

Temperature-Dependent Synthesis of Metal-Organic Frameworks Based on a Flexible Tetradentate Ligand with Bidirectional Coordination Donors

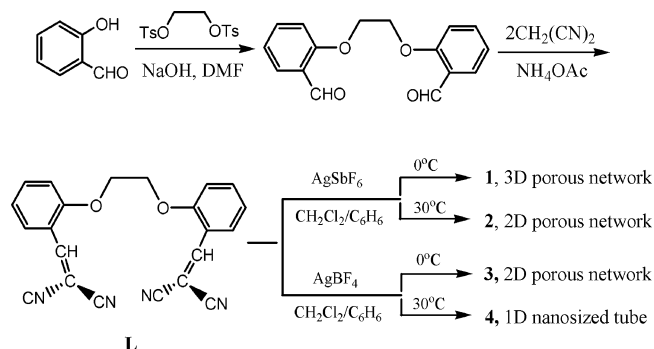
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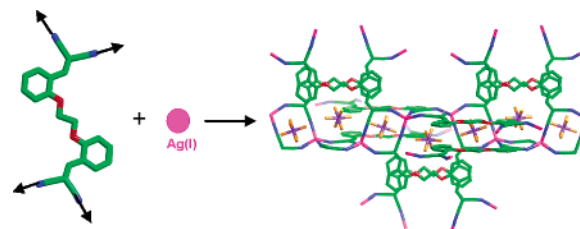
Crystal engineering of metal-organic coordination frameworks based on transition metals and organic spacers is currently attracting significant attention.¹ One of the most important motivations is that programmable crystal engineering may provide a new approach to the synthesis of functional nanoporous materials.² In general, the polymer topology can be modified by the chemical structure of the ligands chosen, the coordination geometry preferred by the metal, the inorganic counterions, the solvent system, and sometimes the metal-to-ligand ratio.³ However, one controlling factor in determining the ultimate topology of metal-organic frameworks, which has not been widely employed to date, is temperature.⁴ It is well-known that flexible organic molecules adopt different conformations under different conditions, especially at different temperatures.⁵ Thus the reaction temperature is an additional important factor that may be utilized in determining the framework topology by controlling the ligand conformation.

Following this idea, we designed and synthesized a flexible ethylene glycol ether-bridging tetradentate ligand **L** (Scheme 1),

Scheme 1. Synthesis of **L**, **1**, and **2**

in which the dicyanomethylene groups act as the terminal coordination donors. The freedom of rotation around the central C–C single bond gives rise to *cis*- or *trans*-conformations which may be frozen at different temperatures. The *cis*- and *trans*-conformations of **L** generate different donor orientations and thus different polymeric patterns. In this contribution, we report four novel silver(I) coordination polymers based on this temperature-dependent approach (Scheme 1).

As shown in Scheme 1, compounds **1–4** were synthesized based on **L** and AgX (for **1–2**, X = SbF₆[−]; for **3–4**, X = BF₄[−]) in a C₆H₆/CH₂Cl₂ mixed solvent system at 0 and 30 °C, respectively. In Ag**L**SbF₆ (**1**), **L** adopts the *trans*-conformation and acts as a tetradentate ligand to bind Ag(I) ions into a porous non-

**Figure 1.** The chiral 1D chain substructure formed in **1**. The intercalated SbF₆[−] anions are also shown. Carbon atoms are shown as green, oxygen as red, nitrogen as blue, silver atoms as pink, antimony atoms as purple, and fluorine atoms as yellow.

interpenetrating 3D network. The structure crystallizes in the chiral tetragonal space group *I*4₁22, and the asymmetric unit contains one Ag(I) cation, one **L** ligand, and one SbF₆[−] anion. Each ligand bonds to four Ag cations via the nitrile nitrogen atoms (Ag–N = 2.240(10)–2.366(8) Å), while in turn each tetrahedral Ag(I) cation coordinates to four ligands. The ligands bridge to create 1D chains of cations connected by pairs of C(CN)₂ moieties (Figure 1). The silver atoms and C(CN)₂ groups form squares; these squares share Ag(I) corners to create the chain. The chains are helical and lie about a 4₁ axis. These 1D chains are cross-linked by the backbones of the ligands, which adopt a *trans*-conformation, such that each chain is connected to four adjoining ones. All chains within the structure have the same handedness, leading to an overall chiral structure. The ligands cross-link the chains in π -stacked pairs (closest C···C contact is 3.55 Å) in which both ligands connect the same chains, but one projects “forward” from the first chain to the second, while the other projects “backward”, relative to the direction of propagation of the chain. The SbF₆[−] anions lie in cavities within the network. The unusual topology of the network may be simplified by considering the ligands and metal ions as 4-connecting nodes. This generates the 3D binodal 4-connected network shown in Figure 2. This is a very unusual network (Schläfli symbol (4².8⁴)_{Ag}(4².8².10²)_L); we are unaware of a precedent despite the large number of 4-connected networks reported in the literature. When viewed down the *c*-axis, very regular square channels (crystallographic dimensions, ca. 10 × 10 Å) are evident in **1** (Figure 2).

When the reaction was carried out at 30 °C, compound Ag**L**SbF₆ (**2**) was generated, with a 2D (6,3) sheet structure (Supporting information). It is noteworthy that, in **2**, the **L** ligands adopt a *cis*-conformation. From **1** to **2**, the dramatic structural change observed clearly results from the different conformations adopted by **L** at different temperatures.

To further investigate the effect of temperature on the structures of Ag(I)–**L** coordination polymers, AgBF₄ was used instead of AgSbF₆ to perform the reactions.

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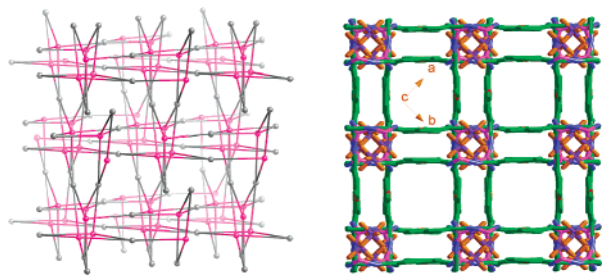


Figure 2. Left: The overall network topology in the structure of **1**; pink spheres represent Ag(I) nodes, while the gray spheres represent the L ligand nodes. Right: stick representation of the non-interpenetrating 3D network containing different square-like channels.

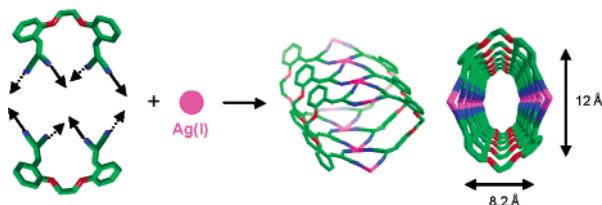


Figure 3. The side and top views of the 1D tube motif in **4**. Carbon atoms are shown as green, oxygen as red, nitrogen as blue, and silver atoms as pink.

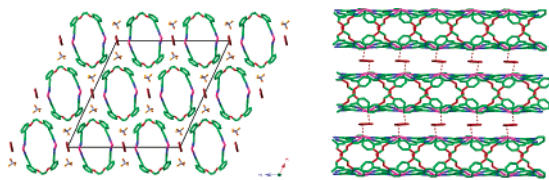


Figure 4. The packing of the tubes in **4** (left). Also shown are the BF_4^- counterions and the bis- η^1 -coordinated benzene molecules. One layer (right) defined by the weak intermolecular $\text{Ag}\cdots\pi$ interactions between the tubes and the intercalated benzene molecules (highlighted in brown).

Compounds $[\text{Ag}_2\text{L}(\text{H}_2\text{O})](\text{BF}_4)_2$ (**3**) and $\text{AgLBF}_4 \cdot 0.5(\text{C}_6\text{H}_6)$ (**4**) were obtained by combination of **L** with AgBF_4 at 0 and 30 °C, respectively. In **3**, the **L** ligands adopt a *trans*-conformation and coordinate to four silver atoms to generate highly corrugated 2D sheets (Supporting information).

The structure of **4** is remarkably different. In **4**, the silver atom acts as square planar 4-connecting nodes, while the ligands adopt the *cis*-conformation, and 1D planar chains are formed. As shown in Figure 3, two of these chains are connected to form a 1D tube motif.

The tubes lie parallel to the crystallographic *b*-axis and have internal dimensions of ca. 8.2×12 Å. Note that the tube walls of **4** are full of oxygen and nitrogen atoms; such a crown-ether-like nanoscale tube is of considerable interest in the broader scientific context. The tubes pack as shown in Figure 4. Intercalated benzene molecules and BF_4^- counterions lie *between* the tubes; the tubes themselves are completely empty. There are, however, weak interactions between the silver ions and the benzene molecules ($\text{Ag}(\text{I})\cdots\text{C}(25) = 2.656(10)$ Å). As shown in Figure 4, each benzene molecule makes an interaction of this type to a silver atom on either side, effectively acting as a weak link between tubes. Each tube is connected to two others in this way to form layers parallel to the crystallographic *bc* plane (Figure 4).

A particularly interesting and challenging subject in metal-organic polymers is the design and construction of metal-organic nanotubular structures. So far, for constructing nanotubular structures, the coordination approach has been shown to be very effective, for example, in the assembly of coordination helices or tape-like secondary building blocks.⁶ Compound **4** provides a new approach for the rational construction of polymeric coordination-driven molecular tubes. That is, the polymeric metallatube is generated by the combination of square planar metal ions with bent tetradentate ligands which each possess two pairs of terminal coordination groups with each pair of coordination donors facing opposite directions.

To gain a deeper insight into the formation of compounds **1–4** based on the temperature-controlled approach, DFT calculations were employed to examine the thermodynamics of the different ligand conformations. The calculated results indicate that the *trans*-conformation is more stable in solution. The transformation barrier between *trans*- and *cis*-conformations is relatively low (13.25 kcal/mol), and the transformation process is very fast ($k = 2.95 \times 10^{10} \text{ s}^{-1}$). Furthermore, the higher temperature clearly enhances the tendency for the transformation from the *trans*- to *cis*-conformation, which supports the current results and discussion.

In summary, we have synthesized four Ag coordination polymers whose structures depend on the reaction temperature. This work demonstrates that the temperature parameter can be used to control the conformation of flexible ligands and, consequentially, the topology of the metal-organic frameworks. Work is in progress to obtain new metal-organic frameworks generated from other flexible ligands and transition metals based on this approach.

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Supporting Information Available: Crystallographic data and CIF files of **1–4**, synthesis of **L**, **1–4**, and structural description of **2** and **3** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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