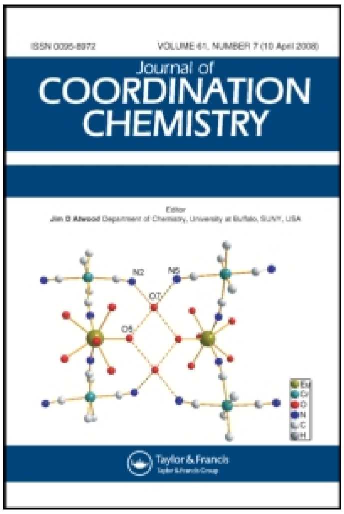

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Four silver-containing coordination polymers based on bis(imidazole) ligands

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Four silver-containing coordination polymers based on bis(imidazole) ligands

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Four coordination polymers, $[Ag(L^1)](m\text{-Hbdc})$ (**1**), $[Ag(L^1)]_2(p\text{-bdc})\cdot 8H_2O$ (**2**), $[Ag(Hbtc)(L^1)][Ag(L^1)]\cdot 2H_2O$ (**3**) and $[Ag_2(L^2)_2](OH\text{-bdc})_2\cdot 4H_2O$ (**4**), where $L^1 = 1,1'$-(1,4-butanediyl)bis(imidazole), $L^2 =$ 1,2-bis(imidazol-1-ylmethyl)benzene, m-H_2bdc = 1,3-benzenedicarboxylic acid, p-H_2bdc = 1,4-benzenedicarboxylic acid, H_3btc = 1,3,5-benzenetricarboxylic acid, and OH–H_2bdc = 5-hydroxisophthalic acid, were synthesized under hydrothermal conditions. Compound **1** contains a –Ag-L^1–Ag-L^1– chain and a hydrogen-bonding interaction induced –(m-Hbdc)-(m-Hbdc)– chain. Compound **2** consists of two independent –Ag-L^1–Ag-L^1– chains. *P*-bdc anions are not coordinated. Hydrogen bonds form a 3D supramolecular structure. A novel $(H_2O)_{16}$ cluster is formed by lattice water molecules in **2**. Compound **3** contains a –Ag-L^1–Ag-L^1– and a –Ag(Hbtc)-L^1–Ag(Hbtc)-L^1– chain. The packing diagram shows a 2D criss-cross supramolecular structure, with $\pi\cdots\pi$ and C–H$\cdots\pi$ interactions stabilizing the framework. Compound **4** contains a $[Ag_2(L^2)_2]^{2+}$ dimer with hydrogen-bonding, $\pi\cdots\pi$, and Ag$\cdots$O interactions forming a 3D supramolecular framework. The luminescent properties for these compounds in the solid state are discussed.

Keywords: Coordination polymer; Carboxylic acid; Bis(imidazole); Silver

1. Introduction

Supramolecular chemistry and crystal engineering based on metal and organic building blocks have been rapidly expanding due to structural topologies, potential applications in host-guest chemistry, catalysis, and electrical conductivity [1]. Generally, extended high-dimensional networks can be obtained by assembly of lower dimensional coordination polymers *via* noncovalent intermolecular forces such as hydrogen-bonding, π–π, C–H$\cdots\pi$, halogen$\cdots$halogen, S$\cdots$S interactions, etc. [2]. Multicarboxylic acids are hydrogen-bonding acceptors but also hydrogen-bonding donors [3]. Bis(imidazoles) are bidentate ligands with flexible skeletons, and therefore excellent candidates for supramolecular architectures [4]. Silver complexes have interesting photophysical properties [5] and high affinity for hard donors such as nitrogen or oxygen and soft donors such as sulfur [6].

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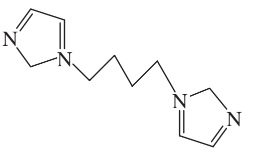
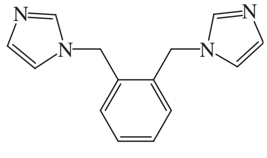
We employ carboxylic acids and bis(imidazole) ligands as mixed organic building units with Ag ions in the assembly process to construct high-dimensional supramolecular networks in expectation that these groups may generate hydrogen-bonding or noncovalent interactions. Herein, we report the syntheses and supramolecular structures of $[Ag(L^1)](m\text{-}Hbdc)$ (**1**), $[Ag(L^1)]_2(p\text{-}bdc)\cdot 8H_2O$ (**2**), $[Ag(Hbtc)(L^1)][Ag(L^1)]\cdot 2H_2O$ (**3**) and $[Ag_2(L^2)_2](OH\text{–}bdc)_2\cdot 4H_2O$ (**4**).


L^1


L^2

2. Experimental

2.1. *Preparation*

All reagents and solvents for syntheses were purchased from commercial sources and used as received. The ligands L^1 and L^2 were synthesized according to the literature [4f].

2.1.1. Synthesis of $[Ag(L^1)](m\text{-}Hbdc)$ (1). A mixture of Ag_2CO_3 (0.124 g, 0.45 mmol), *m*-H_2bcd (0.074 g, 0.45 mmol), and water (7 mL) was stirred for 10 min in air (until no CO_2 was given off). L^1 (0.086 g, 0.45 mmol) and a drop of dilute ammonia was added to the mixture and stirred for 5 min at room temperature., then the mixture was sealed in a Teflon reactor (12 mL) and heated at 100°C for 36 h prior to being cooled to room temperature at $10°C\,h^{-1}$. The final pH of the reaction medium was 7.0. Colorless crystals of **1** were collected from the reaction system by filtration, washed several times with ethanol, and dried in air at ambient temperature (52% yield based on $AgCO_3$). Anal. Calcd for $C_{18}H_{19}AgN_4O_4$ (463.24): C, 46.67; H, 4.13; N, 12.09. Found: C, 46.61; H, 4.22; N, 11.94. IR (cm^{-1}): 3124 (s), 2938 (m), 1693 (m), 1598 (m), 1521 (s), 1426 (w), 1368 (s), 1237 (m), 1105 (w), 1075 (w), 932 (w), 823 (w), 738 (s), 711 (s), 658 (m).

2.1.2. Synthesis of $[Ag(L^1)]_2(p\text{-}bdc)\cdot 8H_2O$ (2). The preparation of **2** was similar to **1** except that *p*-H_2bdc was used instead of *m*-H_2bdc. Colorless crystals of **2** were obtained (40% yield based on $AgCO_3$). Anal. Calcd for $C_{28}H_{48}Ag_2N_8O_{12}$ (904.48): C, 37.18; H, 5.35; N, 12.39. Found: C, 37.24; H, 5.27; N, 12.42. IR (cm^{-1}): 3115 (s), 2932 (m), 2864 (m), 1576 (s), 1517 (m), 1390 (s), 1295 (w), 1235 (m), 1099 (s), 929 (w), 826 (s), 741 (s), 656 (m).

2.1.3. Synthesis of $[Ag(Hbtc)(L^1)][Ag(L^1)]\cdot 2H_2O$ (3). Ag_2CO_3 (0.124 g, 0.45 mmol) was added to an aqueous solution (8 mL) of 1,3,5-btc (0.063 g, 0.3 mmol) and stirred for 5 min until no CO_2 was given off. L^1 (0.086 g, 0.45 mmol) was added to the mixture and stirred for 10 min at room temperature, then the mixture was transferred to a Teflon reactor, heated at 100°C for 24 h and cooled to room temperature at 10°C h^{-1}. Colorless crystals of **3** were obtained (86% yield based on Ag_2CO_3). Anal. Calcd for $C_{29}H_{36}Ag_2N_8O_8$ (840.40): C, 41.45; H, 4.32; N, 13.33. Found: C, 41.59; H, 4.41; N, 13.29. IR (cm^{-1}): 3413 (s), 3114 (m), 2863 (w), 1708 (m), 1623 (s), 1560 (s), 1508 (m), 1431 (m), 1363 (s), 1236 (s), 1105 (vs), 1081 (m), 829 (w), 769 (w), 754 (w), 656 (w).

2.1.4. Synthesis of $[Ag_2(L^2)_2](OH\text{-}bdc)_2 \cdot 4H_2O$ (4). The preparation of **4** was similar to **1** except that OH–H_2bdc and L^2 were used instead of *m*-H_2bdc and L^1. Colorless crystals of **4** were obtained (37% yield based on $AgCO_3$). Anal. Calcd for $C_{36}H_{40}Ag_2N_8O_9$ (944.50): C, 45.78; H, 4.27; N, 11.86. Found: C, 45.84; H, 4.28; N, 11.74. IR (cm^{-1}): 3577 (s), 3292 (s), 3107 (s), 2569 (s), 1712(s), 1620 (s), 1560 (s), 1510 (s), 1393 (s), 1283 (s), 1233 (s), 1106 (m), 1082 (s), 973 (w), 829 (w), 779 (m), 720 (m), 662 (w).

2.2. *Physical measurements and X-ray crystallography*

The C, H, and N elemental analyses were conducted on a Perkin-Elmer 240C elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. The excitation and emission spectra were measured on a Perkin-Elmer LS55 spectrometer.

Single-crystal X-ray diffraction data for **1**–**4** were collected on a Rigaku RAXIS-RAPID single-crystal diffractometer with Mo K_α radiation ($\lambda = 0.71073$ Å) at 293 K. Absorption corrections were applied using multiscan technique. All the structures were solved by the Direct Method of SHELXS-97 [7] and refined by full-matrix least-squares techniques using SHELXL-97 [8]. Non-hydrogen atoms were refined with anisotropic temperature parameters (when no disorder was present). The disordered oxygen atoms in **4** were refined using O atoms split over two sites, with a total occupancy of 1. Aromatic H atoms bound to carbon were refined using a riding model with d(C–H) = 0.93 Å, $U_{iso} = 1.2U_{eq}(C)$ for aromatic and 0.97 Å, $U_{iso} = 1.5U_{eq}(C)$ for CH_2 atoms. Hydroxyl H atoms were refined using a riding model with d(O–H) = 0.82 Å, $U_{iso} = 1.5U_{eq}(O)$. Water H atoms were located in a difference Fourier map and refined as riding atoms with $U_{iso}(H) = 1.5U_{eq}(O)$. Crystal data and details of the data collection and structure refinements are summarized in table 1.

3. Results and discussion

3.1. *Crystal structure*

Selected geometric parameters for **1**–**4** are given in table 2 and hydrogen bond data are listed in table 3.

3.1.1. Structure of $[Ag(L^1)](m\text{-}Hbdc)$ (1). Compound **1** consists of a $[Ag(L^1)]^+$ cation and a noncoordinated *m*-Hbdc anion (figure 1). The Ag^+ is linear with two nitrogen atoms from two L^1 ligands. The Ag–N distance of 2.075(3) Å is within the normal range [9].

Table 1. Crystal data and structure refinements for **1**–**4**.

	1	**2**	**3**	**4**
Formula	$C_{18}H_{19}AgN_4O_4$	$C_{28}H_{48}Ag_2N_8O_{12}$	$C_{29}H_{36}Ag_2N_8O_8$	$C_{36}H_{40}Ag_2N_8O_9$
M	463.24	904.48	840.40	944.50
Crystal system	Monoclinic	Triclinic	Orthorhombic	Triclinic
Space group	$C2/c$	$P\bar{1}$	$Pna2(1)$	$P\bar{1}$
a (Å)	14.129(7)	8.499(4)	32.051(7)	9.965(4)
b (Å)	9.279(7)	13.966(5)	10.630(4)	14.204(6)
c (Å)	14.276(6)	15.863(8)	9.490(3)	14.476(8)
α (°)	90	90.209(2)	90	107.519(2)
β (°)	99.728(2)	97.386(2)	90	91.172(2)
γ (°)	90	90.786(2)	90	108.737(1)
V (Å^3)	1844.7(18)	1867.0(14)	3233.5(16)	1834.8(15)
Z	4	2	4	2
D_{Calcd} g cm^{-3}	1.668	1.609	1.726	1.710
F(000)	936	924	1696	956
θ range (°)	3.13–27.47	3.19–27.48	3.15–27.48	3.06–27.47
R_{int}	0.0237	0.0253	0.0470	0.0283
Reflns collected/unique	8845/2099	18526/8464	30220/7092	17935/8248
Goodness of fitness on F^2	1.175	1.025	1.009	1.039
R_1^a, $wR_2^b[I>2\sigma(I)]$	0.0361, 0.1027	0.0338, 0.0654	0.0365, 0.0743	0.0387, 0.0840
R_1^a, wR_2^b (all data)	0.0500, 0.1085	0.0607, 0.0723	0.0516, 0.0783	0.0674, 0.0944

$R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$. $wR_2 = |\Sigma w(|F_o|^2 - |F_c|^2)|/\Sigma|w(F_o^2)^2|^{1/2}$.

Table 2. Selected bond distances (Å) and angles (°) for **1**–**4**.

1			
Ag(1)–N(1)	2.075(3)	N(1)^i–Ag(1)–N(1)	180.00(13)
2			
Ag(1)–N(4)^i	2.103(2)	Ag(1)–N(2)	2.105(2)
Ag(2)–N(8)^{ii}	2.122(2)	Ag(2)–N(6)	2.129(2)
N(4)^i–Ag(1)–N(2)	171.03(9)	N(8)^{ii}–Ag(2)–N(6)	173.22(9)
3			
Ag(1)–N(4)^i	2.162(4)	Ag(1)–N(1)	2.174(4)
Ag(1)–O(3)	2.532(2)	Ag(2)–N(6)^i	2.072(4)
Ag(2)–N(7)	2.090(4)		
N(4)^i–Ag(1)–N(1)	155.42(11)	N(4)^i–Ag(1)–O(3)	107.02(11)
N(1)–Ag(1)–O(3)	97.36(11)	N(6)^i–Ag(2)–N(7)	178.14(16)
4			
Ag(1)–N(7)	2.109(3)	Ag(1)–N(1)	2.112(3)
Ag(2)–N(3)	2.074(3)	Ag(2)–N(5)	2.075(3)
N(7)–Ag(1)–N(1)	173.80(11)	N(3)–Ag(2)–N(5)	175.19(11)

Symmetry codes for **1**: $^i -x+1/2, -y+1/2, -z$; **2**: $^i x, y+1, z$; $^{ii} x, y-1, z$; **3**: $^i x, y-1, z+1$.

Since the N-donor atom shows stronger coordination ability to silver than O-donor atom, the *m*-Hbdc is only a counteranion [10]. The *m*-Hbdc anions interact with each other by hydrogen bonds to a 1D supramolecular chain. The hydrogen bond distances and angles are illustrated in table 3. The crystal packing of **1** is dominated by van der Waals interactions since no other strong supramolecular interaction is observed.

3.1.2. Structure of $[Ag(L^1)]_2(p\text{-bdc})\cdot 8H_2O$ (2).

Compound **2** consists of two $[Ag(L^1)]^+$ cations, two noncoordinated *p*-bdc anions at half occupancy, and eight lattice water

Table 3. Hydrogen-bond geometry for **1**, **2** and **4** in (Å) and (°).

	D–H···A	d(D–H)	d(D···A)	(D–H···A)
1				
O(2)–H(2A)···O(2)^{i}	0.81(3)	1.66(3)	2.473(4)	175(12)
2				
O(5W)–H(5C)···O(1W)^{iv}	0.86(3)	1.97(3)	2.808(4)	167(5)
O(2W)–H(2D)···O(4)^{v}	0.88(2)	1.93(2)	2.812(3)	176(4)
O(4W)–H(4D)···O(4)^{v}	0.85(2)	1.89(3)	2.742(3)	178(4)
O(7W)–H(7D)···O(5W)^{vi}	0.86(2)	1.93(2)	2.778(3)	169(4)
O(8W)–H(8D)···O(7W)^{vii}	0.86(2)	1.99(2)	2.839(4)	169(4)
O(6W)–H(6D)···O(4W)^{v}	0.83(2)	2.50(4)	3.115(4)	131(4)
O(7W)–H(7C)···O(3W)	0.91(2)	1.93(2)	2.819(4)	163(4)
O(8W)–H(8C)···O(2W)	0.87(2)	1.92(2)	2.770(3)	167(4)
O(1W)–H(1D)···O(2)	0.88(3)	1.91(3)	2.783(4)	172(5)
O(2W)–H(2C)···O(1)	0.83(2)	1.97(2)	2.784(3)	167(4)
O(3W)–H(3C)···O(1)	0.89(2)	1.94(3)	2.786(3)	160(4)
O(3W)–H(3D)···O(8W)	0.74(2)	2.29(3)	2.841(4)	132(3)
O(4W)–H(4C)···O(2)	0.85(3)	1.92(3)	2.729(3)	159(4)
O(5W)–H(5D)···O(3)	0.86(3)	1.98(3)	2.810(4)	162(4)
O(6W)–H(6C)···O(3)	0.86(2)	1.89(3)	2.730(3)	165(5)
C(12)–H(12)···O(4W)^{v}	0.93	2.53	3.193(4)	128.6
O(1W)–H(1C)···O(6W)^{viii}	0.87(3)	1.88(3)	2.739(4)	167(5)
4				
O(1W)–H(1D)···O(1)	0.88(3)	1.88(3)	2.758(3)	174(4)
O(2W)–H(2C)···O(1)	0.91(3)	1.81(3)	2.687(4)	163(4)
O(3W)–H(3D)···O(3)	0.87(3)	1.93(3)	2.765(5)	161(5)
O(1W)–H(1C)···O(3W)^{i}	0.84(3)	2.05(3)	2.799(4)	147(4)
O(3W)–H(3C)···O(2)^{i}	0.88(3)	1.88(3)	2.751(3)	170(5)
O(4W)–H(4D)···O(1W)^{ii}	0.82(3)	2.05(2)	2.862(4)	169(5)
O(5)–H(5A)···O(4)^{iii}	0.82	1.92	2.684(4)	155.7
O(2W)–H(2D)···O(4W)	0.84(3)	2.19(3)	2.969(5)	154(4)

Symmetry code for **1**: $^{i}-x+1, -y+1, -z+2$; **2**: $^{iv}x+1, y, z+1$; $^{v}-x+1, -y, -z$; $^{vi}-x+1, -y, -z+1$; $^{vii}-x, -y+1, -z$; $^{viii}x-1, y, z-1$; **4**: $^{i}-x-1, -y, -z+1$; $^{ii}-x-1, -y+1, -z+2$; $^{iii}-x, -y+1, -z+1$.

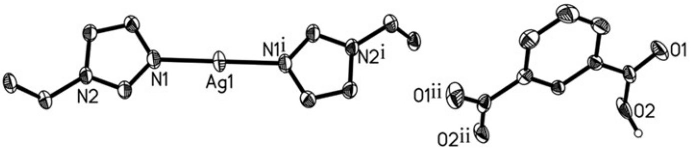


Figure 1. ORTEP drawing of the asymmetric unit of **1**. Symmetry codes: (i) $-x+1/2$, $-y+1/2$, $-z$; (ii) $1-x$, y, $1.5-z$.

molecules [figure 2(a)]. Two independent Ag atoms are each bridged by L^1 ligands to generate two linear polymeric chains,–Ag1-L^1–Ag1-L^1– and –Ag2-L^1–Ag2-L^1–. Ag atoms of each chain are stacked with imidazolyl rings of adjacent chains through Ag–π interactions (centroid-to-centroid distance and centroid-to-ring distance are 3.678 and 3.025 Å for Ag1–π interaction; centroid-to-centroid distance and centroid-to-ring distance are 3.462 and 3.116 Å for Ag2–π interaction) [11], generating two double-chain structures (A) and (B) [figure 2(b)].

The eight crystallographically unique lattice water molecules and their symmetry-related molecules of **2** link to each other to form a $(H_2O)_{16}$ cluster through

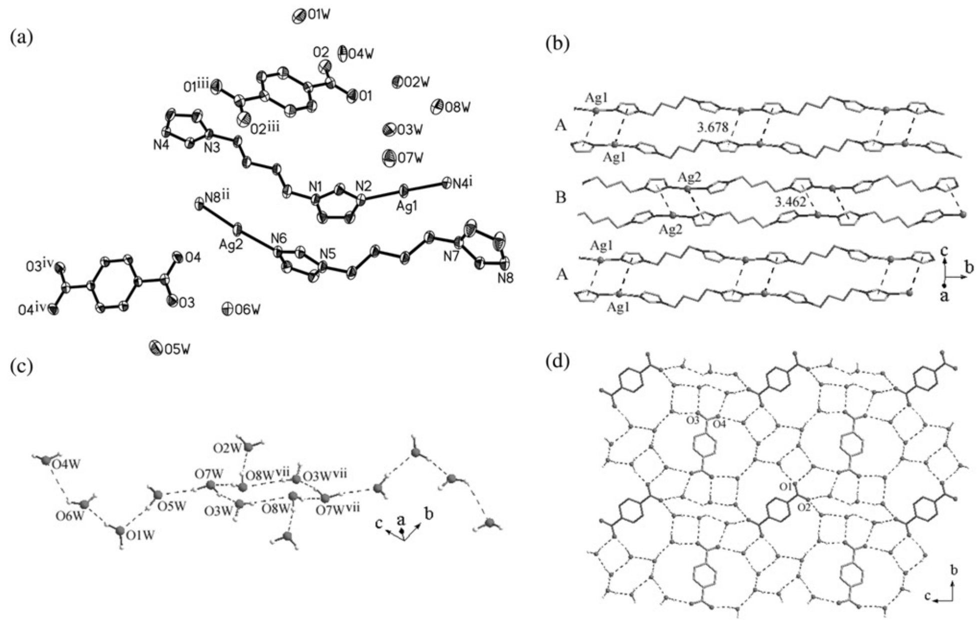


Figure 2. (a) ORTEP drawing of the asymmetric unit of **2**. (b) The Ag-π interactions between the adjacent double $[Ag(L^1)]^+$ chains (3.678 Å for double-chain A and 3.462 Å for double-chain B). (c) Perspective view of the $(H_2O)_{16}$ cluster showing the hydrogen-bonding interaction. (d) The 2D supramolecular layer connected by *p*-bdc anions and $(H_2O)_{16}$ clusters through hydrogen-bonding interactions. Symmetry codes: (i) x, $y+1$, z; (ii) x, $y-1$, z; (iii) $-x$, $-y$, $-z$; (iv) $2-x$, $-1-y$, $1-z$.

hydrogen bonds [figure 2(c)]. A variety of water clusters including tetramers [12], pentamers [13], hexamers [14], octamers [15], decamers [16] and $(H_2O)_{12}$ [17] have been structurally characterized, revealing various configurations in the crystal hosts in the solid states. To the best of our knowledge, only one $(H_2O)_{16}$ cluster has been reported [18]; **2** adds the second example to this water cluster.

A close view of the $(H_2O)_{16}$ cluster of **2** illustrates a new mode of supramolecular association of water molecules. On the middle of the $(H_2O)_{16}$ cluster, six water molecules [O3W, O7W, O8W, O3W^{vii}, O7W^{vii} and O8W^{vii}] are arranged into a hexamer with chair conformation through hydrogen-bonding interactions [figure 2(c)]. The water hexamer further connects with other lattice water molecules via hydrogen-bonding interactions to form a $(H_2O)_{16}$ cluster. Among reported water clusters, the water hexamer is interesting as the building block of ice and also exhibits some of the properties of bulk water [19]. This $(H_2O)_{16}$ cluster provides intriguing and useful information for the study of water clusters. The average O $\cdots$ O distance of $(H_2O)_{16}$ cluster is 2.839 Å, comparable to those in the ice phase (2.77–2.84 Å) [20] and slightly longer than the average distance of the reported $(H_2O)_{16}$ cluster (2.732 Å) [18]. The $(H_2O)_{16}$ clusters gather around *p*-bdc anions via hydrogen bonds to the free carboxylate O atoms leading to a 2D supramolecular structure [figure 2(d)]. All eight water molecules act as hydrogen acceptors and donors simultaneously. The cationic [figure 2(b)] and anionic layers [figure 2(d)] are linked by C–H $\cdots$ O bonds [C12 $\cdots$ O4W^{iii} 3.193(4) Å] to a final 3D supramolecular framework [21].

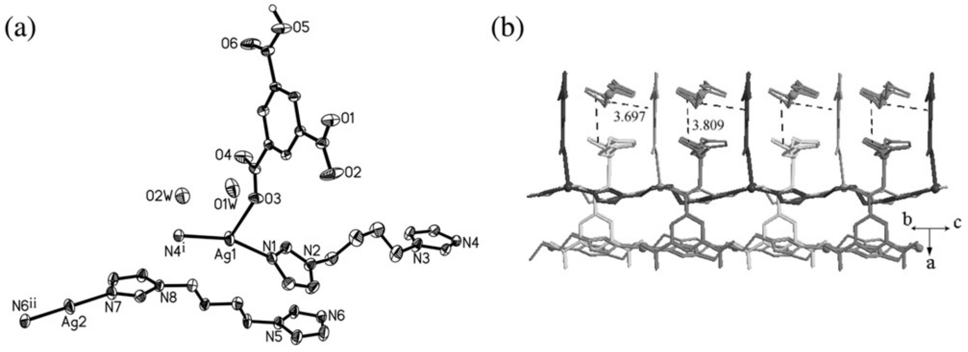


Figure 3. (a) ORTEP drawing of the asymmetric unit of **3**. (b) The π–π interaction (3.809 Å) within the double-stranded chains and C–H $\cdots \pi$ interactions (3.697 Å) among the criss-cross packed supramolecular layer. Symmetry codes: (i) x, $y-1$, $z+1$; (ii) x, $-1+y$, $1+z$.

3.1.3. Structure of [Ag(Hbtc)(L^1)][Ag(L^1)]$\cdot$2H_2O (3). As shown in figure 3(a), **3** contains two crystallographically independent Ag^I centers. Ag1 is three-coordinate, containing a [Ag(Hbtc)(L^1)]$^-$ unit with two symmetry-equivalent L^1 ligands *via* N atoms and a branch-like Hbtc via an O atom. Ag2 is two-coordinate, forming a [Ag(L^1)]$^+$ linear unit. The Ag–O distance is 2.532(2) Å, and Ag–N distances are 2.072(4) to 2.174(4) Å. The two unique polymer chains run parallel to one another, and face-to-face π–π interactions between imidazole rings (centroid-to-centroid distances: 3.809 Å) link them to a double-stranded chain [figure 3(b)].

The remarkable feature of **3** is that the 1D double-stranded chains are interlaced with each other to generate a 2D criss-cross network [figure 3(b)]. In the interlocked structure, there are C–H $\cdots \pi$ interactions between imidazole rings of Ag2 chains and benzene rings of Ag1 chains (edge-to-centroid distance = 3.697 Å, $\angle$C–H $\cdots \pi = 143°$) [22]. Water molecules are scattered among the supramolecular layer.

3.1.4. Structure of [$Ag_2(L^2)_2$](OH-bdc)$_2 \cdot 4H_2O$ (4). X-ray crystal structure analysis shows that **4** consists of one dimeric cation [$Ag_2(L^2)_2$]$^{2+}$, one noncoordinated OH-bdc anion and four water molecules [figure 4(a)]. Each silver is almost linearly coordinated by two L^2 ligands [N–Ag1–N 173.80(11) and N–Ag2–N 175.19(11)]; the two arms of each L^2 ligand adopt a *cis* conformation [23]. The separation of Ag1 and Ag2 is 3.459 Å, indicating Ag $\cdots$ Ag interaction and intramolecular $\pi \cdots \pi$ interactions within the imidazolyl rings of L^2 (centroid-to-centroid distances: 3.480 Å and 3.461 Å, respectively) [24]. Intriguingly, an intermolecular $\pi \cdots \pi$ stacking is present between the phenyl rings of [$Ag_2(L^2)_2$]$^{2+}$ units (with centroid-to-centroid distance of 3.785 Å). Such $\pi \cdots \pi$ interactions link the dimeric [$Ag_2(L^2)_2$]$^{2+}$ cations to form supramolecular chain structures [figure 4(b)].

Adjacent OH-bdc anions are connected to one another *via* symmetry related hydrogen bonds involving –OH of one molecule to an adjacent carboxylate oxygen atom [O5 $\cdots$ O4^{iii} 2.684(4) Å]. The four unique lattice waters link to form a $(H_2O)_4$ chain through hydrogen bonds, and these $(H_2O)_4$ chains further act as "glue" to reinforce the OH-bdc dimers forming a 2D supramolecular layer [figure 4(c)]. O1W, O3W and O4W are hydrogen donors and acceptors, while O2W is only a

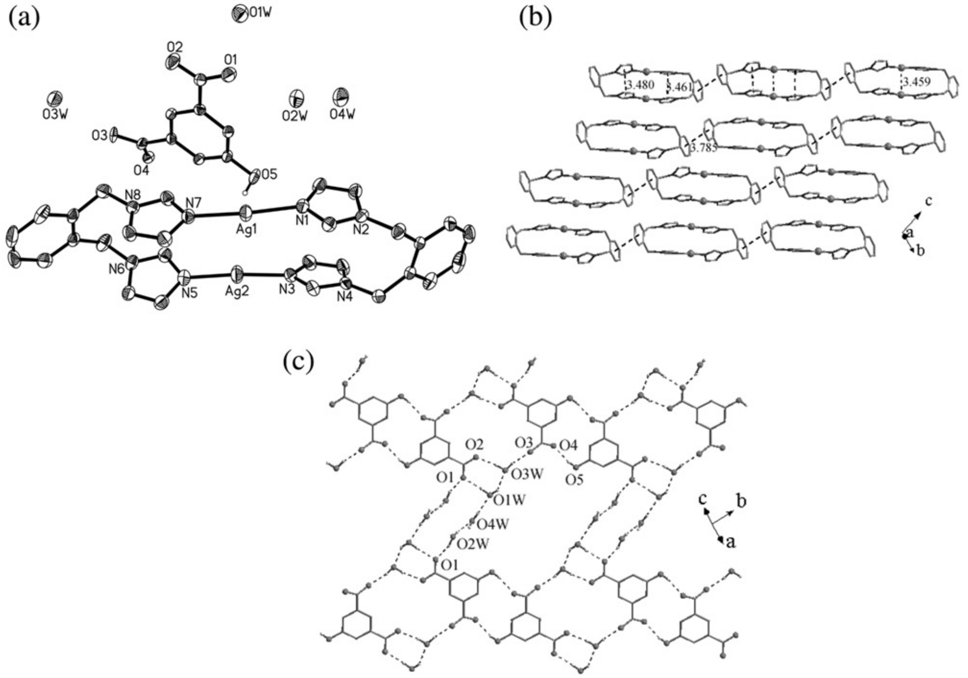


Figure 4. (a) ORTEP drawing of the asymmetric unit of **4**. (b) The Ag $\cdots$ Ag (3.459 Å) and $\pi \cdots \pi$ (3.480 and 3.461 Å) interactions within the $[Ag_2(L^2)_2]^{2+}$ dimers and $\pi \cdots \pi$ (3.785 Å) interactions between the $[Ag_2(L^2)_2]^{2+}$ dimers. (c) The 2D supramolecular layer connected by OH-bdc anions and $(H_2O)_4$ water chains through hydrogen-bonding interactions.

hydrogen donor. The carboxylate oxygen atoms (O1, O2 and O3) are acceptors, hydrogen-bonded to O1W, O2W and O3W, respectively.

The cation chains [figure 4(b)] and the anion layers [figure 4(c)] are further connected through Ag $\cdots$ O interactions between the layers (Ag1 $\cdots$ O2W: 2.831 Å) to a 3D supramolecular structure [25].

3.2. *Luminescent properties*

Solid-state photoluminescent spectra of **1**–**4** are depicted in figure 5. The emission spectra of **1** consist of a main peak at 496 nm ($\lambda_{ex} = 305$ nm). Compound **2** exhibits two intense emission maxima at 486 and 519 nm ($\lambda_{ex} = 320$ nm). Compound **3** has a main peak and a shoulder at 438 and 417 nm ($\lambda_{ex} = 378$ nm). An intense peak at 368 nm and broad band ranging from 410 to 462 nm are observed for **4** ($\lambda_{ex} = 336$ nm). The main emission peak of L^1 and L^2 ligands are at 438 and 468 nm, respectively [4f].

The multicarboxylate ligands (m-H_2bdc, p-H_2bdc, H_3btc and OH-H_2bdc) can also exhibit fluorescence at room temperature as previously reported [26]. With reference to the literature, the peaks at 496 nm and 519 nm of **1** and **2** are probably due to metal-to-ligand charge-transfer (MLCT) transitions [27]. The emission at 486 nm of **2** is assigned to the intra-ligand fluorescent emission since a very weak similar emission (at 466 nm) is also observed for the p-H_2bdc [26b]. The peaks at 438 nm of **3** and the broad emission band of **4** are probably due to $\pi^* \rightarrow \pi$ transitions of neutral ligands because

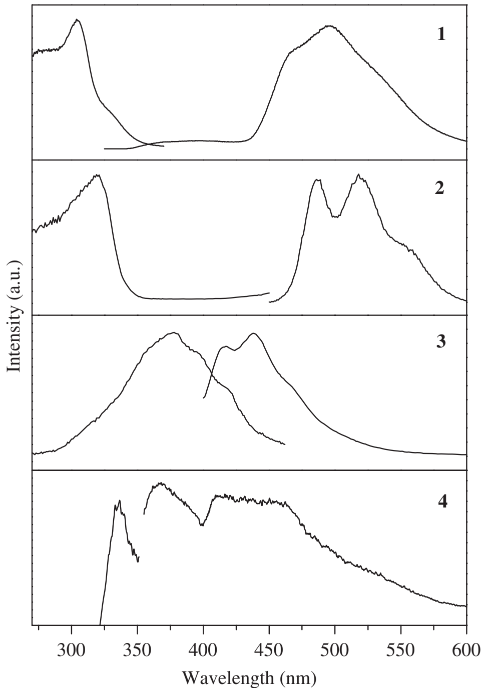


Figure 5. Solid-state photoluminescent spectra of **1**–**4** at room temperature.

similar peaks appear for the free bis(imidazole) ligands [4f]. The spectrum of **4** is significantly different from L^2, due to Ag···Ag interactions. The presence of π–π interactions may also contribute to such luminescent difference [28]. The peaks of 417 nm and 368 nm for **3** and **4** exhibit a red-shift with respect to free H_3btc (380 nm, $\lambda_{ex} = 334$ nm) and OH–H_2bdc (361 nm, $\lambda_{ex} = 280$ nm), respectively, assigned to intra-ligand fluorescent emission of the carboxylate. The N-donor and O-donor ligands show contribution to the fluorescent emissions of **3** and **4** simultaneously.

4. Conclusion

The simultaneous use of the aromatic carboxylic acids and flexible bis(imidazole) ligands to react with silver affords four intriguing polymeric frameworks. The results demonstrate that weak interactions like O–H···O and C–H···O hydrogen bonds, π–π, C–H···π, Ag–π, Ag···Ag, Ag···O and even van der Waals play important roles in the self-assembly of coordination polymers.

Supplementary data

X-ray crystallographic files in CIF format for **1**–**4** have been deposited at the Cambridge Crystallographic Data Centre with deposition number CCDC 664064 to 664067. Copies of the data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk).

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