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# Solvent-Dependent Formations of Supramolecular Isomers and a Single-Crystal to Single-Crystal Transformation from a Cyclic Dimer Complex to a One-Dimensional Coordination Polymer

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**ABSTRACT:** Solvent-dependent supramolecular isomers of a tripodal ligand incorporating two *para*-pyridylmethyl arms, *N*-naphthylmetyl-*N*,*N*-bis(4-pyridylmethyl)amine (L), are reported. A combination of L and copper(II) hexafluoroacetylacetonate,  $Cu(hfac)_{2}$ , in methanol afforded a cyclic dimer complex  $[Cu_2(L)_2(hfac)_4] \cdot CH_3OH(1)$ . In chloroform/methanol, the same reaction furnished an infinite one-dimensional (1D) complex  $\{[Cu_2(L)_2(hfac)_4] \cdot 2CHCl_3\}_n$  (2). When the cyclic dimer 1 was immersed in chloroform/ether, its transformation to the 1D coordination polymer 2 was observed in an single-crystal to single-crystal manner. In silver(I) triflate complexations, three supramolecular isomers (3–5) were isolated. In chloroform/methanol, a multichannel-type three-dimensional (3D) coordination polymer  $\{[Ag(L)](CF_3SO_3) \cdot 0.5CHCl_3\}_n$  (3) was isolated. In isomer 3, the Ag atom link L ligands alternately to form a helix, and these are linked by Ag–Ag contacts to generate an **etb** topology. In acetonitrile/methanol, a multichannel-type 3D coordination polymer  $\{[Ag(L)](CF_3SO_3) \cdot CH_3CN\}_n$  (4) was isolated. In isomer 4, six Ag atoms and six L ligands form an Ag<sub>6</sub>L<sub>6</sub> hexagonal unit, and these are linked via Ag–Ag contacts, resulting in a **pcu-h** topology. In toluene/methanol/ acetonitrile, a cross-linked ladder-type coordination polymer  $\{[Ag_4(L)_4(CF_3SO_3)_2](CF_3SO_3)_2\cdot 3(toluene)\}_n$  (5) was obtained. The isomer 5 is composed of two types of ladders crossed showing a new topology. Considering the formation of the  $(\pi - \pi) \cdot (Ag - Ag) \cdot (\pi - \pi)$  unit in 3–5, it is suggested that the anion–solvent interaction could be a major reason.

## INTRODUCTION

Zaworotko has extended the concept of isomerism in monomeric metal complexes to oligomeric and polymeric coordination compounds and called it supramolecular isomerism.<sup>1-4</sup> Similar to the importance of polymorphism in the pharmaceutical area,<sup>5,6</sup> supramolecular isomerism is academically challenging and may serve the fundamental understanding for the development of metal-organic framework-based functional materials.<sup>7-35</sup> As controlling factors leading to supramolecular isomerism, temperature,<sup>7-12</sup> solvent,<sup>13-22</sup> template,<sup>23-25</sup> guest,<sup>26,27</sup> pH,<sup>28-30</sup> catenation,<sup>31</sup> mole ratio,<sup>32</sup> and concentration<sup>33-35</sup> have been known in the self-assembly of metallosupramolecules. However, the role of the solvent in this area has been less understood than other factors. In some cases,

the solvent-dependent supramolecular isomers show not only the structural differences but also the dimensional changes.<sup>13–16</sup>

Over recent years, we have been interested in the tripodal ligand system incorporating pyridylmethyl arms in conjunction with their metallosupramolecules.<sup>36–39</sup> For example, a series of chiral bidentate ligands in such systems have been employed, and their anion-dependent mercury(II) complexes as well as the

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anion-sensing in CD spectroscopy have been reported.<sup>38</sup> A symmetrical tripodal ligand with three longer arms forms an anion-coordinated trinuclear-bis(ligand) cage in which the anion acts as a terminal ligand, and solvent molecules occupy the cage cavity.<sup>39</sup> In connection with these reflections, we are interested in a tripodal ligand with two pyridylmethyl pendants, N-naphthlmetyl-N,N-bis(4-pyridylmethyl)amine (L). Because of the intrinsic semiflexible nature of the two pyridylmethyl arms in the para-position, the L ligand is expected to behave as a linker ligand rather than a chelating ligand. So the ligand L seems to have a potential for the construction of porous coordination frameworks which have a tendency to maximize their packing density by occupying guests including solvent molecules regardless of their coordinative nature. In particular, the assembled products derived from flexible or semiflexible ligands that are hardly predictable seem to be sensitive to other factors including the solvent (or solvation effect).



N-naphthlmetyl-N,N-bis(4-pyridylmethyl)amine hexafluoroacetylacetonate ion

In this work, by employing the L ligand, we have isolated two copper(II) complexes and three silver(I) complexes, with the same formula for each metal complex but displaying different structural topologies depending on the solvents. Thus, the influence of the solvents on the formations of supramolecular isomers became a key issue in this study. In the copper(II) complexation, copper(II) hexafluoroacetylacetonate, Cu(hfac)<sub>2</sub> was employed due to the bidentating ability of the anion.<sup>40,41</sup> An interesting feature of a cyclic dimer and a one-dimensional (1D) coordination polymer products isolated depending on the solvents is that the observed dimensional difference is mainly being dependent on the coordination modes. In solvent exchange, more interestingly, the cyclic dimer was converted to the 1D polymer in a single-crystal-to-single-crystal (SCSC) manner. When silver(I) triflate was used, the results could be more challenging because of the isolation of three 3D coordination polymers with different structural topologies. The details of our investigations are described below.

# RESULTS AND DISCUSSION

**Synthesis of L.** The bis(4-pyridylmethyl)amine precursor  $6^{42}$  was synthesized by the reaction between 4-(chloromethyl)-pyridine hydrochloride and 4-(aminomethyl)pyridine in a high yield (91%). The ligand L was synthesized by reductive

Scheme 1. Synthesis of N-Naphthlmetyl-N,N-bis(4pyridylmethyl)amine (L)





Figure 1. Crystal structure of L.



Figure 2. Cyclic dimer copper(II) complex 1,  $[Cu_2(L)_2(hfac)_4]$ · CH<sub>3</sub>OH: (a) top view and (b) basic coordination geometry.



Figure 3. One-dimensional copper(II) coordination polymer 2,  $\{[Cu_2(L)_2(hfac)_4] \cdot 2CHCl_3\}_n$ : (a) general view, (b) basic coordination unit (also SBU), (c) local packing structure showing interaction between chloroform and hfac<sup>-</sup> ion, and (d) pseudo 2D structure via cross-linking of chloroform molecules.

amination of bis(4-pyridylmethyl)amine (6) and 2-naphthaldehyde (yield 65%; Scheme 1 and Figure S1). The structure was also confirmed by single crystal X-ray analysis (Figure 1). The single crystals of L were grown by slow evaporation from its dichloromethane/*n*-hexane solution. The conformation of L is basically similar to that of a tribladed propeller, and the distance between two heteronitrogen atoms in the para-position (N1 and N3) is 8.37 Å.



**Figure 4.** Comparison of coordination modes of the L ligands (top) crystal structures and (bottom) schematic representation: (a) closed-bridging (or cis) mode in 1 and (b) extended-bridging (or trans) mode in 2. To clarify the structure, some parts of the L ligand were deleted.





**Figure 5.** (a) Photo of a single crystal of 1 after immersing in  $CHCl_3/$  ether (1:5, v/v). (b) Postulated structural conversion process accompanying the dimensional change from a cyclic dimer (1, cismode) to a 1D coordination polymer (2, trans-mode) by solvent exchange in the crystalline state. To clarify the structure, anions are not shown.

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Scheme 3. Solvent-Dependent 3D Silver(I) Coordination Polymers



**Solvent-Dependent Copper(II) Complexes (1 and 2).** By employing  $Cu(hfac)_2$  and the L ligand, we have isolated two copper(II) complexes 1 and 2, displaying a cyclic dimer and 1D infinite structures in methanol and chloroform/methanol, respectively. Slow evaporation of the reaction solutions at room temperature afforded the products as dark green crystals suitable for X-ray analysis. The homogeneity of 1 and 2 was confirmed by powder X-ray diffraction (XRD) patterns (Figures S2 and S3).

The product 1 on using CH<sub>3</sub>OH solvent is a cyclic dimer complex with the formula  $[Cu_2(L)_2(hfac)_4]$ ·CH<sub>3</sub>OH (Figure 2 and Table S3) with two octahedral copper(II) centers with a Cu1...Cu1A distance of 10.33 Å. The same reaction in  $CHCl_3/$ CH<sub>3</sub>OH solvent instead of CH<sub>3</sub>OH gave a 1D polymeric product 2 with the formula  $\{[Cu_2(L)_2(hfac)_4] \cdot 2CHCl_3\}_n$ (Figure 3 and Table S4), indicating the determinant role of the solvent condition in forming copper(II) supramolecular isomers. In both products, each copper(II) center is sixcoordinate composed of four O donors arising from two hfacions in a bidentate manner. The two remaining sites are occupied by two N donors arising from two different L ligands adopting a  $CuN_2(hfac)_2$  coordination polyhedron, with two pyridine N atoms (N1 and N3A) and two O atoms from two different hfac<sup>-</sup> ions (O2 and O4 in 1 and O1 and O4 in 2) form the square plane, while two O atoms occupy the axial positions [O3-Cu1-O1 165.0(1)° for 1 and O3-Cu1-O2 171.2(1)° for 2].

In 1, two copper(II) centers are doubly linked by two L ligands via Cu–N bonds (Cu1–N1 1.995(4) Å and Cu1–N3A 2.001(4) Å) in a cis fashion (N1–Cu1–N3A 91.5(2)°) (Figure 2b), while the secondary building unit (SBU) in 2 is composed of octahedrally coordinated copper(II) ions which are linked by the L ligands alternately via Cu–N bonds (Cu1–N1 2.011(2) Å and Cu1–N3A 2.000(2) Å) in a trans fashion (N1–Cu1–N3A 177.0(1)°) to form a 1D zigzag structure (Figure 3a,b). Overall, the octahedral CuO<sub>4</sub>N<sub>2</sub> coordination cores with different configurations show distinct roles: a corner piece in 1, while a linker unit in 2. Most copper(II) (d<sup>9</sup>) complexes with Jahn–Teller distortion<sup>43,44</sup> undergo elongation of the axis, and it may





**Figure 6.** 3D silver(I) triflate coordination polymer 3, { $[Ag(L)](CF_3SO_3) \cdot 0.5CHCl_3$ <sub>n</sub>: (a) single framework (solvents not shown), (b) hexagonal column part composed of six trifold helices [three right-handed helices (R, green) and three left-handed helices (L, blue)], (c) simplified framework showing etb topology, (d) core coordination unit (also SBU) showing a Ag–Ag contact,  $\pi - \pi$  stacking, and the anion interaction, and (e) single trifold helix interacting with chloroform molecules.

occur in the bidentate ligands including hfac<sup>-</sup> ion whose bite angle is large. Similarly, the geometry of the Cu1 atoms in 1 and 2 is elongated octahedral; axial bond lengths are 2.279(3) Å (Cu1-O1) and 2.345(3) Å (Cu1-O3) for 1 and 2.261(2) Å (Cu1-O2) and 2.300(2) Å (Cu1-O3) for 2, which are longer than those of the four equatorial bonds (1.982(3)-2.002(3) Å for 1 and 1.992(2)-2.011(2) Å for 2). In 1, the methanol molecule in the lattice is disordered and shows no special interaction with the dimeric product (Figure 2a), while the chloroform molecules in 2 show cross-linking-type interactions to the hfac<sup>-</sup> ions via CH···F H-bonding (2.454 Å) and F···Cl interaction (3.106 Å) to give a pseudo 2D structure (Figure 3c,d).

Altering the solvent condition from  $CH_3OH$  to  $CHCl_3/CH_3OH$  in the complexations of L with  $Cu(hfac)_2$  causes a shift from a discrete to an infinite structure. So, it is important to understand how the different solvent conditions influence the topological changes. In 1, for example, the square planar [Cu(N,N,O,O)] unit has a cis-configuration, and the L ligands show a "closed-bridging" mode (Figure 4a), while that in 2 [Cu(N,O,N,O)] is a trans-form and the L ligands show an "extended-bridging" mode (Figure 4b), indicating that the solvent-dependent local geometrical isomerization and the different bridging modes cause the formations of topologically different copper(II) complexes. More remarkably, when the content of CHCl<sub>3</sub> in the CHCl<sub>3</sub>/CH<sub>3</sub>OH mixed solvent was varied from 10% to 90% (v/v), only product 2 was obtained (Figure S7). Taking the interactions of the chloroform molecules in 2 into account (see Figure 3c,d), this is likely due to the cross-linking-type interactions giving a greater stabilization via the "extended-bridging" (or trans) mode of L leading to the pseudo 2D structure. The methanol molecules in 1, however, simply occupy the empty space without specific interaction with the ligand or metal ion which may promote the "closed-bridging" (or cis) mode of L giving the cyclic dimer product.

A Single-Crystal-to-Single-Crystal (SCSC) Transformation via Solvent Exchange. Structural conversion between products 1 and 2 by solvent exchange was investigated in the crystalline state (Scheme 2). When the dark green single crystals of 1 were immersed in CHCl<sub>3</sub>/ether (1:5, v/v) and left undisturbed at room temperature, the surface of the single crystals showed partial dissolution and recrystallization, while retention of single crystallinity was maintained (Figure 5a). Surprisingly, single crystal X-ray analysis revealed that the structure of the single crystal recovered after 24 h was coincident with that of 2, indicating that the solvent exchange induces the dimensional change of the products in an SCSC manner (Figures S8 and S9 and Table S2). The tiny visual change of the single crystal seems to be associated with the different solubility or kinetics between 1 and 2 during the partial dissolution/ recrystallization process.<sup>45,46</sup> Meanwhile, the fresh single crystals of 2 were dissolved in CH<sub>3</sub>OH/ether (1:5, v/v) and recrystallized to the single crystals of 1 on standing for 3 days.



**Figure 7.** 3D silver(I) triflate coordination polymer 4, {[Ag(L)]-(CF<sub>3</sub>SO<sub>3</sub>)·CH<sub>3</sub>CN}<sub>n</sub>: (a) top view of the 3D framework composed of the hexagonal channels filled with acetonitrile molecules (anions not shown), (b) single hexagonal channel interacting with anions and acetonitrile molecules, (c) simplified framework showing **pcu-h** topology, and (d) core coordination unit showing Ag–Ag contact,  $\pi$ – $\pi$  stacking, and anion interaction.

On the basis of the crystal structures, a stepwise mechanistic process for the structural change of 1 to 2 exhibiting the dimensional change from the cyclic dimer to the 1D polymer was proposed (Figure 5b). Considering the discrete cyclic dimer 1 and the 1D polymeric structure of 2, on immersing in CHCl<sub>3</sub>/ ether, the cyclic dimer 1 (cis-mode) could be rearranged to give an acyclic dimer intermediate (trans-mode) via the Cu–N bond breaking and the rotating of the remaining Cu–N bond. Then, the acyclic dimer intermediate is considered to be converted to the 1D polymeric chain by the Cu–N bond making via the sliding. Among several factors, the transformation might be driven by the solvation effect mainly because the cyclic dimer (1) which is more polar includes methanol molecules, while the less polar 1D polymer (2) interacts with chloroform in the lattice.

Solvent-Dependent Silver(I) Complexes (Supramolecular Isomers 3–5). In an attempt to investigate the effect of solvent variations on the silver(I) complexation toward L, three mixed solvents, such as  $CHCl_3/CH_3OH$ ,  $CH_3CN/CH_3OH$ , and toluene/ $CH_3OH/CH_3CN$ , were employed. By utilizing silver(I) triflate (AgCF<sub>3</sub>SO<sub>3</sub>), the L ligand acts as a good linker to form helix, hexagon, and ladder subunits to yield coordination polymers 3–5, as shown in Scheme 3. Slow evaporation of the solutions afforded colorless crystalline products 3–5. The X-ray analysis reveals that all the complexes are the 3D frameworks of types {[Ag(L)](CF<sub>3</sub>SO<sub>3</sub>) $\cdot 0.5$ CHCl<sub>3</sub>]<sub>n</sub> (3), {[Ag(L)]-(CF<sub>3</sub>SO<sub>3</sub>)(CH<sub>3</sub>CN)}<sub>n</sub> (4), and {[Ag<sub>4</sub>(L)<sub>4</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>]-(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>·3(toluene)]<sub>n</sub> (5) whose structural topologies are dependent on the solvents. The important structural feature of 3–5 is that they are supramolecular isomers with different topologies connected by Ag–Ag contacts.

In CHCl<sub>3</sub>/CH<sub>3</sub>OH, isomer 3, { $[Ag(L)](CF_3SO_3)$ . 0.5CHCl<sub>3</sub> $_n$  crystallizes in the rhombohedral space group R3 with Z = 9 (Figure 6). X-ray analysis reveals that isomer 3 is a 2fold interpenetrated multichannel-type 3D coordination polymer (Figures 6a and S10). The asymmetric unit of isomer 3 contains one formula unit. In isomer 3, the Ag atom link L ligands alternately via Ag–N bonds (Ag1–N1 2.145(5) Å and Ag1–N3A 2.138(5) Å) to form a trifold helical -L-Ag-L-Ag-L-Ag column (Figure 6b).

In the trifold helix, each Ag atom (vertex) is linked to two other Ag atoms on the same helix and to one Ag atom on a different helix. Since the Ag atom acts as a 3-connecting node, the Ag-Ag contact as a linker allows the propagation along the ab-plane, resulting in the 3D multichannel framework. In the framework, the right (R)- and left (L)-handed helices are arranged alternately (Figure 6b). Three asymmetric units (three ligands and three Ag atoms) define one pitch (21.07 Å) of the helix. Accordingly, each helix is linked to their three closest neighboring helices via Ag-Ag contact<sup>47</sup> (3.118 Å), and the linking of six helical columns forms a larger multichannel-type hexagonal column along the *c* axis. By considering the Ag-Ag  $\frac{1}{48-50}$ contact as a linker, the overall topology belongs to an **etb**<sup>4</sup> net, which means the linked trifold helices with both hands (Figure 6c). As we understand, isomer 3 is the first etb topology whose helices are linked with the metallic contact. As expected, the para-pyridylmethyl arm acts as a good linker via the N-Ag-N bonding linkage. Notably, these two parallel linkages are cross-linked by Ag–Ag contact (3.118 Å) and interligand  $\pi - \pi$ stacking (centroid-to-centroid distance 3.982 Å) cooperatively to form a  $(\pi - \pi)$ -(Ag-Ag)- $(\pi - \pi)$  unit to increase the dimensionality (Figure 6d). The triflate ions doubly weak interact with the Ag(I) centers (Ag1…O1 2.756 Å and Ag1A… O1 2.873 Å). The inside of the helical column is occupied by chloroform molecules stabilized by CH…O H-bonding (2.292 Å) and Cl···Cl interaction<sup>51</sup> (3.394 Å) (Figure 6e).

In CH<sub>3</sub>CN/CH<sub>3</sub>OH, isomer 4, { $[Ag(L)](CF_3SO_3)$ ·  $CH_3CN_n$  crystallizes in the rhombohedral space group R3 with Z = 18. The asymmetric unit of 4 contains one formula unit. Again, 4 shows a multichannel-type 3D structure (Figure 7a), but its connectivity pattern is different from that of 3. In 4, six Ag atoms and six L ligands form an Ag<sub>6</sub>L<sub>6</sub> hexagonal unit via Ag–N bonds (Ag1-N1 2.136(7) Å and Ag1-N3A 2.149(7) Å) along the *ab*-plane (Figure 7b), and these further linked up and down via Ag–Ag contact (3.309 Å) along the *c* axis, resulting in the 3D framework. The overall topology belongs to a 3-connected uninodal pcu-h<sup>52</sup> net, which is quite rare in coordination polymers (Figure 7c). Formation of this preferred well-aligned hexagonal columnar structure in 4 is also stabilized by interligand  $\pi - \pi$  stacking interactions (centroid-to-centroid distance 3.759 Å, dashed lines in Figure 7d) in addition to the Ag–Ag contact (3.309 Å). Again, the formation of the  $(\pi - \pi)$ - $(Ag-Ag)-(\pi-\pi)$  unit contributes to increase the dimensionality. Similar to isomer 3, the triflate ions in 4 interact with the Ag(I) center (Ag1…O1 2.677 Å). Six acetonitrile molecules fill the inside of the hexagonal metallacycle via CH---O (2.695 Å, 125.5°) and CH…F H-bondings (2.262 Å, 155.3° and 2.642 Å, 125.0°).

In toluene/CH<sub>3</sub>OH/CH<sub>3</sub>CN, is omer 5,  $\{[Ag_4(L)_4(CF_3SO_3)_2](CF_3SO_3)_2\cdot 3(toluene)\}_n$  crystallizes triclinic space group PI with Z = 2 (Figure 8). X-ray analysis revealed that 5 is a 3D coordination polymer (Figure 8a), and the asymmetric unit contains one formula unit. The overall structure of 5 can be considered that two types of ladders (ladder

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(a)

(b)





Figure 8. 3D silver(I) triflate coordination polymer 5,  $\{[Ag_4(L)_4(CF_3SO_3)_2](CF_3SO_3)_2\cdot 3(toluene)\}_n$ : (a) 3D polymeric structure (solvents, noncoordinated anions, and naphthyl groups not shown), (b) simplified framework showing new topology with 3,3,4-c net, (c) ladder A, (d) ladder B, (e) core coordination unit, and (f) inside of framework filled with toluene molecules.



Figure 9. Solid state photoluminescence spectra of 1-5 at room temperature ( $\lambda_{ex} = 340$  nm).

A and ladder B, see Figure 8b) generated from same components (L and Ag atom) are crossed perpendicularly to form a 3D framework. The unusual 3,3,4-connected network 5 is made up of trigonal nodes of two Ag(I) atoms (Ag1 and Ag3) and one square planar node of one Ag atom (Ag2) created by the Ag1–

Ag2–Ag3 contact. As far as we understand, this is a new topology with point symbol  $\{6^2 \cdot 10^4\}\{6^2 \cdot 10\}\{6^2 \cdot 8\}_2$  net, which was analyzed using TOPOS<sup>53</sup> (Figure 8b).

In ladder A, the Ag1 atoms link the L ligands via Ag1-N4 bonds (2.140(6) Å) to form a -Ag1-L-Ag1-L- rail (Figure 8c). Similarly, the Ag3 atoms link other L ligands to form a -Ag3-L-Ag3-L- rail. Two such parallel rails are cross-linked by Ag1-Ag2-Ag3 contacts as "rungs" (Ag1-Ag2 3.102(1) Å, Ag2-Ag3 3.093(1) Å, and Ag1-Ag2-Ag3 166.1(1)°), while ladder B has two identical -(Ag2-L-Ag4-L)<sub>n</sub>- rails cross-linked by Ag4–Ag4A contact (3.178(1) Å) as rungs (Figure 8d). So, the  $(\pi - \pi)$ -(Ag-Ag)- $(\pi - \pi)$  unit also exists in part (ladder B), similar to 3 and 4. As mentioned, ladders A and B share the Ag2 atom as a 4connecting node (Figure 8e). Among the four triflate ions in the asymmetric unit, two of them are bound to the Ag3 and Ag4 atoms (Ag3-O1 2.586(6) Å and Ag4-O4 2.527(1) Å). Two remaining triflate ions interact with Ag1 and Ag2 atoms (Ag1... O10 2.746 Å and Ag2…O7 2.872 Å). The triflate ions also interact with toluene molecules via CH…F H-bonding (2.373 and 2.710 Å) (Figure 8f).

From the structural comparison of isomers 3, 4, and 5 in terms of the role of solvents, some considerable results were found. (i) the core coordination unit is mainly composed of a tight  $(\pi-\pi)$ -(Ag-Ag)- $(\pi-\pi)$  unit. (ii) The solvent molecules including

(CHCl<sub>3</sub>, CH<sub>3</sub>CN, and toluene) are aprotic rather than protic (CH<sub>3</sub>OH and H<sub>2</sub>O). (iii) The solvent molecules in the voids interact through the anion (CF<sub>3</sub>SO<sub>3</sub>), which interacts with the metal center directly. From the monitoring of the listed aspects (i–iii), it is suggested that the anion–solvent interaction (or anion solvation) which could act as the template to drive the formation of each structure is a major reason, at least in this case, although the origin of the topological differences depending on the solvents is not so clear.

**Thermal Stability.** Thermogravimetric analyses (TGA) were performed in order to investigate the thermal stabilities of **1–5** (Figures S11–S15). The TGA curves revealed that the copper(II) complexes **1** and **2** are stable up to 175 and 140 °C, respectively, while the thermal stabilities of the silver(I) coordination polymers **3**, **4**, and **5** are not significantly different. The TGA curve for **3** indicates no loss of solvent molecules and maintaining of their original weight until 190 °C. For **4**, a weight loss of 6.1% was observed in the range of 30–192 °C, indicating the loss of one acetonitrile molecule (calcd 6.4%). For **5**, a weight loss of 10.3% was observed in the range of 30–205 °C, due to the loss of three toluene molecules (calcd 10.4%). Further heating of each silver(I) complex up to ~450 °C resulted in decomposition.

**Photophysical Properties.** The photoluminescence properties of L and its copper(II) and silver(I) complexes 1-5 were also examined in the solid state (Figure 9). The ligand L shows a blue emission, but its copper(II) complexes 1 and 2 are nonemissive. Meanwhile, silver(I) complexes 3-5 display blue photoluminescence probably resulting from the  $\pi-\pi^*$  transition in the respective aromatic moieties. The emission spectra of 3, 4, and 5 show maxima at 419, 421, and 422 nm, respectively.

## CONCLUSION

Using a semiflexible tripodal ligand (L) incorporating two parapyridylmethyl arms, solvent-dependent supramolecular isomers including two copper(II) complexes and three silver(I) coordination polymers were prepared and structurally characterized. In the systematic investigation of the copper(II) complexes, it was found that the interactions of solvent molecules likely contribute to the influence to the topological structures of the resulting frameworks. We have also demonstrated the conversion of a discrete cyclic dimer complex 1 to a 1D coordination polymer 2 via an SCSC manner simply by dipping the parent species in CHCl<sub>3</sub>/ether. On the basis of the both crystal structures, a mechanistic process involving the conversion of the cis-mode to the trans-mode via the bond breaking-making was proposed. In the case of silver(I), we were able to prepare the 3D coordination polymer with different topologies. In CHCl<sub>3</sub>/CH<sub>3</sub>OH, for example, a supramolecular isomer (3) with a 2-fold interpenetrated multichannel-type 3D structure was obtained. In addition, when CH<sub>3</sub>CN/CH<sub>3</sub>OH was used, a hexagonal multichannel-type 3D isomer (4) was isolated. In toluene/CH<sub>3</sub>OH/CH<sub>3</sub>CN, on the other hand, a cross-linked ladder-type 3D isomer (5) was prepared. The solvent-dependent structural differences between the three supramolecular isomers are considered to be associated with the anion-solvent interaction (or anion solvation) which acts as the template.

# ASSOCIATED CONTENT

## **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.cgd.0c00084.

Experimental section, NMR spectra, PXRD patterns, TGA curves, additional figures (PDF)

#### Accession Codes

CCDC 1957356–1957361 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

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## REFERENCES

(1) Hennigar, T. L.; Macquarrie, D. C.; Losier, P.; Rogers, R. D.; Zaworotko, M. J. Supramolecular Isomerism in Coordination Polymers: Conformational Freedom of Ligands in  $[Co(NO_3)_2(1,2-bis(4-pyridyl)ethane)_{1.5}]_n$ . Angew. Chem., Int. Ed. Engl. 1997, 36, 972–973.

(2) Moulton, B.; Zaworotko, M. J. From Molecules to Crystal Engineering: Supramolecular Isomerism and Polymorphism in Network Solids. *Chem. Rev.* **2001**, *101*, 1629–1658.

(3) Zhang, J.-P.; Huang, X.-C.; Chen, X.-M. Supramolecular isomerism in coordination polymers. *Chem. Soc. Rev.* 2009, 38, 2385–2396.

(4) Robin, A. Y.; Fromm, K. M. Coordination polymer networks with O- and N-donors: What they are, why and how they are made. *Coord. Chem. Rev.* **2006**, *250*, 2127–2157.

(5) Aitipamula, S.; Chow, P. S.; Tan, R. B. H. Polymorphism in cocrystals: a review and assessment of its significance. *CrystEngComm* **2014**, *16*, 3451–3465.

(6) Haleblian, J.; McCrone, W. Pharmaceutical Applications of Polymorphism. J. Pharm. Sci. 1969, 58, 911–929.

(7) Masaoka, S.; Tanaka, D.; Nakanishi, Y.; Kitagawa, S. Reaction-Temperature-Dependent Supramolecular Isomerism of Coordination Networks Based on the Organometallic Building Block  $[Cu_2^{I}(\mu_2-BQ)(\mu_2-OAc)_2]$ . Angew. Chem., Int. Ed. **2004**, 43, 2530–2534.

(8) Dikhtiarenko, A.; Serra-Crespo, P.; Castellanos, S.; Pustovarenko, A.; Mendoza-Meroño, R.; García-Granda, S.; Gascon, J. Temperature-Dependent Supramolecular Isomerism of Lutetium-Aminoterephthalate Metal-Organic Frameworks: Synthesis, Crystallography, and Physical Properties. *Cryst. Growth Des.* **2016**, *16*, 5636–5645.

(9) Kanoo, P.; Gurunatha, K. L.; Maji, T. K. Temperature-Controlled Synthesis of Metal-Organic Coordination Polymers: Crystal Structure, Supramolecular Isomerism, and Porous Property. *Cryst. Growth Des.* **2009**, *9*, 4147–4156.

(10) Nagarkar, S. S.; Chaudhari, A. K.; Ghosh, S. K. Role of Temperature on Framework Dimensionality: Supramolecular Isomers of  $Zn_3(RCOO)_8$  Based Metal Organic Frameworks. *Cryst. Growth Des.* **2012**, *12*, 572–576.

(11) Xie, Z.-n.; Mei, L.; Wu, Q.-y.; Hu, K.-q.; Xia, L.-s.; Chai, Z.-f.; Shi, W.-q. Temperature-induced reversible single-crystal-to-single-crystal isomerisation of uranyl polyrotaxanes: an exquisite case of coordination variability of the uranyl center. *Dalton Trans.* **201**7, *46*, 7392–7396.

(12) Gong, Y.; Zhang, Y.; Qin, C.; Sun, C.; Wang, X.; Su, Z. Bottom-Up Construction and Reversible Structural Transformation of Supramolecular Isomers based on Large Truncated Tetrahedra. *Angew. Chem., Int. Ed.* **2019**, *58*, 780–784.

(13) Cui, P.; Wu, J.; Zhao, X.; Sun, D.; Zhang, L.; Guo, J.; Sun, D. Two Solvent-Dependent Zinc(II) Supramolecular Isomers: Rare kgd and Lonsdaleite Network Topologies Based on a Tripodal Flexible Ligand. *Cryst. Growth Des.* **2011**, *11*, 5182–5187.

(14) Ju, H.; Park, I.-H.; Lee, E.; Kim, S.; Jung, J. H.; Ikeda, M.; Habata, Y.; Lee, S. S. Guest-triggered assembly of zinc(II) supramolecular isomers with accompanying dimensional change and reversible single-crystal-to-single-crystal transformation. *CrystEngComm* **2016**, *18*, 1600–1608.

(15) Song, J.-F.; Luo, J.-J.; Jia, Y.-Y.; Xin, L.-D.; Lin, Z.-Z.; Zhou, R.-S. Solvent-induced construction of two zinc supramolecular isomers: synthesis, framework flexibility, sensing properties, and adsorption of dye molecules. *RSC Adv.* **2017**, *7*, 36575–36584.

(16) Huang, X.-C.; Zhang, J.-P.; Lin, Y.-Y.; Chen, X.-M. Triplestranded helices and zigzag chains of copper(I) 2-ethylimidazolate: solvent polarity-induced supramolecular isomerism. *Chem. Commun.* **2005**, 2232–2234.

(17) Wang, J.; Gao, L.; Zhang, J.; Zhao, L.; Wang, X.; Niu, X.; Fan, L.; Hu, T. Syntheses, Gas Adsorption, and Sensing Properties of Solvent-Controlled Zn(II) Pseudo-Supramolecular Isomers and Pb(II) Supramolecular Isomers. *Cryst. Growth Des.* **2019**, *19*, 630–637.

(18) He, M.; Xu, T.; Jiang, Z.; Yu, X.; Zou, Y.; Yang, L.; Wang, X.; Wang, X.; He, Y. Two copper-based MOFs constructed from a linear diisophthalate linker: supramolecular isomerism and gas adsorption properties. *CrystEngComm* **2019**, *21*, 3192–3198.

(19) Karmakar, A.; Rúbio, G. M. D. M.; Guedes da Silva, M. F. C.; Hazra, S.; Pombeiro, A. J. L. Solvent-Dependent Structural Variation of Zinc(II) Coordination Polymers and Their Catalytic Activity in the Knoevenagel Condensation Reaction. *Cryst. Growth Des.* **2015**, *15*, 4185–4197.

(20) Park, I.-H.; Lee, S. S.; Vittal, J. J. Guest-Triggered Supramolecular Isomerism in a Pillared-Layer Structure with Unusual Isomers of Paddle-Wheel Secondary Building Units by Reversible Single-Crystalto-Single-Crystal Transformation. *Chem. - Eur. J.* **2013**, *19*, 2695–2702. (21) Huang, X.-C.; Li, D.; Chen, X.-M. Solvent-induced supramolecular isomerism in silver(I) 2-methylimidazolate. *CrystEngComm* **2006**, *8*, 351–355.

(22) Lee, I. S.; Shin, D. M.; Chung, Y. K. Novel Supramolecular Isomerism in Coordination Polymer Synthesis from Unsymmetrical Bridging Ligands: Solvent Influence on the Ligand Placement Orientation and Final Network Structure. *Chem. - Eur. J.* **2004**, *10*, 3158–3165.

(23) Zhang, J.-P.; Kitagawa, S. Supramolecular Isomerism, Framework Flexibility, Unsaturated Metal Center, and Porous Property of Ag(I)/Cu(I) 3,3',5,5'-Tetrametyl-4,4'-Bipyrazolate. *J. Am. Chem. Soc.* **2008**, 130, 907–917.

(24) Panda, T.; Pachfule, P.; Banerjee, R. Template induced structural isomerism and enhancement of porosity in manganese(II) based metal–organic frameworks (Mn-MOFs). *Chem. Commun.* **2011**, *47*, 7674–7676.

(25) Jia, Y.; Li, H.; Guo, Q.; Zhao, B.; Zhao, Y.; Hou, H.; Fan, Y. Template-Induced Structural Isomerism of Pyridine-2,3-dicarboxylate and  $Pb^{II}$  with Similar High Stability and Different Fluorescent Properties. *Eur. J. Inorg. Chem.* **2012**, 2012, 3047–3053.

(26) Aitipamula, S.; Nangia, A. Guest-Induced Supramolecular Isomerism in Inclusion Complexes of T-Shaped Host 4,4-Bis(4'hydroxyphenyl)cyclohexanone. *Chem. - Eur. J.* **2005**, *11*, 6727–6742.

(27) Ye, Y.; Chen, S.; Chen, L.; Huang, J.; Ma, Z.; Li, Z.; Yao, Z.; Zhang, J.; Zhang, Z.; Xiang, S. Additive-Induced Supramolecular Isomerism and Enhancement of Robustness in Co(II)-Based MOFs for Efficiently Trapping Acetylene from Acetylene-Containing Mixtures. *ACS Appl. Mater. Interfaces* **2018**, *10*, 30912–30918.

(28) Fan, L.; Zhang, X.; Sun, Z.; Zhang, W.; Ding, Y.; Fan, W.; Sun, L.; Zhao, X.; Lei, H. Ancillary Ligands Dependent Structural Diversity of A Series of Metal–Organic Frameworks Based on 3,5-Bis(3carboxyphenyl)pyridine. *Cryst. Growth Des.* **2013**, *13*, 2462–2475.

(29) Lago, A. B.; Carballo, R.; Rodríguez-Hermida, S.; Vázquez-López, E. M. Control over the preparation of two pH-dependent Cu(II) supramolecular isomers based on 1,3,5-benzenetricarboxylic acid and the bis(4-pyridylthio)methane ligand. *CrystEngComm* **2013**, *15*, 1563– 1570.

(30) Perman, J. A.; Chen, M.; Mikhail, A. A.; Niu, Z.; Ma, S. Acid-base directed supramolecular isomers of isophthalate based MOFs for CO<sub>2</sub> adsorption and transformation. *CrystEngComm* **2017**, *19*, 4171–4174. (31) Haldar, R.; Reddy, S. K.; Suresh, V. M.; Mohapatra, S.; Balasubramanian, S.; Maji, T. K. Flexible and Rigid Amine-Functionalized Microporous Frameworks Based on Different Secondary Building Units: Supramolecular Isomerism, Selective CO<sub>2</sub> Capture, and Catalysis. *Chem. - Eur. J.* **2014**, *20*, 4347–4356.

(32) Lee, E.; Kim, J.-Y.; Lee, S. S.; Park, K.-M. Molar-Ratio-Dependent Supramolecular Isomerism: Ag<sup>I</sup> Coordination Polymers with Bis(cyanobenzyl)sulfides. *Chem. - Eur. J.* **2013**, *19*, 13638–13645.

(33) Cui, P.; Dou, J.; Sun, D.; Dai, F.; Wang, S.; Sun, D.; Wu, Q. Reaction vessel- and concentration-induced supramolecular isomerism in layered lanthanide-organic frameworks. *CrystEngComm* **2011**, *13*, 6968–6971.

(34) Hao, Z.-M.; Zhang, X.-M. Ligand Concentration Controlled Supramolecular Isomerism in Two CuSCN Based Coordination Polymers with in Situ Synthesized 4,4'-Dipyridylsulfide as a Co-Ligand. *Cryst. Growth Des.* **2007**, *7*, 64–68.

(35) Lu, W.-G.; Yang, K.; Jiang, L.; Feng, X.-L.; Lu, T.-B. The concentration controlled 1D and 2D supramolecular isomers of lanthanide with 2,2'-bipyridyl-3,3'-dicarboxylate and phenanthroline. *Inorg. Chim. Acta* **2009**, 362, 5259–5264.

(36) Ikeda, M.; Kuwahara, S.; Lee, S. S.; Habata, Y. Effects of structures of  $HgX_2$  complexes (X = CF<sub>3</sub>SO<sub>3</sub> and Cl) with chiral bidentate ligands on circular dichroism spectra. *Dalton Trans.* **2013**, *42*, 3009–3014.

(37) Ikeda, M.; Matsu-ura, A.; Kuwahara, S.; Lee, S. S.; Habata, Y. Hg<sup>2+</sup>-Sensing System Based on Structures of Complexes. *Org. Lett.* **2012**, *14*, 1564–1567.

## **Crystal Growth & Design**

(38) Ikeda, M.; Kuwahara, S.; Lee, S. S.; Habata, Y. Anion-Controlled Circular Dichroism Spectral Changes in Hg<sup>2+</sup> Complexes with a Chiral Bidentate Ligand. *Inorg. Chem.* **2012**, *51*, 7022–7024.

(39) Ikeda, M.; Ohno, K.; Kasumi, Y.; Kuwahara, S.; Habata, Y. Construction of an  $M_3L_2A_6$  Cage with Small Windows from a Flexible Tripodal Ligand and Cu(hfac)<sub>3</sub>. *Inorg. Chem.* **2014**, *53*, 24–26.

(40) Winter, S.; Weber, E.; Eriksson, L.; Csöregh, I. New coordination polymer networks based on copper(II) hexafluoroacetylacetonate and pyridine containing building blocks: synthesis and structural study. *New J. Chem.* **2006**, *30*, 1808–1819.

(41) Zaman, M. B.; Udachin, K.; Ripmeester, J. A.; Smith, M. D.; zur Loye, H.-C. Synthesis and Characterization of Diverse Coordination Polymers. Linear and Zigzag Chains Involving Their Structural Transformation via Intermolecular Hydrogen-Bonded, Interpenetrating Ladders Polycatenane, and Noninterpenetrating Square Grid from Long, Rigid N,N'-Bidentate Ligands: 1,4-Bis[(x-pyridyl)ethynyl]benzene (x = 3 and 4). *Inorg. Chem.* **2005**, *44*, 5047–5059.

(42) Wong, B. A.; Friedle, S.; Lippard, S. J. Solution and Fluorescence Properties of Symmetric Dipicolylamine-Containing Dichlorofluorescein-Based Zn<sup>2+</sup> Sensors. *J. Am. Chem. Soc.* **2009**, *131*, 7142–7152.

(43) Halcrow, M. A. Jahn–Teller distortions in transition metal compounds, and their importance in functional molecular and inorganic materials. *Chem. Soc. Rev.* **2013**, *42*, 1784–1795.

(44) Lee, E.; Lee, S. S. Syntheses and Crystal Structures of Mercury(II) and Copper(II) Complexes of an 18-Membered NS<sub>4</sub>-Macrocycle. *Bull. Korean Chem. Soc.* **2015**, *36*, 36–42.

(45) Cardew, P. T.; Davey, R. J. The kinetics of solvent-mediated phase transformations. *Proc. R. Soc. London, Ser. A* **1985**, 398, 415–428.

(46) Khlobystov, A. N.; Champness, N. R.; Roberts, C. J.; Tendler, S. J. B.; Thompson, C.; Schröder, M. Anion exchange in coordination polymers: a solid-state or a solvent-mediated process? *CrystEngComm* **2002**, *4*, 426–431.

(47) Jansen, M. Homoatomic  $d^{10}$ - $d^{10}$  Interactions: Their Effects on Structure and Chemical and Physical Properties. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1098–1110.

(48) Fang, Q.-R.; Zhu, G.-S.; Jin, Z.; Ji, Y.-Y.; Ye, J.-W.; Xue, M.; Yang, H.; Wang, Y.; Qiu, S.-L. Mesoporous Metal–Organic Framework with Rare etb Topology for Hydrogen Storage and Dye Assembly. *Angew. Chem., Int. Ed.* **2007**, *46*, 6638–6642.

(49) Hu, H.; Zhu, J.; Yang, F.; Chen, Z.; Deng, M.; Weng, L.; Ling, Y.; Zhou, Y. A robust etb-type metal-organic framework showing polarity-exclusive adsorption of acetone over methanol for their azeotropic mixture. *Chem. Commun.* **2019**, *55*, 6495–6498.

(50) Ge, Y.; Yao, S.; Sun, X.; Yu, C.; Li, G.; Liu, Y. A luminescent metal-organic framework with helical SBUs for highly effective detection of  $Fe^{3+}$  ions. *Inorg. Chem. Commun.* **2018**, *93*, 52–55.

(51) Vener, M. V.; Shishkina, A. V.; Rykounov, A. A.; Tsirelson, V. G. Cl…Cl Interactions in Molecular Crystals: Insights from the Theoretical Charge Density Analysis. *J. Phys. Chem. A* 2013, *117*, 8459–8467.

(52) Zhang, S.-S.; Wang, X.; Su, H.-F.; Feng, L.; Wang, Z.; Ding, W.-Q.; Blatov, V. A.; Kurmoo, M.; Tung, C.-H.; Sun, D.; Zheng, L.-S. A Water-Stable Cl@Ag<sub>14</sub> Cluster Based Metal–Organic Open Framework for Dichromate Trapping and Bacterial Inhibition. *Inorg. Chem.* **2017**, *56*, 11891–11899.

(53) Blatov, V. A.; Shevchenko, A. P.; Proserpio, D. M. Applied Topological Analysis of Crystal Structures with the Program Package ToposPro. *Cryst. Growth Des.* **2014**, *14*, 3576–3586.