Molecular Networks Consisting of Dumbbell-cage Motif: Structure and Anion Exchangeability of $[Ag(Py_2S)_2{\cdot}BF_4]_n$ (Py_2S = 4,4'-Dipyridyl Sulfide)

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The silver(I) network with Py_2S has the face-to-face (π–π) interactions to generate unusual dumbbell-cage motif. The BF_4^-counteranion within each cage has been reversibly exchanged with the similar anions in size.

Open framework structures are of great interest due to their mimicry of microporous solids useful for molecular adsorption,[1] host–guest chemistry,[2,3] exchange,[4,5] and unusual molecular mechanics.[6,7] Recent environmental concern about harmful anions has spurred new field of the open frameworks for reversible encapsulation and removal of such anions.[8] Crystallization of specifically designed building blocks combined with metal ions has resulted in a number of new cavity-materials.[9,10] The discovery of intriguing molecular frames has still been serendipitous since the structures are frequently influenced by induced intra- or intermolecular weak interactions. Among various building spacers, 4,4'-dipyridyl sulfide (Py_2S)[11] has been exploited to produce new coordination polymers.[12] We now describe the structure and anion exchangeability of the unusual cage network which is obtained by the self-assembly of $Ag(CH_3CN)_4BF_4$ (**1**) and Py_2S (**2**).

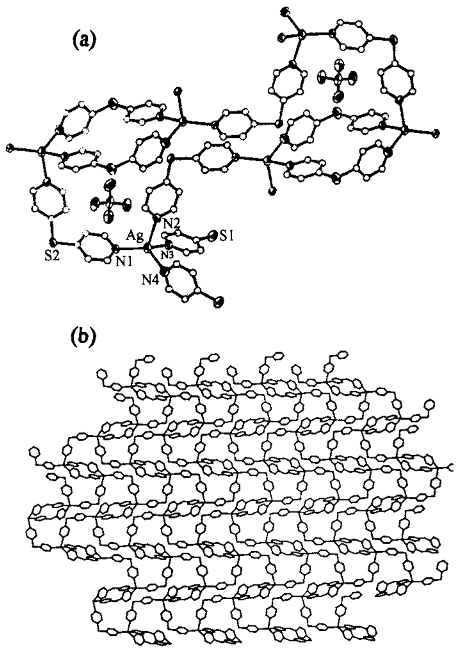
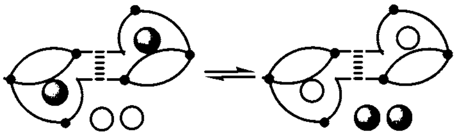


Figure 1. (a) An ORTEP drawing of the unit motif showing the face-to-face (π–π) interactions of **3**. (b) An infinite structure of **3**. Counteranion BF_4^- is omitted for clarity.

The reaction of **1** with **2** in acetonitrile affords beige-colored crystals of $[Ag(Py_2S)_2{\cdot}BF_4]_n$ (**3**).[13] The product is air-stable and is insoluble in water and in organic solvents. Its structure was established by X-ray characterization.[14] The structural motif and infinite structure are depicted in Figure 1. Each Py_2S connects two tetrahedral silver(I) ions defining the edges of 20- and 60-membered rings. The local geometry of the silver(I) ion is severely deviated from typical tetrahedral arrangement to sustain the network. The Ag–N bond distances are in a wide range of 2.246(4)–2.427(5) Å. The most salient feature is the presence of a face-to-face (π–π) stacking of the two pyridine rings (~3.4 Å) within the 60-membered ring, (the corresponding interaction of graphite, 3.35 Å).[15] Thus, the unit motif consisting of 6 Ag ions and 8 Py_2S spacers is two independent bicyclic cages via the π–π interaction, that is, a dumbbell (11 × 13 Å cross section). Each BF_4^- anion is nestled in an independent bicyclic cage. The shortest internetwork Ag···Ag distance is 13.53 Å.


(1)

The anion within each cage can be exchanged in a typical aqueous media (eq 1).[9] To investigate the exchange procedure, the anion exchange of **3** with NO_3^- was monitored by the characteristic IR bands of anions. The addition of $NaNO_3$ to a suspension of microcrystalline **3** in water with a 3 : 1 mole ratio showed that, after 8 h, the BF_4^- anions (> 95%) are exchanged with NO_3^- anions. Intense NO_3^- band at 1370 cm^{-1} appears while the BF_4^- bands at 900–1150 cm^{-1} disappear (Figure 2). The other peaks of the spectrum remain virtually unchanged, suggesting the preservation of the skeletal structure during the

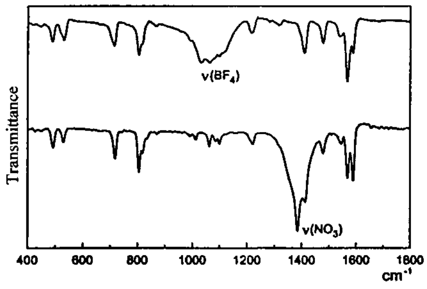


Figure 2. IR spectra of **3** (top) and $[Ag(Py_2S)_2{\cdot}NO_3]_n$ prepared by the anion exchange (bottom).

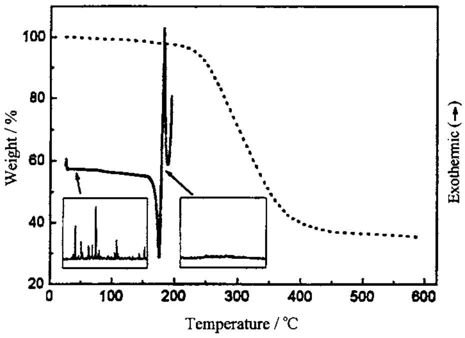


Figure 3. Overlay of TGA and DSC traces of **3**. The XRD patterns for as-synthesized (left) and after-calcination around 185 °C (right) were depicted in the inset.

anion exchange process. The exchanged species still gives a sharp X-ray powder pattern and the satisfactory elemental analysis. The reverse exchange was easily achieved under the same condition. The BF_4^- anions were also exchanged with the octahedral PF_6^- anions as well as the similar tetrahedral ClO_4^- anions. Such exchange reactions may be applied to the development of a tailored synthetic strategy that cannot be approached by general methods. For an instance, the direct reaction of $AgNO_3$ with Py_2S spacer yielded a unique double-stranded coordination polymer, $[Ag_3(Py_2S)_2(NO_3)_3 \cdot 2H_2O]$[16] in contrast to the cage network, $[Ag(Py_2S)_2 \cdot NO_3]_n$, obtained from the anion exchange. The TGA curve of **3** shows a weight-loss corresponding to two **2** linkers (obsd 64.4%, calcd 65.9%) in the temperature range 230–380 °C (Figure 3). In contrast to a typical ionic coordination polymer, the DSC trace shows that the compound sharply melts at 176 °C (endothermic peak), and then is melt-transformed into new species around 185 °C (exothermic peak) just above the melting point. The resulting material seems to exist as amorphous composite as shown in the X-ray powder pattern. Such thermal properties provide that the thermal energy collapses the face-to-face interactions, resulting in the change from the highly ordered arrangement to the more random state.

The unusual molecular networks consisting of a dumbbell motif induced by the face-to-face (π–π) interaction show significant anion exchangeability. Further experiments and pervasive applications are in progress, and will provide more detailed information on the development of the molecular networks that exhibit characteristic properties including auxetic behavior.[6]

References and Notes

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13 **3**: an acetonitrile solution (15 mL) of **1** (180 mg, 0.5 mmol) and **2** (188 mg, 1.0 mmol) was stirred for 5 min at room temperature. The solution was slowly evaporated. Colorless crystals, **3**, suitable for X-ray crystallography were obtained in 3 days in 80% yield. IR (KBr, cm^{-1}): $\nu(BF_4$, s, multibands), 1130 (sh), 1090 (sh), 1062 (s), 1032 (s). Anal. found: C, 42.60; H, 2.79; N, 9.70%. Calcd for $C_{20}H_{16}N_4BF_4S_2Ag$: C, 42.06; H, 2.82; N, 9.81%.

14 Crystal data for **3**: MW= 571.17, monoclinic, a = 17.060(3) Å, b = 15.858(2) Å, c = 8.561(2) Å, β = 103.30(2)°, U = 2254.0(7) $Å^3$, T = 293(2) K, space group $P2_1/a$, Z = 4, D = 1.683 g/cm^3, μ (Mo Kα) = 1.128 mm^{-1}, 5862 unique reflections in all calculations. $R1$ = 0.072 ($wR2$ = 0.1210), GOF = 1.178 for 290 parameters.

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