Unique Nanometer-Thick Layered Network

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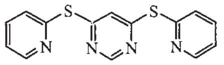
4,6-Bis(2′-pyridylthio)pyrimidine coordinates to three Ag(I) ions in a bridged tridentate fashion to generate the anion exchangeable nanometer-thick layered network.

Nanoscale mimics of simple molecules or natural minerals have surged into mesoscopic physics and materials science during the last decade.[1–3] Significant progress can be made in the development of nanochemistry by transfering concepts found in the real worlds into the chemical arena.[4,5] Central to this mission is the development of the simple chemical system capable of instructing their own organization into large aggregates of molecule through their mutual recognition properties.[6] Though some strategies for the construction of molecular materials have still been serendipitous, various ligands containing multiple donor atoms have been used as chelating modes or bridging modes.[7] Appropriate angles and flexible components of the multidentate ligands play important roles in self-assembly via coordination. We have demonstrated recently that Py_2X (X=O, S) produce interesting structures.[5,8–11] Among various building spacer ligands, 4,6-bis(2′-pyridylthio) pyrimidine (bptp) is an interesting spacer.[12] The bptp is a noninnocent spacer that possesses a magic angle (C-S-C, about 100°), conformational nonrigidity, and potential multidentate donors (N_4S_2). We report herein unique nanometer-thick silver(I)-bptp network and related properties.



bptp

The reaction of $AgCF_3CO_2$ (**1**) with bptp (**2**) affords colorless crystals of $[Ag(bptp){\cdot}CF_3CO_2]_n$ (**3**).[13] **3** is air-stable and is insoluble in water and in organic solvents. The structure of **3** was established by X-ray characterization.[14] The structural unit and infinite structure are depicted in Figure 1. **2** acts as a tridentate and connects three Ag(I) ions defining the edges of 48-membered rings. The local geometry of the silver(I) ion approximates to a rare trigonal pyramid rather than a tetrahedral arrangement. The Ag–N bonds are in the range of 2.261(9)–2.35(1) Å. The trifluoroacetate anion weakly interacts with the silver(I) ion as a fourth ligand (Ag–O(1), 2.50(1) Å). The skeletal structure seems to be affected by the presence of a face-to-face (π–π) stacking of two pyridine rings (3.8 Å). There are two silver planes in the network. The interplanar shortest Ag(I)···Ag(I) distance is 5.63 Å. The intraplanar shortest distance Ag(I)···Ag(I) is 7.24 × 9.83 Å. Thus, a pyridyl and a pyrimidine of **2** are coordinated to Ag(I) at the same plane whereas another pyridyl is coordinated to Ag(I) at the next plane. The dihedral angles between the pyridyl and the pyrimidine planes around the sulfur atom are 85.8(2)° and 80.2(3)°. The most salient feature is the nanometer-thick layered network covered by trifluoro groups. The side view of the complicate network can be diagrammatically depicted in Scheme 1.

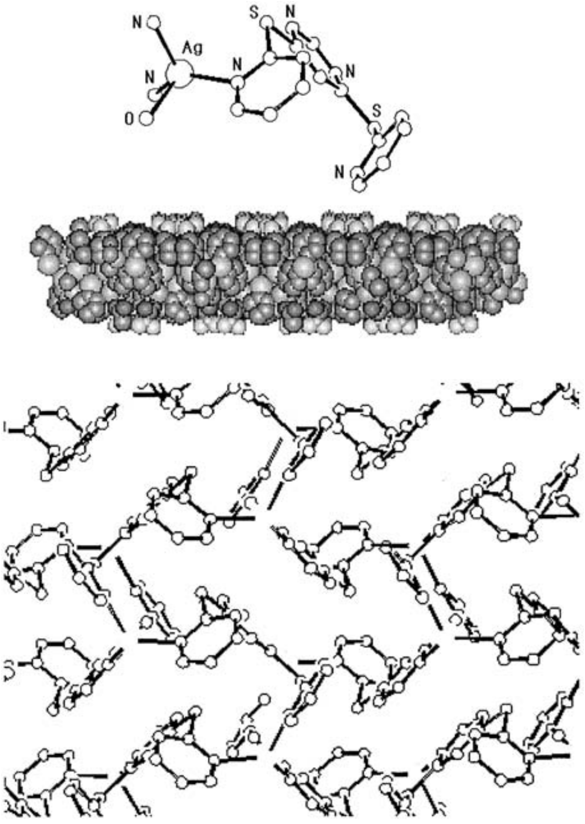
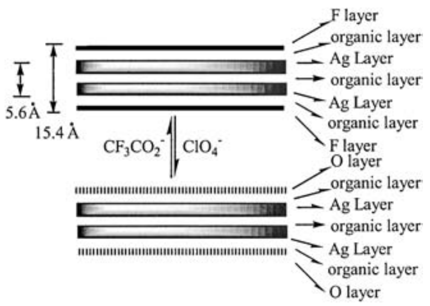


Figure 1. An ORTEP drawing of the unit of **3** (top). Side view space-filling of the infinite structure (middle). Top view of the infinite structure. Counteranion $CF_3CO_2^-$ is omitted for clarity (bottom).



Scheme 1.

The anions at the surface of the network can be exchanged in a typical aqueous media.[5] To investigate the exchange procedure, the anion exchange of **3** with ClO_4^- was monitored by the characteristic IR bands of anions. The addition of $NaClO_4$ to a

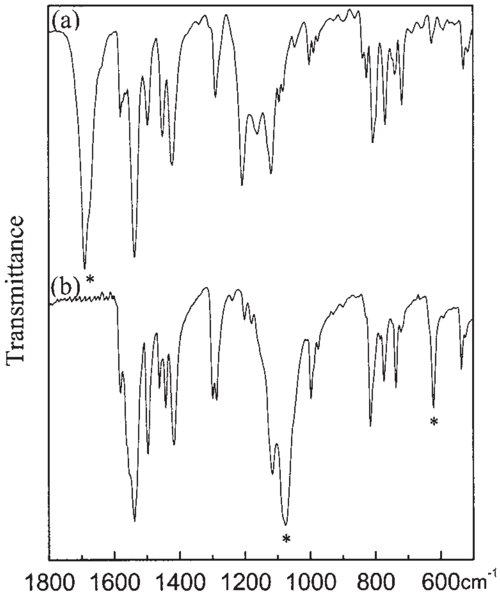


Figure 2. IR spectra of **3** (a) and $[Ag(bptp)\cdot ClO_4]_n$ prepared by the anion exchange (b). Asterisk indicates the bands induced by each anion.

suspension of microcrystalline **3** in water with a 3 : 1 mole ratio showed that, after 24 h, the $CF_3CO_2^-$ anions (>98%) are exchanged with ClO_4^- anions. Intense ClO_4^- band at $1016\,cm^{-1}$ appears while the $CF_3CO_2^-$ band at $1690\,cm^{-1}$ disappears (Figure 2). The other peaks of the spectrum remain virtually unchanged, suggesting the preservation of the skeletal structure during the anion exchange process. The exchanged species still gives a sharp X-ray powder pattern and the satisfactory elemental analysis.[15] The reverse exchange was easily achieved under the same condition. The $CF_3CO_2^-$ anions were also exchanged with the octahedral PF_6^- anions. Such anion exchange may be applied to the modification of surface of the network (Scheme 1). The TGA curve of **3** shows a weight-loss corresponding to **2** (obsd 58.2%, calcd 57.5%) in the temperature range 198–300 °C, and thus **1** remains above that temperature range.

The unique nanometer-thick network was induced by the three-connected linker and face-to-face (π–π) interactions. The present system is significant as a rare example of metalloid nanoplate covered by the organic group with a periodic array of atomic scale. Further experiments and pervasive applications including anion exchange are in progress, and will provide more detailed information on the development of the molecular networks that exhibit desirable properties.

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13 **3**: an ethanolic solution (15 mL) of **1** (110 mg, 0.5 mmol) was slowly diffused into an a chloroform solution (15 mL) of **2** (149 mg, 0.5 mmol). Colorless crystals of **3** formed at the interface, and were obtained in 3 days in 78% yield. IR (KBr, cm^{-1}): $\nu(CO_2, s)$, 1690 (s). Anal. found: C, 37.60; H, 1.89; N, 10.70%. Calcd for $C_{16}H_{10}N_4F_3O_2S_2Ag$: C, 37.01; H, 1.94; N, 10.79%.

14 Crystal data for **3**: fw = 519.27, monoclinic, $a = 9.832(2)$ Å, $b = 12.382(2)$ Å, $c = 15.418(2)$ Å, $\beta = 96.33(2)°$, $U = 1865.5(5)$ Å^3, $T = 293(2)$ K, space group $P2_1/a$, $Z = 4$, $D = 1.849\,g/cm^3$, μ(Mo Kα) = $1.353\,mm^{-1}$, 2216 unique reflections in all calculations. $R1 = 0.0778$ ($wR2 = 0.2363$), $GOF = 1.146$ for 253 parameters.

15 Anal. found: C, 33.40; H, 1.90; N, 11.70%. Calcd for $C_{14}H_{10}N_4O_4S_2Cl\,Ag$: C, 33.25; H, 1.99; N, 11.19%.