Water Molecules as Binders in Transformation of 2D Coordination Polymer $[Cu(4,4'\text{-bpy})_2(OTf)_2]_n$ into Parallel Aligned 3D Architectures

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Solvent-mediated structural transformation of $\{[Cu(4,4'\text{-bpy})_2(OTf)_2]\cdot 2CH_3CN\}_n$ coordination polymer (CP) was crystallographically characterized and confirmed the formation of infinite linear water networks that bind metal centers through the interplay of coordination and hydrogen bonding of water molecules.

Coordination complexes with infinitely repeating cavities of regular shapes and sizes have been the focus of intense research for their superb properties useful in the development of heterogeneous catalysis[1–6] and small molecule absorption materials to name but a few.[7–12] Adaptive expansion of the framework geometries in the event of gas absorption recognized in some 2D architectures is particularly interesting for studying dynamic phenomena in crystal structures.[4,7,8,13–17] In addition, recent studies show promising results in the development of novel proton conductors, which employ infinite assembly of water molecules in the internal cavities of CPs as conducting pathways.[18] Generally, the synthesis of CPs relies on spontaneous assembly that leads to a thermodynamic product, and further modification of the coordination sphere, with the exception of anion exchange,[19,20] has hardly been performed mainly due to limited solvation capability or considerable disintegration of the framework. However, if the parent polymer were dissolved in an appropriate solvent system without extensive structural decomposition, a drastic rearrangement may be inflicted on the framework topology via complexation with incoming solvents and/or solutes.

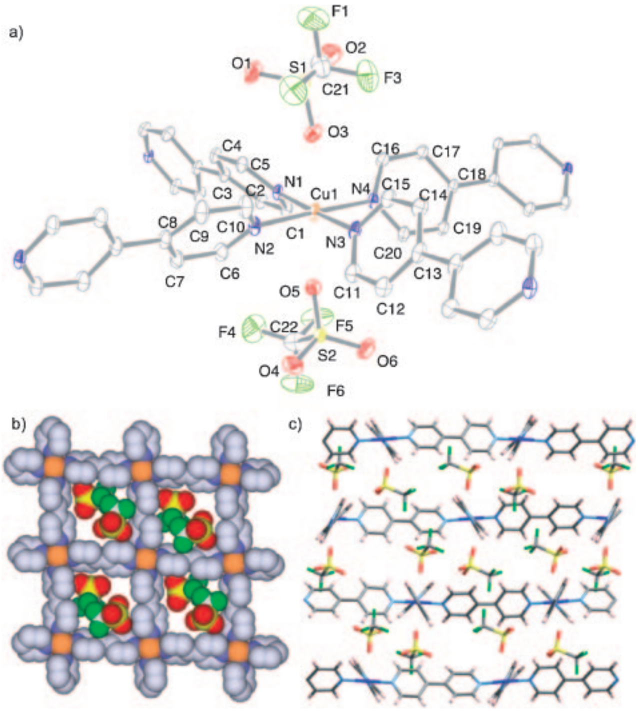

Figure 1. (a) ORTEP drawing of complex **1**. Selected bond distances/Å: Cu(1)–N(1) = 2.025(2), Cu(1)–N(2) = 2.028(2), Cu(1)–N(3) = 2.030(2), Cu(1)–N(4) = 2.028(2), Cu(1)–O(3) = 2.408(3), Cu(1)–O(5) = 2.367(3). (b) Space filling model of the framework (*bc* plane). Hydrogen atoms on 4,4′-bpy and solvent molecules are omitted. Only triflate ligands belong to adjacent layers are shown. (c) Wireframe model of **1** along the *bc* plane showing the layer arrangement. Atom colors: copper, brown; carbon, gray; nitrogen, blue; oxygen, red; fluorine, green; sulfur, yellow; and hydrogen, pink.

In this report, solvent-assisted structural reorganization of a 2D open grid CP is demonstrated in water rich media and characterized by single crystal X-ray diffraction, which shows striking differences in topology due to the formation of unprecedented water networks that bind 2D sheets into an aligned 3D architecture. We employed a 2D open grid framework of $\{[Cu(4,4'\text{-bpy})_2]^{2+}\}_n$ assembled from Cu^{II}, which favors a square planar arrangement, and 4,4′-bipyridine (4,4′-bpy), a ubiquitous linear spacer ligand, as the initial constituents.[21,22] To date, several analogs have been prepared from BF_4^-, PF_6^-, and $CF_3SO_3^-$ (triflate; OTf^-) salts of Cu^{II}, and their crystal structures have been determined by single crystal X-ray diffraction[13,14,19,23,24] except $\{[Cu(4,4'\text{-bpy})_2(OTf)_2]\cdot 2C_2H_5OH\cdot H_2O\}_n$, which was solved primarily from its powder diffraction pattern.[13] Therefore, we attempted complexation of $Cu(OTf)_2$ with 4,4′-bpy that provided X-ray quality crystals. A subsequent diffraction study confirmed a structure of $\{[Cu(4,4'\text{-bpy})_2(OTf)_2]\cdot 2CH_3CN\}_n$ (**1**), in which two triflate anions loosely coordinated to the axial sites of the metal (Figure 1a). Equatorial coordination environments are virtually identical to those found in complexes prepared using other Cu^{II} salts. The planar frameworks have no bonding interaction with each other and stack in the sequence ABAB··· with interlayer separation being ca. 6.23 Å. The layer stacking is offset laterally because the terminal fluorine atoms in trans coordinated triflate anions penetrate into the adjoining grids (Figures 1b and 1c). Two acetonitrile molecules are also found in the crystal lattice.

As documented by Khlobystov et al., a CP with $Cu(4,4'\text{-bpy})_2$ framework is much less soluble in water than Ni, Co, Cd, and Zn analogs,[20] and complex **1** is no exception. However, it becomes moderately soluble if 20–50% (v/v) of water is added in acetonitrile, and blue crystals of $\{[Cu(4,4'\text{-bpy})_2(H_2O)_2](OTf)_2\cdot(4,4'\text{-bpy})\cdot 6H_2O\}_n$ (**2**) are obtained in several days (Figure 2a). The ORTEP drawing of the Cu^{II} center shows

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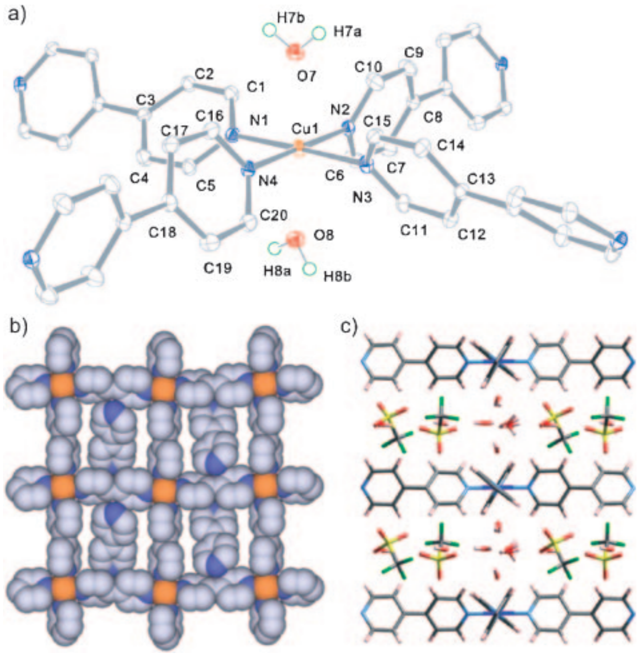

Figure 2. (a) ORTEP drawing of complex **2**. Selected bond distances/Å: Cu(1)–N(1) = 2.0245(14), Cu(1)–N(2) = 2.0388(14), Cu(1)–N(3) = 2.0243(14), Cu(1)–N(4) = 2.0447(14), Cu(1)–O(7) = 2.4196(19), Cu(1)–O(8) = 2.3815(19). (b) Space filling model of the framework (*bc* plane). Hydrogen atoms, water molecules, and triflate anions are omitted. (c) The layer structure viewed in the *ab* plane.

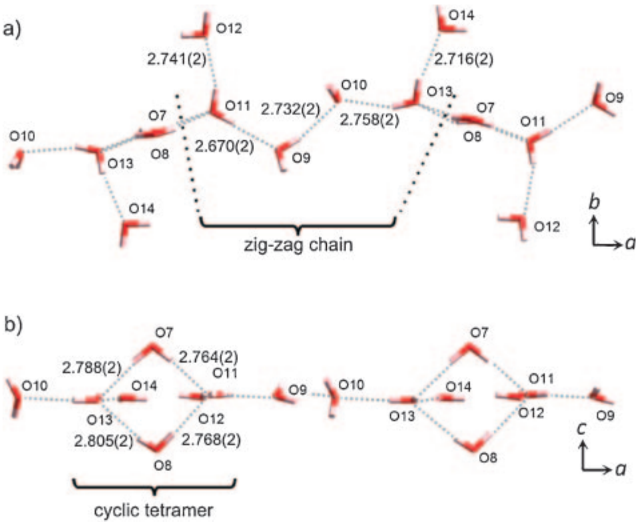

Figure 3. Drawings of the hydrogen-bond network viewed in the *ab* plane (a) and in the *ac* plane (b). Hydrogen bonds are shown as gray dashed lines with selected O···O distances/Å.

that while the equatorial coordination is essentially preserved, the axial positions are occupied by water molecules. Interestingly, the square grids of the frameworks are blocked by guest 4,4′-bpy molecules, providing a unique molecular panel-like appearance (Figure 2b). The most notable aspect of complex **2** is the manner in which eight (two coordinated and six uncoordinated) water molecules assemble in the inter-layer space, forming an infinite hydrogen-bond network. Six uncoordinated water molecules are hydrogen bonded with each other in a zig-zag chain, lying almost flat in the *ab* plane (Figure 3). The zig-zag chains are further hydrogen bonded to metal-coordinated water molecules that occupy diagonal corners of a water tetramer (Figure 3b), and to the nearest two guest 4,4′-bpy molecules via N–HO(10) interactions ($d_{av} = 2.795$ Å), thereby forming an infinite water chain along the crystallographic *a* axis. All the O···O hydrogen bonding distances are comparable to the value found in regular ice (2.74 Å),[25] and the average distances among the cyclic water tetramer (2.782 Å) is similar to that (2.794 Å) of another model in $\{[Cu(C_4H_6N_2)_2(C_4H_2O_4)](H_2O)_3\}_n$.[26] A projection along the chain direction helps to understand the manner hydrogen bonds link the metal centers and vertically align adjacent layers with the inter-layer separation of 8.42 Å as well as a templating effect of triflate anions (Figure 2c). To note, Noro et al. also trapped eight water molecules per Cu^{II}, however in quite a different manner, inside a 3D channel of Cu^{II}–4,4′-bpy based CP.[19]

This structural conversion is not specific to the above experimental conditions but the same results are obtained when acetone or methanol is employed in place of acetonitrile, implying the importance of labile coordination of the triflate anions in complex **1** for the succeeding conversion. In the solvent mixture, we assume that solvation of the 4,4′-bpy moiety in **1** with organic molecules facilitates expansion of the inter-layer spaces, while water molecules occupy trans positions due to their higher affinities for Cu^{II} than the triflate anions. Subsequently, the hydrogen-bond network extends to span the nearest two metal-coordinated water molecules and eventually pull adjacent layers together. In the meantime, although the framework is considered reasonably stable in its solid state,[19] partial disruption of the coordination interactions must occur in the solution to generate free 4,4′-bpy molecules, whose high affinity for hydrophobic environment drive themselves inside cavities to accomplish the panel-like morphology in **2**.

In conclusion, we achieved self-assembly of a hydrogen bond assisted 3D architecture, in which water molecules serve as molecular aligners that interlink the adjacent layers. Besides the synthetic interest, our discovery may serve to address several hot areas of research. For instance, preparation of stable water clusters or low-dimensional networks in crystalline host material has been intensively investigated aiming at better understanding of the unusual properties of water,[25,27,28] and our finding will be yet another example of those.[29–31] Also, solvent-mediated crystal engineering will enable surface self-assembly of polymer thin films through reorganization of the parent complex, and to this end we are actively investigating oriented growth of Cu(4,4′-bpy)$_2$ on a hydroxy-terminated surface for applications in separation membranes or sensors.[32,33]

Experimental

Synthesis. Complex **1** was prepared by dissolving Cu(CF$_3$SO$_3$)$_2$ (150 mg, 0.415 mmol) in mixed solvents of 2 mL of acetonitrile and 3 mL of distilled water in a small test tube. An acetonitrile buffer layer (3 mL) and a solution of 4,4′-bpy

(315.2 mg, 2.08 mmol) in acetonitrile (10 mL) were carefully layered. After a week, X-ray quality blue crystals were collected from the wall. Yield 163 mg (53.8%). Elemental analyses were performed with dried samples on a Perkin-Elmer 2400 element analyzer. Elemental analysis. Found: C, 37.34; H, 2.96; N, 8.05%. Calcd for $C_{22}H_{20}F_6N_4O_8S_2Cu$: C, 37.21; H, 2.84; N, 7.89%.[34] Complex **2** was obtained by dissolving complex **1** (10.4 mg, 14.3 μmol) in a mixture of acetonitrile (2 mL) and distilled water (1 mL). The solution was filtered and stood for 5 days under ambient atmosphere before blue crystals of **2** suitable for X-ray analysis precipitated. Yield 3.79 mg (23.5%). Elemental analysis. Found: C, 43.15; H, 2.87; N, 9.48%. Calcd for $C_{32}H_{30}F_6N_6O_9S_2Cu$: C, 43.46; H, 3.42; N, 9.50%.[35]

Structure Determination. X-ray diffraction data were collected on a Rigaku Saturn CCD area detector system using Mo Kα radiation ($\lambda = 0.71073$). A suitable crystal was coated with paraffin oil, mounted on a glass fiber, and immediately placed in a cold stream ($-150 \pm 10\,°C$) of N_2. Structure solution and refinements were carried out using SIR 2004 and SHELXL-97, respectively. The positions of H atoms in water molecules were taken from the difference electron density map and refined isotropically. Other H atoms were placed at calculated positions and refined as a riding model. One triflate anion in **1** was disordered over two positions and fixed at the position with a larger site occupancy factor of 0.81. The methyl group of one acetonitrile molecule and the nitrile group of another were also disordered with site occupancy factors of 0.64 and 0.5, respectively. Crystal data for **1**: $C_{26}H_{22}F_6N_6O_6S_2Cu$, monoclinic, $C2/c$ (No. 15), $a = 27.462(2)$, $b = 15.0421(9)$, $c = 16.4251(13)$ Å, $\beta = 107.459(4)°$, $V = 6472.4(8)$ Å^3, $Z = 8$, $R_1 = 0.0731$ ($I > 2\sigma(I)$), $wR_2 = 0.1861$, 30043 reflections measured, 7810 unique ($R_{int} = 0.0470$), 511 parameters. CCDC-739255. Crystal data for **2**: $C_{32}H_{40}F_6N_6O_{14}S_2Cu$, orthorhombic, $Pca2_1$ (No. 29), $a = 22.212(4)$, $b = 11.1351(19)$, $c = 16.837(3)$ Å, $V = 4164.2(12)$ Å^3, $Z = 4$, $R_1 = 0.0332$ ($I > 2\sigma(I)$), $wR_2 = 0.0800$, 38237 reflections measured, 9472 unique ($R_{int} = 0.0235$), 637 parameters. CCDC-737504. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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34 We assume that two water molecules occupy the axial positions instead of acetonitrile because the dried sample is prepared under ambient atmosphere.

35 It is difficult to determine the exact formula due to rapid loss of water molecules. Calculation includes only one out of six non-coodinated water molecules.