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Interweaving of Triple-Helical and Extended Metal–O–Metal Single-Helical Chains with the Same Helix Axis in a 3D Metal–Organic Framework

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A novel 3D metal–organic framework $[Cd_2(m\text{-}bptc)(4,4'\text{-}bpy)_{0.5}(H_2O)_4]\cdot H_2O$ (**1**; m-H_4bptc = 1,1′-biphenyl-2,3′,3,4′-tetracarboxylic acid, 4,4′-bpy = 4,4′-bipyridine) with interweaving of triple- and single-helical chains has been obtained based on hydro(solvo)thermal reactions.

The construction of novel coordination polymers is the current interest in the field of supramolecular chemistry and crystal engineering stemming from their potential applications as functional materials,[1−3] as well as their intriguing variety of architectures and molecular topologies.[4] Among them, the construction of helical coordination polymers has aroused a great more deal of attention[5−8] owing to the wide appearance of helical structures in, for example, proteins, collagens, quartz, single-walled carbon nanotubes, and many more natural or artificial fiber-type derivatives.[9] Consequently, many single-, double-, triple-, and higher-order stranded helical complexes have been generated by self-assembly processes. Recently, scientists have found that the DNA double helix can accommodate a third strand in its major groove under certain contains and the resulting interweaved triplex DNA could be used to induce genetic mutations.[10] At the same time, some topologies with interlocked or interweaved helices have also been reported in metal−organic frameworks.[11] However, networks with interweaving of two kinds of helices that possess the same helix axis are extremely rare.[12] Recently, we have introduced a new versatile asymmetrical ligand of 1,1′-biphenyl-2,3,3′,4′-tetracarboxylic acid (m-H_4bptc; Chart 1) to construct novel coordination polymers in view of its following characteristics: (a) The two phenyl rings are severely twisted across the C−C single bond, and the skew coordination orientation of the carboxy groups provide the potential of the formation of a helix. (b) Upon coordination as a bridge,

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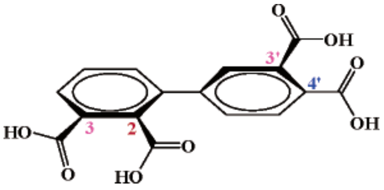
Chart 1. Structure of m-H_4bptc



the freedom of the ligand to rotate around the C−C single bond is restrained and the ligand can be locked in a twisted chiral conformation. Herein, we report fascinating interweaved helices based on a Cd^{II} complex with the versatile m-H_4bptc ligand. To the best of our knowledge, this is the first example of a metal−organic framework that has interweaving of triple- and single-helical chains with the same chirality. Moreover, it shows an interesting behavior in which the single-helical chain is based on a −Cd−O−Cd−O− chain.

Needle crystals of **1** were obtained by the hydrothermal reaction of $Cd(NO_3)_2{\cdot}4H_2O$, m-H_4bptc, and 4,4′-bpy in water in the presence of triethylamine at 120 °C for 3 days.[13] Single-crystal X-ray analysis[14] revealed that **1** has a novel 3D metal−organic framework. In the asymmetrical unit of **1** (Figure 1), there are two crystallographically independent Cd^{2+} ions, one m-bptc ligand, half of 4,4′-bpy molecule, and four coordinated and two disordered solvated water molecules. The coordination geometries for the seven-coordinate Cd1 and Cd2 atoms are all close to those of distorted capped octahedra with long Cd1−O3 (2.805 Å) and Cd2−O5 (2.751 Å) bonds (Figures 1 and S1in the Supporting Information). The Cd1 center coordinates to three carboxylate groups (3′- and 4′-COO^- in one m-bptc ligand in monochelating fashion and 3-COO^- from a neighboring molecule in bichelating fashion), one N atom of 4,4′-bpy (N1), and two O atoms of water (O9 and O10) in cis conformation. In contrast, the Cd2 center coordinates to four carboxylate groups (4′-COO^- in one m-bptc ligand, 2- and 3-COO^- from other molecules in a monochelating fashion, and 3′-COO^- in a third m-bptc ligand in a bischelating fashion) and two O atoms of water (O11 and O12) in trans conformation. According to the m-bptc ligand, the dihedral angle between the two phenyl rings is 58.8°; the 2,4′-carboxylate groups are almost perpendicular to the plane of correspondingly linked phenyl rings with dihedral angles of 92.6° and 84.0°, respectively.

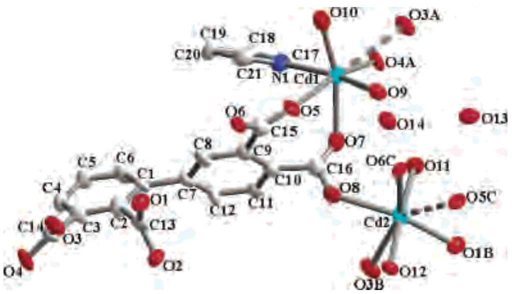


Figure 1. Molecular structure of **1**. Selected bond lengths [Å]: Cd1−O3A 2.805(1), Cd1−O4A 2.273(3), Cd1−O5 2.501(3), Cd1−O7 2.310(4), Cd1−O9 2.298(3), Cd1−O10 2.234(4), Cd1−N1 2.320(4), Cd2−O1B 2.252(3), Cd2−O3B 2.331(3), Cd2−O5c 2.746(4), Cd2−O6c 2.276(3), Cd2−O8 2.359(3), Cd2−O11 2.266(3), Cd2−O12 2.327(3). Symmetry codes: A, $1 + x$, $-1 + y$, z; B, x, $-1 + y$, z; C, $^1/_2 - x$, $-^1/_2 + y$, $^1/_2 - z$.

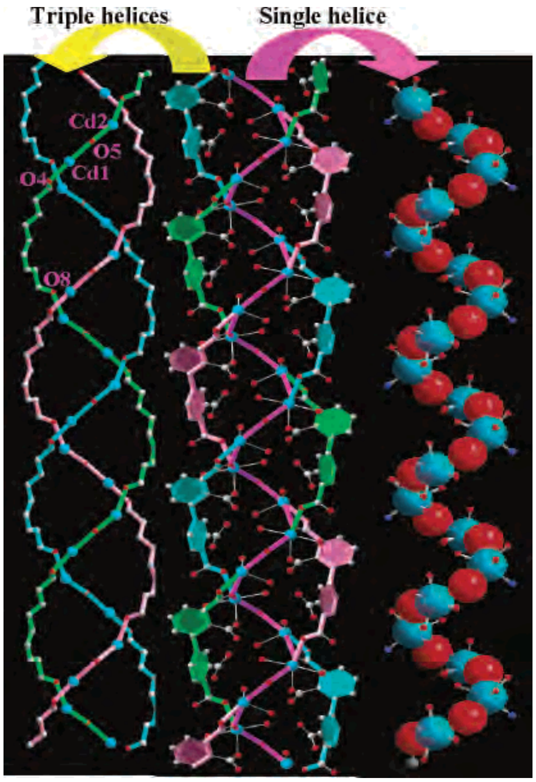


Figure 2. Left: Triple-helical chains that are marked as sky, rose, and bright green, respectively. Middle: Interweaved triple- and single-helical chains. The single-helical chain is marked as purple. Right: −Cd1−O5−Cd2−O3− single-helical chain. Blue and red represent Cd and O atoms, respectively.

The first feature of **1** is its triple-helical topology. The Cd octahedra are linked into an extended chain via 3- and 4′-carboxylate groups of one m-bptc ligand and the O5 atom of the 3′-carboxylate group in another m-bptc ligand from the neighboring helical chain (Figures 2 and 3 and the Supporting Information). Each helical chain in **1**, therefore, results from metal−ligand interactions and can be described as $(-Cd1-O5-Cd2-bptc-)_n$. The separation between the adjacent chains in the triple-helical chains is the same as the length of the *b* axis (10.801 Å). The pitch of the helical chain running along the *b* axis is 3 times the length of the *b* axis.

A more interesting feature of **1** is the existence of a single-helical chain that is made up of −Cd2−O5−Cd1−O3− repeat units and interweaves with triple-helical chains across Cd2−O5−Cd1 (Figures 2 and S2 in the Supporting Information). Among helical coordination polymers, a −metal−O−

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(13) Synthesis of the compound: A mixture of m-H_4bptc (0.1 mmol), 4,4′-bpy (0.05 mmol), and $Cd(NO_3)_2{\cdot}4H_2O$ (0.2 mmol) in 8 mL of water was heated at 120 °C for 3 days in a Teflon-lined 23-mL bomb, and white crystals were obtained (yield: 82%). Anal. Calcd: C, 35.07; H, 2.80; N, 1.95. Found: C, 35.15; H, 2.68; N, 2.01. IR (KBr/pellet, cm^{-1}): 3300 (vs), 2360 (vs), 1600 (vs), 1546 (vs), 1452 (ms), 1402 (vs), 1368 (ms), 1216 (w), 1098 (w), 1062 (w), 935 (w), 846 (m), 816 (ms), 768 (ms), 631 (ms), 575 (w), 475 (w), 441(w).

(14) Crystal data were measured as follows: $C_{21}H_{20}Cd_2NO_{13}$, $M_r = 719.18$, white crystal (0.4 × 0.2 × 0.2 mm), monoclinic, space group $P2_1/n$, $a = 8.094(2)$ Å, $b = 10.801(3)$ Å, $c = 28.324(7)$ Å, $\beta = 94.804(5)°$, $V = 2467.6(10)$ Å^3, $Z = 4$, $T = 293(2)$ K, $\rho_{calcd} = 1.936$ g cm^{-1}, $F(000) = 1412$, $\mu = 1.792$ mm^{-1}, R1 (wR2) 0.0430 (0.0739), and $S = 1.034$ for 3491 reflections with $F_o > 2\sigma(F_o)$. CCDC 291361.

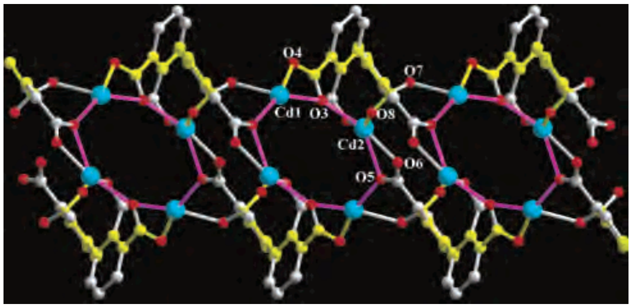

Figure 3. Section of one chiral layer showing coordination interactions between helical bundles. Bonds of the single-helical chain are marked as purple, while atoms and bonds in triple-helical chains are all presented as yellow.

metal– helix is extremely rare.[15] In **1**, the arrangements of the triple-helical chains provided an opportunity to form the single-helical chain, which, in turn, should play an important role in the stability of triple-helical chains. The pitch of the single-helical chain running along the *b* axis is the same length as the *b* axis. More wonderfully, the single-helical chain has the same chirality as the triple-helical chain. In fact, the limited examples that have interweaving of two kinds of helical ribbons with the same helix axis have opposite orientations.[12]

It should be noted that all helices have the same handness in the same layer. As shown in Figure 3, these helical chains are united together through the m-bptc ligands in one layer. Each m-odta in one helica chain provides O6 of the 3′-COO^- group and O7 of the 4′-COO^- group to coordinate to Cd2 and Cd1 ions in adjacent chain, respectively, besides the O5 atom of the 3′-COO^- group directly participating in the formation of an adjacent helix. Homochiral helix assembly in two dimensions in **1** is accomplished by the m-bptc ligand itself. This can be interpreted by the configuration of this ligand, in which two phenyl rings are united together by the C–C single bond. Upon coordination as a bridge, the ligand can be locked into a twisted chiral conformation, and the homochiral information can effectively transfer through this versatile ligand.

Another feature of **1** is that these 2D chiral layers with opposite chirality can be supported by the second rigid pillaring spacer (4,4′-bpy) to give a 3D centric framework having small channels (7.8% of the cell volume calculated by PLATON[16]) to host the guest water (Figures 4 and S3 in the Supporting Information).

The existence of the guest molecules in the porous framework inspired us to investigate the thermal stability of the framework. Thermal gravimetric analysis (TGA) for crystal sample **1** was performed from 25 to 800 °C. The weight loss of 12.22% in the range of 25–150 °C corresponds to the loss of solvent and coordinated water molecules (calculated 12.65% for five water molecules per two Cd atoms), as shown in Figure S4 in the Supporting Information. To further test the stability of the porous framework, we examined the powder samples by X-ray diffraction (XRD) analysis. Water molecules were removed by heating **1** at 150 °C for 2 h. Powder XRD patterns of as-synthesized **1** and dehydrated samples show only minor changes (Figure S5 in the Supporting Information), which indicates that the porous framework can still stably exist even when water molecules are lost.

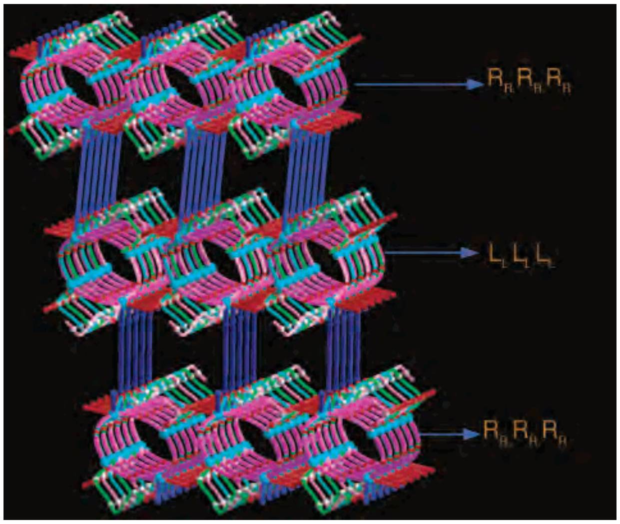

Figure 4. 3D framework of **1** showing its chiral layers and micropores. Triple-helical chains are marked as sky, rose, and bright green, while single-helical chains are marked as purple. Blue sticks represent 4,4′-bpy molecules. R, L = triple helices. Subscripted R, L = single-helical chains.

Excitation of solid samples at $\lambda = 360$ nm produces luminescence peaks with a maximum at 406 nm for **1** (Figure S6a in the Supporting Information). The emission band might be attributed to the intraligand emission from m-bptc (392 nm; Figure S6b in the Supporting Information).

In summary, a new flexible ligand of m-H_4bptc having the potential to form a helix has been introduced to construct helical coordinational polymers. In this paper, we present an unprecedented architecture: a 3D microporous coordination network having chiral layers constructured from interweaving homoaxis triple- and single-helical chains. XRD analyses show that the framework is stable subject to loss of both guest and coordination water molecules. More efforts will focus on the construction of novel coordination polymers by reacting this ligand and its isomeric analogue with other metal ions.

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Supporting Information Available: X-ray crystallographic data in CIF format, hydrogen-bond table, packing diagram, thermal gravimetric curve, powder XRD patterns, and fluorescent emission spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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