

Homochiral 3D open frameworks assembled from 1- and 2-D coordination polymers†

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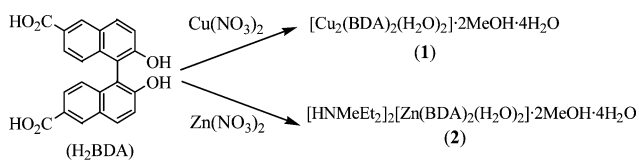
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Homochiral 3D open frameworks have been assembled from 1- and 2-D coordination structures via hydrogen bonding and are stable towards the removal of included guest molecules.

The design of metal–organic coordination frameworks has been extensively studied in recent year because of their intriguing structures and, more importantly, their potential applications as functional materials.¹ A particularly interesting and challenging area in this field is the synthesis of homochiral porous metal–organic networks and exploration of their potential applications in heterogeneous asymmetric catalysis and enantioselective separations.^{2,3} Although chiral coordination networks can be constructed using several different strategies,⁴ we believe that the combination of rigid chiral linkers and metal nodes or metal–organic secondary building units (SBUs) represent the most straightforward and reliable approach toward homochiral solids. We have recently demonstrated the synthesis of homochiral solids based on multitopic rigid linkers derived from axially chiral 1,1'-bi-2-naphthol and their potential applications in enantioselective processes.^{2b–c} Herein we wish to report the assembly of homochiral 3D open frameworks from 1- and 2-D coordination polymers via hydrogen bonding.

[Cu₂(BDA)₂(H₂O)₂]₂·2MeOH·4H₂O, **1**, was obtained in 60% yield by slow diffusion of *N,N'*-dimethylaniline into a mixture of copper nitrate, (*S*)-2,2'-dihydroxy-1,1'-binaphthalene-6,6'-dicarboxylic acid (H₂BDA),⁵ methanol and water at r.t. [HNMeEt₂]₂[Zn(BDA)₂]₂·2MeOH·4H₂O, **2**, was obtained in 36% yield by treating zinc nitrate and (*S*)-H₂BDA in a mixture of *N,N'*-diethylformamide (DEF), MeOH and *N,N'*-dimethylaniline at 50 °C. Both **1** and **2** are insoluble in water and common organic solvents. The IR spectra of **1** and **2** exhibit bands characteristic of carboxylate groups at 1650–1320 cm⁻¹; the very strong and broad peaks around 3430 cm⁻¹ are indicative of strong hydrogen bonds in their solid structures. Thermogravimetric analyses show that **1** lost 12.5% of total weight by 165 °C, corresponding to the loss of two MeOH and four water guest molecules per formula unit (expected 13.0%). **2** lost 12.3% of total weight by 192 °C, corresponding to the loss of four water and two methanol guest molecules (expected 12.1%). The formulations of **1** and **2** are also supported by microanalysis results.† We have also prepared compounds **1** and **2** using (*R*)-H₂BDA. Solid-state CD spectra of the products made from (*R*)- and (*S*)-H₂DBA are exact mirror image of each other, and conclusively demonstrate the enantiomeric nature of **1** and **2** made from (*R*)- and (*S*)-H₂BDA.



† Electronic supplementary information (ESI) available: synthesis of compounds **1** and **2**, removal and reintroduction of guest molecules, and Figs. S1–S6. See <http://www.rsc.org/suppdata/cc/b211916a/>

A single-crystal X-ray analysis of **1** reveals a H-bonded 3D chiral open framework assembled from 1D coordination polymer that is constructed from BDA-bridged Cu₂(carboxylate)₄ paddle-wheels (Fig 1). **1** crystallizes in the chiral space group *I*222, and contains one Cu center, one half BDA group, one coordinated water and one methanol molecule and two water guest molecules in the asymmetric unit. Four crystallographically equivalent carboxylate groups of four BDA ligands bridge two Cu(II) centers to form a paddle-wheel structure with a Cu...Cu distance of 2.66(1) Å. Each Cu is also coordinated to a terminal water molecule to result in a slightly distorted square pyramidal geometry. Adjacent Cu₂(carboxylate)₄ paddle-wheels are doubly bridged by the binaphthyl backbones of two BDA groups to form an infinite 1-D chain running along the *b*-axis. The naphthyl subunits of each BDA ligand have a dihedral angle of 92.6°. A space-filling model indicates that the formation of cavities of ~6.2 × 6.2 Å within each Cu₄(BDA)₂ macrocycle.

The OH groups of the BDA ligands of the polymeric chains are pointing outward and well positioned to form interchain H-bonds with the carboxylate oxygen atoms. Indeed, the hydroxyl oxygen atoms and two coordinated carboxylate oxygen atoms of each BDA ligand form interchain H-bonds (O2...O7, 3.00 Å); each coordination polymer chain is thus linked to four adjacent chains. Interestingly, interchain H-bonds have steered the stacking of all Cu₄(BDA)₂ metallocycles on top of each

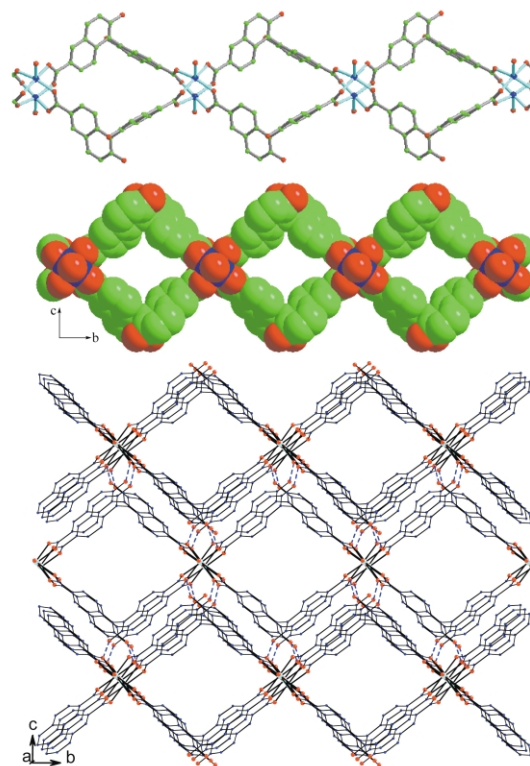


Fig. 1 Top, 1D chain of **1** composed of Cu₂(carboxylate)₄ paddle-wheels. Middle, a space-filling model of the 1D chain. Bottom, a view slightly off the *a* axis showing the 3-D H-bonded open framework.

other to form a 3D chiral open framework. The open channels constitute $\sim 48.8\%$ (1492.6 \AA^3) of the crystal volume (PLATON) and are occupied by methanol and water guest molecules.⁶

Compound **2** adopts a H-bonded 3D chiral open framework assembled from 2D rhombohedral grids and crystallizes in the chiral space group $P4_22_12$ (Fig 2). The asymmetric unit of **2** consists of one half $[\text{HMeNEt}_2]^+$ cation, one fourth Zn center, one half BDA ligand, one half methanol and one water guest molecule. The Zn center coordinates to four oxygen atoms of four monodentate carboxylate groups from four different BDA ligands to adopt a distorted tetrahedral geometry. The naphthyl subunits of BDA have a dihedral angle of 77.1° , while the $\text{Zn}\cdots\text{Zn}$ distance in the 2D grid is $11.738(2) \text{ \AA}$. The BDA ligands link adjacent Zn centers to form a corrugated 2D grid.

Interestingly, all OH groups of the BDA ligands are pointing towards the opposite sides of the 2D grids, and are positioned to form a H-bonded network. 2D grids in **2** stack on top of each other in a staggered arrangement along the c -axis (Fig 2). The adjacent layers are shifted by $1/2a$ and $1/2b$ along the a and b axis, respectively, and have a layer-to-layer separation of 7.17 \AA . Such a staggered arrangement orients uncoordinated carboxylate O atoms and OH group of BDA ligands from adjacent

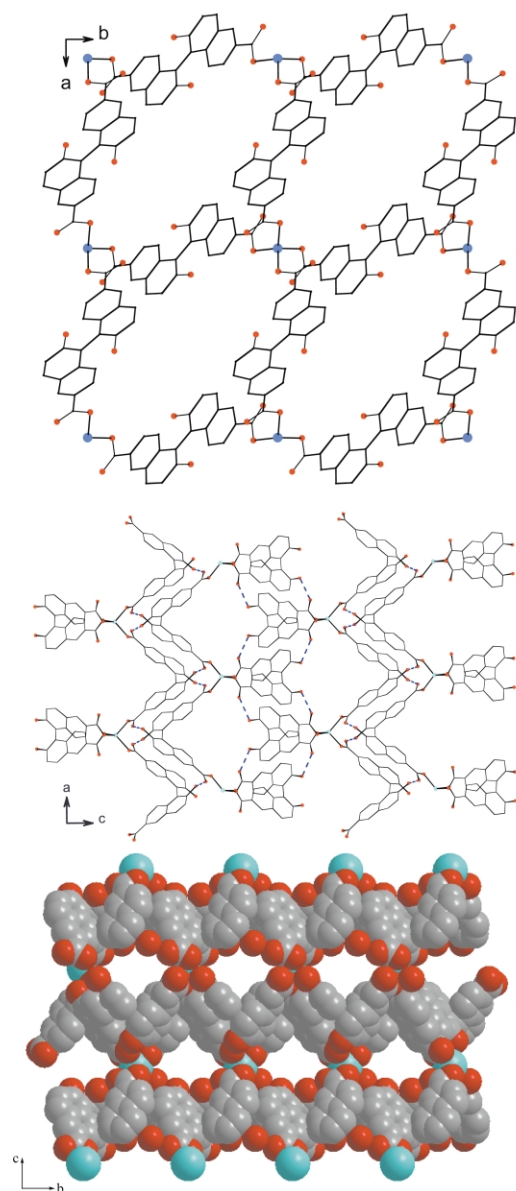


Fig. 2 Top, a view of the 2D rhombohedral grid of **2** down the c axis. Middle, 3D H-bonded open framework of **2** as viewed down the b axis. Bottom, a space-filling model of **2** as viewed down the a axis.

layers close to each other. As a result, the OH groups and uncoordinated carboxylate oxygen atoms from adjacent layers form strong interlayer H-bonds with an $\text{O2}\cdots\text{O2}$ distance of $2.622(1) \text{ \AA}$. **2** thus adopts an interesting homochiral 3D open framework structure with open channels running along both a - and b -axes. These open channels constitute $\sim 53.4\%$ (1650 \AA^3) of the crystal volume (PLATON) and are occupied by two $[\text{HMeNEt}_2]^+$ counter ions and four water and two methanol guest molecules per formula unit.

The ability of the 2,2'-dihydroxyl groups of BDA ligands in forming directional H-bonds undoubtedly steers the formation of 3D open frameworks of **1** and **2**. More importantly, the H-bonds also stabilize open framework structures to allow for the hierarchical assembly of chiral solids that are stable towards the removal of their included guest molecules. MeOH and water guest molecules of **1** and **2** can be removed in vacuo, and PXRDs of evacuated solids of **1** and **2** are similar to those of their pristine solids. Interestingly, evacuated solids of **1** and **2** readily adsorb expected amounts of guest molecules upon exposure to their vapors, which provides further evidence for their framework stability. Although coordination bonds¹ or H-bonds alone⁷ have been extensively used to construct extended networks, this work represents one of the few attempts in designing novel materials using a combination of coordination and H-bonds.⁸

In summary, we have synthesized homochiral 3D open frameworks via interchain or interlayer H-bonds of 1D or 2D polymeric coordination structures. Such 3D networks based on both coordination and H-bonds are stable towards the removal of their included guest molecules.

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Notes and references

† Anal. calc. for $\text{C}_{46}\text{H}_{44}\text{Cu}_2\text{O}_{20}$, **1**: C, 52.92; H, 4.25; N, 0%. Found: C, 52.02; H, 4.45; N, 0.18%. Anal. calc. for $\text{C}_{56}\text{H}_{68}\text{ZnN}_2\text{O}_{18}$, **2**: C, 59.92; H, 6.11; N, 2.50%. Found: C, 58.89; H, 5.87; N, 2.43%.

§ X-ray single-crystal diffraction data for **1** and **2** were collected on a Siemens SMART CCD diffractometer. Crystal data for **1**: orthorhombic, space group $I222$, $a = 10.92(3)$, $b = 14.03(4)$, $c = 19.96(6) \text{ \AA}$, $U = 3060(16) \text{ \AA}^3$, $Z = 2$, $\rho_{\text{calcd}} = 1.13 \text{ g}\cdot\text{cm}^{-3}$. Least-squares refinement based on 1256 reflections with $I > 2\sigma(I)$ and 151 parameters led to convergence, with a final $R1 = 0.119$, $wR2 = 0.263$, and $\text{GOF} = 1.36$. Flack parameter = $0.15(10)$. Crystal data for **2**: tetragonal, space group $P4_22_12$, $a = 11.739(2)$, $b = 11.739(2)$, $c = 22.408(5) \text{ \AA}$, $U = 3087.6(9) \text{ \AA}^3$, $Z = 2$, $\rho_{\text{calcd}} = 1.19 \text{ g}\cdot\text{cm}^{-3}$. Least-squares refinement based on 1540 reflections with $I > 2\sigma(I)$ and 164 parameters led to convergence, with a final $R1 = 0.098$, $wR2 = 0.248$, and $\text{GOF} = 1.02$. Flack parameter = $-0.01(7)$. CCDC 199492 and 199493. See <http://www.rsc.org/suppdata/cc/b2/b211916a/> for crystallographic data in .cif or other electronic format.

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