Porous Coordination Networks

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Ab Initio Powder Diffraction Structure Analysis of a Host–Guest Network: Short Contacts between Tetrathiafulvalene Molecules in a Pore**

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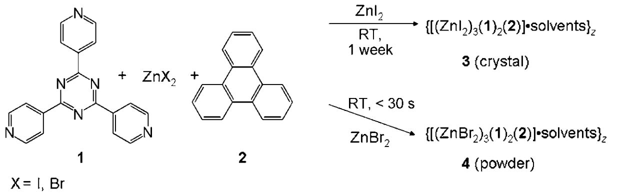
Many crystal structures of porous coordination networks have been solved by single-crystal X-ray crystallography, providing detailed molecular structural information on framework, guest arrangement, and even reactive intermediates generated in situ.[1] Such detailed structural analysis facilitated the explosive development of porous coordination networks in the last 15 years. On the other hand, although there are many examples of ab initio powder X-ray diffraction (PXRD) analysis of inorganic materials, organic solids, nonporous coordination networks, and discrete small molecules,[2] there are only few reports of ab initio PXRD analysis of porous coordination networks describing guest behavior (guest exchange, gas adsorption, etc.).[3] This is because ab initio PXRD analysis is considerably more challenging than single-crystal structure determination. Porous coordination networks usually have large unit cells and often low symmetry that contribute to severe peak overlap which hampers accurate structure determination. By using high-resolution synchrotron PXRD and the simulating annealing method, we have now succeeded in solving the crystal structure of a biporous coordination network having an unprecedented arrangement of tetrathiafulvalene (TTF) molecules and a unit cell larger than 15000 Å^3.[4] The PXRD analysis revealed very short intermolecular S⋯S contacts between TTF molecules (3.370 Å) that have a nonplanar shape indicating a neutral form. Those findings agree with solid-state spectroscopic features.

A key issue in inducing intriguing physical properties in TTF is how to arrange the molecules.[5–8] We tried to achieve a unique arrangement of TTF molecules by using the pores of a porous coordination network.[9] We used the previously reported network $[(\mathrm{ZnI_2})_3(\mathbf{1})_2(\mathbf{2})]_n{\cdot}x\,\mathrm{C_6H_5NO_2}{\cdot}y\,\mathrm{CH_3OH}$ (**3**, where **1** is 2,4,6-tris(4-pyridyl)-1,3,5-triazine (TPT) and **2** is triphenylene; $x \approx 4$ and $y \approx 2$)[10] and prepared new isostructural $\mathrm{ZnBr_2}$ network **4** (Scheme 1) by instant synthesis.[3b] Compound **4** can only be synthesized kinetically as a uniform microcrystalline powder by fast addition of a solution of $\mathrm{ZnBr_2}$ in methanol to a vigorously stirred solution of **1** and **2** in nitrobenzene/methanol.[11] Hence, complete structure determination of **4** and host–guest system **4**·TTF was carried out by ab initio synchrotron PXRD analysis.[12]



Scheme 1. Selective synthesis of networks **3** and **4**.

When a light yellow single crystal of **3** was immersed in a solution of TTF (12.26 mg, 0.06 mmol) in cyclohexane (20 mL) for 12 h at 300 K, the crystal turned green. Synchrotron X-ray crystallography revealed the coordination network $[(\mathrm{ZnI_2})_3(\mathbf{1})_2(\mathbf{2})]_n{\cdot}\mathrm{TTF}{\cdot}2\,\mathrm{C_6H_{12}}$ (**3**·TTF). Network **3** has two types of pores, A and B.[10] The original nitrobenzene molecules in the pores were replaced by TTF and cyclohexane. The TTF molecules are selectively included in pore A, whereas cyclohexane molecules are located in both pores A and B (Figure 1). The TTF molecules interact with TPT through S⋯H−C (3.42 and 3.32 Å) contacts. The color change of the crystal indicates charge-transfer (CT) interaction

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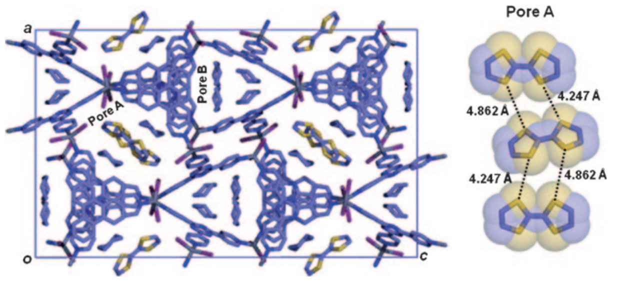

Figure 1. Synchrotron X-ray structure of **3**·TTF. Inclusion of TTF molecules occurs only in one of the two pore types. The TTF molecules are stacked along the *b* axis and the S···S distances are depicted.

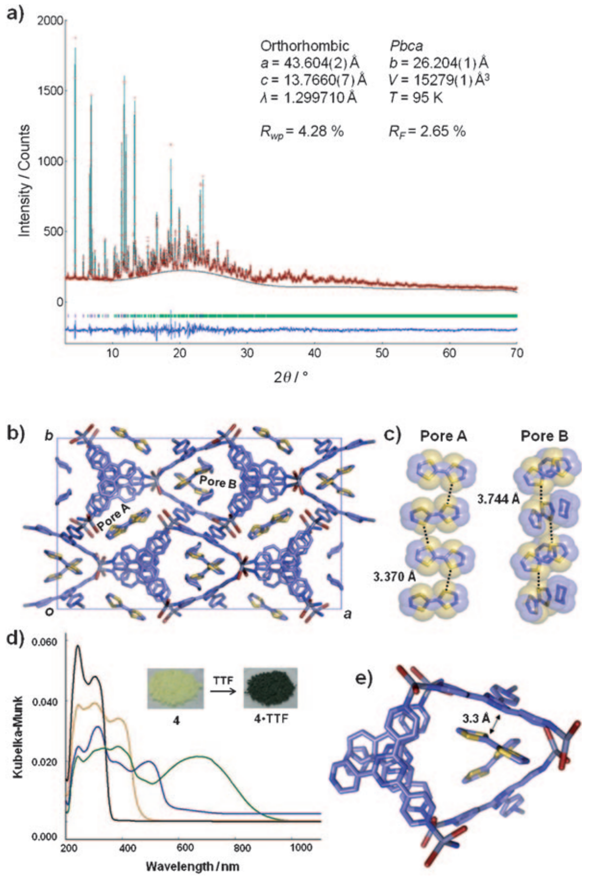

Figure 2. a) Experimental (red), calculated (pale blue), and difference (dark blue) PXRD profiles from the final Rietveld refinement of **4**·TTF. b) Crystal structure of **4**·TTF determined directly from ab initio synchrotron PXRD data. c) Pores A and B contain TTF molecules. Cyclohexane is included only in pore B. d) Diffuse-reflectance UV/Vis spectra of TPT (black), TTF (blue), network **4** (yellow), and **4**·TTF (green) and photographs of powder samples of **4** and **4**·TTF. e) Detailed view of pore B. Cyclohexane molecules have been omitted for clarity.

between electron-rich TTF and the electron-deficient triazine ligand.[13] The TTF molecules are oriented in the same direction and form one-dimensional columns along the *b* axis. The S···S distances among stacked TTF molecules are 4.247 Å (Figure 1), which are too large to expect conductivity along the one-dimensional array of TTF molecules. In fact, conductivity measurements on single crystals of **3**·TTF did not show electron transport.[14]

When the yellow microcrystalline powder of network **4** was immersed in a solution of TTF (12.26 mg, 0.06 mmol) in cyclohexane (20 mL) for 12 h at 300 K, the powder turned dark green overnight while maintaining good crystallinity. Elemental analysis suggested inclusion of two TTF and one cyclohexane molecules. To fully determine the crystal structure, ab initio PXRD analysis was carried out[15] by using the SA method[4] (i.e., global optimization method) implemented in the program DASH,[16] followed by Rietveld[17] refinement with the program RIETAN-FP.[18] The good agreement between the calculated and experimental PXRD patterns in the final Rietveld refinement clearly indicates that the structure is correct (Figure 2a). The resulting crystal structure, $[(\mathrm{ZnBr_2})_3(\mathbf{1})_2(\mathbf{2})]_n\cdot 2\,\mathrm{TTF}\cdot \mathrm{C_6H_{12}}$ (**4**·TTF), has the same topology as **3**·TTF. However, in **4**·TTF the TTF molecules are included in both pores A and B and cyclohexane molecules are only in pore B (Figure 2b) under the same guest-exchange conditions as for **3**·TTF.

The S···S distances among stacked TTF molecules in pore A of **4**·TTF are shorter (ca. 3.370 Å) than those in pore B (3.744 Å). In both pores, the TTF molecules are not stacked through π–π interactions but through S···S contacts, probably due to the pore-confinement effect (Figure 2c). Such a short contacts among TTF molecules may allow conductivity along the pores (*c*-axis direction). However, due to the small crystal size (< 10 μm), single-crystal conductivity measurement was unsuccessful, and measurements on pellets after gently grinding the network showed no conductivity. The absence of conduction bands in solid-state UV/Vis spectra (Figure 2d and Figure S4 of the Supporting Information) of both **3**·TTF and **4**·TTF are also in agreement with the experimental results.

In solid-state UV/Vis spectra, we observed a strong characteristic CT band (500–950 nm) for **4**·TTF, but a comparatively weak CT band (500–925 nm) for **3**·TTF. In pore A, TTF molecules of both networks lie almost perpendicular to TPT (Figures 1 and 2b), and the shortest distance in **3**·TTF between TTF (C44) and TPT (N29) of 4.65 Å is far from a van der Waals contact (3.25 Å) and prevents efficient electron transfer between them. However, in pore B of **4**·TTF, TTF molecules lying close (ca. 3.3 Å) and almost parallel to TPT (Figure 2e) facilitate electron transfer between host and guest. Such interactions rather than S···S contacts result in a different TTF stacking to that observed in pore A.

We have demonstrated by ab initio PXRD analysis of a kinetically prepared biporous coordination network that the network pore can force TTF molecules to form a unique arrangement that results in induction of host–guest CT interactions and short guest–guest (S···S) contacts. Interestingly, an isostructural network containing $\mathrm{ZnI_2}$ instead of $\mathrm{ZnBr_2}$ could not form such intermolecular interactions. It indicates that slight modification of a pore can make a big difference in guest recognition and arrangement. Such an approach can be extended to other porous coordination networks, which may find intriguing applications.[19]

Experimental Section

C,H,N analysis calcd (%) for $[(ZnI_2)_3(\mathbf{1})_2(\mathbf{2})]\cdot TTF\cdot 2\,C_6H_{122}$ (**3**·TTF): C 38.15, H 2.59, N 7.94; found: C 38.20, H 2.47, N 8.00.

C,H,N analysis calcd for $[(ZnBr_2)_3(\mathbf{1})_2(\mathbf{2})]\cdot 2\,TTF\cdot 0.45\,C_6H_{12}$ (**4**·TTF): C 41.78, H 2.52, N 8.51; found: C 41.75, H 2.78, N 8.11.

Single crystal X-ray diffraction data for **3**·TTF: $C_{78}H_{76}I_6N_{12}S_4Zn_3$, $M_r = 2267.26$, orthorhombic, space group *Pbca*, $a = 27.4690(1)$, $b = 13.6888(3)$, $c = 45.9961(5)$ Å, $V = 17\,295.3$ Å^3, $T = 85$ K, $Z = 8$, $\rho_{calcd} = 1.741\ g\,cm^{-3}$, 17483 unique reflections out of 26240 with $I > 2\sigma(I)$, 928 parameters, $1.44 < \theta < 29.48$, final $R_1 = 0.0478$ and $wR_2 = 0.1251$.

A high-quality powder X-ray diffraction pattern of **4**·TTF was recorded at 95 K in transmission mode (0.3 mm capillary; synchrotron radiation, $\lambda = 1.299710$ Å; 2θ range: 3.0–70.0; step width: 0.01°; data collection time 20 s) on a diffractometer equipped with a blue imaging plate detector at SPring-8 BL19B2 beam line.

Ab initio structure determination of **4**·TTF: The PXRD pattern was indexed by using the program DICVOL[20] to give an orthorhombic unit cell ($a = 43.63793$, $b = 26.19466$, $c = 13.77310$ Å) with good figures of merit. The space group was assigned from systematic absences as *Pbca*. Unit cell and profile refinement, carried out by using the Pawley method, led to excellent fit ($R_{wp} = 13.49$, $\chi^2 = 6.347$) for these lattice parameters and space group. Structure solution was carried out by the simulated annealing method with the program DASH.[16] $[(ZnBr_2)_3(TPT)_2]$ in which rotation about the Zn−N bond is allowed, triphenylene, two TTF molecules, and cyclohexane as rigid groups in the asymmetric unit and $Z = 8$ for space group *Pbca* were introduced by using a constrained Z-matrix description. Twenty runs of 2×10^6 Monte Carlo moves each were performed. The best structure obtained (profile $\chi^2 = 36.30$) was taken as the starting structural model for Rietveld refinement. The Rietveld refinement of **4**·TTF was performed with the program RIETAN-FP[18a] and VESTA.[18b] Restraints but no constraints for all bond lengths were employed to maintain the molecular geometry. Thermal temperature factors were refined isotropically, and uniform values were applied to the framework, triphenylene, and cyclohexane. Uniform thermal temperature factors were applied to two independent TTF molecules individually. Final Rietveld refinement: $a = 43.604(2)$, $b = 26.204(1)$, $c = 13.7660(7)$ Å, $V = 15\,729(1)$ Å^3, $R_{wp} = 4.28\,\%$ ($R_e = 7.11\,\%$), $R_p = 3.32\,\%$, $R_B = 4.11\,\%$, $R_F = 2.65\,\%$; 6701 profile points; 443 refined variables.

CCDC 806586 (**3**·TTF), 806587 (**5**) and 806588 (**4**·TTF) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[10] Pore A is roughly cylindrical and is mainly surrounded by the hydrogen atoms of an infinite aromatic stacking of TPT and triphenylene. Pore B is trigonal-prismatic and is surrounded by three walls: two of them are π faces of ligand TPT and the third corresponds to the edges of TPT and triphenylene. Detailed description of network **3**: O. Ohmori, M. Kawano, M. Fujita, *Angew. Chem.* **2005**, *117*, 1998–2000; *Angew. Chem. Int. Ed.* **2005**, *44*, 1962–1964.

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[14] For electron conductivity measurements of (**3·TTF**) and (**4·TTF**), see SI.

[15] For the structure solution, [$(ZnBr_2)_3(TPT)_2$] in which rotation about the Zn−N bond is allowed, triphenylene, two TTF molecules, and cyclohexane were used as rigid groups in the asymmetric unit. For details, see Experimental Section.

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