

## Anion-controlled formation of two silver lamella frameworks based on *in situ* ligand reaction†

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Two 2D silver lamella frameworks,  $[\text{Ag}_4(\text{C}_5\text{H}_4\text{NS})_2(\text{NO}_3)_2]_n$  (**1**) and  $[\text{Ag}_3(\text{C}_5\text{H}_4\text{NS})_2]_n \cdot n\text{ClO}_4$  (**2**) based on binuclear units have been solvothermally synthesized. The  $\text{C}_5\text{H}_4\text{NS}$  ligand was *in situ* generated from the cleavage of bis(2,4,6-trimethyl-3,5-bis((pyridin-2-ylthio)methyl)phenyl)methane (bmpm). Furthermore, the formation of **1** and **2** was also controlled by anions involved in the reaction. Short Ag–Ag interactions were also found in **1** and **2**.

Design and synthesis of coordination polymers with desired topology is still a great challenge to chemists because many factors such as solvents, pH value, reaction temperature and time, cations, anions *etc.* influence the crystal growth as well as the final structures of the product.<sup>1–4</sup> As is known, anions have significant effect on the formation of product. For example, some anions such as  $\text{HCOO}^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{NO}_3^-$  *etc.* with strong coordination ability can coordinate to metal ions or bridge metal ions to generate high-nuclear units or high-dimensional frameworks;<sup>5</sup> however, some other anions such as  $\text{ClO}_4^-$ ,  $\text{BF}_4^-$  *etc.* possess very weak coordination ability and normally act as counterions in the formation of the frameworks.<sup>6</sup> In the past decade, studies on anion-controlled formation of coordination complexes have been widely documented.<sup>5,6</sup> Very recently, our group studied the anion effect on the formation of a series of metal–organic coordination cages.<sup>7</sup> In this communication, we report anion-controlled formation of two silver lamella frameworks based on *in situ* generated pyridine-2-thiol.

Thiolates are a subject of great interest in the chemistry of transition-metal complexes for their special potential to construct coordination architectures. They can act as  $\mu_2$ ,  $\mu_3$  or even  $\mu_4$  bridges and often yield structural versatile polynuclear or polymeric complexes.<sup>8,9</sup> To design polymeric d<sup>10</sup> metal complexes with fascinating structures is also one of most exciting and rapidly developing fields in current coordination

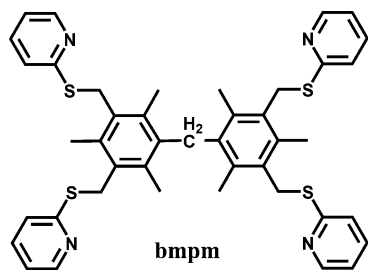
and supramolecular chemistry due to their potential applications in many areas.<sup>10–12</sup> Especially silver(I) polymers with chains or network structures are potential optics and semiconductor materials<sup>13,14</sup> and studies have shown that direct metal–metal interactions are one of the most important factors for the manifestation of such properties.<sup>15</sup> Recently, many flexible ligands containing dithiolate or monothiolate have been synthesized to construct novel polymeric complexes with infinite chains or high-dimensional frameworks.<sup>16,17</sup> In order to construct silver complexes with interesting topology and property, we designed and synthesized a new flexible ligand, bis(2,4,6-trimethyl-3,5-bis((pyridin-2-ylthio)methyl)phenyl)methane (bmpm) (Scheme 1). However, to our surprise, solvothermal reaction of bmpm and different silver salts resulted in the formation of two silver lamella frameworks involving pyridine-2-thiolate,  $[\text{Ag}_4(\text{C}_5\text{H}_4\text{NS})_2(\text{NO}_3)_2]_n$  (**1**) and  $[\text{Ag}_3(\text{C}_5\text{H}_4\text{NS})_2]_n \cdot n\text{ClO}_4$  (**2**) ( $\text{C}_5\text{H}_4\text{NS}$  = pyridine-2-thiolate ( $\text{PyS}^-$ )). Through a series of analysis involving <sup>1</sup>HNMR, ESI-MS, single crystal X-ray diffraction of bmpm and some comparative experiments, we conformed that the pyridine-2-thiolate was *in situ* generated from the cleavage of bmpm.

The formation of **1** and **2** was controlled by anions in the reaction. The solvothermal reaction of  $\text{AgNO}_3$  or  $\text{AgClO}_4$  and bmpm in DMF for three days at 90 °C resulted in the formation of a large amount of brown block crystals of **1** and gray rod-like crystals of **2**, respectively. In **1**,  $\text{NO}_3^-$  anions were involved in the coordination to form the 2D neutral framework, however,  $\text{ClO}_4^-$  anions did not coordinate to the metal ion and act as counterions to generate a 2D cationic framework of **2** (Fig. S1†). Both complexes contain a binuclear silver cluster as the basic building unit (Fig. 1a). The phase purity of the bulk samples were confirmed by powder XRD (PXRD) (Fig. S3†). The simulated and experimental PXRD patterns of **1** and **2** indicate the phase purity of the products. The most peak positions of simulated and experimental patterns are in good agreement with each other, and the differences in intensity may be due to the preferred orientation of

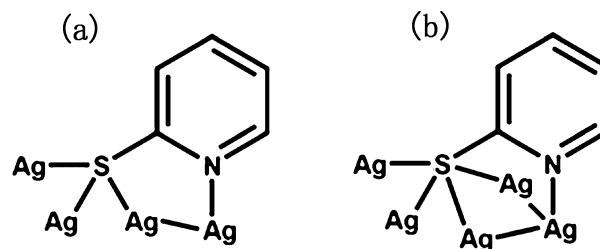
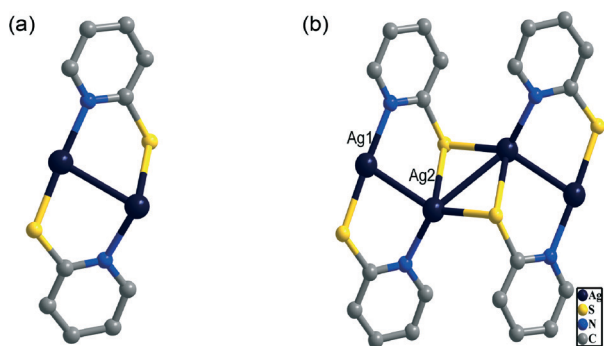
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† Electronic supplementary information (ESI) available: Synthesis, crystallographic information, additional figures, <sup>1</sup>HNMR spectrum, ESI-MS, configurations of bmpm, IR, TGA and XRD pattern. CCDC 937450 for **1**, 937451 for **2**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3ce40809d



Scheme 1 The bmpm ligand.

Scheme 2 Coordination modes of pyridine-2-thiolate ligand in **1** (a) and **2** (b). All hydrogen atoms are omitted for clarity.Fig. 1 (a) The basic building unit of a binuclear silver cluster in **1** and **2**. (b) A tetranuclear  $\text{Ag}_4(\text{C}_5\text{H}_4\text{NS})_4$  cluster in **1**. All hydrogen atoms are omitted for clarity.

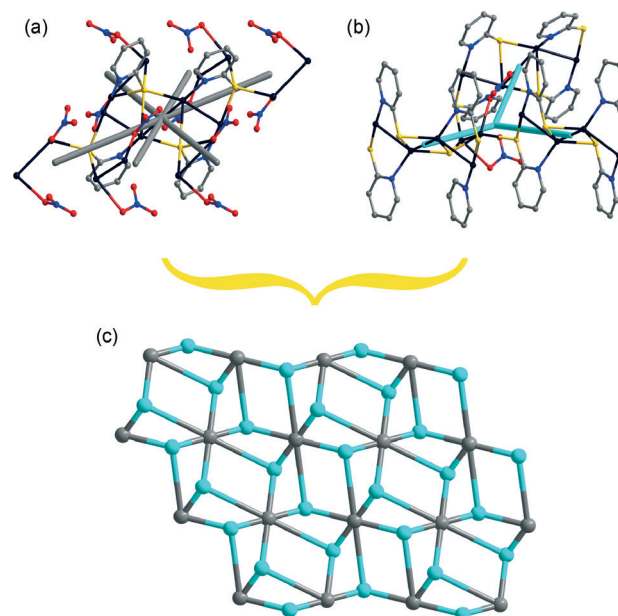
the powder samples. In **1** and **2** the observed strong peak (Fig. S4†) at  $1379\text{ cm}^{-1}$  in **1** and  $1619\text{ cm}^{-1}$  in **2** are attributed to  $\text{NO}_3^-$  and  $\text{ClO}_4^-$ , respectively, indicating the existence of  $\text{NO}_3^-$  and  $\text{ClO}_4^-$  in **1** and **2**.

Complex **1** crystallizes in monoclinic  $P2_1/c$  space group and the asymmetric unit consists of four silver ions (Ag1, Ag2, Ag3 and Ag4), two  $\text{C}_5\text{H}_4\text{NS}$  ligands and two coordinated  $\text{NO}_3^-$  anions (Fig. S1(a)†). There are two types of pyridine-2-thiolate ligands with different coordination modes: the sulfur atom acts as a  $\mu_3$ -bridge linking three metal centers (Scheme 2a) or as a  $\mu_4$ -bridge linking four metal centers (Scheme 2b). Ag1 and Ag2 were engaged by two  $\text{C}_5\text{H}_4\text{NS}$  ligands to generate a binuclear unit with strong  $\text{Ag}\cdots\text{Ag}$  interaction (distance:  $2.899\text{ \AA}$ ). Two such units were connected each other through the bridging S atom of  $\text{C}_5\text{H}_4\text{NS}$  ligand and ligand-unsupported  $\text{Ag}\cdots\text{Ag}$  interaction (distance:  $3.373\text{ \AA}$ ) to form a tetranuclear  $\text{Ag}_4(\text{C}_5\text{H}_4\text{NS})_4$  cluster (Fig. 1b). Ag3 and Ag4 were bridged by ligand-unsupported  $\text{Ag}\cdots\text{Ag}$  interaction (distance:  $3.006\text{ \AA}$ ) to generate

† Crystal data for **1**: monoclinic  $P2_1/c$  space group,  $a = 11.552(5)\text{ \AA}$ ,  $b = 14.116(6)\text{ \AA}$ ,  $c = 10.387(4)\text{ \AA}$ ,  $\alpha = 90.00^\circ$ ,  $\beta = 96.412(7)^\circ$ ,  $\gamma = 90.00^\circ$ ,  $V = 1683.2(12)\text{ \AA}^3$ ,  $Z = 4$ ,  $\rho = 3.062\text{ g cm}^{-3}$ ,  $F(000) = 1456$ ,  $\mu = 4.871\text{ mm}^{-1}$ , 8104 reflection measured, 2964 unique ( $R_{\text{int}} = 0.0227$ ), final  $R_1 = 0.0382$ ,  $wR_2 = 0.0740$  for all data; **2**: monoclinic  $C2/c$  space group,  $a = 10.0593(19)\text{ \AA}$ ,  $b = 23.506(5)\text{ \AA}$ ,  $c = 7.2278(14)\text{ \AA}$ ,  $\alpha = 90.00^\circ$ ,  $\beta = 116.631(3)^\circ$ ,  $\gamma = 90.00^\circ$ ,  $V = 1527.7(5)\text{ \AA}^3$ ,  $Z = 4$ ,  $\rho = 2.763\text{ g cm}^{-3}$ ,  $F(000) = 1185$ ,  $\mu = 4.269\text{ mm}^{-1}$ , 3716 reflection measured, 1342 unique ( $R_{\text{int}} = 0.0318$ ), final  $R_1 = 0.0324$ ,  $wR_2 = 0.0711$  for all data; data collection of **1** and **2** were performed with Mo K $\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ) on a Bruker APEX-II diffractometer. The structures were solved by direct methods and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on  $F^2$  using the SHELXTL program.

a  $\text{Ag}_2(\text{NO}_3)_2$  unit. Thus, each  $\text{Ag}_4(\text{C}_5\text{H}_4\text{NS})_4$  cluster connected six  $\text{Ag}_2(\text{NO}_3)_2$  units and every  $\text{Ag}_2(\text{NO}_3)_2$  unit attached to three  $\text{Ag}_4(\text{C}_5\text{H}_4\text{NS})_4$  clusters to generate a 2D layer. If the  $\text{Ag}_4(\text{C}_5\text{H}_4\text{NS})_4$  cluster can be considered as a six-connected node and  $\text{Ag}_2(\text{NO}_3)_2$  unit as a three-connected node, then, complex **1** is a (6,3)-connected net, as shown in Fig. 2. There exist several  $\text{Ag}\cdots\text{Ag}$  interactions in **1** with the distances of  $2.899\text{ \AA}$ ,  $3.373\text{ \AA}$ ,  $3.078\text{ \AA}$ ,  $3.006\text{ \AA}$  (Fig. 3 and Table S1†), which are comparable to other silver complexes containing  $\text{Ag}\cdots\text{Ag}$  interactions.<sup>14,18</sup> Due to the coordination of  $\text{NO}_3^-$  anions, the 2D layer is neutral.

As mentioned above, anions involved in the reaction have significant influence on the formation of the product. Hence, when we used  $\text{AgClO}_4$  to replace  $\text{AgNO}_3$  in the preparation of **1**, gray rod-like crystals of **2** were isolated in a very low yield. Different from **1**, complex **2** crystallizes in the monoclinic  $C2/c$  space group and the asymmetric unit consists of one and a half silver ions (Ag1 and Ag2), one  $\text{C}_5\text{H}_4\text{NS}$  ligand and a half  $\text{ClO}_4^-$  anion. The S atom in the  $\text{C}_5\text{H}_4\text{NS}$  ligand adopts a  $\mu_3$ -bridge to link three silver ions. As found in **1**, two Ag1 ions

Fig. 2 (a) Each  $\text{Ag}_4(\text{C}_5\text{H}_4\text{NS})_4$  cluster linking six  $\text{Ag}_2(\text{NO}_3)_2$  unit is defined as a 6-connected node. (b) Every  $\text{Ag}_2(\text{NO}_3)_2$  unit is attached to three  $\text{Ag}_4(\text{C}_5\text{H}_4\text{NS})_4$  clusters, forming a 3-connected node. (c) A schematic representation of the (6,3)-connected net of **1**.

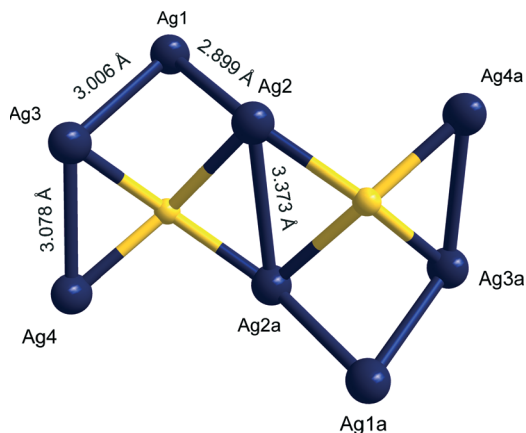


Fig. 3 The existence of Ag $\cdots$ Ag interactions in **1**.

were engaged by two  $C_5H_4NS$  ligands to generate a binuclear cluster (Fig. 1a), which can be considered as the basic building unit. The Ag $\cdots$ Ag distance in the unit is 2.982 Å, which is slightly longer than that in **1**. The binuclear units were connected each other along the  $c$  axis through the bridging S atom of  $C_5H_4NS$  ligand to form a 1D double chain, which was further linked by Ag2 ions through the bridging S atoms of  $C_5H_4NS$  ligand to form a 2D layer (Fig.S1(b) $\dagger$ ). Thus, Ag1 ion is three-coordinated by two S atoms and one N atom in a triangular geometry, whereas Ag2 is coordinated by two S atoms of  $C_5H_4NS$  ligand in a linear geometry. If we further simplify the structure by considering the binuclear unit as a four-connected node, the S atom of  $C_5H_4NS$  ligand as a three-connected node and Ag2 as a linear linker, then, complex **2** is a 2D (4,3)-connected net, as shown in Fig. 4. Due to the weak coordination ability of  $ClO_4^-$ , the 2D layer is cationic and the  $ClO_4^-$  anions are located between the layers as counterions.

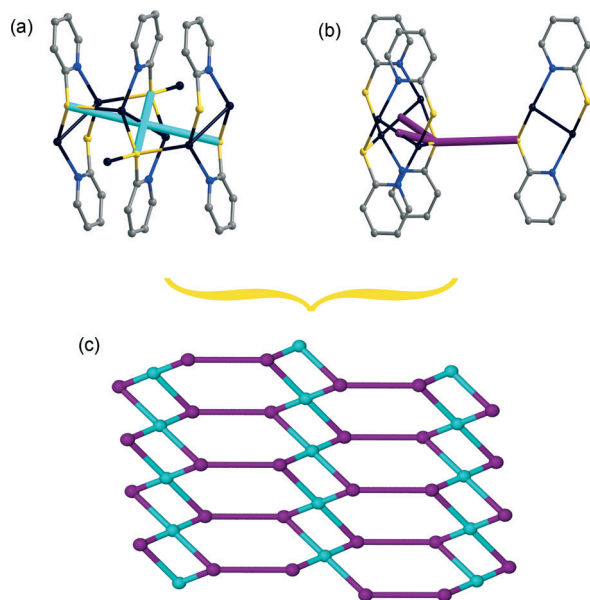


Fig. 4 (a) Each binuclear unit is defined as a four-connected node. (b) Each S atom of  $C_5H_4NS$  ligand is defined as a three-connected node and Ag2 is defined as a linear linker. (c) A schematic representation of 2D (4,3)-connected net of **2**.

To prove the origin of the  $C_5H_4NS$  ligand in **1** and **2**, a series of analyses including  $^1H$ NMR, ESI-MS, X-ray single crystal diffraction of bmpm and comparative experiments were carried out. However, when we used pyridine-2-thiol ligand to directly assemble with silver ions under the same conditions, only some unknown precipitates were obtained. We made sure that they were not the same as the complex **1** and **2** by PXRD comparison (Fig. S10 $\dagger$ ), indicating that the *in situ* ligand reaction plays an important role in the formation of **1** and **2**. The purity of the original bmpm ligand was further confirmed by  $^1H$ NMR, ESI-MS and single crystal X-ray diffraction analysis [Fig. S2 $\dagger$ ], indicating the  $C_5H_4NS$  ligand is not from the starting material. Recently, *in situ* ligand formation has largely been an attractive process in the assembly of coordination polymers. Because of C–S bond formation or cleavage, among many others processes, the organic starting material may undergo a variety of reactions, so the products of these reactions are not always intuitive.<sup>19,20</sup> Due to the special space configuration of bmpm and the strong coordination ability of S atom to Ag ions, the C–S bond became weakened and broken during the solvothermal reaction. When other metal ions such as  $Zn^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$  were used in the same reaction, only clear solution was obtained. Then the clear solution were slow evaporation at 50 °C, the crystal of bmpm ligand was obtained, indicating the *in situ* ligand reaction did not occur and the dual role of Ag ions in forming **1** and **2**. Hence, we concluded that  $C_5H_4NS$  ligand in **1** and **2** was formed by *in situ* cleavage of bmpm ligand mediated by  $Ag^+$  ions.

Complexes **1** and **2** are stable in air and insoluble in water and common organic solvents. To better understand the thermal stability of **1** and **2**, thermal gravimetric analysis (TGA) was performed. Thermogravimetric analysis of **1** and **2** was carried out under a nitrogen-flow atmosphere with a heating rate of 10 °C  $min^{-1}$  in the temperature region of 20–600 °C (Fig. S5 $\dagger$ ). TGA indicates that **1** is stable up to *ca.* 200 °C and **2** is stable up to 315 °C, corresponding to the decomposition of  $NO_3^-$  anions involved in the coordination and  $ClO_4^-$  counterions as well as organic ligands, which are nearly in agreement with the single-crystal analysis.

The solid-state luminescent spectra of **1**, **2** and the pyridine-2-thiol ligand were also investigated at room temperature. As shown in Fig. 5, complexes **1** and **2** display emission peaks at 332, 469 nm and 358, 469 nm upon excitation at 275 nm. The pyridine-2-thiol ligand displays emission at similar positions upon excitation at 275 nm. Compared with the emission peaks of the ligand, the luminescent behaviors of **1** and **2** are almost no change, except the intensity at 332 and 358 nm for **1** and **2**, respectively, increases significantly. Since  $Ag^+$  ions are difficult to oxidize or to reduce due to their  $d^{10}$  configuration and the free ligand shows approximate emissions also, the emissions in **1** and **2** are neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT) in nature and may originated from the  $\pi-\pi^*$  transition of the  $C_5H_4NS$  ligand.<sup>21</sup>

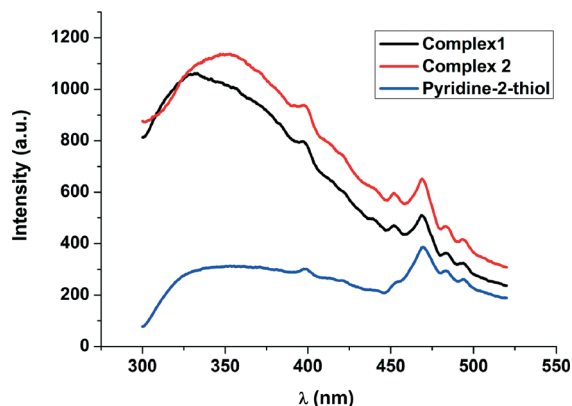


Fig. 5 Solid-state emission spectra of complexes **1** and **2** and the  $C_5H_4NS$  ligand at room temperature.

In summary, the syntheses and characterization of two new Ag(I) complexes (**1** and **2**) are described. *In situ* ligand reaction plays an important role in the formation of these two complexes. Furthermore, the formation of **1** and **2** is controlled by anions involved in the reaction. Silver ions play a dual role in the formation of **1** and **2**: mediating the *in situ* ligand reaction and participating in the coordination to form the frameworks. Although many *in situ* ligand reactions or anion-controlled coordination polymers have been widely reported, our results reveal the synergistic effect of the *in situ* ligand reaction and anion-controlled synthesis as well as the dual role of silver ion in the reaction.

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