# The role of Ag…O and Ag…Ag interactions in silver(I) supramolecular frameworks constructed from benzene multicarboxylate and nitrogen ligands

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Abstract Using a hydrothermal synthesis method, two Ag(I) coordination polymers,  $\{[Ag_2(bbbm)_2] \cdot (Hbtc)\}_n$  (1) and  $\{[Ag_2(mbim)_2(Hsip)] \cdot H_2O\}_n$  (2) (bbbm = N,N'-(1,4-butanediyl)bis-(benzimidazole), mbim =  $N_N'$ -(1,1-methyl)-bis-(imidazole),  $H_3btc = 1,3,5$ -benzenetricarboxylic acid.  $H_3 sip = 5$ -sulfoisophthalic acid) were synthesized and characterized by physicochemical and spectroscopic methods and single crystal diffraction. The complex 1 features a 2D supramolecular network formed by left- and right-handed cationic  $[Ag(bbbm)]_n$  helical chains and Hbtc ligands with the link of Ag...O interactions, displaying an unusual trinodal (3,3,4)connected 3,3,4L12 topology net. The complex 2 has a lefthanded and a symmetric right-handed double-stranded  $[Ag_2(mbim)_2(Hsip)]_n$  helical chains. The adjacent  $[Ag_2(m$  $bim)_2(Hsip)]_n$  helical chains are further linked by Hsip ligands through the combination of weak Ag...O coordinative interactions and ligand-supported Ag...Ag interactions to generate a 3D supramolecular framework, exhibiting a new type of topology of a trinodal (4,5,5)-connected net. The solid-state fluorescence properties of the compounds 1 and 2 were investigated.

# Introduction

In recent years, the design and synthesis of coordination architectures with controlled dimensionality is a rapidly developing field in supramolecular chemistry and crystal engineering [1-4]. Apart from using multidentate and symmetric ligands as building blocks to form highdimensional frameworks through coordinate covalent bonding [5–7], extended high-dimensional networks also can be obtained by assembly of lower dimensional coordination polymers via noncovalent intermolecular forces such as hydrogen bonding,  $\pi - \pi$  and other weak interactions [8, 9]. One such weak interaction is the closed-shell Ag...Ag interaction (argentophilicity) [8], which can be either ligand-supported or ligand-unsupported by the ancillary ligands [10], and its strength is comparable to a weak hydrogen bond [11]. Most short Ag...Ag distances were observed in structurally characterized complexes with bridging ligands (ligand-supported), and the attractive phenomenon was generally accepted after examples of ligand-unsupported Ag...Ag interactions were reported [12, 13].

Recently, the chemistry of metal-organic frameworks (MOFs) related to Ag(I) complexes has been an attractive research area, since the Ag(I) complexes have interesting photophysical properties [14] and high affinity for hard donors such as nitrogen or oxygen and soft donors such as sulfur [15–17]. To date, many Ag(I) complexes constructed by oxygen-containing carboxylates and nitrogen-containing mixed ligands have been reported [18-20]. Among them, the imidazole-containing ligands always coordinate to Ag(I) atoms with coordinate bonds (2.0-2.3 Å), while most oxygen-containing carboxylates connect Ag(I) centers via weak Ag…O coordinative bonds (2.6–3.24 Å), and in some cases, weak Ag...O interactions can extend the structure to a higher-dimensional supramolecular network [21]. For example, Wang et al. [22] reported an Ag(I) coordination polymer  $\{[Ag(bpy)][Ag(Hsip)(bpy)](H_2O)_2\}_n$ , showing a 2D supramolecular network extended by Ag(I)-bpy double

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chains and Hsip ligands through ligand-unsupported Ag...Ag interactions and weak Ag...O coordinative interactions.

In this paper, we selected N, N'-(1, 1-methyl)-bis(imidazole) (mbim) and N,N'-(1,4-butanediyl)-bis(benzimidazole) (bbbm) as nitrogen-containing ligands, which have proved to be good candidates for the N-donor bridging ligands [23–25]. Two kinds of oxygen-containing benzene multicarboxylic acids, 1,3,5-benzenetricarboxylic acid (H<sub>3</sub>btc) and 5-sulfoisophthalic acid (H<sub>3</sub>sip) were chosen as auxiliary ligands to increase the possibility of getting highdimensional networks. After the mixed ligands reacted with Ag(I) salts by hydrothermal methods, we successfully obtained and characterized two novel Ag(I) coordination polymers, namely  $\{[Ag_2(bbbm)_2] \cdot (Hbtc)\}_n$  (1) and  $\{[Ag_2(mbim)_2(Hsip)] \cdot H_2O\}_n$  (2). The two structures are both extended to 2D or 3D supramolecular networks from chain structures through Ag...O or/and Ag...Ag interactions and both exhibit unusual trinodal topology nets.

# **Experimental section**

## Materials and physical measurements

The reagents and solvents for synthesis were commercially available and used as received without further purification. The ligands bbbm and mbim were synthesized according to a literature method [26]. Elemental analyses of C, H and N were carried out with a Perkin-Elmer 240C elemental analyzer. The IR spectra were recorded on KBr disks on a Tensor 27 FT-IR spectrometer Bruker in the 4,000-400 cm<sup>-1</sup> range. Thermal analysis was performed on a NETZSCH TG 209 thermal analyzer from room temperature to 800 °C under nitrogen atmosphere with a heating rate of 10 °C/min<sup>-1</sup>. Photoluminescence spectra for the solid samples were recorded with a Cary Eclipse fluorescence spectrophotometer. X-ray powder diffraction (XRPD) was recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA with CuKa radiation  $(\lambda = 1.54178 \text{ Å})$ . UV–Vis spectra of **1**, **2**, bbbm and mbim ligands were obtained with a Hitachi UV-3010 spectrophotometer in integrating sphere of solid-state sample.

# Synthesis of $\{[Ag_2(bbbm)_2] \cdot (Hbtc)\}_n$ (1)

A mixture of AgOAc (33 mg, 0.2 mmol), bbbm (58 mg, 0.2 mmol) and H<sub>3</sub>btc (48 mg, 0.5 mmol) in 20 mL H<sub>2</sub>O was sealed in a Teflon-lined stainless vessel (25 mL) and heated to 140 °C and held for 72 h and then cooled to room temperature at 5 °C/h rate. Colorless block-shaped crystals of **1** were filtered off, washed with distilled water and dried in the air. Yield 58 % (based on AgOAc). Anal. Calc. for  $C_{45}H_{40}N_8O_6Ag_2$  (*Fw* = 1,004.59): C 53.8 H 4.0, N

11.2 %; found: C 53.6, H 3.9, N 11.0 %. FT-IR (KBr,  $cm^{-1}$ ): 3,100 m, 2,929 w, 1,700 m, 1,613 m, 1,557 m, 1,509 m, 1,461 m, 1,393 w, 1,356 m, 1,263 m, 1,182 m, 758 s.

# Synthesis of $\{[Ag_2(mbim)_2(Hsip)] \cdot H_2O\}_n$ (2)

By employing the above-described procedure with a mixture of AgOAc (83 mg, 0.5 mmol), mbim (74 mg, 0.5 mmol), NaH<sub>2</sub>sip (134 mg, 0.5 mmol) and 18 mL H<sub>2</sub>O, colorless block-shaped crystals of **2** were obtained with a yield of 45 % (based on AgOAc). Anal. Calc. for  $C_{22}H_{22}N_8O_8Ag_2S$  (*Fw* = 774.28): C 34.1, H 2.9, N 14.5 %; found: C 33.9, H 3.0, N 14.3 %. FT-IR (KBr, cm<sup>-1</sup>): 3,441 m, 3,109 m, 1,691 s, 1,604 m, 1,560 s, 1,508 m, 1,354 m, 1,286 w, 1,210 s, 1,185 s, 1,091 s, 1,039 s, 746 m, 682 m, 623 s.

# X-ray crystallography

The single crystal X-ray data for complexes 1 and 2 were collected on a Bruker SMART 1000 CCD diffractometer with graphite monochromatic Mo Kα radiation  $(\lambda = 0.71073 \text{ Å})$  at 298 K. The structures were solved by direct method of SHELXS-97 and refined by full-matrix least squares on  $F^2$  using the SHELXL-97 program [27]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to carbon and nitrogen atoms were generated geometrically. Hydrogen atoms of the undeprotonated carboxylic acid group of the Hbtc/Hsip moiety and the water molecules were located from Fourier difference maps and refined isotropically with the O-H distances fixing on 0.85 Å. The absolute configuration of chiral compound 1 was determined by Flack's method [28]. The crystallographic data and experimental details and structure refinements are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

# **Results and discussion**

Crystal structure of  $\{[Ag_2(bbbm)_2] \cdot (Hbtc)\}_n$  (1)

The crystals of **1** conform to the chiral monoclinic  $P2_1$  space group, and each asymmetric unit contains two  $[Ag(bbbm)]^+$  cations and one uncoordinated Hbtc diatomic anion (Fig. 1a). Two independent Ag centers are each bridged by bbbm ligands to generate two cationic helical chains, a left-handed -Ag1-bbbm-Ag1-bbbm-(**chain-1**) and a right-handed -Ag2-bbbm-Ag2-bbbm-(**chain-2**) (Fig. 1b). The Ag-N distances of 2.077(6)-2.130(6) Å are within the normal range [18]. The coordination geometry of Ag1 and Ag2 in the two chains is nearly linear with N-

 Table 1 Crystallographic data and structure refinement for 1 and 2

Coordination polymers	1	2
Formula	$C_{45}H_{40}Ag_2N_8O_6$	C22H22Ag2N8O8S
Formula weight	1,004.59	774.28
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_{1}/c$
a (Å)	9.7689(8)	8.7806(7)
<i>b</i> (Å)	13.6291(10)	25.0804(19)
<i>c</i> (Å)	16.7263(13)	13.0384(10)
α (°)	90	90
β (°)	96.9890(10)	108.1870(10)
γ (°)	90	90
$V(\text{\AA}^3)$	2,210.4(3)	2,727.9(4)
Ζ	2	4
$\rho_{calcd}$ (g cm <sup>-3</sup> )	1.509	1.885
$\mu/\mathrm{mm}^{-1}$	0.942	1.574
<i>F</i> (000)	1,016	1,536
R <sub>int</sub>	0.0882	0.0195
Refins collected/unique	17,185/7,725	16,038/5,964
Goodness-of-fit on $F^2$	0.689	1.009
$R_1, wR_2 [I > 2\sigma(I)]$	0.0440, 0.0570	0.00260, 0.0723
$R_1$ , $wR_2$ (all data)	0.0953, 0.0688	0.0295, 0.0745

 $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|; \ wR_2 = \{ \Sigma \ [w \ (F_0^2 - F_c^2)^2] / \Sigma \ [w \ (F_0^2)^2] \}^{1/2}$ 

Table 2 Selected bond lengths (Å) and angles (°) for 1 and 2

1			
Ag1–N5	2.129(5)	Ag1–N7	2.130(6)
Ag2–N3	2.077(6)	Ag2–N1	2.087(6)
Ag1…O4	3.015(7)	Ag1…O2A	2.930(5)
Ag2…O5B	3.119(8)	N5-Ag1-N7	171.9(3)
N3-Ag2-N1	174.6(3)		
2			
Ag1–N1	2.158(2)	Ag1–N5A	2.163(2)
Ag2–N8	2.129(2)	Ag2–N4A	2.1333(19)
Ag1–O1	2.6359(16)	Ag1…O2	2.9136(16)
Ag1…O4B	2.977(2)	Ag2…O6C	2.785(2)
Ag2…O6D	2.881(3)	Ag1…Ag2	3.0995(3)
N8-Ag2-N4A	170.74(8)	N1-Ag1-N5A	169.83(8)

Symmetry codes for 1 A: -x + 1, y + 1/2, -z + 1; B: -x, y + 1/2, -z + 1; A: x - 1, y, z; B: x, -y + 1/2, z - 1/2, C: -x, -y, -z + 1, D: x, y, z - 1

Ag–N angles of  $171.9(3)^{\circ}$  and  $174.6(3)^{\circ}$ , respectively. The dihedral angles of the two benzimidazole rings of bbbm are 79.801° (for **chain-1**) and 81.213° (for **chain-2**). The Ag…Ag distances bridged by bbbm are 7.508 Å (for **chain-1**) and 7.306 Å (for **chain-2**), and the Ag–Ag–Ag angles are 130.349° (for **chain-1**) and 137.735° (for **chain-2**). There are three kinds of weak Ag…O interactions between Ag(I) centers (Ag1 or Ag2) and three carboxylate oxygen

atoms from different Hbtc dianions  $[Ag1\cdots O2A = 2.930(5)$  Å,  $Ag1\cdots O4 = 3.015(7)$  Å,  $Ag2\cdots O5B = 3.119(8)$  Å, symmetry codes, A: -x + 1, y + 1/2, -z + 1; B: -x, y + 1/2, -z + 1]. The upper limit of Ag–O bond is 2.3–2.6 Å, and van der Waals contact of Ag and O atoms is 3.24 Å [29]. Therefore, Hbtc ligands connect the two cationic helical chains alternately to form a 2D supramolecular network through three such kinds of weak Ag…O interactions (Fig. 1b).

In order to understand the architecture of 1, which is more intuitive, the topological method was used to simplify and analyze the structure. Obviously, Ag1 should be considered as a 4-connected node since it is connected by two bbbm and two carboxylic groups from distinct Hbtc ligands, while Ag2 linking two bbbm and one carboxylic group from an Hbtc ligand can be regarded as a 3-connected node, and each Hbtc ligand connecting two symmetric Ag1 nodes and one Ag2 node should be viewed as a 3-connected node. The bridging  $\mu_2$ -bbbm ligand is only considered as a linker. Therefore, after analysis by TOPOS40 [30], the 2D supramolecular network is detected to be an unusual trinodal (3,3,4)-connected 3,3,4L12 topology, and the point symbol of the net is  $(3^2 \times 7^2 \times 8^2)(7^3)(3 \times 7^2)$ . To the best of our knowledge, 1 displays a rare 2D supramolecular framework with 3,3,4L12 topology [31].

Crystal structure of  $\{[Ag_2(mbim)_2(Hsip)] \cdot H_2O\}_n$  (2)

Single crystal X-ray diffraction reveals that 2 has a 3D supramolecular network generated from a combination of coordination bonds, ligand-supported Ag-Ag interactions and weak Ag...O coordinative interactions. The 3D network contains a left-handed and a symmetric right-handed  $[Ag_2(mbim)_2(Hsip)]_n$  double-stranded helical chains since 2 crystallizes in the centrosymmetric monoclinic space group  $P2_1/c$ . The asymmetric unit of 2 consists of two Ag(I) centers, one Hsip dianion, two mbim ligands and one solvent water molecule, as shown in Fig. 2a. Ag1 coordinates with one carboxylate oxygen atom and two imidazolyl nitrogen atoms to generate a T-shaped coordination geometry, having a longer covalent Ag1-O1 distance of 2.6359(16) Å and Ag1-N distances of 2.158(2) and 2.163(2) Å, respectively. Different from that of Ag1, the coordination geometry of Ag2 is linear with the Ag2-N distances being 2.129(2) and 2.1333(19) Å, respectively. The N-Ag-N angles are 169.83(8)° (for Ag1) and 170.74(8)° (for Ag2). The mbim ligands bridge Ag1 and Ag2 atoms alternately to form two left-handed and two symmetric right-handed single helices, and the two left-/ right-handed single helices are self-encircled along the b axis with pitches of 35.12(3) Å to form a left-handed and a right-handed  $[Ag_2(mbim)_2(Hsip)]_n$  double-stranded



**Fig. 1** a The coordination environment (at 30 % probability level) of the Ag(I) centers in 1 (*dotted line* indicates weak Ag…O interactions). All H atoms are omitted for clarity. Symmetry codes: A = -x + 1, y + 1/2, -z + 1; B = -x, y + 1/2, -z + 1; C = -x, y-1/2, -z + 2. **b** The *left* (chain-1)- and *right* (chain-2)-handed helical chains based on bbbm and Ag(I). **c** View of the 2D supramolecular

network in 1 along the *bc* axis extended by weak Ag…O bonds (*dotted line* indicates weak Ag…O interactions). **d** Topological view of the trinodal (3,3,4)-connected 3,3,4L12 net in 1 (Ag1 nodes are shown as *pink balls*; Ag2 nodes, as *red balls*; and Hbtc nodes, as *green balls*). (Color figure online)

helical chains, as depicted in Fig. 2b. The Hsip ligands are located at the same side of the left-/right-handed doublestranded  $[Ag_2(mbim)_2(Hsip)]_n$  chains. In each strand of single helix, there are two kinds of mbim ligands with different dihedral angles of imidazole rings of 75.034° and 83.983°. The Ag1...Ag2 distances bridged by the two kinds of mbim ligands are 9.0067(7) Å and 9.6068(7) Å, respectively, and the Ag-Ag-Ag angle in each single helix is 141.162(3)°. The two single helices in each doublestranded helical chain are further linked by ligand-supported argentophilic Ag…Ag interactions [Ag1 - Ag2 = 3.0995(3) Å] (Fig. 2c). The Ag-Ag distance is comparable to the value of 2.89 Å in metallic silver

and of 3.0356(14) Å in the complex of  $\{[Ag(bpy)][Ag(H-sip)(bpy)](H_2O)_2\}_n$  [22].

As illustrated in Fig. 2a, the Ag···O weak interactions also exist around Ag1 and Ag2 [Ag1···O2 = 2.9136(16) Å, Ag1···O4B = 2.977(2) Å, Ag2···O6C = 2.785(2) Å, Ag2···O6D = 2.881(3) Å, symmetry codes, B: x, -y + 1/2, z - 1/2; C: -x, -y, -z + 1; D: x, y, z - 1]. The carboxylate oxygen atoms (O2, O4) make a linkage to two symmetric Ag1 atoms, and the sulfonate oxygen atom (O6) connects two symmetric Ag2 atoms of the double-stranded helix with the weak Ag···O bonding distances of 2.785(2)–2.977(2) Å (Table 2). Similar weak Ag···O bonds are reported in other silver sulfonate complexes [32]. Thus, the adjacent double-



**Fig. 2** a The coordination environment (at 30 % probability level) of the Ag(I) centers in 2 (*dotted line* indicates Ag...Ag interaction and weak Ag...O interactions). All H atoms are omitted for clarity. Symmetry codes: A = x - 1, y, z; B = x, -y + 1/2, z - 1/2, C = -x, -y, -z + 1, D = x, y, z-1. **b** The *right-handed* and *left-handed* [Ag<sub>2</sub>(mbim)<sub>2</sub>(Hsip)]<sub>n</sub> double-stranded helices viewed along the b axis

stranded  $[Ag_2(mbim)_2(Hsip)]_n$  helical chains are extended by the Hsip ligands through a number of weak Ag...O bonding interactions to generate a 3D complicated supramolecular network as depicted in Fig. 2c. Furthermore, from a topological perspective, considering the Ag…O and Ag…Ag interactions, if the silver (Ag1 and Ag2) centers and Hsip ligands are considered as the 5- and 4-connected nodes, respectively, this framework becomes an unprecedented topology of trinodal (4,5,5)-connected net with the point symbol  $(4 \times 5^2 \times 6 \times 7 \times 8)(4^2 \times 5^2 \times 6^4 \times 7^2)(4^3 \times 7^2)$  $5 \times 6^4 \times 7^2$ ) (Fig. 2d). In addition, the solvent water molecules fill in the cavities of the network and are hydrogenbonded with the network. The related O-H…O hydrogen bonds are found between the oxygen atoms of carboxylate (O1) and sulfonate oxygen atoms (O5) with the H atoms of water molecules. The O1 W-H1<sup>I</sup>...O1 bond distances  $(O1\cdots H1^{I} and O1\cdots O1 W)$  and angle are 1.99 Å, 2.806 Å and

in 2. c View of the 3D supramolecular structure of 2 extended by Ag...Ag interactions and weak Ag...O interactions (*dotted line*). d Topological view of trinodal (4,5,5)-connected  $(4 \times 5^2 \times 6 \times 7 \times 8)(4^2 \times 5^2 \times 6^4 \times 7^2)(4^3 \times 5 \times 6^4 \times 7^2)$  net in 2 (Ag1 nodes represented as *pink balls*; Ag2 nodes, as *red balls*; and Hsip nodes, as *green balls*). (Color figure online)

177°, respectively, while the O1 W–H1<sup>II...</sup>O5 bond distances (O5…H1<sup>II</sup> and O5…O1 W) and angle are 2.60 Å, 2.925 Å and 105°, respectively The weak noncovalent interactions are important in the formation of the final supramolecular structure of **2**.

IR and UV absorption spectra

The IR spectrum of **1** shows the stretching vibrations of the C–H bands at 3,100 cm<sup>-1</sup>. The O–H of lattice water and C–H stretching vibrations of **2** are centered at 3,441 and 3,109 cm<sup>-1</sup>, respectively. The characteristic asymmetric and symmetric vibration bands of the carboxylic groups can be observed at 1,613 and 1,356 cm<sup>-1</sup> for **1** and 1,604 and 1,354 cm<sup>-1</sup> for **2**. The characteristic bands at 1,700 cm<sup>-1</sup> for **1** and 1,691 cm<sup>-1</sup> for **2** are attributable to the protonated carboxylic group of the Hbtc and Hsip

ligands, respectively. The frequencies characteristic of the S–O stretching modes are observed in the region  $1,039-1,210 \text{ cm}^{-1}$  for **2** [33].

The absorption spectra of solid-state bbbm, mbim, **1** and **2** were measured by integrating sphere at room temperature (Figure S1–S2, Supporting Information). The strong bands at 272 nm for bbbm, 273 nm for **1**, 228 nm for mbim and 243 nm for **2** are assigned to the  $\pi \rightarrow \pi^*$  transitions within the imidazolyl rings.

# XRPD results

To confirm the phase purity of the bulk materials, X-ray powder diffraction (XRPD) experiments have been carried out for complexes **1** and **2**. The XRPD experimental and computer-simulated patterns of the corresponding complexes are shown in Figure S3–S4 (see in the Supporting Information). The different structures of **1** and **2** also have been indicated by their different XRPD patterns. It can be well concluded that the bulk synthesized materials and the crystals used for diffraction are homogeneous.

### Thermal analysis

The decomposition behaviors of complexes 1 and 2 were examined by thermogravimetric analysis (TGA) with a heating rate of 10 °C/min from room temperature to 800 °C, as shown in Fig. 3. The TGA trace of 1 exhibits two main steps of weight losses. The first step starts at 220 °C and completes at 288 °C, which corresponds to the decomposition of Hbtc ligand. The observed weight loss of 19.52 % is close to the calculated value of 19.11 %. The second step covers from 303 to 580 °C, during which the bbbm ligands are lost, with a weight loss of 58.72 % (calcd. 57.82 %); the remaining weight corresponds to the formation of Ag<sub>2</sub>O (obsd. 22.17 %, calcd. 23.07 %). Complex 2 loses its lattice water molecule from 72 to 147 °C (obsd. 2.57 %, calcd. 2.32 %), and the departure of Hsip ligand occurs from 245 to 358 °C (obsd. 28.36 %, calcd. 29.48 %). The last weight loss between 390 and 525 °C is attributable to the mbim ligand decomposition, and the remaining weight corresponds to the formation of Ag<sub>2</sub>O (obsd. 28.95 %, calcd. 29.93 %).

#### Photoluminescence properties

The Ag(I) coordination complexes with aromatic ligands have received much attention for the development of hybrid photoluminescent materials [34]. Thus, solid-state photoluminescent properties of complexes 1 and 2 as well as the free ligands were examined at room temperature. The photoluminescence spectra of the free ligands and complexes 1-2are shown in Fig. 4. The free ligands display



Fig. 3 The TG curves of 1 (a) and 2 (b)



Fig. 4 Photoluminescences of the free ligands and complexes 1 and 2

photoluminescence with emission maxima at 400 nm (upon irradiation at 349 nm for bbbm) and 352 nm (upon irradiation 318 nm for mbim). It can be presumed that these peaks originate from the  $\pi \rightarrow \pi^*$  transitions [35]. The complexes exhibit an emission peak at 403 nm for 1 and 486 nm for 2 upon excitation at 284 nm, respectively. When compared to the photoluminescence spectra of the corresponding ligands, the emission band of 1 is similar to that of bbbm and should be assigned to the intraligand transition of the coordinated N-donor ligand. The emission of **2** is red-shifted by 134 nm, which may come from the electronic transition between the p orbitals (filled orbitals) of coordinated N atoms and the 5 s orbital (empty orbital) of Ag(I) center, i.e., ligand-to-metal charge transfer (LMCT), mixed with metal-centered (d–s/ d–p) transitions [36].

# Conclusions

In conclusion, the self-assembly of silver acetate with different organic nitrogen-containing ligands and benzene multicarboxylates afforded two novel Ag(I) coordination polymers 1 and 2. The two coordination polymers are both chain structures and extend to higher-dimensional frameworks by weak Ag...O or Ag...Ag interactions. 1 displays first 2D trinodal (3,3,4)-connected the 3,3,4L12 Ag(I) supramolecular topology supported by Ag...O interactions, while 2 exhibits a 3D supramolecular framework with a new type of trinodal (4,5,5)-connected  $(4 \times$  $5^2 \times 6 \times 7 \times 8)(4^2 \times 5^2 \times 6^4 \times 7^2)(4^3 \times 5 \times 6^4 \times 7^2)$ topology linked by Ag...Ag and Ag...O interactions. This work demonstrates that the weak Ag...O and Ag...Ag interactions are thus important in determining the structural diversity and dimensionalities of the Ag(I) complexes.

## Supplementary material

X-ray crystallographic files in CIF format for **1** and **2** have been deposited at the Cambridge Crystallographic Data Centre with CCDC No: 921031 and 921032. These data can be obtained free of charge via https://www.ccdc.cam. ac.uk/services/structure\_deposit/Unless or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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