

Interweaving 3D Network with Double Helical Tubes Filled by 1D Coordination Polymer Chains

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Received May 16, 2004

The hydrothermal reaction of mellitic acid, 4,4'-bipyridine, and Cu(CH₃COO)₂·H₂O gave rise to a novel 3D supramolecular architecture interpenetrated by three types of coordination polymer motifs. Two independent {[Cu₂(mellitate)(4,4'-bpy)(H₂O)₂]²⁻} 3D polymers incorporating helical substructures were interwoven into a 3D network with double-stranded helical tubes that host 1D linear polymers [Cu(4,4'-bpy)(H₂O)₄]²⁺]_n.

Helical structures have received much attention in coordination chemistry and materials chemistry¹ over the past decade because of the fundamental role of helicity in biology; the potential applications of such structures in the fields of supramolecular chemistry, asymmetric catalysis, and non-linear optical material; and the aesthetically appealing structural topology. Consequently, many single-, double, and higher-order stranded helical complexes have been generated by self-assembly processes. However, the infinite double helices remain quite rare.^{2,3} No examples of infinite double helices with large tubes in the spiral direction have been described, although there are some reports of cavities in other directions of the helices.^{3,4}

Structural interpenetration has been widely involved in supramolecular chemistry systems,⁵ and some helical structures reported in the literature have been constructed by interpenetration.² Usually, interpenetration precludes the existence of frameworks with very large cavities.⁶ Yaghi and co-workers made use of the strategy for the design of a highly porous and structurally stable coordination network in which interwoven pairs of metal–organic frameworks were mutually reinforced.⁷ Several examples of coordination networks constructed by chemically or crystallographically distinct polymeric building motifs⁸ have been reported. In this communication, we present a first example of a self-assembled 3D architecture that comprises interesting double helical host tubes filled by 1D guest metal–organic polymer chains.

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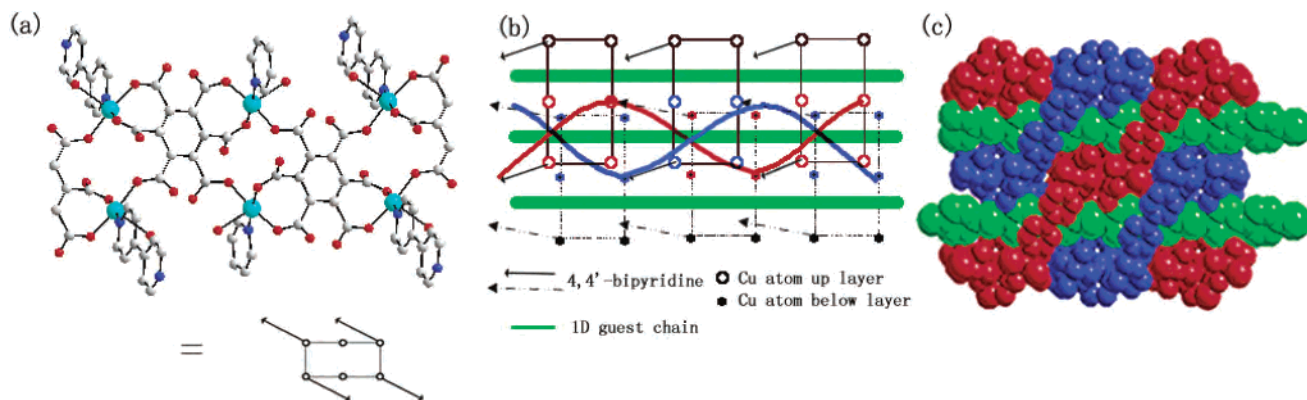


Figure 1. (a) ORTEP plot of the expanded building block of host polymers; Cu = sky blue, N = deep blue, O = red. (b) Schematic representation of constructing host polymer (deep blue line represents one helix, and red represents the other) and the 1D guest chains through the double-stranded helix, where the rectangle represents the zigzag chain. (c) View of the architecture along [001]; red represent one helical coordination polymer, deep blue represents the other, and green represents the 1D infinite guest chain. H and H₂O molecules are omitted for clarity.

The hydrothermal reaction of mellitic acid, 4,4'-bpy, and Cu(CH₃COO)₂·H₂O produced blue crystals⁹ of a novel 3D interpenetrated supramolecular complex in high yield. X-ray crystal structural analysis¹⁰ revealed that the architecture consists of three polymeric motifs (Figure 1): one is the guest cation with a [Cu(4,4'-bpy)(H₂O)₄]²ⁿ⁺ infinite 1D chain, the other two have the same component of {[Cu₂(mellitate)(4,4'-bpy)(H₂O)₂]²⁻]_n. In total, the architecture can be formulated as {[Cu₂(mellitate)(4,4'-bpy)(H₂O)₂]²⁻·[Cu(4,4'-bpy)(H₂O)₄]²⁺]_n. TGA data suggest that the complex is almost unchanged when heated to 153 °C (Figure S3, Supporting Information)

The host anion network is based on the expanded building block consisting of three mellitate anions, five 4,4'-bpy ligands, and six square-pyramidally coordinated Cu(II) ions (Figure 1a). The interesting feature of the host polymer is that each mellitate ligand links four Cu(II) ions into an infinite zigzag chain that is represented by a rectangle. These rectangles are stacked into layers as shown in Figure 1b. Each rectangle connects to the adjacent rectangle at the other plane by the bridging 4,4'-bpy ligands to complete the infinite host 3D polymer. The other infinite host polymer is formed in the same way. These two host polymers are structurally independent, and they are interwoven into 3D architecture with double-stranded helical tubes along the spiral direction. Examination of the crystal packing shows that host building blocks construct three-dimensional networks similar to the PtS structure (Figure S1). Large tubes are arranged along the spiral direction. The most significant structural feature is that the tubes are filled with guest infinite 1D linear [Cu-

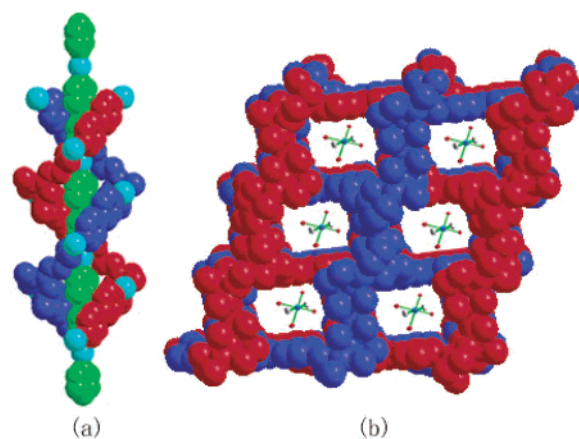


Figure 2. (a) Description of the helical tube in detail; red and deep blue represent the two strands of the double-stranded helix; Cu = blue; some C and O atoms of the mellitate and water molecules were omitted for clarity. (b) Representation of the space-filling 3D anion framework with 1D open tubes and the cationic chains through the tubes viewed along [010].

(4,4'-bpy)(H₂O)₄]²ⁿ⁺ polymer chains just like cables (Figure 1b and c and Figure 2b). Each tube is composed of two 2(1) helices with right-handedness (Figure 2a). The period of the helix is 22.3 Å by the centroid of Cu(II) ions; the distance within the double helix is about 11.16 Å along the spiral direction, and the dimension of the helical tube is approximately 8 Å × 7 Å. Cu(II) in the 1D guest polymer is six-coordinated in slightly distorted octahedral coordination, with the equatorial plane consisting of two oxygen atoms from H₂O molecules and two nitrogen atoms from 4,4'-bpy ligands, with the other two oxygen atoms from the H₂O molecules occupying the axial sites.

It should be noted that there are π-π and C-H...π interactions^{2a,11} between the three 4,4'-bpy moieties from the guest and host polymers and that the 4,4'-bpy ligands of the framework interact with each other in an offset fashion, with face-to-face and centroid-to-centroid distances of ca. 3.43 and 3.93 Å, respectively. Thus, π-π and C-H...π interactions, as well as the electrostatic attraction between the guest polymers and the double helices, are undoubtedly responsible for the cohesion of the whole architecture. These interactions

- (9) Synthesis of the compound: A mixture of mellitic acid (0.25 mmol), 4,4'-bpy (0.50 mmol), and Cu(CH₃COO)₂·H₂O (0.75 mmol) in 15 mL of H₂O was heated at 145 °C for 3 days in a Teflon-lined 23-mL bomb, and blue crystals were obtained (yield: 70.7%). Anal. Calc. for C₃₂H₂₈Cu₃N₄O₁₈ (%): C, 40.58; H, 2.98; N, 5.91. Found: C, 40.38; H, 2.58; N, 6.03. IR (KBr/pellet, cm⁻¹): 3434 (vs), 1634 (vs), 1613 (s), 1563 (ms), 1544 (sh), 1422 (vs), 1398 (sh), 1334 (ms), 1221 (w), 1080 (w), 1067 (w), 904 (m), 839 (m), 818 (s), 645 (s).
- (10) Crystal data were measured as follows: C₃₂H₂₈N₄O₁₈Cu₃, *M*_r = 947.20, blue crystal (0.52 × 0.32 × 0.26 mm), monoclinic, space group *P2*/*c*, *a* = 10.173(4) Å, *b* = 11.1598(4) Å, *c* = 14.8557(5) Å, β = 107.0350(10)°, *V* = 1613.07(10) Å³, *Z* = 2, *T* = 293(2) K, ρ_{calcd} = 1.950 g cm⁻³, *F*(000) = 958, μ = 2.057 mm⁻¹, *R*1 (wR2) = 0.0417 (0.1071) and *S* = 1.068 for 2817 reflections with *F*_o > 4σ(*F*_o).

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imply host–guest molecular recognition, and the chain polymer $[\text{Cu}(4,4'\text{-bpy})(\text{H}_2\text{O})_4]^{2n+}$ plays an important role to the formation of the 3D double helical¹² interwoven architecture.

In summary, we present an unprecedented architecture: a PtS-like interpenetrating network with large helical tubes that are suitable for the incorporation of 1D guest metal–organic polymers. The results show that the interpenetrating network can include other infinite linear polymers. They also show that the guest polymers play an important role in the formation of double-stranded helical tubes through specific

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host–guest interactions. We are presently exploring a method of replacing the guests by other polymers.

Acknowledgment. The authors acknowledge financial support from the State Key Basic Research and Development Plan of China (001CB108906), the NNSF of China (Nos. 29733090 and 20173063), Key Project in KIP of the CAS (KJCX2–H3), and the NSF of Fujian Province (E0020001).

Supporting Information Available: Experimental section and crystal data, figures of magnetic susceptibility and TGA curves, X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC049363G