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Hierarchical Assembly of Homochiral Porous Solids Using Coordination and Hydrogen Bonds

Yong Cui, Helen L. Ngo, Peter S. White, and Wenbin Lin*

Department of Chemistry, Venable and Kenan Laboratories CB#3290,
University of North Carolina, Chapel Hill, North Carolina 27599

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A family of homochiral metal carboxylate coordination polymers have been synthesized by treating 2,2′-dihydroxy-1,1′-binaphthalene-6,6′-dicarboxylic acid (H_2BDA) with metal salts at elevated temperatures. BDA ligands link adjacent metal centers to form 1D coordination polymeric chains using the carboxylate functionality, while the hydroxyl groups of BDA ligands form H-bonds with carboxylate oxygen atoms to link 1D coordination polymeric chains into open frameworks of higher dimensionality. We also present evidence for the important role played by H-bonds in the stabilization of open framework structures which allows for the hierarchical assembly of chiral porous solids.

Recent advances in the field of solid-state supramolecular chemistry have led to many organic−inorganic hybrid materials with interesting chemical and physical properties.[1] Metal−organic coordination networks have particularly provided a fertile ground for the design of single-crystalline porous solids.[2] On the other hand, it is now well-established that hydrogen bonds (H-bonds) present an ideal synthetic paradigm for the rational design of functional organic crystalline materials.[3] Only very recently have attempts been made to combine both coordination bonds and H-bonds to crystal engineer hybrid organic−inorganic materials.[4]

Our recent efforts in the rational design of homochiral porous metal−organic coordination networks have led to a family of porous lamellar lanthanide phosphonates with interesting catalytic and enantioselective separation properties,[5] as well as homochiral open frameworks based on metal−carboxylate coordination.[6] We report here the hierarchical assembly of homochiral porous solids using a combination of coordination and H-bonds. The bridging ligand used for this study, 2,2′-dihydroxy-1,1′-binaphthalene-6,6′-dicarboxylic acid (H_2BDA), can link adjacent metal centers to form 1D coordination polymeric chains using the carboxylate functionality. The hydroxyl groups in BDA ligands can then form H-bonds with carboxylate oxygen atoms to link 1D coordination polymeric chains into open frameworks of higher dimensionality. We also present evidence for the important role played by H-bonds in the stabilization of open framework structures which allows for the hierarchical assembly of chiral porous solids. The placement of enantiopure 2,2′-dihydroxyl functionality in these porous solids represents the first step toward highly porous chiral solids for applications in heterogeneous asymmetric catalysis and chiral separations.[7]

Enantiopure H_2BDA was prepared in excellent yield from 6,6′-dicyano-2,2′-dihydroxy-1,1′-binaphthalene. $[Mn(BDA)(DEF)_2(MeOH)]\cdot Lu$, **1**, $[Co(BDA)(DEF)(H_2O)]\cdot Lu\cdot DEF$, **2**, $[Cd(BDA)(Py)_3]\cdot Py\cdot H_2O$, **3**, and $[HNMe_3]_2[Cd_2Cl_2(BDA)_2]\cdot 6H_2O$, **4**, were synthesized in good yields by treating enantiopure H_2BDA with corresponding metal salts according to conditions shown in Scheme 1. The formulations of **1**−**4** are supported by TGA, IR, and microanalysis results.[8]

Compound **1** adopts a H-bonded chiral 2D framework structure that crystallizes in space group $P2_12_12_1$.[9] The Mn center adopts a distorted octahedral geometry by coordinating to six oxygen atoms of one chelating carboxylate group and one monodentate carboxylate group of two BDA ligands, two DEF molecules, and one methanol molecule. The *trans* angles around the Mn center range from 148.0(2)° to 165.6(2)°, whereas the cis angles range from 58.2(2)° to 113.9(2)°. The naphthyl rings of each BDA ligand have a dihedral angle of 84.4°. Adjacent Mn centers are thus linked by the

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* Author to whom correspondence should be addressed. E-mail: wlin@unc.edu.

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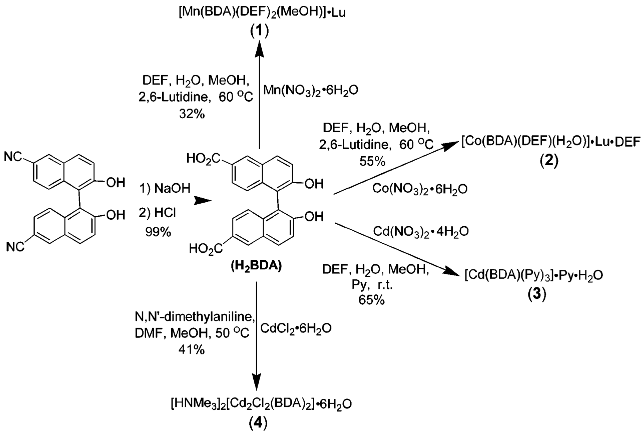
Scheme 1



BDA ligands to form 1D zigzag chains running along the *b* axis (Figure 1a). The two hydroxy groups of each BDA ligand form strong H-bonds with two carboxylate oxygen atoms of two BDA ligands from adjacent 1D zigzag chains to form a chiral 2D corrugated network as shown in Figure 1b (O1···O3, 2.63 Å; O5···O6, 2.59 Å). The 2D network is surrounded by Lu guest molecules, which are H-bonded to coordinated methanol molecules (O9···N3, 2.69 Å). 2D networks of **1** stack on top of each other along the *c* axis to result in a lamellar solid with a layer-to-layer separation of 12.9 Å ($^1/_2c$). The void space between the layers is occupied by included Lu molecules.

Compound **2** also adopts a H-bonded chiral 2D framework structure that is assembled from 1D coordination polymeric chains and crystallizes in space group $P2_12_12_1$.[9] The Co center adopts a highly distorted octahedral geometry by coordinating to six oxygen atoms of two chelating carboxylate groups of two different BDA ligands, one DEF molecule, and one methanol molecule, with *trans* angles ranging from 146.3(3)° to 165.4(3)° and cis angles ranging from 60.8(3)° to 104.0(3)°. The binaphthyl subunits of BDA ligands have a dihedral angle of 86.5°. Adjacent Co centers are linked by the BDA ligands to form an infinite 1D zigzag chain running along the *b* axis (Figure 2). Similar to **1**, the two hydroxy groups of each BDA ligand in **2** form strong H-bonds with two carboxylate oxygen atoms of two BDA ligands from adjacent 1D zigzag chains to form a chiral 2D corrugated network (O1···O6, 2.68 Å; O3···O4, 2.63 Å). The 2D network is also surrounded by Lu molecules, which are H-bonded to coordinated water molecules (O8···N2, 2.76 Å). The 2D slabs stack on top of each other along the *c* axis to form a lamellar structure with a layer-to-layer separation of 13.3 Å; the void space between the layers is occupied by DEF and Lu guest molecules.

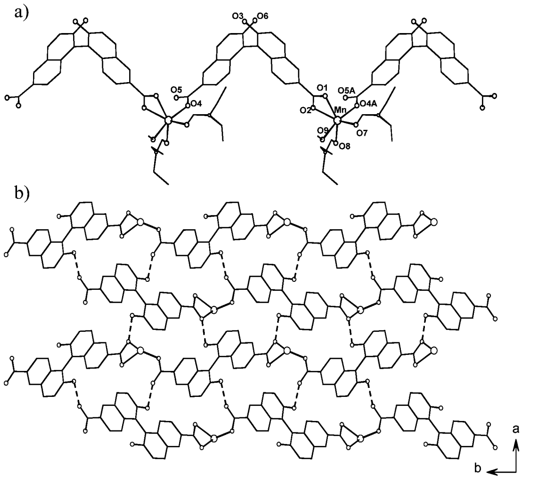


Figure 1. (a) A view of a 1D zigzag chain of [Mn(BDA)(DEF)$_2$(MeOH)] in **1**. (b) A view of a H-bonded 2D network of **1** down the *c* axis.

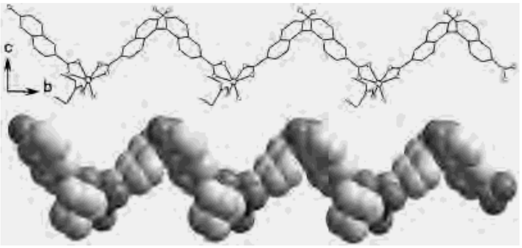


Figure 2. Ball-and-stick and space-filling representations of a 1D zigzag chain of [Co(BDA)(DEF)(H$_2$O)] in **2**.

Compound **3** adopts a H-bonded 3D chiral porous network that crystallizes in space group $C222_1$.[9] The Cd center adopts a distorted pentagonal bipyramid geometry by coordinating to four chelating carboxylate oxygen atoms of two different BDA ligands and three pyridine molecules. The binaphthyl subunits of BDA ligands have a dihedral angle of 80.4°. Adjacent Cd centers are linked by the BDA ligands to form an infinite 1D helix running along the *c* axis (Figure 3a). The left-handed 2_1 helix has a pitch of 23.6 Å. The two hydroxyl oxygen atoms and two carboxylate oxygen atoms of two coordinated carboxylate groups of each BDA ligand form strong interhelix H-bonds (O2···O3, 2.70 Å) which link four adjacent helices to form a 3D chiral porous network with a channel opening of 2.3 × 2.5 Å (Figure 3b). The open cavities are occupied by one pyridine molecule and one water guest molecule per formula unit.

Compound **4** adopts a H-bonded 3D chiral porous framework that is built from 1D coordination chains of $Cd_2(\mu\text{-}Cl)_2(BDA)_2$ and crystallizes in space group $C2$.[9] The asymmetric unit of **4** consists of one $[HNMe_3]^+$ cation, one [CdCl(BDA)] anionic unit, and three water guest molecules. The Cd center adopts a highly distorted octahedral geometry by coordinating to four oxygen atoms of two chelated carboxylate groups from two different BDA ligands and two chlorine atoms. The two chlorine atoms bridge two Cd

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(8) See Supporting Information.

(9) X-ray single-crystal diffraction data for **1**−**4** were collected on a Siemens SMART CCD diffractometer. Crystal data for **1**: orthorhombic, space group $P2_12_12_1$, $a = 10.741(2)$ Å, $b = 13.818(3)$ Å, $c = 25.741(5)$ Å, $V = 3820.5(13)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.34$ g·cm^{-3}, μ(Mo Kα) = 4.04 cm^{-1}. R1 = 0.065, wR2 = 0.151, and GOF = 1.04. Flack parameter = −0.02(4). Crystal data for **2**: orthorhombic, space group $P2_12_12_1$, $a = 9.937(2)$ Å, $b = 14.482(3)$ Å, $c = 26.758(5)$ Å, $V = 3850.9(13)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.31$ g·cm^{-3}, μ(Mo Kα) = 5.03 cm^{-1}. R1 = 0.091, wR2 = 0.206, and GOF = 1.09. Flack parameter = 0.00(5). Crystal data for **3**: orthorhombic, space group $C222_1$, $a = 11.448(1)$ Å, $b = 14.302(2)$ Å, $c = 23.552(2)$ Å, $V = 3856.2(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.41$ g·cm^{-3}, μ(Mo Kα) = 6.21 cm^{-1}. R1 = 0.062, wR2 = 0.157, and GOF = 1.15. Flack parameter = 0.06(5). Crystal data for **4**: monoclinic, $C2$, $a = 28.707(11)$ Å, $b = 14.507(6)$ Å, $c = 10.000(5)$ Å, $\beta = 110.4(1)$°, $V = 3904(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.08$ g·cm^{-3}, μ(Mo Kα) = 6.64 cm^{-1}. R1 = 0.088, wR2 = 0.213, and GOF = 1.00. Flack parameter = 0.0(1).

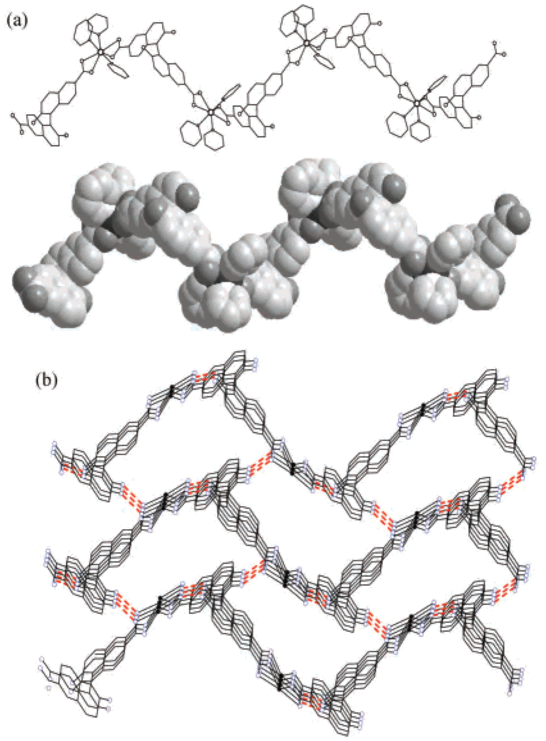

Figure 3. (a) Ball-and-stick and space-filling representations of a 1D left-handed helix of $[Cd(BDA)(Py)_3]$ in **3**. (b) 3D H-bonded network of **3** as viewed slightly off the $[1\bar{1}0]$ axis.

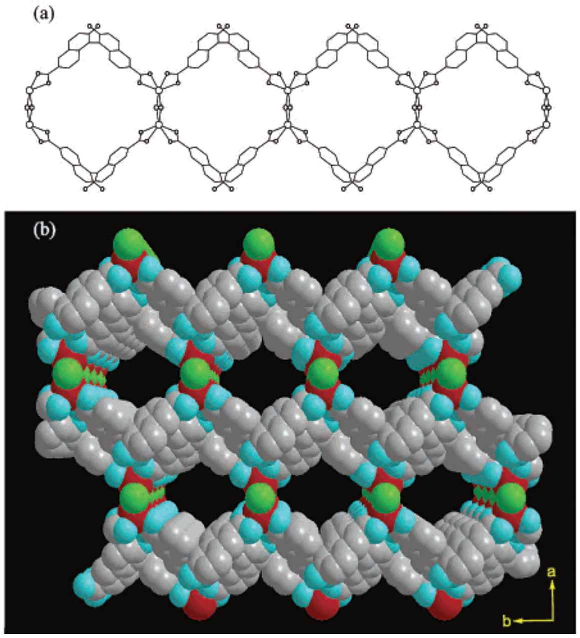

Figure 4. (a) View of a 1D coordination polymeric chain based on $Cd_4(\mu\text{-}Cl)_4(BDA)_2$ metallocycles in **4**. (b) Space-filling model of **4** as viewed down the *c* axis. Open channels have dimension of ~1.1 × 1.2 nm^2.

centers to give a dicadmium unit with a Cd−Cd separation of 3.597(1) Å and a Cl−Cl distance of 3.577(2) Å. Adjacent $Cd_2(\mu\text{-}Cl)_2$ units are doubly bridged by BDA ligands to form 1D double chains based on 34-membered $Cd_4(\mu\text{-}Cl)_4(BDA)_2$ macrocyclic building units (Figure 4a). The 1D chains of $Cd_2(\mu\text{-}Cl)_2(BDA)_2$ run along the *b* axis. The naphthyl subunits of BDA ligands have a dihedral angle of 87.2°. A space-filling model indicates the formation of a nanoscopic rectangular cavity of dimensions of 1.1 × 1.2 nm^2 within each $Cd_4(\mu\text{-}Cl)_4(BDA)_2$ macrocycle.

The hydroxyl groups of the BDA ligands of **4** are also engaged in interchain H-bonding with carboxylate oxygen atoms (O2···O3, 2.60 Å; O5···O6, 2.62 Å). Each 1D coordination polymeric chain of $Cd_2(\mu\text{-}Cl)_2(BDA)_2$ is thus further linked to four adjacent chains to form a 3D H-bonded network. Interestingly, interchain H-bonds have steered the stacking of all $Cd_4(\mu\text{-}Cl)_4(BDA)_2$ metallocycles on top of each other to result in a highly porous solid with open channels running along both the *b* and *c* axes (Figure 4). The void space in **4** accounts for 59.1% of the crystal volume and is occupied by $[HNMe_3]^+$ cations and water guest molecules.[10]

The synthesis of **1**−**4** clearly illustrates the important role of the 2,2′-dihydroxyl groups of BDA ligands in steering the supramolecular structures via directional H-bonds between hydroxyl and carboxylate groups. Moreover, interchain H-bonds are also key to the stabilization of open framework structures to allow for the hierarchical assembly of chiral porous solids of **3** and **4** based on both coordination and H-bonds. Although Lu and DEF guest molecules can be removed from **1** and **2** under vacuum at elevated temperatures, their framework structures have collapsed as evident from powder X-ray diffraction patterns (PXRDs). In stark contrast, py and water guest molecules of **3** and **4** can be readily removed by subjecting their freshly ground samples to a 10^{-2} Torr vacuum, and PXRDs of evacuated solids of **3** and **4** are essentially the same as those of pristine solids of **3** and **4**, respectively. Interestingly, evacuated solids of **3** and **4** readily adsorb expected amounts of guest molecules upon exposure to their vapors, which provides further evidence for the framework stability of **3** and **4**. Undoubtedly, the strikingly different behaviors of **1** and **2** vs **3** and **4** are a direct consequence of their varied dimensionalities. We have prepared crystalline solids of **1**−**4** using both (*R*)- and (*S*)-enantiomers of H_2BDA. Solid-state CD spectra of compounds **1**−**4** made from (*R*)- and (*S*)-H_2DBA are exact mirror images of each other and demonstrate their supramolecular enantiomeric nature.

In summary, directional H-bonds have been utilized to construct 2D and 3D homochiral network materials based on 1D coordination polymeric chains. Interchain H-bonds also stabilize open framework structures to lead to homochiral porous solids.

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Supporting Information Available: Experimental procedures, analytical data, 17 figures, and an X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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