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**Transition Metal Chemistry**

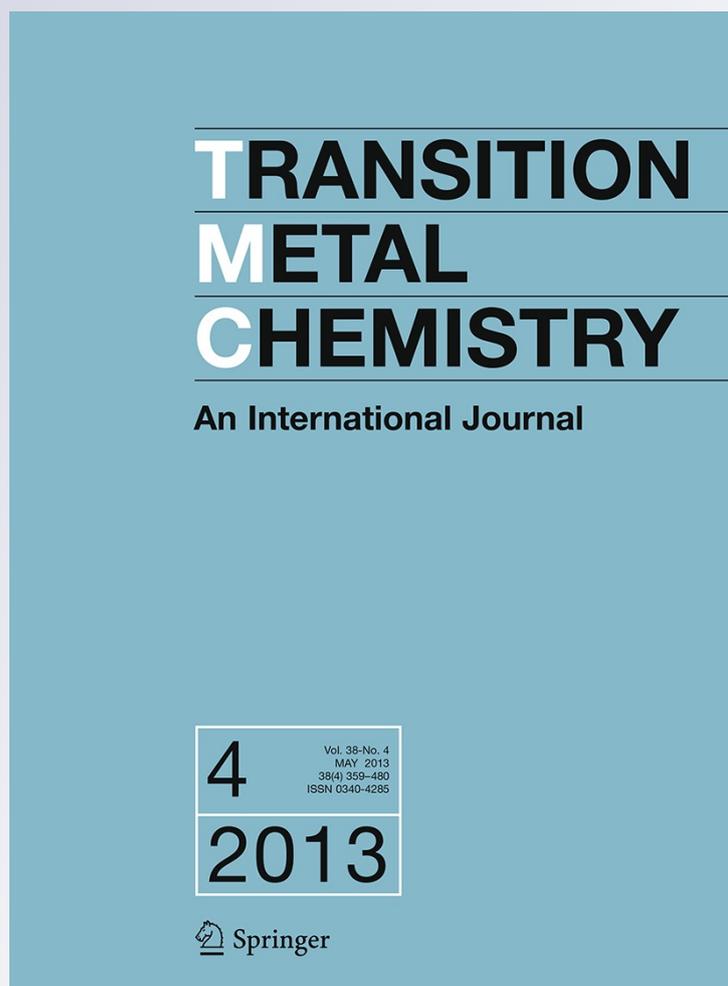
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# Synthesis, structure, and luminescent properties of three silver(I) complexes with organic carboxylic acid and 4,4'-bipyridine-like ligands

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**Abstract** The reactions of  $\text{AgNO}_3$  with combinations of 1,2-bis(4-pyridyl)ethane(bpa)/4,4'-bipyridine (bpy), 4,4'-stilbenedicarboxylic acid ( $\text{H}_2\text{sda}$ )/2,2'-diphenylaminedicarboxylic acid ( $\text{H}_2\text{dpadc}$ )/2,6-naphthalenedicarboxylic acid ( $\text{H}_2\text{ndc}$ ) in aqueous alcohol/ammonia at room temperature produce block-like crystals of  $[\text{Ag}_2(\text{bpa})_{1.5}(\text{sda})_{0.5}](\text{sda})_{0.5} \cdot 7\text{H}_2\text{O}$ ,  $[\text{Ag}_2(\text{bpa})_2(\text{H}_2\text{O})_3](\text{dpadc})$ ,  $[\text{Ag}_2(\text{bpy})_2](\text{ndc}) \cdot 4\text{H}_2\text{O}$ . All three complexes consist of 1D infinite silver–ligand cationic chains, interspersed with organic carboxylate anions that provide charge compensation in the crystal structures. The lattice water molecules are situated among the framework of the crystal structure and show rich hydrogen-bonding interactions, which help to orientate the organic carboxylate anions in the crystal packing, and the presence of  $\text{Ag} \cdots \text{N}$  and  $\text{Ag} \cdots \text{Ag}$  contacts contributes to strengthen the frameworks. The luminescent properties and thermogravimetric analyses of the three complexes are also presented.

## Introduction

The growing interest in the design and assembly of silver coordination polymers is not only because of their intricate

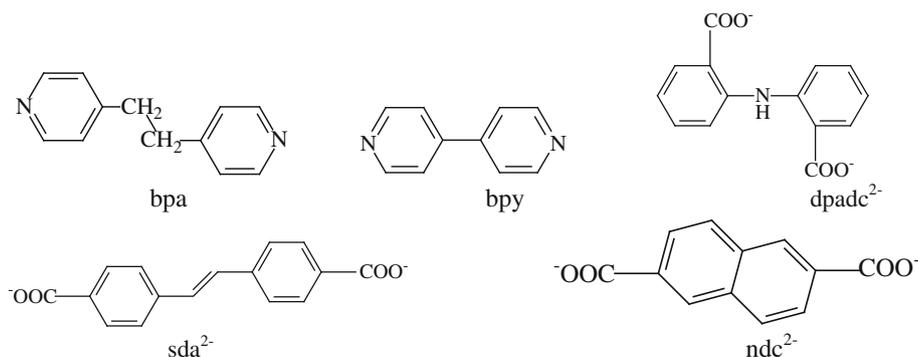
coordination architectures [1–5], but also because of their distinctive conductivity, luminescence, antimicrobial activity, and magnetism properties [6–18]. The silver(I) cation has a  $d^{10}$  electronic configuration and is not expected to significantly alter the emission color of luminescent ligands. Because of its larger size, silver(I) cation has a tendency to adopt more bonding modes and coordination geometries to facilitate the formation of a diverse range of silver-based complexes and also affords an opportunity to explore how the self-assembly of silver-based complexes can be influenced by factors such as the structural characteristics of polydentate organic ligands, the metal–ligand ratio, solvents, and the counter-ions [1–5, 9–11]. It is noteworthy that counter-ions, especially anions, often play important roles in determining the structures of silver-based complexes. The size, coordination ability, and supramolecular interactions of these anions exert different influences on the final silver(I) complexes. Compared to inorganic anions, the organic carboxylate anions are more numerous and versatile; we have therefore chosen to focus our efforts on the synthesis of silver complexes containing different organic carboxylate anions in order to explore how the self-assembly process can be influenced by these organic anions. [2–5, 19].

In this paper, we present three silver-based complexes, namely  $[\text{Ag}_2(\text{bpa})_{1.5}(\text{sda})_{0.5}](\text{sda})_{0.5} \cdot 7\text{H}_2\text{O}$  (**1**),  $[\text{Ag}_2(\text{bpa})_2(\text{H}_2\text{O})_3](\text{dpadc})$  (**2**), and  $[\text{Ag}_2(\text{bpy})_2](\text{ndc}) \cdot 4\text{H}_2\text{O}$  (**3**), constructed from flexible bpa and rigid bpy as typical neutral N-donor ligands, and organic carboxylate anions, namely  $\text{sda}^{2-}$ ,  $\text{dpadc}^{2-}$ , and  $\text{ndc}^{2-}$  (Scheme 1), as counter-ions/secondary ligands, in order to investigate the influence of different organic anions on the crystal structures and properties of the resulting silver-based complexes. The complexes **1–3** show interesting luminescent and thermal properties.

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**Scheme 1** The structural formulae of bpa, bpy, dpadc<sup>2-</sup>, sda<sup>2-</sup> and ndc<sup>2-</sup>



## Experimental section

### Materials and measurements

All chemicals were commercially available reagent grade and used without further purification. Elemental analysis for the title complexes was performed using an Elementar Vario EL-III instrument. FTIR spectra, in the region (400–4,000 cm<sup>-1</sup>), were recorded on a Perkin-Elmer Spectrum 100 Fourier Transform infrared spectrophotometer. Luminescence spectra were recorded on a Tianjin Gangdong F-280 spectrophotometer at room temperature. TGA was performed from room temperature to 800 °C in an air stream at a flow rate of 5 °C min<sup>-1</sup> on a SDT Q600 Simultaneous DSC-TGA Instrument (TA Instruments) using  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as reference material.

### Synthesis of [Ag<sub>2</sub>(bpa)<sub>1.5</sub>(sda)<sub>0.5</sub>](sda)<sub>0.5</sub>·7H<sub>2</sub>O (**1**)

An ammonia solution (25 mL, 0.5 mol/L) containing AgNO<sub>3</sub> (0.0085 g, 0.05 mmol) and H<sub>2</sub>sda (0.013 g, 0.05 mmol) was added dropwise to an EtOH solution (25 mL) of bpa (0.009 g, 0.05 mmol). The clear mixture was stirred for a few minutes and then allowed to evaporate slowly at room temperature. Block-like colorless crystals of [Ag<sub>2</sub>(bpa)<sub>1.5</sub>(sda)<sub>0.5</sub>](sda)<sub>0.5</sub>·7H<sub>2</sub>O (**1**) were obtained after several weeks. Anal. Calcd. for C<sub>34</sub>H<sub>42</sub>Ag<sub>2</sub>N<sub>3</sub>O<sub>11</sub>: C, 46.2; H, 4.8; N, 4.8. Found: C, 46.4; H, 4.9; N, 4.8. IR (KBr)/cm<sup>-1</sup>: 3,444, 1,928, 1,632, 1,600, 1,480, 1,425, 1,376, 1,351, 1,290, 1,259, 1,208, 1,180, 1,125, 1,083, 1,031, 1,009, 997, 988, 972, 954, 896, 837, 826, 674, 601, 547, 411.

### Synthesis of [Ag<sub>2</sub>(bpa)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>](dpadc) (**2**)

Synthesis of block-like colorless crystals of [Ag<sub>2</sub>(bpa)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>](dpadc) (**2**) followed the same procedure as for **1**, except that H<sub>2</sub>sda was replaced with H<sub>2</sub>dpadc. Anal. Calcd. for C<sub>38</sub>H<sub>39</sub>Ag<sub>2</sub>N<sub>5</sub>O<sub>7</sub>(%): C, 51.1; H, 4.4; N, 7.8. Found: C, 52.0; H, 4.5; N, 7.8. IR (KBr)/cm<sup>-1</sup>: 3,434, 3,028, 1,662, 1,600, 1,496, 1,450, 1,384, 1,324, 1,270, 1,215, 1,163, 1,144, 1,066, 1,041, 1,010, 997, 989, 972, 954, 847, 838, 826, 752, 735, 697, 548.

### Synthesis of [Ag<sub>2</sub>(bpy)<sub>2</sub>](ndc)·4H<sub>2</sub>O (**3**)

Synthesis of block-like colorless crystals of [Ag<sub>2</sub>(bpy)<sub>2</sub>](ndc)·4H<sub>2</sub>O (**3**) followed the same procedure as for **1**, except that H<sub>2</sub>sda and bpa were replaced with H<sub>2</sub>ndc and bpy, respectively. Anal. Calcd. for C<sub>32</sub>H<sub>30</sub>Ag<sub>2</sub>N<sub>4</sub>O<sub>8</sub> (%): C, 47.2; H, 3.7; N, 6.9. Found: C, 47.4; H, 3.8; N, 7.0. IR (KBr)/cm<sup>-1</sup>: 3,377, 3,049, 1,956, 1,681, 1,643, 1,598, 1,561, 1,530, 1,493, 1,407, 1,358, 1,138, 1,323, 1,219, 1,191, 1,093, 1,072, 1,042, 1,004, 994, 959, 923, 903, 855, 827, 806, 792, 782, 736, 728, 683, 626, 571, 538, 507, 488, 475.

### X-ray crystallography

Diffraction intensities for all three complexes were recorded with a Bruker smart APEX CCD area-detector diffractometer with graphite-monochromatized MoK $\alpha$  radiation ( $\lambda = 0.71, 0.73\text{\AA}$ ) using  $\varphi$ - $\omega$  mode at 298(2) K. Semi-empirical absorption corrections were applied using the SADABS program [19]. The structures were solved by direct methods [20] and refined by full-matrix least-squares on  $F^2$  using SHELXS 97 and SHELXL 97 programs, respectively [20]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of organic ligands were added according to theoretical models, and those of water molecules were found by difference Fourier maps. Crystallographic data and structural refinements for the complexes are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

## Results and discussion

### Crystallographic analysis of complex (**1**)

The analysis of the crystal structure reveals that [Ag<sub>2</sub>(bpa)<sub>1.5</sub>(sda)<sub>0.5</sub>](sda)<sub>0.5</sub>·7H<sub>2</sub>O (**1**) is made up of 1D cationic [Ag<sub>2</sub>(bpa)<sub>1.5</sub>(sda)<sub>0.5</sub>]<sup>n+</sup> chains, discrete sda<sup>2-</sup> counter-ions, and lattice water molecules. There are two crystallographically non-identical silver(I) atoms, in which Ag1 atom is linearly coordinated by one N atom from bpa

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

	1	2	3
Formula	C <sub>34</sub> H <sub>42</sub> Ag <sub>2</sub> N <sub>3</sub> O <sub>11</sub>	C <sub>38</sub> H <sub>39</sub> Ag <sub>2</sub> N <sub>5</sub> O <sub>7</sub>	C <sub>32</sub> H <sub>30</sub> Ag <sub>2</sub> N <sub>4</sub> O <sub>8</sub>
M	884.45	893.48	814.34
Crystal system	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	11.4627(4)	10.8888(7)	7.1440(12)
<i>b</i> (Å)	12.6360(5)	12.1961(11)	9.6170(13)
<i>c</i> (Å)	13.6132(5)	13.6590(8)	11.4194(15)
$\alpha$ (°)	114.877(2)	87.561(2)	90.4940(12)
$\beta$ (°)	93.1080(10)	85.4950(10)	94.9050(15)
$\gamma$ (°)	90.9710(10)	77.0610(10)	108.7940(10)
<i>V</i> (Å <sup>3</sup> )	1,784.46(11)	1,761.8(2)	739.46(19)
<i>Z</i>	2	2	1
$\mu$ (Mo, K $\alpha$ ) (mm <sup>-1</sup> )	1.160	1.170	1.385
Total reflections	10,735	11,189	3,740
Unique	6,284	6,205	2,584
<i>F</i> (000)	898	904	408
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.029	1.051	1.074
<i>R</i> <sub>int</sub>	0.0215	0.0223	0.0224
<i>R</i> 1	0.0339	0.0362	0.0332
$\omega R$ 2	0.0738	0.0793	0.0865
<i>R</i> 1 (all data)	0.0512	0.0515	0.0408
$\omega R$ 2 (all data)	0.0833	0.0885	0.0915
Largest diff. peak and hole(e/Å <sup>3</sup> )	0.643, -0.332	0.477, -0.526	0.341, -1.047

ligand and one oxygen atom from sda<sup>2-</sup> ligand, with Ag–N distance of 2.124(2) Å, Ag–O distance of 2.121(2) Å, and O–Ag–N angle of 169.58(10)°, while Ag2, also in linear geometry, is joined by two N atoms from bpa ligand, with Ag–N distances of 2.119(2) and 2.125(2) Å, respectively, and N–Ag–N angle of 176.05(10)°. The Ag–N bond lengths and N–Ag–N bond angles are comparable with those observed in related complexes [2–5]. The bpa acts as a typical N,N'-bidentate ligand to join two silver(I) atoms, and the dihedral angles between the two pyridyl rings of the same bpa ligands are 0.00° and 7.46(10)°. There are two types of completely deprotonated sda<sup>2-</sup> in complex 1, in which one type sda<sup>2-</sup> acts as bis-monodentate ligand to link silver(I) atoms into 1D cationic chains alternately along with the bpa ligands, while the other type sda<sup>2-</sup> acts as counterion to balance the charge of cationic [Ag<sub>2</sub>(bpa)<sub>1.5</sub>(sda)<sub>0.5</sub>]<sup>n+</sup>.

The adjacent cationic chains of [Ag<sub>2</sub>(bpa)<sub>1.5</sub>(sda)<sub>0.5</sub>]<sup>n+</sup> are connected by ligand-unsupported Ag...Ag and Ag...N interactions (the shortest distances of Ag...Ag and Ag...N are 3.20(5) Å and 3.79(4) Å, respectively) into 2D cationic sheets, as shown in Fig. 1b. The deprotonated sda<sup>2-</sup> anions are linked into anionic sheets with the aid of lattice water molecules via intermolecular hydrogen-bonding interactions, as listed in Table 3. The neighboring cationic and anionic sheets are further joined into a 3D sandwich-like framework by weak Ag...O interactions and electrostatic interactions. Viewed from the *a*-axis, it can be seen that the anionic sheet is inserted into the two cationic sheets to form a typical sandwich-like framework (Fig. 1c).

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

[Ag <sub>2</sub> (bpe) <sub>1.5</sub> (sda) <sub>0.5</sub> ](sda) <sub>0.5</sub> ·7H <sub>2</sub> O ( <b>1</b> )							
Bond lengths (Å)							
Ag(1)–O(1)	2.121(2)	Ag(1)–N(1)	2.124(2)	Ag(2)–N(2)	2.119(2)	Ag(2)–N(3)	2.125(2)
Bond angles (°)							
O(1)–Ag(1)–N(1)	169.58(10)	N(2)–Ag(2)–N(3)	176.05(10)				
[Ag <sub>2</sub> (bpe) <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ](dpac) ( <b>2</b> )							
Bond lengths (Å)							
Ag(1)–N(3)	2.183(3)	Ag(1)–N(1)	2.188(3)	Ag(1)–O(6)	2.475(3)	Ag(1)–O(5)	2.586(3)
Ag(2)–N(4)	2.150(3)	Ag(2)–N(2)	2.154(3)	Ag(2)–O(7)	2.516(3)		
Bond angles (°)							
N(3)–Ag(1)–N(1)	152.46(11)	N(3)–Ag(1)–O(6)	102.60(11)	N(1)–Ag(1)–O(6)	96.86(11)		
N(3)–Ag(1)–O(5)	99.92(10)	N(1)–Ag(1)–O(5)	101.85(10)	O(6)–Ag(1)–O(5)	82.31(11)		
N(4)–Ag(2)–N(2)	155.42(12)	N(4)–Ag(2)–O(7)	102.88(10)	N(2)–Ag(2)–O(7)	98.45(10)		
[Ag <sub>2</sub> (bpy) <sub>2</sub> ](ndc)·4H <sub>2</sub> O ( <b>3</b> )							
Bond lengths (Å)							
Ag(1)–N(2)#1	2.157(3)	Ag(1)–N(1)	2.162(2)				
Bond angles (°)							
N(2)#1–Ag(1)–N(1)	176.14(9)						

Symmetry transformations used to generate equivalent atoms: #1 *x*, *y*, *z* – 1



**Table 3** Hydrogen bonds for compound (1)–(3) [Å and °]

D–H	d(D–H)	d(H···A)	<DHA	d(D···A)	A
<b>[Ag<sub>2</sub>(bpe)<sub>1.5</sub>(sda)<sub>0.5</sub>](sda)<sub>0.5</sub>·7H<sub>2</sub>O (1)</b>					
O5–H5C	0.850	1.842	177.55	2.691	O4
O5–H5D	0.850	1.991	177.83	2.841	O1 [–x + 1, –y + 1, –z + 1]
O6–H6C	0.850	1.985	179.13	2.835	O2 [x, y – 1, z]
O6–H6D	0.850	2.046	179.26	2.896	O10 [–x + 1, –y, –z + 1]
O7–H7C	0.850	1.911	168.47	2.749	O3
O7–H7D	0.850	2.020	168.60	2.858	O3 [–x, –y + 1, –z + 1]
O8–H8C	0.850	1.893	174.32	2.740	O5
O8–H8D	0.850	1.954	174.96	2.802	O2 [x, y – 1, z]
O9–H9C	0.850	2.040	167.64	2.876	O7
O9–H9D	0.850	2.013	167.46	2.849	O8 [x, y + 1, z]
O10–H10C	0.850	1.978	175.47	2.826	O6 [x, y, z – 1]
O10–H10D	0.850	1.949	174.96	2.797	O9 [–x + 1, –y + 1, –z + 1]
O11–H11E	0.850	1.989	173.81	2.836	O4 [x + 1, y, z]
O11–H11F	0.850	2.170	174.69	3.017	O5 [–x + 1, –y, –z + 1]
<b>[Ag<sub>2</sub>(bpe)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>](dpadc) (2)</b>					
N5–H5	0.860	1.994	134.01	2.665	O1
N5–H5	0.860	2.156	126.27	2.753	O3
O5–H5D	0.850	1.822	165.94	2.654	O3 [–x + 1, –y, –z + 1]
O5–H5E	0.850	2.013	166.55	2.846	O7 [x + 1, y – 1, z]
O6–H6B	0.850	1.939	153.20	2.725	O4 [x + 1, y, z]
O6–H6C	0.850	1.927	153.28	2.713	O2
O7–H7B	0.850	1.993	166.75	2.827	O5 [–x, –y + 1, –z + 1]
O7–H7C	0.850	1.845	160.40	2.661	O1 [x – 1, y + 1, z]
<b>[Ag<sub>2</sub>(bpy)<sub>2</sub>](ndc)·4H<sub>2</sub>O (3)</b>					
O3–H3C	0.850	2.001	159.31	2.812	O1 [–x + 1, –y + 1, –z + 1]
O3–H3D	0.850	2.394	160.16	3.206	O4 [–x + 1, –y + 1, –z]
O4–H4C	0.850	1.963	168.96	2.802	O1 [x + 1, y, z – 1]
O4–H4D	0.850	1.911	168.72	2.749	O2 [–x + 1, –y + 2, –z + 1]

155.42(12)°, and by an oxygen atom from aqua ligand [Ag–O bond distance being 2.516(6) Å, N–Ag–O being 102.88(10)° and 98.45(10)°] [2–4], as illustrated in Fig. 2a and Table 2. Bpa thus acts as typical 4,4'-bipyridine-like bidentate ligand, linking two Ag atoms via nitrogen atoms from two pyridyl rings to form infinite 1-D chains. The dihedral angles between the two pyridyl rings of the bpa ligand are 7.62(10)° and 12.06(13)°. The dihedral angle between the two benzene rings of the dpadc<sup>2-</sup>, which acts as counter-ion to balance the charge of the cationic [Ag<sub>2</sub>(bpa)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>]<sub>n</sub><sup>2n+</sup> chains, is 44.974(92)°, similar to the previously reported complexes constructed from 4,4'-bipyridine-like ligands and dpadc<sup>2-</sup> anion [3].

In the complex 2, no apparent Ag···Ag, Ag···N or π–π stacking interactions are found, which is different from similar complexes [2–4, 15]. The adjacent chains are interconnected by the dpadc<sup>2-</sup> counterions via electrostatic interactions to build up a 3D sandwich-like network. The

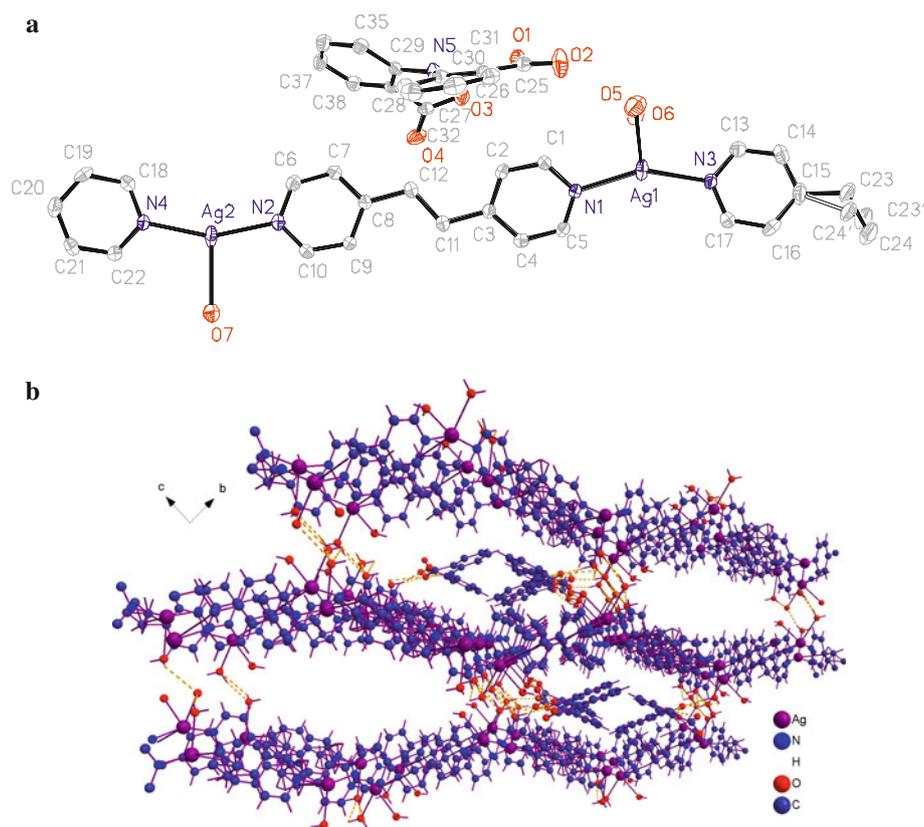
lattice water molecules are held within the framework and stabilized by hydrogen-bonding interactions (Table 3).

#### Crystallographic analysis of complex (3)

As illustrated in Fig. 3a, in the complex [Ag<sub>2</sub>(bpy)<sub>2</sub>](ndc)·4H<sub>2</sub>O (3), the Ag atoms, in a linear coordination geometry, are coordinated by the two nitrogen atoms from two different rigid bpy ligands (Ag–N being 2.157(3) and 2.162(2) Å; N–Ag–N being 176.14(9)°) [2–5]. The oxygen atoms of the aqua ligands also interact with the Ag(1) centers through weak Ag···O interactions [Ag···O = 2.794(3) and 2.885(3) Å]. The Ag···O distances are thus shorter than their van der Waals contact distance of 3.24 Å [12]. The dihedral angles between the pyridyl rings of bpy linked to two silver(I) atoms are 3.43°.

The adjacent cationic [Ag<sub>2</sub>(bpy)<sub>2</sub>]<sub>n</sub><sup>2n+</sup> chains are connected by Ag···N interactions and Ag···Ag interactions (Ag···N

**Fig. 2** **a** Asymmetric unit of  $[\text{Ag}_2(\text{bpe})_2(\text{H}_2\text{O})_3](\text{dpadc})$  (**2**) and coordination environments around the Ag atoms. **b**. Packing view of the sandwich-like framework built from anionic and cationic sheets along the *c*-axis for **2**



contacts and Ag...Ag contacts being 3.38 Å and 3.42 Å, respectively) into 2D cationic sheets (A sheet), as shown in Fig. 3b. The completely deprotonated  $\text{ndc}^{2-}$  anions are joined into anionic sheets (B sheets) with the aid of lattice water molecules via intermolecular hydrogen-bonding interactions, as depicted in Fig. 3c and Table 3. The neighboring cationic and anionic sheets are further joined into a 3D sandwich-like framework with the order of "...ABAB..." by hydrogen bonding and electrostatic interactions (Fig. 3d).

### Fluorescence properties of complexes 1–3

The solid-state emission spectra of complexes **1–3** have been investigated at room temperature (Fig. 4). The broad intense band in the emission spectra was observed at 458 nm, 455 nm, and 459 nm with  $\lambda_{\text{ex}} = 360$  nm for **1–3**, respectively. The above results suggest that the fluorescent emissions arise from bpa and bpy (intense emissions at 439 nm and 451 nm with  $\lambda_{\text{ex}} = 360$  nm for free bpy and free bpa ligands, respectively), which are probably attributed to the intraligand ( $\pi-\pi^*$ ) fluorescence [7, 12, 21–23].

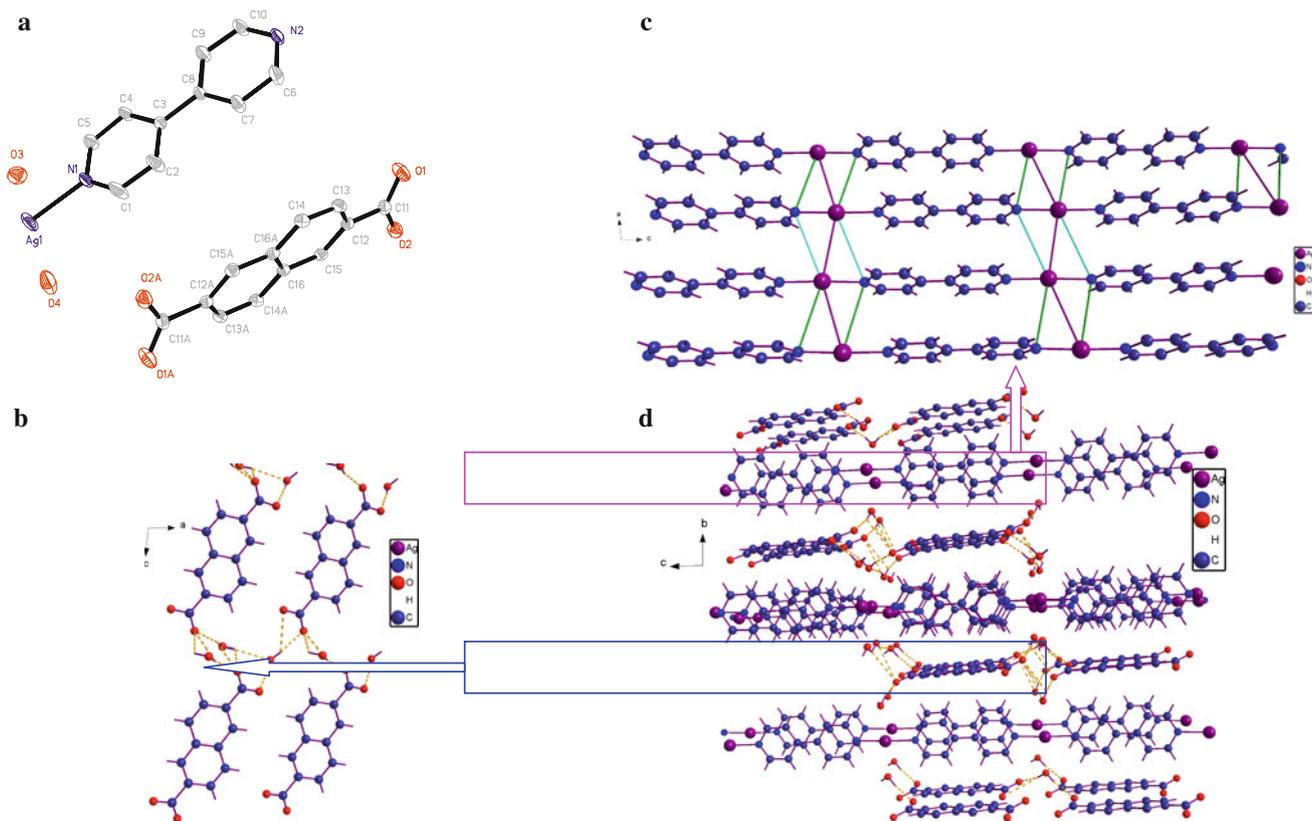
### Thermal properties of complexes 1–3

The thermal properties of the three silver coordination polymers were investigated with thermogravimetric analysis (TGA) under air atmosphere, as shown in Fig. 5.

For complex **1**, the weight loss of 15.0 % from 28 to 160 °C is equivalent to the loss of 7 lattice water molecules per formula unit (calcd: 14.25 %). A total weight loss of 68.0 % is achieved higher than 160 °C, which corresponds to the loss of 0.5 coordinated  $\text{sda}^{2-}$ , 0.5 uncoordinated  $\text{sda}^{2-}$ , and two bpa ligands (calcd. 57.2 %), and the decomposition ends above 600 °C. The final residue,  $\text{Ag}_2\text{O}$ , is 27.5 % (calcd. 26.2 %), in which Ag is 25.6 %, in good agreement with  $[\text{Ag}_2(\text{bpa})_{1.5}(\text{sda})_{0.5}](\text{sda})_{0.5}\cdot 7\text{H}_2\text{O}$  (requires 24.4 %).

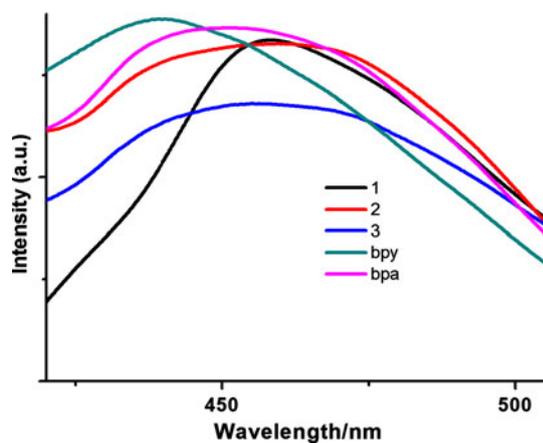
The TGA curve of complex **2** presents two main stages of decomposition. The first step, from 28 to 175 °C, is assigned to loss of 3 coordinated water molecules, with a weight decrease of 6.6 % (calcd. 6.0 %). The second, from 175 to 590 °C, is due to the decomposition of bpa and  $\text{dpadc}^{2-}$  ligands, which shows a weight decrease of 66.2 % (calcd. 69.8 %). The final residue,  $\text{Ag}_2\text{O}$ , is 26.2 % (calcd. 25.9 %), in which Ag is 24.4 %, in good agreement with  $[\text{Ag}_2(\text{bpa})_2(\text{H}_2\text{O})_3](\text{dpadc})$  (requires 24.2 %).

The TGA curve of complex **3** presents two main stages of decomposition. The first step, from 28 to 135 °C, is assigned to loss of 4 lattice water molecules, with a weight decrease of 9.6 % (calcd. 8.8 %). The second, from 135 to 500 °C, is due to the decomposition of bpy and  $\text{ndc}^{2-}$ , which shows a weight decrease of 61.6 % (calcd. 64.6 %). The final residue,  $\text{Ag}_2\text{O}$ , is 28.8 % (calcd. 28.5 %), in which Ag is 26.4 %, in good agreement with  $[\text{Ag}_2(\text{bpy})_2](\text{ndc})\cdot 4\text{H}_2\text{O}$  (requires 26.0 %).



**Fig. 3** **a** Asymmetric unit of  $[\text{Ag}_2(\text{bpy})_2](\text{ndc})\cdot 4\text{H}_2\text{O}$  (**3**) and coordination environments around the Ag atoms. Lattice water molecules and corresponding H atoms are omitted for clarity. **b** The 2D anionic layer constructed from  $\text{ndc}^{2-}$  and lattice water molecules via

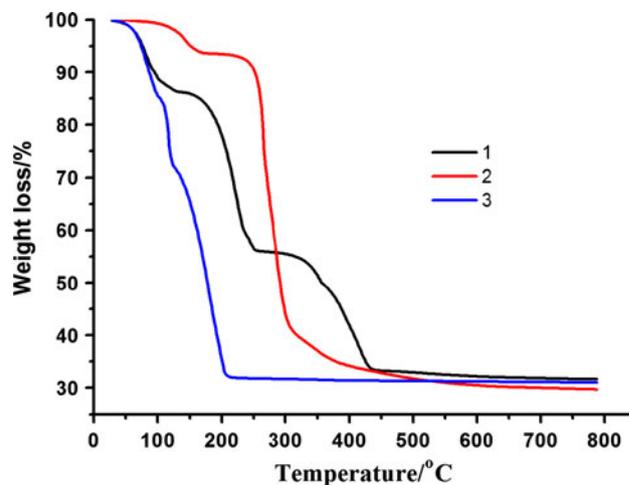
hydrogen-bonding interactions. **c** The cationic 2D sheet built up of  $[\text{Ag}_2(\text{bpy})_2]_n^{2n+}$  chains via  $\text{Ag}\cdots\text{N}$  and  $\text{Ag}\cdots\text{Ag}$  interactions. **d** Packing view of the sandwich-like framework built from anionic and cationic sheets along the  $a$ -axis for complex **3**



**Fig. 4** Luminescent emission spectra of complexes **1–3**, free bpy, and bpa ligands in the solid state at room temperature

## Conclusions

The three silver(I) complexes reported here all contain sandwich-like frameworks, showing that the different anions play an important role in constructing the crystal structures. In these complexes, the flexible bpa and rigid



**Fig. 5** TGA curve of complexes **1–3**

bpy act as typical bidentate ligands to join the silver(I) centers into 1D cationic chains, balanced by the different anions, like completely deprotonated  $\text{sda}^{2-}$ ,  $\text{dpadc}^{2-}$ , and  $\text{ndc}^{2-}$ . The coordination numbers of silver range from 2 to 4, resulting in linear (complexes **1** and **3**), trigonal (complex **2**), and tetrahedral (complex **2**)

geometries. Except for  $\text{sda}^{2-}$  acting as coordinated counterion to link the silver (I), the other organic carboxylate anions only act as counter-ions to balance the charge of the cationic chains. In complexes **1** and **3**, the ligand-unsupported  $\text{Ag}\cdots\text{Ag}$  and  $\text{Ag}\cdots\text{N}$  interactions facilitate the formation of 3D sandwich-like structures, which are further supported by rich hydrogen-bonding interactions, while in complex **2**, there are no apparent  $\text{Ag}\cdots\text{N}$  and  $\text{Ag}\cdots\text{Ag}$  contacts, but hydrogen-bonding interactions contribute to build up the 3D crystal structure. Considering the similar silver-based complexes [2–5] and complexes **1–3** in this paper, we can see that the coordination modes of the ligands and the supramolecular interactions of the anions both help to determine the crystal structures of such complexes. Generally, the counter-ions can be present in coordinated, uncoordinated, or mixed modes. Coordinated anions normally increase the dimensionality of the crystal structures, while uncoordinated anions may help to extend the crystal structures via hydrogen bonding,  $\pi$ – $\pi$  stacking, and/or ligand-unsupported  $\text{Ag}\cdots\text{Ag}$  and  $\text{Ag}\cdots\text{N}$  interactions. Luminescent measurements reveal that complexes **1–3** are potential candidates for photoactive materials owing to their luminescent emissions. The thermogravimetric analyses show that the frameworks of all three complexes are stable under 200 °C, due to the discrete carboxylate ions.

### Supplementary material

CCDC 915,783, 915,784, and 915,786 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](http://www.ccdc.cam.ac.uk/data_request/cif).

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