Coexistence of chiral hydrophilic and achiral hydrophobic channels in one multi-helical-array metal–organic framework incorporating helical water cluster chains†

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A novel host–guest metal–organic compound with both chiral hydrophilic and achiral hydrophobic channels has been obtained through the reaction of Cd(II) ion and a versatile asymmetrical ligand of H_4bptc (H_4bptc = 1,1′-biphenyl-2,2′,3,3′-tetracarboxylic acid) based on hydro(solvo)thermal reactions.

Helicity is a topological motif that is highly attractive not only because of its fascinating structure but also for its realistic and potential applications in many fields.[1–3] There is no doubt that the search for new structural motifs for helical architectures has been an intensive research area to date.[4] Though the basic features of the design necessary to assemble discrete helices or low dimensional helical coordination polymers are now fairly well established, the design and control of the assembly of the helical unit into a multi-helical-array still remains a challenge.[5]

Meanwhile, metal–organic frameworks with high porosity have attracted a great deal of attention,[6] especially the helical tubular structure with chiral porosities that are capable of recognizing special guests.[7] While most of the effort has so far focused on the assembly of the porous metal–organic open frameworks with large and identical cavities for molecular absorption and stabilization, one framework with two distinct cavities or channels remains largely unexplored and difficult to construct, notwithstanding the interesting phenomena which have been found in these rare examples.[8]

Here we report a novel d^{10} metal–organic coordination polymer $[Cd_4(bptc)_2(bpy)(H_2O)_8]\cdot 5.5H_2O$ (**1**) (H_4bptc = 1,1′-biphenyl-2,2′,3,3′-tetracarboxylic acid) having large hydrophilic helical channels with alternately arranged chirality and small hydrophobic achiral microchannels of two initially interwoven double-stranded helices. Meanwhile, each hydrophilic helical channel acting as a host incorporates a helical stream of water clusters.

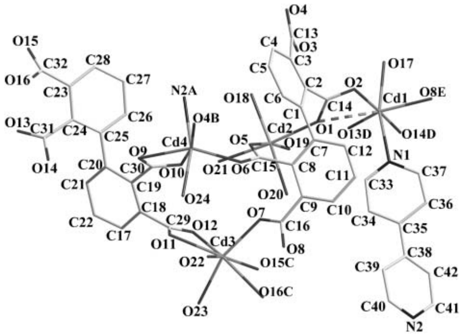
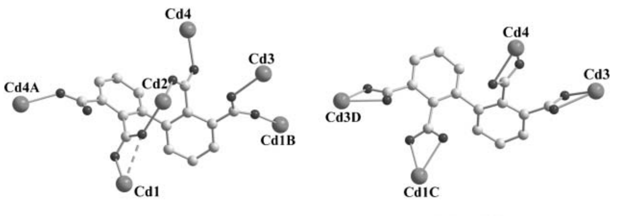


Fig. 1 The asymmetric unit of **1**. Solvent water molecules and hydrogen atoms are omitted for clarity. (Symmetry code: A: *x*, *y*, −1 + *z*; B: −1/4 + *y*, 5/4 − *x*, 5/4 − *z*; C: *x*, *y*, 1 + *z*; D: −1/4 + *y*, 3/4 − *x*, 3/4 + *z*; E: 5/4 − *y*, 1/4 + *x*, 9/4 − *z*).

Needle shaped crystals of **1** were obtained by the hydrothermal reaction of $Cd(NO_3)_2\cdot 4H_2O$, H_4bptc and bpy in water in the presence of triethylamine at 120 °C for five days.‡ The X-ray crystal structure analyses§ reveal that **1** crystallizes in the high symmetry tetragonal space group $I4_1/a$. The asymmetric unit of **1** (Fig. 1) contains four crystallographically independent Cd^{2+} ions, two unique bptc ligands in different coordination modes (Scheme 1 and Fig. 1), and one 4,4′-bpy molecule. The Cd1 ion (mode **1** in Scheme 1) is seven-coordinate and is described as having a distorted pentagonal-bipyramidal geometry with one long axis (Cd1–O1 = 2.826 Å) (Fig. 1 and S1). The coordination geometry for the six-coordinate Cd2 and Cd4 ions (Scheme 1) is close to octahedral (Fig. 1 and S1). The Cd3 ion (Scheme 1, Fig. 1 and S1) is seven-coordinate and is described as having a pentagonal-bipyramidal geometry.

A survey down the *c*-axis easily identifies the existence of two distinct types of channels (Fig. 2). The small channels (diameter[9] of 1.73 Å) are located at (0, ¼, *z*), (0, ¾, *z*), (½, ¼, *z*) and (½, ¾, *z*) while the large channels (diameter[9] of 7.83 Å) are located at (¼, 0, *z*), (¼, ½, *z*), (¾, 0, *z*) and (¾, ½, *z*) (Fig. 2 and S2).

The first feature of **1** is that the small channel consists of two interwoven double-stranded helical chains with opposite orientations (Fig. 3a and S3). In the double-stranded helices, chains with the same chirality are interconnected through bpy molecules



Mode I **Mode II**

Scheme 1 Two different coordination modes of the bptc ligand in **1**. Each of the two modes is actually chiral and has its mirror coexisting in the crystal. (Symmetry code: A: 5/4 − *y*, 1/4 + *x*, 5/4 − *z*; B: 1/4 + *y*, 5/4 − *x*, 5/4 − *z*; C: 3/4 − *y*, 1/4 + *x*, −3/4 + *z*; D: *x*, *y*, −1 + *z*).

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† Electronic supplementary information (ESI) available: Selected bond distances and angles, hydrogen bond table, packing diagram, TG curve, and PXRD patterns. See DOI: 10.1039/b611994h

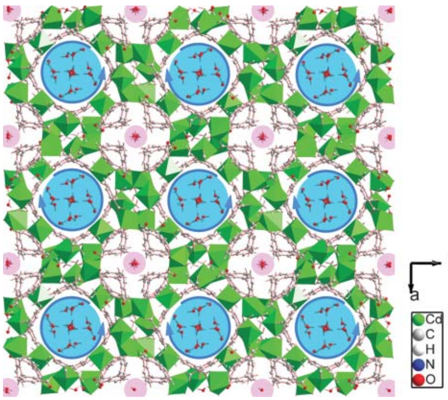

Fig. 2 The framework of **1** viewed down the *c* axis, showing the two distinct types of channels in the structure of **1**. Cd^{2+} ions are represented by polyhedra. The small hydrophobic channels are colored red while the large hydrophilic channels are colored blue with surrounding arrows representing their chirality.

coordinating to Cd1 and Cd4 (Fig. S3). The smallest repeat unit of each strand employs two bptc ligands in mode **I** that are connected through Cd1, Cd2 and Cd4 ions (Scheme 1 and Fig. S3). The separation between adjacent chains of the double-stranded helices is the same as the cell period *c* (13.523 Å) while the pitch of each chain is 2*c*. Chains with opposite orientations are connected through 2- and 2′-carboxylate groups and interweave with each other up and down (Fig. 3a and S3). The benzene rings of the bptc ligands are alternately trapped inside the helical channels to give hydrophobic small tubules (Fig. 2). As divinable, the water (O25) suspended in this hydrophobic channel is disordered and its occupancy is 50%. Four helical chains are essentially symmetry equivalents that are related by an S_4-axis passing through them (Fig. S5 and S6 in supporting information). Therefore the small channel is achiral. From our understanding of helical coordination polymers, frameworks with two interwoven double helical chains are uncommon.

In contrast to the small channel comprising only mode **I**, the large channel employs both modes **I** and **II** (Scheme 1 and Fig. S7). Mode **I** is connected to mode **II** through Cd1 and Cd4 ions to form a helical chain (Scheme 1 and Fig. S7). As for the large channel, it consists of a triple-helical-strand with each strand a 4_3 helical chain (Fig. 3b and Fig. S7). The separation between adjacent chains is *c* while the pitch of each chain is 3*c*. The chirality of these channels is alternately distributed and depends on the location where the triple-helical-strand resides—right-handed with a 4_3-axis at $(\frac{1}{4}, 0, z)$ and $(\frac{3}{4}, \frac{1}{2}, z)$, left-handed with a 4_1-axis at $(\frac{1}{4}, \frac{1}{2}, z)$ and $(\frac{3}{4}, 0, z)$ (Fig. 2 and S2). In addition to the bpy molecules coordinating to Cd1 and Cd4, adjacent chains in triple-stranded helices are as well connected through Cd3 ions coordinated by the 3- and 3′-carboxylate groups in mode **II** (Fig. S7 and S8). Wonderfully, the severely twisted bptc ligands further lead to local chirality in every single chain, giving a *quasi*-helical ribbon arrangement (Fig. S7 and S9). Interestingly, Cd2 ions are embedded in the inner wall of the large channel by coordinating with the 2- and 2′-carboxylate groups in mode **I** (Fig. 2 and S10). The coordination waters pointing to the inside of the channel (four on Cd2 along with two on Cd3), acting as functional adornments, make the large channel remarkably hydrophilic. As a matter of fact, no metal–organic framework that has both a triple-helical-strand and interweaving of two double-stranded helices has been reported before.

Another interesting structural feature of **1** is the helical stream of guest waters in the host hydrophilic helical channels. This helical water stream is made up of co-edged (O27···O28) V-shaped water heptamers sharing the same screw axis and keeping its chirality with its host channel (Table S1 and Fig. 4a, 4b). Alternatively, this helical 1D polymer can also be regarded as two intra-hydrogen-bonded helical water chains (namely a double-stranded helical chain) connected to each other through inter-chain hydrogen bonds (O27···O28) (Fig. 4c). The helical water stream is further supported and stabilized by maintaining hydrogen bond networks to the aqua ligands (O20) in the wall of the hydrophilic channel, which in turn transfers its chirality to the water stream inside it and hence determines the orientation of the helical water stream (Table S2, Fig. 4c and S11). In this sense, the helical tubular host

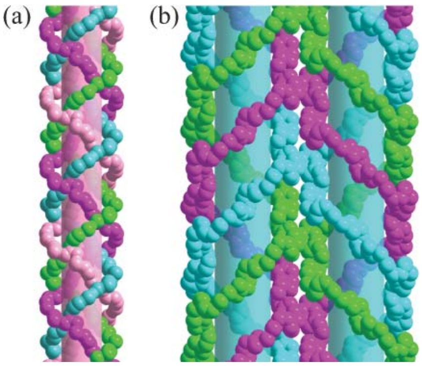

Fig. 3 (a) Two interwoven double-stranded helical chains with the reverse orientation. Two right-orientated chains are colored cyan and green while two left-orientated chains are colored magenta and pink. (b) Two adjacent large helical channels with opposite chirality. The triple-helical chains are colored magenta, cyan, and green. In (a) and (b), bpy molecules and Cd3 atoms are omitted for clarity.

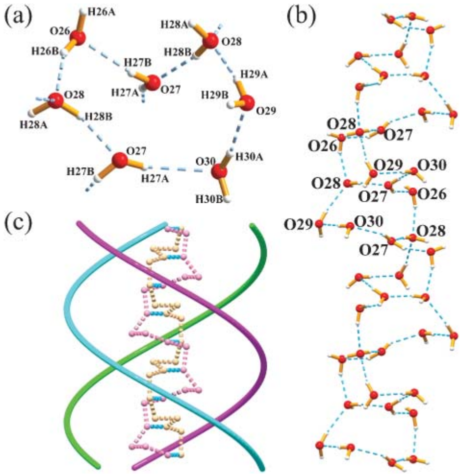

Fig. 4 (a) V-shaped water heptamers. (b) The helical water cluster stream. Hydrogen bonds are marked as light blue broken lines. (c) Each hydrophilic chiral host helical tubular channel incorporates a guest helical water cluster chain with the same chirality. This water chain can be seen as double-stranded helical water chains. Two water chains are colored pink and gold, while interchain interactions (O27···O28) are presented as light greenish blue. Hydrogen atoms are omitted for clarity.

acts as a template for the formation of the helical chain of water molecules. In fact, water molecules can form various interesting topologies depending on the shape of the void afforded by the host frameworks.[10] Water chains are attracting more and more attention[11] in the respect that many fundamental biological processes appear to depend on the unique properties of water chains.[12] Though limited examples of 1D helical water chains have been found in the past two years,[13] helical water chains constructed from water clusters are rare.

In summary, we have successfully constructed a novel biporous metal–organic coordination polymer. From our understanding of biporous MOFs, this is the first example with both chiral hydrophilic and achiral hydrophobic helical channels. Moreover, the observed template effect of the helical tubule on the formation of the helical water cluster chain is very important for correctly describing the association of water molecules in biological systems.

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Notes and references

‡ Synthesis of the compound: Colorless needle shaped crystals of compound **1** were synthesized hydro(solvo)thermally in a 23-ml Teflon-lined autoclave by heating a mixture of 2,2′,3,3′-H_4bptc (0.1 mM, 0.033 g), bpy (0.05 mmol, 0.008 g), $Cd(NO_3)_2\cdot 4H_2O$ (0.2 mM, 0.062 g) and one drop of triethylamine at 120 °C in 8 ml water and 2 ml ethanol for five days. Small crystals of **1** suitable for structure determination were picked out from the white precipitate. Yield: about 12% (based on $Cd(NO_3)_2\cdot 4H_2O$). Anal. Calc. (%) for **1** ($C_{168}H_{188}Cd_{16}N_8O_{118}$): C 33.60, H 3.16, N 1.87; found: C 33.87, H 3.01, N 2.01; IR (KBr pellet): 3609, 3379, 3081, 1606, 1571, 1560, 1440, 1371, 1233, 1072, 889, 831, 815, 790, 768, 701, 654, 601, 530, 451 cm^{-1}.

§ Crystal data were measured as follows: $C_{168}H_{188}Cd_{16}N_8O_{118}$, M_r = 6005.66, tetragonal, space group $I4_1/a$, a = 40.698(2), b = 40.698(2), c = 13.523(1) Å, V = 22399(2) Å^3, Z = 4, ρ = 1.781 g cm^{-3}, μ = 1.588 cm^{-1}, $F(000)$ = 11856, GOF = 0.96. Of 60083 total reflections collected, 11021 were unique (R_{int} = 0.0895). R_1 (wR_2) = 0.0535 (0.1276) for 739 parameters and 9150 reflections [$I > 2\sigma(I)$]. The intensity data were collected on a Smart CCD diffractometer with graphite-monochromated MoKa radiation (λ = 0.71073 Å) at room temperature. All absorption corrections were performed by using the *SADABS* program. The structure was solved by direct methods and refined by full-matrix least squares on F^2 using the *SHELXTL-97* program package. The nonhydrogen atoms were refined anisotropically. The hydrogen atoms of the coordination water molecules and aromatic rings were included in the structure factor calculation at idealized positions by using a riding model. The hydrogen atoms of the solvent water molecules were located from the difference Fourier maps and refined isotropically. CCDC 601759 (**1**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b611994h

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