

Three Topological Isomeric Coordination Polymer Networks from the Assembly of a Rigid Linear Spacer and a Square Planar Metal Node: Structures, Isomerism Control, and Solid-to-Solid Transformation

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Received September 22, 2003

Assemblies of 1-methyl-1',2-bis(4-pyridyl)ethene (mpe) and $\text{Co}(\text{NCS})_2$ afford three isomeric framework networks and different topological features depending on the assembly conditions. Isomerism control and solid-to-solid transformation phenomena are observed among them.

Over the past decade, the judicious combination of organic ligand “spacers” and metal ion “nodes” has been the most common synthetic approach to producing predictable networked coordination polymers.¹ In particular, the self-assembly of 4,4'-bipyridine type rigid linear ligands and square planar or octahedral metal centers has afforded many noteworthy 2-D and 3-D frameworks.² In synthesizing these, the topological isomerism including interpenetration difference was found to be a widely encountered phenomenon influenced by subtle environmental changes.³ They may afford significant variations in chemical and physical properties as well as overall structures. Thus, control over them lies at the very heart of the concept of crystal engineering.⁴ However, there is presently very little understanding concerning the factors that determine their synthesis, and the attainment of rational control over desired topologies and specific properties still remains a great challenge.⁵

Herein we report three remarkable topological isomeric coordination polymer networks generated from an assembly of 1-methyl-1',2-bis(4-pyridyl)ethene (mpe) and $\text{Co}(\text{NCS})_2$ and the solid-to-solid transformation phenomena observed among them. To the best of our knowledge, this kind of transformation has been explored very little in the context of coordination polymers.^{2a,5a,6} Moreover, we also wish to report the controlled and reproducible access to a particular polymorph among them.

When a CH_3OH solution of $\text{Co}(\text{NCS})_2$ was layered onto a solution of mpe in CH_3NO_2 , needlelike crystals of **1** were grown just at the interface of the two solutions within 1 day. While the solution was kept standing for several days, crystals of **2** with a block shape gradually appeared from the same batch in succession. The X-ray crystallographic analyses of **1** and **2** revealed that each of them consisted of isomeric framework networks with an identical chemical composition of $[\text{Co}(\text{mpe})_2(\text{NCS})_2]_\infty$ and different topological features, which denoted the occurrence of concomitant polymorphism.⁷ The crystal of **1** is constituted by 2-D layers of rhombic grids with diagonal distances of 21.33 and 17.26 Å. Two sets of parallel layers, stacked with a separation of 17.23 Å, give a perpendicular interpenetration, and, thus, the cavities of each layer are partially filled by the other layer

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- (7) Crystal data for **1**: $\text{C}_{28}\text{H}_{24}\text{CoN}_6\text{S}_2$ (293 K). $M = 567.58$, tetragonal, space group $P4_2/c$, $a = 21.310(1)$ Å, $c = 17.2600(10)$ Å, $V = 7838.0(7)$ Å³, $Z = 8$, $\rho_{\text{calc}} = 0.962$ g/cm⁻³, absorption coefficient = 0.564 mm⁻¹, total reflections collected 30319, unique 8583 ($R_{\text{int}} = 0.098$), GOF = 1.220, $R_1 = 0.1177$, $R_w = 0.3278$ ($I > 2\sigma(I)$). **2**: $\text{C}_{42}\text{H}_{36}\text{Co}_{1.50}\text{N}_6\text{S}_3$ (293 K). $M = 851.37$, monoclinic, space group $C2/c$, $a = 19.5758(6)$ Å, $b = 19.3887(6)$ Å, $c = 27.3461(6)$ Å, $\beta = 108.4899(16)^\circ$, $V = 9843.4(5)$ Å³, $Z = 8$, $\rho_{\text{calc}} = 1.149$ g/cm⁻³, absorption coefficient = 0.674 mm⁻¹, total reflections collected 20267, unique 11221 ($R_{\text{int}} = 0.055$), GOF = 1.088, $R_1 = 0.1180$, $R_w = 0.3179$ ($I > 2\sigma(I)$).

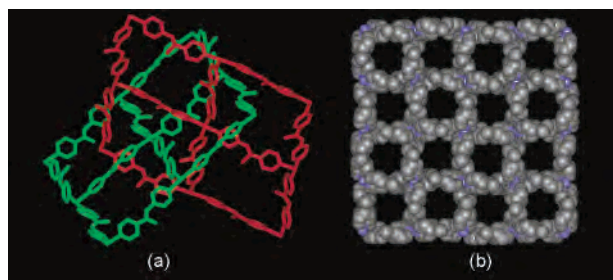


Figure 1. Perpendicularly interpenetrating grid networks (a) and square channel structures (b) found in **1**.

(Figure 1a). Despite the interpenetration, the intersection of the grids gives rise to large square channels parallel to the crystallographic c axis (Figure 1b).⁸ These channels have an effective size of $6.12 \times 6.12 \text{ \AA}$ and are occupied by disordered solvent molecules. The volume fraction occupied by solvent molecules is estimated to be 49% out of the total space.⁹

The crystal structure of **2** consists of two mutually interpenetrating independent 3-D frameworks belonging to CdSO_4 topology and 2-D square grid layers (Figure 2). This structure is almost equivalent to an isomer of $\{\text{Co}[1\text{-methyl-}1'-(4\text{-pyridyl})\text{-}2\text{-(4-pyrimidyl)ethene}]_2(\text{NCS})_2\}_\infty$ recently reported by us.¹⁰ The structure of **2** is also porous such that solvent molecules account for 18% of the crystal volume.⁹

The high porosity and relatively low density of the structure found in **1** suggested that its crystal form was thermodynamically metastable and its formation could be controlled by the variation of kinetic factors such as diffusion rate, concentration, and crystallization temperature.¹¹ Following on from this assumption, it is discovered that the crystals of **1** are exclusively raised when highly concentrated solutions are diffused rapidly through a wide area. The crystals of **2** can be formed as a sole product when dilute solutions are allowed to diffuse slowly. The crystal of **1** loses the included solvent and turns opaque immediately upon removal from the mother liquor. The XRPD measurements of solvated and desolvated forms of **1** and comparison between them showed that the porous and metastable topology of **1** was converted to the denser and thermodynamically stable one of **2** in the course of the removal of included solvent molecules (Figure 3).

When the self-assembly was carried out by the diffusion of a solution of mpe in MeOH into an aqueous solution of $\text{Co}(\text{NCS})_2$ for several days, crystals with a block shape were raised. Thorough investigation using single crystallography and XRPD methods discloses that they are of another concomitant polymorphism involving **2** and a third topological isomer of $[\text{Co}(\text{mpe})_2(\text{NCS})_2]_\infty$, **3**.¹² The network structure

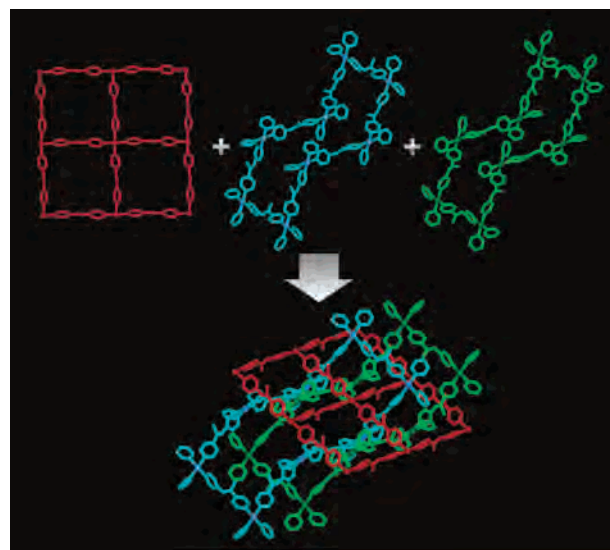


Figure 2. (a) Network structure of **2** with two independent 3-D frames and 2-D grid layers mutually interpenetrated. (b) Schematic representation of **2**.

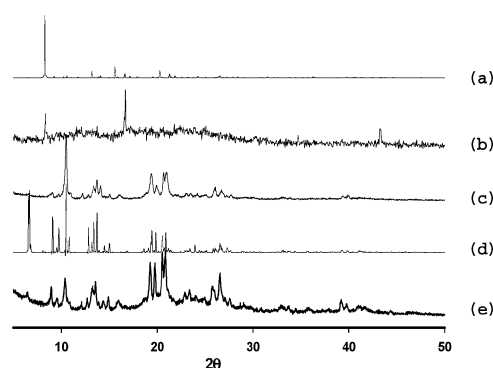


Figure 3. XRPD results: (a) simulated for **1**; (b) measured for **1** in the mother liquor; (c) measured for **1** after the removal of included solvent, indicating the transformation to **2**; (d) simulated for **2**; (e) measured for **2**.

in **3** has a catenane isomeric relation to that of **1**. Thus, while 2-D rhombic grid layers constituting **3** are almost equivalent

- (8) For examples of large channel containing interpenetrated network structures, see: (a) Chen, B.; Eddaoudi, M.; Hyde, S. T.; O'Keeffe, M.; Yaghi, O. *Science* **2001**, *291*, 1021. (b) Kondo, M.; Shimamura, M.; Noro, S.; Minakoshi, S.; Asami, A.; Seki, K.; Kitagawa, S. *Chem. Mater.* **2000**, *12*, 1288.
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- (12) Crystal data for **3**: $\text{C}_{28}\text{H}_{24}\text{CoN}_6\text{S}_2$ (293 K). $M = 567.58$, orthorhombic, space group $Pbca$, $a = 16.4866(2) \text{ \AA}$, $b = 15.2905(2) \text{ \AA}$, $c = 22.4722(4) \text{ \AA}$, $V = 5664.98(14) \text{ \AA}^3$, $Z = 8$, $\rho_{\text{calc}} = 1.331 \text{ g/cm}^{-3}$, absorption coefficient = 0.781 mm^{-1} , total reflections collected 11874, unique 6461 ($R_{\text{int}} = 0.022$), GOF = 1.091, $R_1 = 0.0508$, $R_w = 0.1562$ ($I > 2\sigma(I)$).

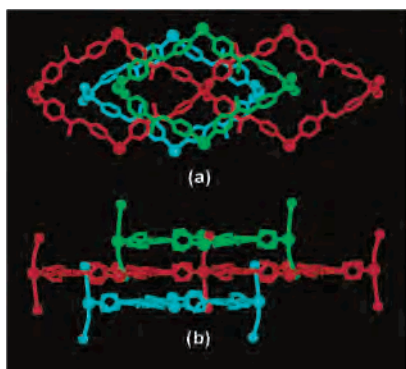


Figure 4. Stacked 2-D grid layer structures found for **3**: (a) a view down the plane; (b) a side view.

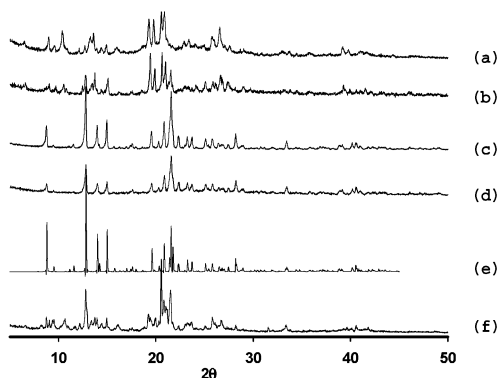
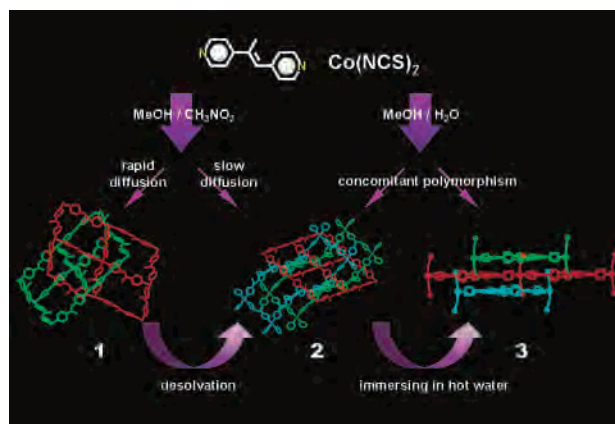


Figure 5. XRPD results: (a) measured for **2**; (b) measured after immersing **2** in hot water for 12 h; (c) measured after immersing **2** in hot water for 2 days, indicating the transformation to **3**; (d) measured after immersing **3** in hot MeOH for 2 days; (e) simulated for **3**; (f) measured for mixture of **2** and **3** as synthesized.

to those found in **1**, they are not interpenetrated. Instead, they are stacked and staggered relative to each other so that the SCN groups protrude through the cavity of the adjacent sheet (Figure 4). In this manner, the voids are effectively filled and, consequently, a closely packed structure results. The crystal of **3** includes no solvent molecules.

Variation of the assembly conditions does not significantly influence the polymorphism for the above case. However, in another attempt to obtain a pure polymorph, a mixture of **2** and **3** was immersed in refluxing water for several days, and then, only crystals of **3** were found to remain. To clarify this phenomenon, the same treatment was done with the pure crystals of **2**. When they were immersed in reflux water for 12 h, a portion of them was found to be converted to **3**. And, after the immersion for 2 days, their complete transformation to **3** was revealed by XRPD measurement. When the

Scheme 1



resulting powders of **3** were immersed in warm CH_3OH for 2 days, any change was not observed in XRPD experiment (Figure 5). This phenomenon can be understood on the basis of the supposition that the porous polymorph is transformed into the energetically most favorable packing structure in the solid state.

In summary, we have demonstrated three coordination polymer network structures of the topological isomerism and interesting solid-to-solid transformation phenomena involving them. Furthermore, we have also demonstrated the rational control of their formation through simple variation of the reaction conditions. It is quite noteworthy that any polymorph in this work can be accessed as a unique product through the combination of the control of the assembly condition and the utilization of the solid transformation (Scheme 1). We believe that this result offers very valuable information for the engineering of solid materials with desired topologies and specific properties.

Acknowledgment. This work was supported by Grant No. R01-1999-000-0041-0 of the Korea Science and Engineering Foundation (KOSEF) and KOSEF through the Center for Molecular Catalysis. D.M.S. thanks the Ministry of Education for the Brain Korea 21 Fellowship. We thank Dr. Seung-Tae Hong in LG Chem. for the assistance in the XRPD experiment and helpful discussions.

Supporting Information Available: Experimental procedures for the syntheses, the control of polymorph, and solid-to-solid transformation, TGA measurement results (S1), crystal photographs (S2), a 3-D interpenetration structure of **2** (S3), and X-ray crystallographic information files (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC035111O