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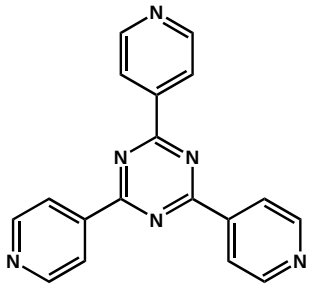
A Springlike 3D-Coordination Network That Shrinks or Swells in a Crystal-to-Crystal Manner upon Guest Removal or Readsorption**

Kumar Biradha and Makoto Fujita*

The recent upsurge in the crystal engineering of coordination nets is caused by their several useful functional properties such as porosity, use in separation and catalysis, and magnetism.[1] Particularly, some metal–organic 3D networks were shown to be porous: the networks and their crystalline nature are intact after the guest removal and the emptied network had the ability to reabsorb and desorb guest molecules.[2] Here we show another class of compounds in which a 3D network contracts after guest removal and expands after a guest is readsorbed; this class of molecules can also exchange guest molecules without affecting the 3D network or its crystalline nature. Linear and rigid bifunctional ligands (1D) such as 4,4′-bipyridine form several networks with various properties.[3] However, its 3D analogue, 2,4,6-tris(4-pyridyl)triazine (TPT, **1**), has not been explored to that extent.[4] In solution chemistry we have already shown that panel-like ligands such as **1** self-assemble into 3D polyhedra upon reaction with



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convergent metal centers.[5] Simultaneously, in coordination polymers, Robson and co-workers showed that ligand **1** can self-assemble into 3D networks upon reaction with transition metals.[6] We report here the unprecedented dynamic nature of a doubly interpenetrated (10,3)-b network that assembles from **1** and ZnI_2: that is, it shrinks when guest molecules are removed and swells when they are returned (Figure 1)

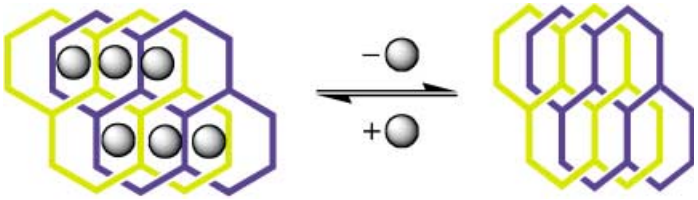

Figure 1. Schematic representation of the contraction or expansion of the 3D network on the removal or addition of guest molecules, respectively.

without destruction of the crystalline nature.[7] Furthermore, we show that guest molecules can control the formation of doubly interpenetrated and non-interpenetrated networks of the same (10,3)-b configuration. Batten and Robson disclosed that **1** with $ZnCl_2$ forms a similar type of doubly interpenetrated network.[8]

The diffusion of a solution of ZnI_2 in MeOH into a nitrobenzene/MeOH solution of **1** resulted in single crystals of the complex $[\{(ZnI_2)_3(\mathbf{1})_2{\cdot}6\,C_6H_5NO_2\}_n]$ (**2**). Single-crystal analysis of the complex revealed the formation of a doubly interpenetrated 3D network.[9]

In the crystal structure of **2**, the Zn atoms adopt a tetrahedral geometry as the I atoms and pyridine moieties of TPT occupy two sites each. The shortest circuits in the 3D network contain ten molecules of **1** and ten Zn atoms (Figure 2a) and the network can be classified as having a (10,3)-b configuration, if the Zn atoms are considered to be spacers and the moieties of **1** to be three connected nodes. Along the (010) axis, the network can be regarded as a helical, hexagonal 3D network with a pitch length of 15 Å (Figure 2b).[10] Two of these nets are interpenetrated such that continuous channels exist (Figure 2c,d). Despite this interlinking of the networks, 60% of the unit-cell volume is occupied by the nitrobenzene molecules, which are partially disordered. Interestingly, the interpenetration of the networks does not interfere in channel formation as the channels run in a direction overlapping that of the two networks (Figure 2d). The use of cyanobenzene in place of nitrobenzene also resulted in a similar complex $[\{(ZnI_2)_3(\mathbf{1})_2{\cdot}6\,C_6H_5CN\}_n]$ (**3**).[11]

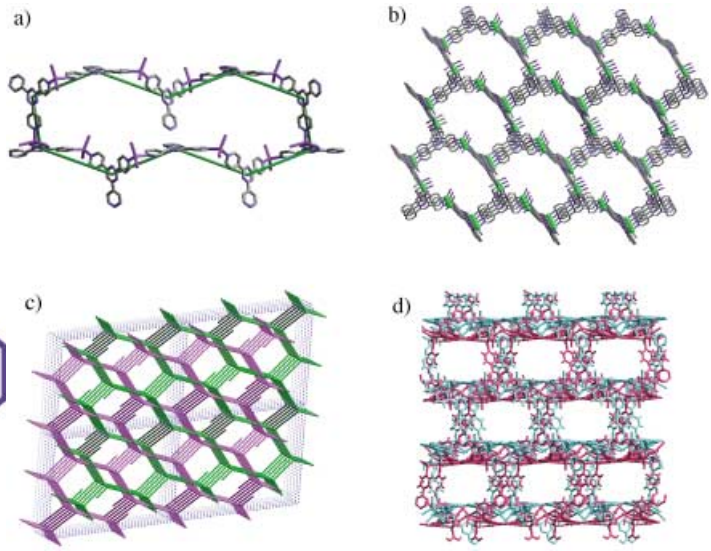

Figure 2. The crystal structure of **2**: a) the shortest circuit formed by ten molecules of **1** and ten Zn atoms (C = gray, N = blue, and Zn and I = magenta). The centers of the **1** molecules are joined by a green line; b) view of 3D network in the (010) direction (C = gray, N = blue, Zn = light green, and I = magenta); c) view of the interpenetrated networks from the (010) direction. Note that the ligands are denoted by nodes and the Zn atoms by lines; d) the formation of channels through the interpenetrated networks. In c) and d) the networks are differentiated with two different colors.

A remarkable feature of the complexes **2** and **3** is the compression of the networks, without destroying the crystalline nature, when the guest molecule is released from the crystals (Figure 1). The crystals of **2** or **3** were left at room temperature to equilibrate with the atmosphere for one day. The color of the crystals changed from colorless to light yellow. The single-crystal analysis of these crystals of **2** and **3** from which the some of the guest molecules have escaped (**2′** and **3′**, respectively) indicated large differences in unit-cell parameters from their parent crystals. The crystal-structure determinations revealed the compression of the networks with unchanged network connections. Although the crystal structures of complexes **2** and **3** are very similar, those of **2′** and **3′** are not the same because of differences in the compression of the networks.

The crystal system of **2′** is triclinic while the crystals of **2** are monoclinic.[12] In contrast, the crystal system of **3′** is the same as that of **3** or **2**, because contraction of the network occurred only in the (100) direction.[13] The unit-cell volumes of **2′** and

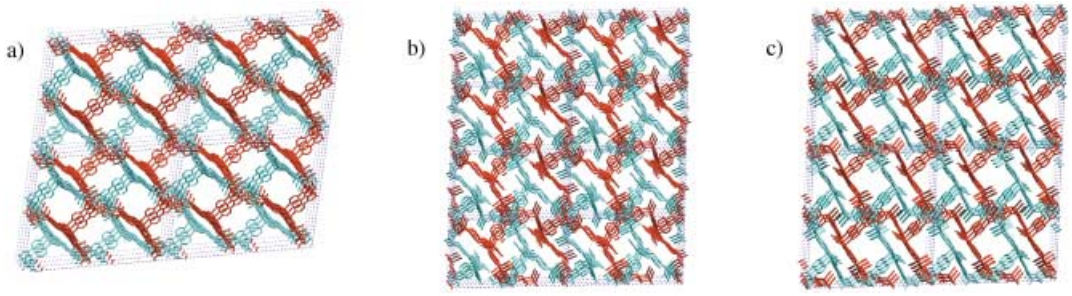

Figure 3. Illustration of interpenetrated networks before and after contraction of the crystal structure: a) **2** or **3**; b) **2′**, and c) **3′**. Notice the massive changes which occurred.

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3′ are reduced by 23 and 20% from those of **2** and **3**, respectively, because of the network compression (Figure 3). The intermolecular Zn–Zn distances became much shorter after compression, both in **2′** and **3′**. For example, before compression the shortest intermolecular Zn–Zn distances in **2** and **3** are 6.9 and 7.0 Å, respectively, while after compression they are 5.2 and 5.8 Å in **2′** and **3′**, respectively. Similarly, the shortest centroid–centroid distances of the ligand before compression are 8.2 Å for both **2** and **3**; after compression they are 5.1 and 7.0 Å for **2′** and **3′**, respectively. Remarkably, when the crystals of **2′** were placed in nitrobenzene for one day, the network expanded to reproduce the original crystals of **2**.[14] The guest molecules were removed completely from **2** or **3** by heating the crystals. The diffraction of these crystals, from which the guest molecules had been fully removed, enabled the determination of the cell parameters which are the same as those for **2′**.[15] This result indicates that complete guest elimination favors the structure **2′** over **3′**. Powder diffraction studies on these transformations at room temperature indicated continuous changes in the powder patterns with time.[16]

Interestingly, the crystals of **2** and **3** exhibited a remarkable ability to exchange nitrobenzene and cyanobenzene guest molecules for a variety of other guest molecules such as benzene, mesitylene, *cis*-stilbene, and $CHCl_3$. In a typical reaction, the crystals of **2** were immersed in benzene for a day and then the absorbed guest was extracted into diethyl ether after addition of HCl to the dried crystals. GC analysis of the extracted layer showed no trace of nitrobenzene but only the new guest. Importantly, the crystalline nature was not destroyed during the exchange process and hence crystals suitable for an X-ray analysis were obtained even after guest exchange.

The single crystal analysis of the crystals of **2** with the guest molecule exchanged for benzene, $[\{(ZnI_2)_3(\mathbf{1})_2{\cdot}6\,C_6H_6\}_n]$ (**4**) revealed that the crystal structure is virtually identical to that of **2**.[17] Interestingly, unlike the nitrobenzene molecules, which are disordered, the benzene molecules (except one) in **4** are ordered and refined well isotropically. As a result, the crystal structure of **4** refined with a better *R* factor than the parent crystal ($R_1 = 5.5\%$ vs. 7.9%). The benzene molecules in **4** interact with each other through aromatic interactions to form a column of molecules that will pass through the channels of the network (Figure 4).

Our efforts to synthesize the non-interpenetrated (10,3)-b network using TPT and ZnI_2 were successful when we conducted the reaction in the presence of bromoform–MeOH. Crystals of the complex $[\{(ZnI_2)_3(\mathbf{1})_2{\cdot}2\,CHBr_3\}_n]$, (**5**) grew in four days when the MeOH solution of ZnI_2 was layered onto the bromoform solution of TPT.[18] The crystal structure of the complex **5** shows the formation of a (10,3)-b network without interpenetration. In **5**, the pitch of the helix was reduced to nearly half that in **2** or **3**. The hexagonal channels shown in Figure 2b for **2** or **3** are divided into two channels in **5** (Figure 5). The disordered bromoform molecules occupy these channels.

Figure 4. Space-filling representation of the column of benzene molecules exhibited in the crystal structure of **4**: a) top view and b) side view (C = red and H = light brown). Note that these columns fit into the channels shown in Figure 2d.

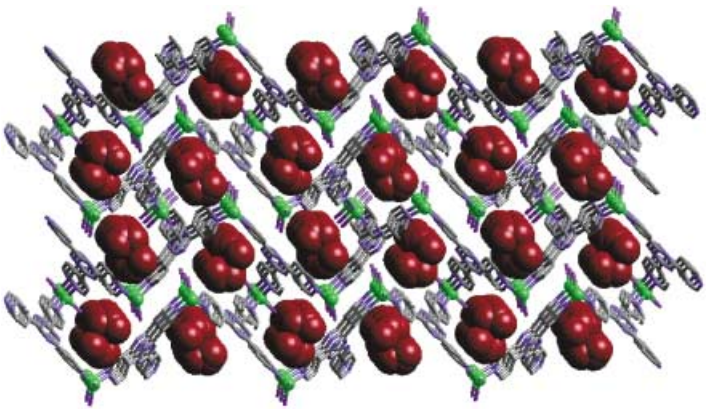

Figure 5. Illustration of 3D network in complex **5**. Bromoform molecules are shown in space-filling mode in brown (Zn = light green, I = magenta, C = gray, and N = blue).

Experimental Section

Synthesis of **2/3**: Single crystals of **2/3** were prepared by layering a MeOH solution of ZnI_2 (9.6 mg in 1 mL) onto a nitrobenzene/cyanobenzene solution of **1** (6.3 mg in 4 mL). After the solution was allowed to stand for 7 days, the crystals formed were isolated in 63%/57% yield, respectively, by filtration. Similarly, the crystals of **5** were prepared by layering the MeOH solution of ZnI_2 (9.6 mg in 1 mL) onto the bromoform solution of **1** (6.3 mg in 3 mL). Single crystals suitable for X-ray studies were obtained in 15% yield in two days.

Synthesis of **2′/3′**: The crystals of **2′/3′** were prepared by leaving the crystals of **2/3** at room temperature to equilibrate with atmosphere for one day. The elemental analysis suggests the presence of a lower proportion of guest molecules than in **2/3**.

Synthesis of **4**: The single crystals of **4** were obtained by immersing the crystals of **2** in benzene for a day. GC analysis of these crystals suggests the presence of benzene and the complete absence of nitrobenzene.

Elemental analysis: for **2**, found: C 36.60, H 2.28, N 10.57; calcd for $[(ZnI_2)_3(\mathbf{1})_2{\cdot}5.5\,C_6H_5NO_2]$: C 36.68, H 2.30, N 10.85; for **2′**, found: C 33.75, H 2.12, N 10.08; calcd for $[(ZnI_2)_3(\mathbf{1})_2{\cdot}3.33\,C_6H_5NO_2]$: C 33.94, H 2.06, N 10.78.

Elemental analysis: for **3**, found: C 42.45, H 2.50, N 11.60; calcd for $[(ZnI_2)_3(\mathbf{1})_2{\cdot}6\,C_6H_5CN]$: C 42.56, H 2.47, N 11.45; for **3′**, found: C 38.60, H 2.25, N 11.35; calcd for $[(ZnI_2)_3(\mathbf{1})_2{\cdot}4\,C_6H_5CN]$: C 38.54, H 2.22, N 11.23.

Crystal data collection and refinement: The data for all the structures were measured on a Bruker SMART/CCD diffractometer (MoK_α radiation λ = 0.71073 Å) at 193 K. An empirical absorption correction was applied using the SADABS program. Non-hydrogen atoms were refined anisotropically except for guest molecules and hydrogen atoms, which were fixed at calculated positions and refined using a riding model. CCDC-187829(**2**), CCDC-187830 (**2′**), CCDC-187831 (**3**), CCDC-187832 (**3′**) CCDC-187833(**4**) and CCDC-187834 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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[10] Crystal data for **2**: Monoclinic, *C*2/*c*, $a = 36.079(10)$, $b = 14.978(4)$, $c = 30.734(9)$ Å, $\beta = 102.470(2)°$, $V = 16217(12)$ Å^3, $Z = 8$, $D_c = 1.851$ g cm^{-3}, 9066 reflections out of 14243 unique reflections with $I > 2\sigma(I)$, $1.16 < \theta < 25.00°$, final *R* factors $R_1 = 0.079$, $wR_2 = 0.2316$.

[11] Crystal data for **3**: Monoclinic, *C*2/*c*, $a = 35.487(8)$, $b = 15.080(4)$, $c = 31.542(7)$ Å, $\beta = 102.107(4)°$, $V = 16504(7)$ Å^3, $Z = 8$, $D_c = 1.772$ g cm^{-3}, 9884 reflections out of 14518 unique reflections with $I > 2\sigma(I)$, $1.32 < \theta < 25.00°$, final *R* factors $R_1 = 0.0638$, $wR_2 = 0.1922$.

[12] Crystal data for **2′**: Triclinic, $P\bar{1}$, $a = 14.297(3)$, $b = 17.164(3)$, $c = 27.333(5)$ Å, $\alpha = 89.970(5)°$; $\beta = 77.104(4)°$, $\gamma = 74.591(4)°$, $V = 6291(2)$ Å^3, $Z = 4$, 6564 reflections out of 21852 unique reflections with $I > 2\sigma(I)$, $1.16 < \theta < 25.00°$, final *R* factors $R_1 = 0.1194$, $wR_2 = 0.2720$.

[13] Crystal data for **3′**: Monoclinic, *C*2/*c*, $a = 27.482(8)$, $b = 15.096(4)$, $c = 31.846(7)$ Å, $\beta = 94.143(6)°$, $V = 13177(6)$ Å^3, $Z = 8$, 8052 reflections out of 11604 unique reflections with $I > 2\sigma(I)$, $1.28 < \theta < 25.00°$, final *R* factors $R_1 = 0.0623$, $wR_2 = 0.1462$.

[14] Crystals of **2′** placed in nitrobenzene: The crystals broke into small pieces, monoclinic, *C*2/*c*, $a = 36.370(7)$, $b = 15.090(3)$, $c = 31.266(6)$ Å, $\beta = 103.782(4)°$, $V = 16665(5)$ Å^3, $Z = 8$, 5583 reflections out of 14665 unique reflections with $I > 2\sigma(I)$, $1.15 < \theta < 25.00°$, final *R* factors $R_1 = 0.0994$, $wR_2 = 0.2486$.

[15] Unit cell parameters for **2** after complete guest removal by heating on hotplate for 10 mins at 170 °C, the crystals broke into small pieces and became less transparent. The complete guest removal was confirmed by GC analysis: $a = 14.573(19)$, $b = 17.268(23)$, $c = 28.044(38)$ Å, $\alpha = 89.685(15)°$; $\beta = 76.956(14)°$; $\gamma = 73.794(12)°$. Heating the crystals of **3** to 170 °C resulted in similar cell parameters to those described above.

[16] The powder diffraction patterns for **2** monitored at various time intervals are in the Supporting Information.

[17] Crystal data for **4**: Monoclinic, *C*2/*c*, $a = 35.316(3)$, $b = 14.7247(14)$, $c = 31.766(3)$ Å, $\beta = 101.906(2)°$, $V = 16163(7)$ Å^3, $Z = 8$, $D_c = 1.686$ g cm^{-3}, 10419 reflections out of 14232 unique reflections with $I > 2\sigma(I)$, $1.50 < \theta < 25.00°$, final R factors $R_1 = 0.0557$, $wR_2 = 0.1589$.

[18] Crystal data for **5**: Orthorhombic, *Fdd*2, $a = 35.252(5)$, $b = 39.509(5)$, $c = 8.153(1)$ Å, $V = 11355(3)$ Å^3, $Z = 8$, $D_c = 2.442$ g cm^{-3}, 3752 reflections out of 4976 unique reflections with $I > 2\sigma(I)$, $1.55 < \theta < 24.99°$, final *R* factors $R_1 = 0.0456$, $wR_2 = 0.1038$.

Crystal-to-Crystal Sliding of 2D Coordination Layers Triggered by Guest Exchange**

Kumar Biradha, Yoshito Hongo, and Makoto Fujita*

Metal–organic frameworks containing channels or voids have attracted current interest because of their functional properties, which are similar to those of zeolites and clays.[1–4] Although the porosity is one of the most studied properties of metal–organic frameworks, there are very few studies on dynamic porous coordination networks.[5] 2D-network materials have the potential to provide such dynamic porous materials as they can adopt changes caused by external stimuli, either within the layer or in between the layers. Here we present one such unique and novel dynamic process in the crystals of a 2D net containing square grids of dimension 20 × 20 Å.

The crystal-to-crystal sliding of the 2D nets between two packing modes A and B (Figure 1) is triggered by guest exchange, and results in considerable increase in the dimensions of channels. This crystal-to-crystal transformation was evidenced by single crystal and powder X-ray diffraction studies before and after the transformation. The single-crystal

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