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Three silver complexes constructed from organic carboxylic acid and 1,2-bis(4-pyridyl)ethane ligands: syntheses, crystal structures, and luminescent properties

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Abstract Three silver-based complexes, namely $[Ag_2(bpa)_2](Brtp)\cdot 6H_2O$ (**1**), $[Ag_3(bpa)_3](Hdcdcpb)\cdot 9H_2O$ (**2**), and $[Ag_2(bpa)_2(oa)]\cdot 2H_2O$ (**3**), were synthesized via the reactions of $AgNO_3$, 1,2-bis(4-pyridyl)ethane (bpa), and 2-bromoterephthalic acid (H_2Brtp), 2,3-dicarboxyl-(2′,3′-dicarboxylazophenyl)benzene (H_4dcdcpb) or 4,4′-oxybisbenzoic acid (H_2oa) in aqueous alcohol/ammonia solution at room temperature. Complexes **1** and **2** consist of 1D infinite cationic $[Ag(bpa)]_n^{n+}$ chains, interspersed with non-coordinated and completely deprotonated $Brtp^{2-}$ or partly deprotonated $Hdcdcpb^{3-}$ anions acting as discrete counter-ions to balance the charge. The lattice water molecules are situated among the framework of the crystal structure and show rich hydrogen-bonding interactions, while the presence of Ag…N and Ag…Ag contacts strengthens the frameworks. Complex **3** consists of 2D neutral $[Ag_2(bpa)_2(oa)]$ in which the completely deprotonated oa^{2-} units both act as bidentate ligands and as counter-ions. All three complexes exhibit luminescent properties, which can be assigned to ligand-to-metal charge transfer and Ag…Ag interactions.

Introduction

Metal–organic frameworks (MOFs, also called coordination polymers) are a relatively new class of porous materials with high diversity, which have attracted much attention in recent decades due to not only their diverse structures [1–3], but also their many potential applications, such as gas storage [4, 5], catalysis [6, 7], conductive materials [8, 9], drug delivery systems [10, 11], sensors [12, 13], magnetic materials [14, 15], gas separation materials [16], and photocatalysis [1, 17–20].

MOFs constructed from metal atoms as templates linked together by multifunctional organic ligands as linkers, can display a variety of infinite supramolecular networks [2, 7, 8, 19, 21, 22]. The construction of such MOFs is highly influenced by such factors as the coordination preferences of the metal, the structural characteristics of polydentate organic ligands, the metal–ligand ratio and the choice of counter-ions [2, 7, 8, 21, 23–26]. It is noteworthy that counter-ions, especially anions, often play important roles in determining the structures of sliver(I) complexes [2, 7, 8, 21, 22]. Compared to inorganic anions, organic carboxylate anions are more numerous and versatile [2, 7, 8, 21, 22, 24]. Therefore, in recent years, our group has focused on syntheses of silver complexes containing different organic carboxylate anions in order to explore how the self-assembly process can be influenced by these organic anions [1, 2, 7, 8, 21, 22, 24, 27–29]. The key to targeted construction of a desired framework is usually the selection of organic carboxylate anions as ligands or/and counter-ions. In some cases, a subtle alteration of organic ligands can lead to a new architecture. Furthermore, with the aid of supramolecular interactions such as hydrogen-bonding, π–π staking interactions, Ag…Ag and Ag…N contacts, various high-dimensional silver(I) coordination polymers can

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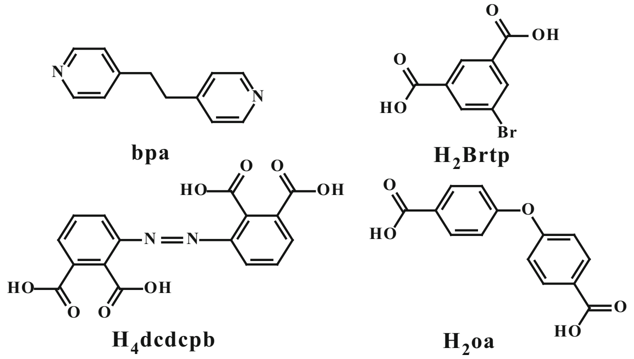

Scheme 1 Structural formulae of bpa, H_2Brtp, H_4dcdcpb, and H_2oa

be built up from low-dimensional Ag(I) complexes [2, 7, 8, 20–22, 24].

In this paper, we present three silver complexes, namely $[Ag_2(bpa)_2](Brtp)\cdot6H_2O$ **(1)**, $[Ag_3(bpa)_3](Hdcdcpb)\cdot9H_2O$ **(2)** and $[Ag_2(bpa)_2(oa)]\cdot2H_2O$ **(3)**, constructed from 1,2-bis(4-pyridyl)ethane (bpa), 2-bromoterephthalic acid (Br-H_2tp), 2,3-dicarboxyl-(2′,3′-dicarboxylazophenyl)benzene (H_4dcdcpb), and 4,4′-oxybisbenzoic acid (H_2oa) (as shown in Scheme 1), in order to investigate the influence of different organic anions on the crystal structures and properties of the resulting silver complexes.

Experimental

All chemicals were commercially available reagent grade and used without further purification. C, H, N elemental analyses were obtained with an Elementar Vario EL-III instrument. FTIR spectra in the region (400–4000 cm^{-1}) were recorded on a PerkinElmer Spectrum 100 Fourier transform infrared spectrophotometer with KBr pellets. Powder X-ray diffraction (PXRD) patterns were recorded using a Dandonghaoyuan DX-2700B diffractometer employing Cu Kα radiation. Luminescence spectra were recorded on a Hitachi F-7000 fluorescence spectrophotometer equipped with a Xenon flash lamp at room temperature.

Synthesis of complex 1

An ammonia solution (125 mL, 0.5 mol/L) of $AgNO_3$ (0.21 g, 1.25 mmol) and 2-bromoterephthalic acid (0.31 g, 1.25 mmol) was added dropwise to an EtOH solution (125 mL) of bpa (0.23 g, 1.25 mmol). The clear mixture was stirred for 15 min and then allowed to evaporate slowly at room temperature. Block-like light white crystals of $[Ag_2(bpa)_2](Brtp)\cdot6H_2O$ **(1)** were obtained after 4 weeks. Anal. calcd. for $C_{32}H_{39}Ag_2BrN_4O_{10}$ (%): C, 41.1; H, 4.2; N, 6.0. Found: C, 41.2; H, 4.3; N, 6.0. IR (KBr)/cm^{-1}: 3333(m), 3030(m), 2925(w), 1933(w), 1606(s), 1557(s), 1495(w), 1423(m), 1360(s), 1219(w), 1177(s), 1100(m), 1076(w), 1012(m), 991(w), 917(w), 828(s), 810(m), 778(s), 718(m), 659(w), 546(m), 488(m), 409(w).

Synthesis of complex 2

Synthesis of block-like red crystals of $Ag_3(bpa)_3](Hdcdcpb)\cdot9H_2O$ **(2)** followed the same procedure as for **1**, except that 2-bromoterephthalic acid was replaced by 2,3-dicarboxyl-(2′,3′-dicarboxylazophenyl)benzene. Anal. calcd. for $C_{52}H_{61}Ag_3N_8O_{17}$ (%): C, 44.8; H, 4.4; N, 8.0. Found: C, 44.7; H, 4.4; N, 8.0. IR (KBr)/cm^{-1}: 3369(m), 3070(m), 1931(w), 1660(w), 1606(s), 1580(s), 1560(s), 1500(w), 1460(m), 1441(m), 1420(m), 1410(w), 1380(s), 1221(w), 1154(s), 1080(m), 1062(w), 1011(m), 989(w), 854(m), 827(s), 797(w), 776(m), 659(w), 574(s), 546(m), 400(w).

Synthesis of complex 3

Synthesis of block-like white crystals of $[Ag_2(bpa)_2(oa)]\cdot2H_2O$ **(3)** followed the same procedure as for **1**, except that 2-bromoterephthalic acid were replaced with 4,4′-oxybisbenzoic acid. Anal. calcd. for $C_{38}H_{36}Ag_2N_4O_7$ (%): C, 52.0; H, 4.1; N, 6.4. Found: C, 52.1; H, 4.1; N, 6.4. IR (KBr)/cm^{-1}: 3417(m), 3030(m), 2926(m), 1599(s), 1553(s), 1500(m), 1400(m), 1311(m), 1290(m), 1266(m), 1251(m), 1218(w), 1161(s), 1114(m), 1010(m), 991(w), 866(m), 828(s), 809(m), 777(m), 659(w), 547(m), 495(m).

X-ray crystallography

X-ray single-crystal data collection for all three complexes was performed with a Bruker Smart 1000 CCD area detector diffractometer with graphite-monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) using φ–ω mode at 298(2) K. The SMART software [30] was used for data collection and the SAINT software [30] for data extraction. Empirical absorption corrections were performed with the SADABS program [31]. The structures were solved by direct methods (SHELXS-97) [32] and refined by full-matrix least-squares techniques on F^2 with anisotropic thermal parameters for all of the non-hydrogen atoms (SHELXL-97) [32]. All hydrogen atoms were located by Fourier difference synthesis and geometrical analysis. These hydrogen atoms were allowed to ride on their respective parent atoms. All structural calculations were carried out using the SHELX-97 program package [32]. Crystallographic data and structural refinements for the complexes are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

Table 1 Details of X-ray data collection and refinement for the complexes **1**–**3**

	1	2	3
Formula	$C_{32}H_{39}Ag_2BrN_4O_{10}$	$C_{52}H_{61}Ag_3N_8O_{17}$	$C_{38}H_{36}Ag_2N_4O_7$
M	935.32	1393.70	876.45
Crystal system	Triclinic	Orthorhombic	Monoclinic
Space group	$P\bar{1}$	Pna2(1)	P2(1)/c
a (Å)	10.9303(7)	21.8702(19)	9.3557(8)
b (Å)	11.3512(8)	13.6500(11)	28.920(3)
c (Å)	15.2302(14)	18.2601(17)	13.5709(11)
α (°)	91.2980(10)	90	90
β (°)	106.978(2)	90	109.963(2)
γ (°)	98.1940(10)	90	90
V (Å^3)	1784.7(2)	5451.2(8)	3451.3(5)
Z	2	4	4
μ(Mo, Kα) (mm^{-1})	2.277	1.147	1.192
Total Reflections	8955	26,856	17,253
Unique	6531	9500	6052
F(000)	936	2824	1768
Goodness-of-fit on F^2	1.012	0.957	1.220
R_{int}	0.0299	0.0864	0.0374
R_0	0.0410	0.0494	0.0756
ωR_2	0.0958	0.0726	0.1705
R_1 (all data)	0.0745	0.1027	0.0973
ωR_2 (all data)	0.1067	0.0817	0.1770
Largest diff. peak and hole (e/Å^3)	0.813, −1.227	1.181, −0.512	0.856, −0.832

Results and discussion

IR spectra

In the IR spectra of all three complexes, a strong and broad absorption at 3333, 3369, and 3417 cm^{-1} for **1**, **2,** and **3**, respectively, is assigned to the O–H stretching vibration, showing the presence of lattice water molecules. Sharp bands at 1557 and 1423 m^{-1} (for **1**), 1580 and 1420 cm^{-1} (for **2**), and 1599 and 1410 cm^{-1} (for **3**) are attributed to the asymmetric and symmetric vibrations of the respective carboxylate groups.

Crystallographic analysis of complex **1**

The crystal structure of complex **1** reveals infinite cationic chains of $[Ag_2(bpa)_2]_n^{2n+}$ cations, Brtp^{2-} anions, and lattice water molecules, as illustrated in Fig. 1a. In the cationic chains of $[Ag_2(bpa)_2]_n^{2n+}$, the Ag(1) and Ag(2) atoms, in linear geometry, are coordinated by the two nitrogen atoms from two different bpa ligands, as also seen for previously reported Ag$^{\text{I}}$ complexes [1, 2, 7, 8, 21, 22] (Fig. 1a; Table 2). The oxygen atoms of the lattice water molecules interact with the Ag centers through weak Ag…O interactions [Ag(1)…O(5) = 2.734(4) Å and Ag(2)…O(6) = 2.859(4) Å, respectively], in which the Ag…O distances are shorter than their van der Waals contact distance of 3.24 Å [33].

In complex **1**, bpa acts as a typical 4,4′-bipyridine-like bidentate ligand, linking two Ag centers via the nitrogen atoms from two pyridyl rings to form infinite 1-D $[Ag_2(bpa)_2]_n^{2n+}$ chains. The dihedral angles between the two pyridyl rings of the two different bpa ligands, are 171.3°. The adjacent cationic $[Ag_2(bpa)_2]_n^{2n+}$ chains are packed into 2-D cationic sheets in an ABBA pattern via Ag…N interactions [Ag…N contacts ranging from 3.502(46) to 3.840(45) Å], as shown in Fig. 1d, similar to a previously reported Ag$^{\text{I}}$ complex [7]. The completely deprotonated Brtp^{2-} anion acts as counter-ion to compensate the charge of $[Ag_2(bpa)_2]_n^{2n+}$, which is joined into anionic sheets with the aid of lattice water molecules via intermolecular hydrogen-bonding interactions, as depicted in Table 3 and Fig. 1c. The neighboring cationic and anionic sheets are further joined into a 3D sandwich-like framework along the *a*-axis, as shown in Fig. 1b. The lattice water molecules of complex **1** are situated within the 3D framework and stabilized by hydrogen-bonding interactions.

Table 2 Selected bond lengths (Å) and angles (°) for complexes **1–3**

(1)					
Bond lengths (Å)					
Ag(1)–N(1)	2.129(4)	Ag(1)–N(3)	2.138(4)	Ag(2)–N(4)#1	2.153(4)
Ag(2)–N(2)	2.154(4)				
Bond angles (°)					
N(1)–Ag(1)–N(3)	172.10(16)		N(4)#1–Ag(2)–N(2)	178.13(13)	
Symmetry transformations used to generate equivalent atoms: #1 $x-2$, $y+1$, $z-1$ #2 $x+2$, $y-1$, $z+1$					
(2)					
Bond lengths (Å)					
Ag(1)–N(3)	2.124(6)	Ag(1)–N(4)	2.157(4)	Ag(2)–N(6)#1	2.141(5)
Ag(2)–N(5)	2.144(6)	Ag(3)–N(7)	2.152(5)	Ag(3)–N(8)	2.153(5)
Bond angles (°)					
N(3)–Ag(1)–N(4)	174.2(3)		N(6)#1–Ag(2)–N(5)	168.6(2)	
N(7)–Ag(3)–N(8)	172.5(2)				
Symmetry transformations used to generate equivalent atoms: #1 x, $y+1$, z #2 x, $y-1$, z					
(3)					
Bond lengths (Å)					
Ag(1)–N(1)	2.162(8)	Ag(1)–N(2)	2.215(8)	Ag(1)–O(1)	2.406(7)
Ag(2)–N(4)	2.166(8)	Ag(2)–N(3)	2.173(8)	Ag(2)–O(3)	2.441(7)
Bond angles (°)					
N(1)–Ag(1)–N(2)	157.8(3)		N(1)–Ag(1)–O(1)	110.2(3)	
N(2)–Ag(1)–O(1)	91.0(3)		N(4)–Ag(2)–N(3)	154.8(3)	
N(4)–Ag(2)–O(3)	93.7(3)		N(3)–Ag(2)–O(3)	111.0(3)	
Symmetry transformations used to generate equivalent atoms: #1 $x+1$, y, $z+1$ #2 $x-1$, y, $z-1$ #3 x, y, $z+1$ #4 x, y, $z-1$					

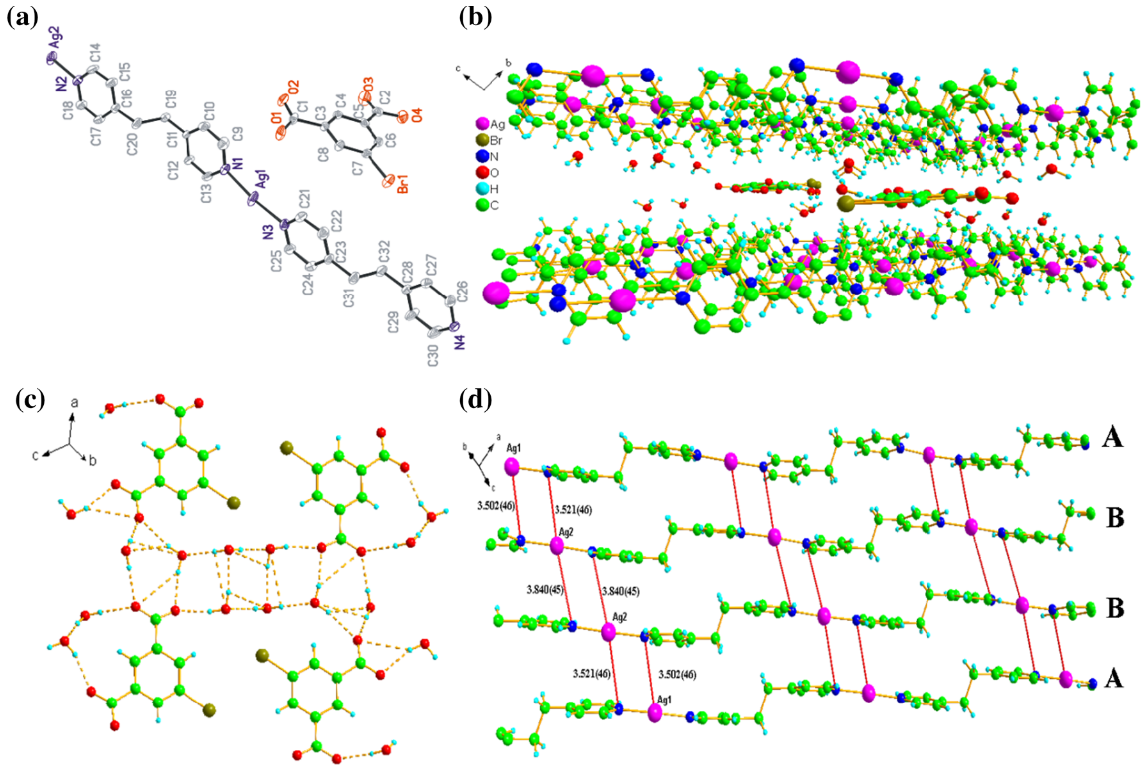

Fig. 1 **a** Asymmetric unit of $[Ag_2(bpa)_2](Br\text{-}tp)\cdot 6H_2O$ (1) and coordination environments around the Ag^I atoms. Water molecules and corresponding H atoms are omitted for clarity. **b** Packing view of the sandwich-like framework built from anionic and cationic sheets along the *a*-axis for complex **1**. **c** The anionic layer constructed from $Br\text{-}tp^{2-}$ and water molecules in complex **1**. **d** The cationic layer formed from Ag-bpa chains in complex **1** via Ag…N interactions

Table 3 Hydrogen bonds for complexes **1**–**3** [Å and °]

D–H	d(D–H)	d(H..A)	<DHA	d(D..A)	A
(1)					
O5-H5C	0.850	2.090	169.89	2.931	O2 $[-x+1, -y+1, -z]$
O5-H5D	0.850	2.117	170.19	2.958	O7 $[x, y-1, z-1]$
O6-H6C	0.850	1.960	176.88	2.809	O2 $[-x, -y+2, -z]$
O6-H6D	0.850	1.875	177.21	2.724	O4 $[-x+1, -y+2, -z]$
O7-H7C	0.850	2.015	163.72	2.841	O3 $[x-1, y, z+1]$
O7-H7D	0.850	2.023	164.47	2.851	O3 $[-x+1, -y+2, -z+1]$
O8-H8C	0.850	1.905	170.37	2.746	O1
O8-H8D	0.850	2.098	170.76	2.940	O4 $[x-1, y, z]$
O9-H9C	0.850	1.914	174.17	2.761	O8
O9-H9D	0.850	2.006	174.46	2.853	O10 $[-x+1, -y+1, -z+1]$
O10-H10C	0.850	1.887	170.92	2.729	O1
O10-H10D	0.850	2.072	170.96	2.915	O9
(2)					
O3-H3	0.820	1.837	154.69	2.602	O5 $[x-1/2, -y+1/2, z]$
O9-H9C	0.850	1.984	179.15	2.834	O1 $[-\mathrm{x}+1/2, y-1/2, z-1/2]$
O9-H9D	0.850	1.857	178.96	2.707	O7 $[-x+1, -y+1, z-1/2]$
O10-H10C	0.850	2.032	175.12	2.880	O14
O10-H10D	0.850	1.915	176.14	2.764	O17 $[x+1/2, -y+3/2, z]$
O11-H11C	0.850	1.928	169.34	2.767	O1 $[x+1/2, -y+3/2, z]$
O11-H11D	0.850	1.987	169.74	2.827	O8
O12-H12C	0.850	2.026	178.82	2.876	O9
O12-H12D	0.850	1.924	179.40	2.774	O13 $[-x+1, -y+1, z-1/2]$
O13-H13C	0.850	1.891	175.55	2.739	O6
O13-H13D	0.850	2.151	175.68	2.999	O4 $[x+1/2, -y+1/2, z]$
O14-H14C	0.850	1.961	172.15	2.806	O11
O14-H14D	0.850	2.053	172.70	2.898	O12 $[-x+1, -y+1, z+1/2]$
O15-H15C	0.850	2.016	168.03	2.853	O1 $[\underline{x}+1, y, z]$
O15-H15D	0.850	2.001	168.34	2.839	O8 $[x+1/2, -y+3/2, z]$
O16-H16C	0.850	1.847	172.81	2.693	O2 $[x+1, y, z]$
O16-H16D	0.850	1.919	173.18	2.764	O5 $[x+1/2, -y+1/2, z]$
O17-H17C	0.850	1.947	175.48	2.795	O15 $[x-1/2, -y+3/2, z]$
O17-H17D	0.850	1.923	174.77	2.771.	O16 $[x-1/2, -y+3/2, z]$
(3)					
O6-H6C	0.850	2.021	179.33	2.871	O2
O6-H6D	0.850	2.003	179.41	2.853	O3 $[-x, y-1/2, -z+3/2]$
O7-H7C	0.850	1.950	179.09	2.800	O4
O7-H7D	0.850	2.040	179.08	2.890	O1 $[-x+1, y+1/2, -z+3/2]$

Crystallographic analysis of complex **2**

As illustrated in Fig. 2a, the crystal structure of complex **2** consists of three chains of $[\mathrm{Ag(1)(bpa)}]_n^{n+}$, $[\mathrm{Ag(2)(bpa)}]_n^{n+}$,and $[\mathrm{Ag(3)(bpa)}]_n^{n+}$ cations, partly deprotonated Hdcdcpb^{3-} moieties, and lattice water molecules. The coordination environment of Ag$^{\mathrm{I}}$ is similar to that observed in complex **1**, involving a linear coordination geometry with two nitrogen atoms from different bpa ligands. The Ag atoms interact with the oxygen atoms of the water molecules through weak Ag…O interactions, and the partly deprotonated Hdcdcpb^{3-} anions act as counter-ions to balance the cationic $[\mathrm{Ag_3(bpa)_3}]_n^{3n+}$ chains.

The adjacent cationic $[\mathrm{Ag(1)(bpa)}]_n^{n+}$, $[\mathrm{Ag(2)(bpa)}]_n^{n+}$ and $[\mathrm{Ag(3)(bpa)}]_n^{n+}$ chains are connected by Ag…Ag and Ag…N interactions [Ag(1)…Ag(2) contacts 3.4846(10) Å, Ag(1)…Ag(3) contacts 3.5903(10) Å, Ag(1)…N contacts 3.5346(65) and 3.521(66) Å, Ag(2)…N contacts 3.3988(65) Å, and Ag(3)…N contacts 3.5045(65) Å] into 2D cationic sheets (A sheets), as shown in Fig. 2c. The partly

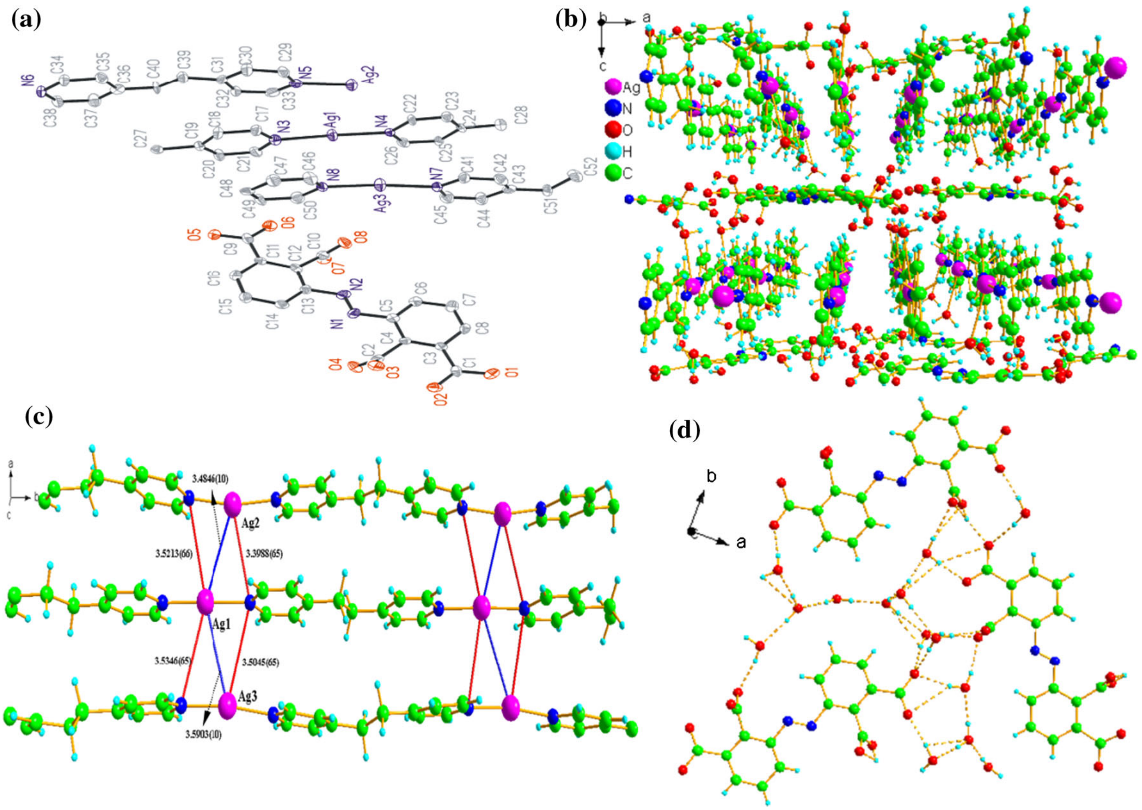

Fig. 2 **a** Asymmetric unit of $[Ag_3(bpa)_3](Hdcdcpb)\cdot 9H_2O$ (**2**) and coordination environments around the Ag^I atoms. Lattice water molecules and corresponding H atoms are omitted for clarity. **b** Packing view of the sandwich-like framework built from anionic and cationic sheets along the *b*-axis for complex **2**. **c** The cationic layer formed from Ag-bpa chains in complex **2**. **d** The anionic layer constructed from $Hdcdcpb^{3-}$ and water molecules in complex **2**

deprotonated $Hdcdcpb^{3-}$ anions are linked into anionic sheets (B sheets) with the aid of lattice water molecules via intermolecular hydrogen-bonding interactions, as depicted in Table 3 and Fig. 2d. The neighboring cationic and anionic sheets are further joined into a 3D sandwich-like framework (as shown in Fig. 2b) with the ABAB pattern by hydrogen-bonding and electrostatic interactions, which is similar to previously reported Ag^I complexes [22, 24].

Crystallographic analysis of complex 3

The crystal structure of complex **3** reveals that $[Ag_2(bpa)_2(oa)]\cdot 2H_2O$ is made up of infinite neutral 2D sheets of $[Ag_2(bpa)_2(oa)]_n$ moieties and lattice water molecules, as illustrated in Fig. 3a. In the 2D sheet of $[Ag_2(bpa)_2(oa)]_n$, each Ag atom has a T-shaped coordination geometry provided by two nitrogen atoms from different bpa ligands and an oxygen atom from a COO^-, as illustrated in Table 2.

The coordination mode of bpa is similar to those of bpy-like ligands in similar complexes [2, 7, 8, 20–22], such that two Ag atoms are linked via the nitrogen atoms from two pyridyl rings to form 1-D $[Ag(bpa)]_n^{n+}$ chains. The fully deprotonated oa^{2-} ligand, in which the dihedral angle between the two benzene rings is 123.2°, connects two Ag atoms via O(1) and O(3) in bis-monodentate mode, to form 1-D anionic chains. The neighboring cationic $[Ag(bpa)]_n^{n+}$ chains are further linked into 2-D sheets, as illustrated in Fig. 3b and Table 2. The 2-D sheets are connected into a 3-D framework by rich hydrogen-bonding interactions provided by lattice water molecules, as illustrated in Fig. 3c.

A series of complexes of silver(I) with sandwich-like frameworks has been reported previously [1, 2, 7, 8, 21, 22]. These complexes consist of 2D cationic sheets constructed from parallel 1-D infinite bpy/bpe/bpp-silver cationic chains via ligand-unsupported Ag…Ag and Ag…N interactions, interspersed with anionic sheets constructed from organic anions and water molecules via rich hydrogen-bonding interactions. The coordination environment of the Ag^I is generally either linear [1, 2, 7, 8, 21, 22, 24], T-shaped [2, 7, 8, 21, 22], trigonal or tetrahedral [8, 22]. Generally, the counter-ions can be present in coordinated, uncoordinated, or mixed modes, such that coordinated anions normally increase the dimensionality of the

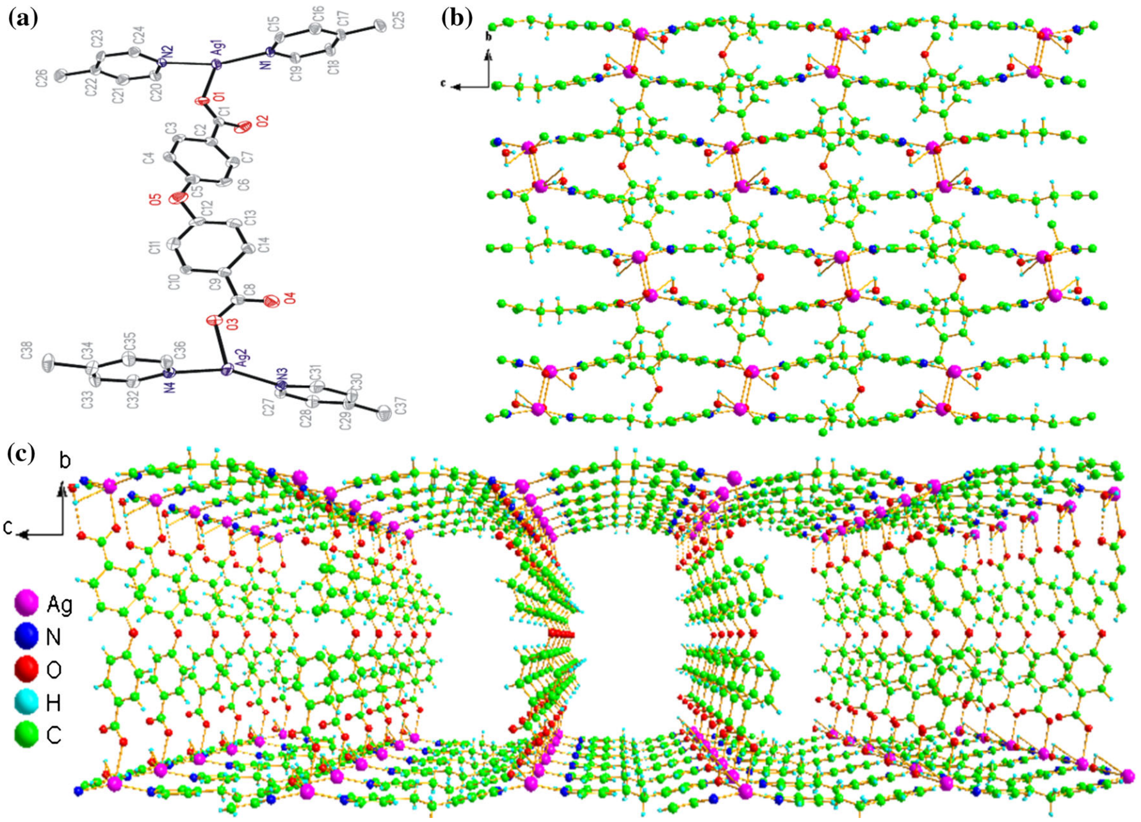

Fig. 3 **a** Asymmetric unit of $[Ag_2(bpa)_2(oba)]\cdot 2H_2O$ (**3**) and coordination environments around the Ag^I atoms. Lattice water molecules and corresponding H atoms are omitted for clarity. **b** 2-D network built up of 1-D cationic silver-bpa chains linked by oa^{2-} ligands. **c** Packing view of the 3-D framework built from rich hydrogen-bonding interactions along *a*-axis for **3**

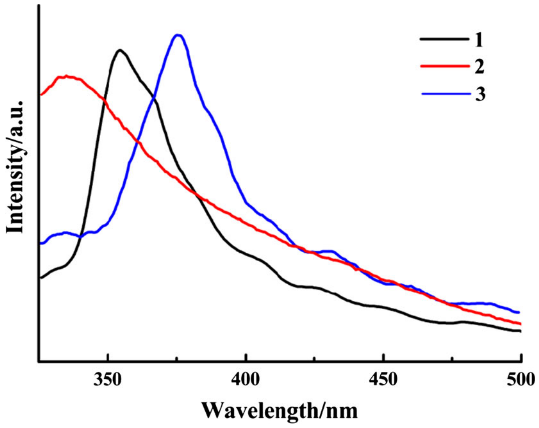

Fig. 4 Luminescent emission spectra of complexes **1**–**3** in the solid state at room temperature

crystal structures, while uncoordinated anions may help to extend the crystal structures via hydrogen-bonding, π–π stacking, and/or ligand-unsupported Ag…Ag and Ag…N interactions [2].

Fluorescence properties of the complexes

The solid-state emission spectra of these complexes have been investigated at room temperature (Fig. 4). Intense bands in the emission spectra were observed at 354 nm ($\lambda_{ex} = 290$ nm) for **1**, 335 nm ($\lambda_{ex} = 308$ nm) for **2** and 375 nm ($\lambda_{ex} = 310$ nm) for **3**. According to the literature, these emission bands can be assigned to ligand-to-metal charge transfer and Ag…Ag interactions. Some silver-based complexes with Ag…Ag interactions show emission with similar energies [21, 34].

In order to check the phase purities of the complexes which were used to study their fluorescence properties, powder X-ray diffraction (PXRD) patterns have been checked at ambient temperature, as listed in Fig. 5. For all three complexes, the measured PXRD patterns agree well with those calculated from the X-ray single-crystal diffraction data, confirming high-phase purities. The slight differences in intensities may be attributed to the preferred orientations of the crystalline powder samples [19, 35].

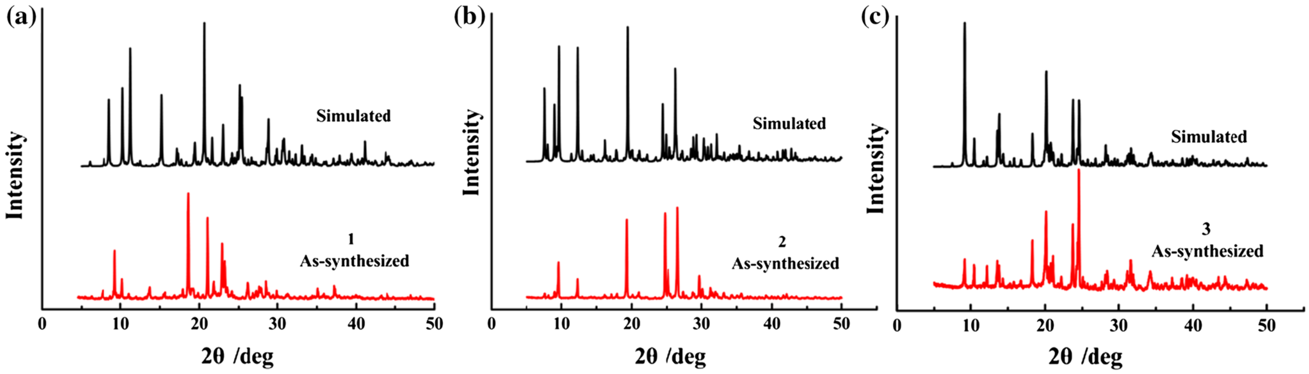

Fig. 5 Simulated (*black*) and experimental (*red*) PXRD patterns for complexes **1**–**3**. (Color figure online)

Conclusions

Three silver(I) complexes have been synthesized and characterized by single-crystal diffraction. Complexes **1** and **2** contain novel and fascinating sandwich-like frameworks built up of cationic $[Ag(bpa)]_n^{n+}$ layers and anionic layers with the aid of supramolecular interactions, via ligand-unsupported Ag…Ag and Ag…N interactions and hydrogen-bonding interactions, in which the deprotonated $Brtp^{2-}$ and $Hdcdcpb^{3-}$ moieties do not participate in coordination with silver, only playing the role of charge compensation. Complex **3** is built up of 2D $[Ag_2(bpa)_2(oa)]$ sheets, in which the exo-multidentate oa^{2-} ligands not only act as O-donors to link the silver centers, but also as counter-ions to compensate the cationic charge of the crystal structure. All three complexes are luminescent.

Supplementary materials

CCDC 1412329, 1412330, and 1412331 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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