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Rational Design and Crystal Structure Determination of a 3-D Metal–Organic Jungle-Gym-like Open Framework

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A new three-dimensional (3-D) jungle-gym-like open metal–organic framework has been synthesized from a two-dimensional (2-D) layer compound using a heterogeneous pillar insertion reaction. Both the starting 2-D layer and the resulting 3-D open compounds have been characterized using X-ray crystallography.

A new class of porous materials, known as coordination polymers, which are constructed from transition metal ions and organic bridging ligands, have attracted a great deal of attention recently,[1] and a great deal of research effort has been devoted to the development, design, and synthesis of novel high porous metal−organic frameworks. One of the most rational methods used for the construction of three-dimensional (3-D) porous frameworks is to insert pillar moieties between the layers of two-dimensional (2-D) layered compounds (Figure 1).

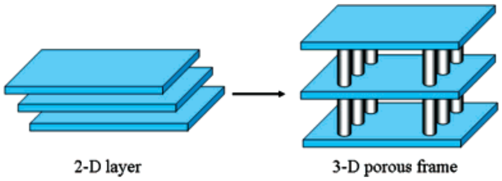

Figure 1. Schematic representation of a construction of 3-D porous framework by a pillar insertion strategy.

This strategy has already been successfully used in inorganic compounds, resulting in many pillared layer porous materials being synthesized, such as pillared montmorillonite and smectite.[2] On the other hand, the number of coordination compounds designed using this strategy is still low.[3] Recently, a series of 3-D Cu^{II}−dicarboxylate−dabco (where dabco = 1,4-diazabicyclo[2.2.2]octane) coordination frameworks, which exhibit an exceptionally high methane storage capacity, have been synthesized using a pillar insertion strategy.[4] However, due to difficulties in achieving crystallization and in structural characterization, the crystal structures of both the starting 2-D layer compounds and the resulting 3-D framework compounds have not been elucidated. In this paper, we report on the synthesis and determination of the crystal structure of novel 2-D and 3-D Cu^{II}−dicarboxylate coordination frameworks, hereafter referred to as 2-D and 3-D frameworks **1** and **2**, respectively. The 3-D framework, $[Cu(tfbdc)(dabco)_{0.5}]$ (**2**), was prepared by a heterogeneous pillar insertion reaction of $[Cu(tfbdc)(MeOH)]$ (**1**), in which tfbdc = tetrafluorobenzene-1,4-dicarboxylate and the pillar ligand = dabco. This pillar insertion reaction involves a sliding of the 2-D layers, resulting in a considerable increase in the channel size and

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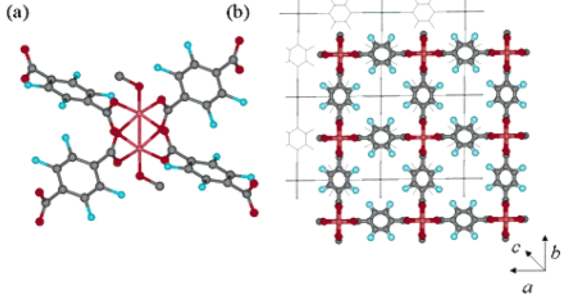

Figure 2. Crystal structure of **1**. (a) Paddle-wheel Cu^{II} building unit of **1**. (b) 2-D grid layer of **1**. The neighboring layer is drawn as black line. H atoms are omitted for clarity (Cu, orange; F, light blue; O, red; C, gray).

pore volume dimensions. The repulsion between the F atoms probably facilitates this reaction.

Compound **1** was prepared by reacting $Cu(HCOO)_2 \cdot 4H_2O$ and H_2tfbdc in MeOH/EtOH at $T = 298$ K. One of the green, plate-shaped crystals formed was chosen for the X-ray crystallography studies.[5] Figure 2 displays the crystal structure of **1**, showing the paddle-wheel-like clusters of Cu^{II} ions with axial MeOH ligands (Figure 2a) that are bridged by tfbdc ligands to form 2-D infinite layers. These layers form in a square grid configuration, with dimensions of 10.87 × 10.87 Å^2 (Figure 2b). These layers are stacked alternately, so that the paddle wheel Cu^{II} clusters of neighboring 2-D layers are located in the middle of the grid layer (i.e., an ABAB mode, see Figure 2b).

This results in there being no cavities large enough to accommodate any guest molecules (as the channel dimensions are ca. 3.8 × 3.1 Å^2, the only possible guest molecule candidates are He and H_2). The benzene rings of the tfbdc ligands are highly tilted against the *ac*-plane with a dihedral angle of 115.9°, which is attributed to the repulsion between F atoms of neighboring 2-D layers, and from the steric hindrance between the F atoms and carboxylate oxygen atoms. Compound **1** is not soluble in common organic solvents, such as MeOH, EtOH, and THF.

Compound **2** was prepared by the heterogeneous reaction of compound **1** with dabco in MeOH at $T = 373$ K in a stainless reaction vessel. (Although we confirmed that this reaction proceeds at ambient temperature, a high reaction temperature of $T = 373$ K was utilized to speed up the reaction.) During the reaction, the color of the crystals changed from green to yellow-green, but the crystal morphology did not alter with the slight change in crystal transparence. This degradation is attributed to structural changes in the crystals arising from the pillar insertion reaction. Single crystals are able to endure this type of drastic structural change, resulting in the degradation of the crystal transparence. To elucidate the crystal structure of **2**, we performed synchrotron X-ray powder diffraction measurements at the SPring-8, BL02B2 synchrotron facility in Japan.[6] Figure 3 shows the powder diffraction pattern of **2** and the result of the final Rietveld fitting.

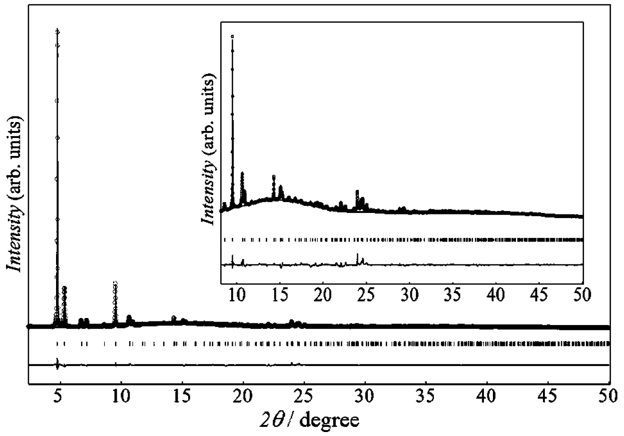

Figure 3. Synchrotron X-ray powder diffraction pattern of **2**, and the final result of Rietveld fitting.

The reliability factors based on the powder pattern, R_{wp}, and the integrated intensities, R_I, were 3.04% and 3.75%, respectively.[7] Compared with **1**, both the cell parameters and the space group were drastically changed after the reaction (**1** = monoclinic, $C2/m$, $a = 15.139$ Å, $b = 15.426$ Å, $c = 10.676$ Å, and $\beta = 131.27°$, and **2** = tetragonal, $P4/mmm$, $a = 10.866$ Å, $c = 9.6705$ Å). Figure 4a,b shows the crystal structure of **2** looking down the *c*- and *a*-axes, respectively.

Two-dimensional grid layers constructed by the Cu^{II} ions and the tfbdc groups are linked by dabco groups to form a 3-D jungle-gym-like open framework. The dihedral angle between the benzene rings and the *ac*-plane decreased from

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(5) Data collection for a green plate single crystal of **1** was performed on a Rigaku mercury charge coupled device (CCD) system using graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$) at 298 K. The structure was solved by direct methods and refined by full-matrix least-squares methods with the teXsan crystallographic software package from Molecular Sructure Corporation. Hydrogen atoms were placed at calculated positions, and their parameters were not refined. Crystallographic data for **1**: $C_9F_4H_4O_5Cu$, $M = 335.70$, monoclinic, space group $C2/m$ (No. 12), $a = 15.139(4)$ Å, $b = 15.426(9)$ Å, $c = 10.676(1)$ Å, and $\beta = 131.270(3)°$, $U = 1873(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.190$ g·cm^{-3}, $2\theta_{max} = 54.18°$, 1962 reflections measured, 1297 observed ($I > 3.00\ \sigma(I)$), 91 parameters, $R = 0.0776$, $R_w = 0.0841$. These data are available from the Crystallographic Data Centre as supplementary publication CCDC-235831. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (Fax: (+44)1223-336-033. E-mail: deposit@ccdc.cam.ac.uk.)

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(7) The crystal structure determination of **2** was carried out from synchrotron X-ray powder diffraction data. Data collection was performed using a Debye−Scherrer camera and imaging plate as a detector at SPring-8, BL02B2. The powder crystal was sealed in the glass capillary (0.4 mm inside diameter). Cell parameters were determined by indexing program DICVOL91.[8] A Le Bail structureless profile fitting algorithm affords refined cell parameters, peak shift parameters, and profile parameters. The peak shape was modeled by a Split−Pearson function. The structure refinement was performed by the Rietveld method with RIETAN software.[9] Soft constraints about bond angles and bond distances were adapted throughout the refinement. Hydrogen atoms were placed at calculated positions, and their parameters were not refined. Crystallographic data for **2**: $C_{11}F_4H_6O_4$-Cu, $M = 341.70$, $\lambda = 0.90229$ Å, tetragonal, space group $P4/mmm$ (No. 123), $a = 10.8661(1)$ Å, $c = 9.6703(5)$ Å, $U = 1141.79(6)$ Å^3, $Z = 2$, $T = 298$ K, $2\theta_{min} = 2.4°$, $2\theta_{max} = 50.0°$, step size 0.1°, number of reflections = 337, $R_{wp} = 0.0304$, $R_I = 0.0375$. These data are available from the Crystallographic Data Centre as supplementary publication CCDC-236931. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (Fax: (+44)1223-336-033. E-mail: deposit@ccdc.cam.ac.uk.)

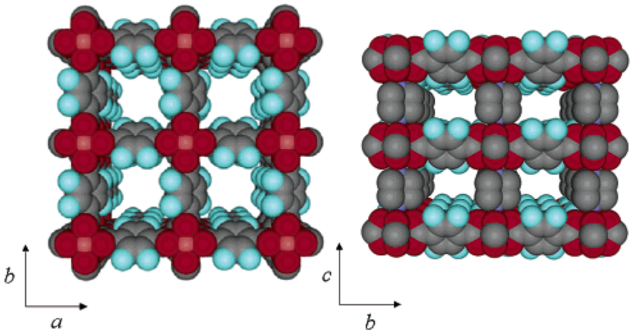

Figure 4. Crystal structure of **2** with CPK model: (a) down from *c*-axis, (b) down from *b*-axis. H atoms and disordered atoms are omitted for clarity (Cu, orange; F, light blue; O, red; C, gray).

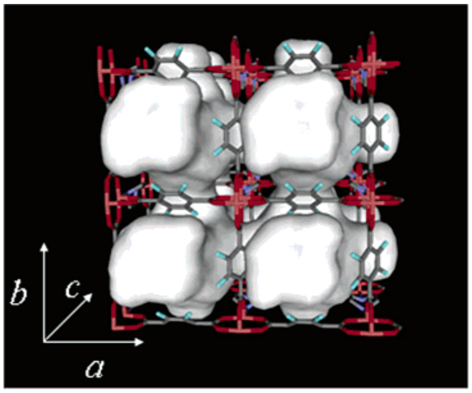

Figure 5. A stick representation of the crystal structure of **2** with accessible 3-D interconnected open channel along the *c*-axis, which is shown as a white surface (Cu, orange; F, light blue; O, red; C, gray).

115.9° to 35.8°. This results from the increase in distance between the 2-D layers, as induced by the pillar insertion reaction. Figure 5 shows the solvent-accessible pore surface, which is defined by the possible surface of a rolling sphere with a diameter = 3.0 Å.

As illustrated in Figure 5, 3-D interconnected channels exist, and their dimensions looking down the *c*- and *a*-axis are approximately 6.3 × 6.3 and 3.5 × 4.7 Å^2, respectively. The calculated solvent-accessible pore volume and surface area are 0.54 cm^3/g (0.55% of unit cell volume) and 2020 m^2/g, respectively (using a sphere with diameter of 3.0 Å).[10] No guest molecules were found in the channels of **2**, probably due to disorder in the guest molecules. This type of 3-D open framework has been reported before, but this is the first characterization of such a compound's crystal structure using X-ray crystallography.

Interestingly, the sliding of the 2-D layers during the heterogeneous pillar insertion reaction resulted in a drastic change of stacking mode of the 2-D layers from the ABAB mode to a nonoffset mode. This probably is associated with the repulsion between the F atoms, which facilitates the sliding of the 2-D layers. This framework is stable and retains its original structure after desolvation, which was confirmed by X-ray diffraction measurements under reduced pressure at higher temperatures.

In conclusion, we have succeeded in synthesizing novel fluorinated 3-D open frameworks[11] using a heterogeneous pillar insertion reaction that involved the sliding of the 2-D layers, and we have successfully characterized their structure using single crystal and synchrotron X-ray powder crystallography.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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