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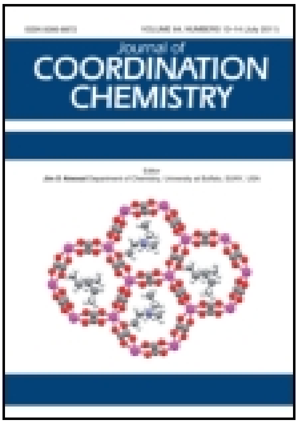

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Syntheses, structures, and photo-luminescence of three silver complexes with N-heterocyclic multicarboxylic acids and 4,4′-bipyridine

Jing Qu [a] , Yong-Ling Yi [a] , Yao-Min Hu [a] , Wei-Tao Chen [a] , Hong-Ling Gao [a] , Jian-Zhong Cui [a] & Bin Zhai [b]

[a] Department of Chemistry , Tianjin University , Tianjin 300072 , P.R. China

[b] College of Chemistry & Chemical Engineering, Shangqiu Normal University , Henan 476000 , P.R. China

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Syntheses, structures, and photo-luminescence of three silver complexes with N-heterocyclic multicarboxylic acids and 4,4′-bipyridine

JING QU†, YONG-LING YI†, YAO-MIN HU†, WEI-TAO CHEN†,
HONG-LING GAO†, JIAN-ZHONG CUI*† and BIN ZHAI‡

†Department of Chemistry, Tianjin University, Tianjin 300072, P.R. China
‡College of Chemistry & Chemical Engineering, Shangqiu Normal University,
Henan 476000, P.R. China

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Three coordination polymers, $[Ag_4(bpy)_3(pztc)]_n$ (**1**), $\{[Ag_6(bpy)_2(pztc)(CN)_2]\cdot 2.6H_2O\}_n$ (**2**), and $\{[Ag_2(H_2pdtc)(bpy)_2]\cdot 3H_2O\}_n$ (**3**) (H_4pztc = pyrazine-2,3,5,6-tetracarboxylic acid, H_4pdtc = pyridine-2,3,5,6-tetracarboxylic acid, bpy = 4,4′-bipyridine), have been synthesized and characterized by elemental analysis, IR spectra, thermogravimetric analysis, UV spectra, fluorescent spectra, and single-crystal X-ray diffraction. Complex **1** displays a 3-D network with infinite channels of about $6.4 \times 3.1\ Å^2$ along the *a*-axis. The structure of **1** can be simplified as a 3,4,4-connected framework. Complex **2** displays a 3-D network and can be simplified as a 6,6-connected *pcu* framework. Complex **3** shows a 1-D chain structure and the chains form a 2-D layer structure by hydrogen bonds. Complexes **1**–**3** emit intense fluorescence at around 500 nm on excitation at 340 nm, 320 nm, and 340 nm, respectively.

Keywords: Silver(I) complex; Pyrazine-2,3,5,6-tetracarboxylic acid; Pyridine-2,3,5,6-tetracarboxylic acid; Fluorescent properties

1. Introduction

Synthesis of transition metal coordination frameworks have interest owing to potential applications in catalysis, gas storage, magnetism, optics, etc. [1–5]. Well-designed bridging ligands in combination with metal centers of diverse geometries has led to construction of numerous coordination frameworks with ladders, honeycombs, brick walls, helices, and networks [6–8]. Silver(I) principally exhibits linear, trigonal, and tetrahedral coordination and has high affinity for hard donors (nitrogen or oxygen) and soft donor (sulfur), being a favorable building block for coordination frameworks [9–12]. Short Ag···Ag contacts and ligand-unsupported interaction are two of the most important factors contributing to fascinating structures and photo-luminescent properties of these kinds of complexes [10–13].

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*Corresponding author. Email: cuijianzhong@tju.edu.cn

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There are a few complexes containing silver(I) and bridging N- and O-donors [10, 12, 14–16]. Since silver compounds are unstable, the synthesis conditions are demanding. There is no study of silver(I) complexes with pyrazine-2,3,5,6-tetracarboxylic acid or pyridine-2,3,5,6-tetracarboxylic acid and 4,4′-bipyridine. Pyrazine-2,3,5,6-tetracarboxylic acid and pyridine-2,3,5,6-tetracarboxylic acid containing O- and N-donors have rich coordination modes and function as hydrogen-bond accepters as well as hydrogen-bond donors [17–20]. Ligands, such as 4,4′-bipyridine, often have a significant effect on metal N-containing polycarboxylate complexes [21–23]. We report herein the syntheses and structures of three silver complexes, $[Ag_4(bpy)_3(pztc)]_n$ (**1**), $\{[Ag_6(bpy)_2(pztc)(CN)_2] \cdot 2.6H_2O\}_n$ (**2**), and $\{[Ag_2(H_2pdtc)(bpy)_2] \cdot 3H_2O\}_n$ (**3**), where H_4pztc = pyrazine-2,3,5,6-tetracarboxylic acid, H_4pdtc = pyridine-2,3,5,6-tetracarboxylic acid, and bpy = 4,4′-bipyridine.

2. Experimental

2.1. *Materials and methods*

H_4pztc was synthesized by Wolff's synthesis [24] and H_4pdtc was synthesized by our reported method [25]. Other chemicals purchased were of reagent grade and used without purification. Elemental analysis (C, H, and N) was performed on a Perkin-Elmer 240 CHN elemental analyzer. IR spectra were recorded from 400 to 4000 cm^{-1} with a Bruker TENOR 27 spectrophotometer using KBr pellets. Thermogravimetric analyses (TGA) were performed on a NETZSCH TG 209 instrument with a heating rate of $10°C\,min^{-1}$. Ultraviolet spectra were measured by a Hewlett Packard 8453 ultraviolet spectrometer. Fluorescence spectra were measured on an F-4500 fluorescence spectrophotometer with a xenon arc lamp as the light source.

2.2. *Syntheses*

2.2.1. Synthesis of $[Ag_4(bpy)_3(pztc)]_n$ (1). An ethanolic solution of bpy (0.0156 g, 0.1 mmol), an aqueous solution of H_4pztc (0.0128 g, 0.05 mmol), and acetonitrile were added to aqueous solution of $AgNO_3$ (0.0340 g, 0.2 mmol). The mixture was adjusted to pH = 5–6 and stirred for 2 h. After filtering the solution, the solvent was allowed to evaporate slowly at room temperature, whereupon (after a week) 0.0184 g (0.016 mmol) colorless rectangular crystals of **1** were obtained. All the processes should avoid exposure to light. Yield 32% based on Ag. Anal. Calcd for $C_{38}H_{24}Ag_4N_8O_8$ (fw = 1152.14) (%): C, 39.61; H, 2.10; N, 9.73. Found (%): C, 39.62; H, 2.09; N, 9.75. IR (KBr pellet, cm^{-1}): 1603vs, 1438m, 1407m, 1306m, 806m, 616w, 491w.

2.2.2. Synthesis of $\{[Ag_6(bpy)_2(pztc)(CN)_2] \cdot 2.6H_2O\}_n$ (2). An ethanolic solution of bpy (0.0156 g, 0.1 mmol), an aqueous solution of H_4pztc (0.0128 g, 0.05 mmol), and acetonitrile were added to aqueous solution of $AgNO_3$ (0.0170 g, 0.1 mmol). The mixture was adjusted to pH = 5–6 and stirred for 2 h. After filtering the solution, the solvent was allowed to evaporate slowly at room temperature, whereupon (after a week) 0.0076 g (0.006 mmol) colorless parallelogram crystals of **2** were obtained. All the processes should avoid exposure to light. Yield 35% based on Ag. Anal. Calcd for $C_{30}H_{21.20}Ag_6N_8O_{10.60}$ (fw = 1310.57) (%): C, 27.49; H, 1.63; N, 8.55. Found (%): C, 27.48; H, 1.61; N, 8.58. IR (KBr pellet, cm^{-1}): 3420s, 2140w, 1620vs, 1439m, 1415m, 1304m, 808m, 636w, 576w.

2.2.3. $\{[Ag_2(H_2pdtc)(bpy)_2] \cdot 3H_2O\}_n$ (3). An ethanolic solution of bpy (0.0156 g, 0.1 mmol), an aqueous solution of H_4pdtc (0.0128 g, 0.05 mmol), and acetonitrile were added to aqueous solution of $AgNO_3$ (0.0255 g, 0.15 mmol) and stirred for 1 h. After filtering the solution, the solvent was allowed to evaporate slowly at room temperature, whereupon (after five days) 0.019 g (0.023 mmol) colorless rectangular crystals of **3** were obtained. All the processes should avoid exposure to light. Yield 31% based on Ag. Anal. Calcd for $C_{29}H_{25}Ag_2N_5O_{11}$ (fw = 835.28) (%): C, 41.70; H, 3.02; N, 8.38. Found (%): C, 41.72; H, 3.01; N, 8.35. IR (KBr pellet, cm^{-1}): 3440s, 1709m, 1603vs, 1416m, 1324m, 812m, 636w, 597w.

2.3. *X-ray crystallography*

Diffraction data for **1**–**3** were collected on a computer-controlled Rigaku Saturn diffractometer. The detector was equipped with graphite-monochromated Mo-Kα radiation (0.71073 Å) by using the ω-scan technique. The structure was solved by direct methods and refined with full-matrix least-squares on F^2 using SHELXS-97 [26] and SHELXL-97 [27]. All non-hydrogen atoms were refined anisotropically. The organic and water hydrogen atoms in **3** were assigned with common isotropic displacement factors and included in the final refinement by geometrical restraints, while in **2**, not all hydrogen atoms of water were located because of disorder. Crystallographic data for **1**–**3** are summarized in table 1. Selected bond distances and angles for the complexes are given in tables 2–4, respectively.

3. Results and discussion

3.1. *Crystal structures of 1–3*

The crystal structure of **1** consists of a centrosymmetric polynuclear $[Ag_4(bpy)_3(pztc)]$ structural unit (figure 1a). There are two crystallographically independent Ag(I) ions (Ag1 and Ag2) in different coordination environments. Ag1 is three-coordinate in a distorted Y-shaped geometry, coordinated by O2 and N1 from a chelating $pztc^{4-}$ and N3B from a bpy. The coordination geometry around Ag2 is a distorted Y-shaped too, coordinated by O1 from $pztc^{4-}$ and N2 and N4 from different bpy molecules. Adjacent Ag1 and Ag2 are alternately connected by $pztc^{4-}$ and bpy to generate an infinite 1-D stair-like chain (figure 1b). Parallel bpy molecules extend the 1-D chain into a 2-D grid structure (figure 1c). The 2-D layers are further assembled *via* Ag···Ag ligand-unsupported interaction to form a 3-D network (figure 1d with distance between Ag1 and Ag2 of 3.1685(11) Å). The structure shows infinite channels of 6.4×3.1 Å^2 along the *a*-axis (figure 1e), and the effective volume of the channels is 137.8 Å^3. Ag1, Ag2, and $pztc^{4-}$ can be considered as 3-connected, 4-connected and 4-connected nodes,

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Table 1. Crystal data and structure refinement details for **1–3**.

Complex	**1**	**2**	**3**
Empirical formula	$C_{19}H_{12}Ag_2N_4O_4$	$C_{30}H_{21.20}Ag_6N_8O_{10.60}$	$C_{29}H_{25}Ag_2N_5O_{11}$
Formula weight	576.07	1310.57	835.28
Temperature (K)	113(2)	113(2)	113(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions (Å, °)			
a	7.0100(14)	8.083(8)	9.4971(18)
b	9.1462(18)	8.312(8)	10.7428(18)
c	15.496(3)	13.645(15)	15.528(3)
α	97.96(3)	75.38(6)	78.562(7)
β	98.39(3)	74.92(5)	87.414(8)
γ	92.01(3)	70.29(5)	66.025(10)
Volume (Å^3), Z	971.8(3), 2	819.5(15), 1	1417.7(5), 2
Calculated density (Mg m^{-3})	1.969	2.655	1.957
Absorption coefficient (mm^{-1})	2.049	3.590	1.457
$F(000)$	560	624	832
Crystal size (mm^3)	$0.18 \times 0.06 \times 0.04$	$0.20 \times 0.18 \times 0.10$	$0.20 \times 0.20 \times 0.12$
θ range for data collection (°)	2.69–25.02	2.65–27.81	1.34–25.01
Limiting indices	$-8 \le h \le 8$; $-9 \le k \le 10$; $-18 \le l \le 18$	$-10 \le h \le 10$; $-10 \le k \le 10$; $-17 \le l \le 17$	$-11 \le h \le 11$; $-12 \le k \le 12$; $-18 \le l \le 18$
Reflections collected	7190	8161	14,895
Independent reflection	3391 [R(int) = 0.0259]	3801 [R(int) = 0.0338]	4995 [R(int) = 0.0458]
Max. and min. transmission	0.9225 and 0.7093	0.7154 and 0.5338	0.7594 and 0.7594
Data/restraints/parameters	3391/0/263	3801/18/262	4995/9/432
Goodness-of-fit on F^2	1.045	1.003	1.044
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0259$, $wR_2 = 0.0761$	$R_1 = 0.0239$, $wR_2 = 0.0542$	$R_1 = 0.0407$, $wR_2 = 0.1008$
R indices (all data)	$R_1 = 0.0307$, $wR_2 = 0.0777$	$R_1 = 0.0289$, $wR_2 = 0.0550$	$R_1 = 0.0451$, $wR_2 = 0.1045$
Largest difference peak and hole (e Å^{-3})	0.657 and −0.404	0.567 and −1.155	1.076 and −2.347

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

Ag(1)–N(3)^{i}	2.203(3)	Ag(1)–N(1)	2.363(3)
Ag(1)–O(2)	2.393(2)	Ag(1)–Ag(2)^{ii}	3.1682(10)
Ag(2)–N(4)	2.199(3)	Ag(2)–N(2)	2.219(3)
Ag(2)–O(1)	2.446(3)		
N(3)^{i}–Ag(1)–N(1)	133.16(10)	N(3)^{i}–Ag(1)–O(2)	144.60(10)
N(1)–Ag(1)–O(2)	71.30(9)	N(4)–Ag(2)–N(2)	145.25(11)
N(4)–Ag(2)–O(1)	125.25(10)	N(2)–Ag(2)–O(1)	89.32(10)

Symmetry transformations used to generate equivalent atoms: ^{i} $x, y, z-1$; ^{ii} $-x+1, -y+1, -z+1$.

respectively, and bpy molecules are simplified as lines. Complex **1** can be described as a 3,4,4-connected framework with Schläfli symbol $\{4.6^2.8^3\}_2\{4.6^2\}_2\{6^4.10^2\}$, as shown in figure 1(f).

The molecular structure and coordination environments of metal centers in **2** are shown in figure 2(a). The asymmetric unit of **2** consists of three silver ions, half pztc^{4-}, one bpy molecule, one cyanide, and 1.3 lattice water molecules. Ag1 is four-coordinate in a distorted tetrahedral geometry. The ion is coordinated by O2A, O4B, and N1 from

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Table 3. Selected bond lengths (Å) and angles (°) for **2**.

Ag(1)–O(2)^{i}	2.270(3)	Ag(1)–N(1)	2.362(3)
Ag(1)–O(4)^{ii}	2.377(3)	Ag(1)–N(4′)	2.612(4)
Ag(1)–Ag(2)	3.115(3)	Ag(2)–N(4′)	2.077(4)
Ag(2)–N(2)	2.140(3)	Ag(2)–Ag(2)^{iii}	3.230(3)
Ag(3)–N(4)	2.078(3)	Ag(3)–N(3)^{iv}	2.146(3)
Ag(3)–O(1)^{v}	2.612(4)		
O(2)^{i}–Ag(1)–N(1)	133.78(9)	O(2)^{i}–Ag(1)–O(4)^{ii}	144.23(9)
N(1)–Ag(1)–O(4)^{ii}	70.01(10)	O(2)^{i}–Ag(1)–N(4′)	91.90(10)
N(1)–Ag(1)–N(4′)	121.85(11)	O(4)^{ii}–Ag(1)–N(4′)	93.65(11)
N(2)–Ag(2)–N(4′)	174.54(11)	N(4)–Ag(3)–N(3)^{iv}	166.70(12)
N(4)–Ag(3)–O(1)^{v}	103.82(12)	N(3)^{iv}–Ag(3)–O(1)^{v}	89.45(11)

Symmetry transformations used to generate equivalent atoms: ^{i} $-x+1, -y+1, -z+1$; ^{ii} $-x, -y+1, -z+1$; ^{iii} $-x+1, -y+2, -z+1$; ^{iv} $x-1, y+1, z-1$; ^{v} $-x, -y+2, -z+1$.

Table 4. Selected bond lengths (Å) and angles (°) for **3**.

Ag(1)–N(4)	2.136(3)	Ag(1)–N(1)	2.143(3)
Ag(1)–O(6)	2.711(3)	Ag(2)–N(3)^{i}	2.128(3)
Ag(2)–N(2)	2.133(3)	Ag(2)–Ag(2)^{ii}	3.2196(9)
N(4)–Ag(1)–N(1)	167.83(13)	N(1)–Ag(1)–O(6)	82.16(4)
N(4)–Ag(1)–O(6)	109.65(8)	N(3)^{i}–Ag(2)–N(2)	171.69(14)

Symmetry transformations used to generate equivalent atoms: ^{i} $x+2, y-1, z+1$; ^{ii} $-x+3, -y-1, -z+2$.

three different pztc^{4-} and one CN^{-} which likely originates from decomposition of acetonitrile. Ag2 exhibits a slightly distorted linear geometry, coordinated by N2 from bpy and CN′. The coordination geometry around Ag3 is a distorted T-shape, coordinated by N3D from bpy, O1F from pztc^{4-}, and CN^{-}. The Ag3···OF distance is 2.612 Å, beyond the usual range of 2.32–2.52 Å for silver(I) carboxylate complexes, yet are shorter than the sum of van der Waals radii (3.24 Å) of silver(I) and oxygen, suggesting the existence of significant Ag···O interactions [28, 29]. All Ag ions are connected by pztc^{4-} and Ag···Ag interactions to construct a 2-D layer structure (figure 2b). The Ag···Ag distances are 3.115(3) Å (Ag(1)–Ag(2)) and 3.230(3) Å (Ag(2)–Ag(2)^{iii}), shown in table 3. The former Ag···Ag is a ligand supported interaction while the latter Ag···Ag is a ligand-unsupported interaction. The 2-D layer structures are linked by parallel bpy molecules to form a 3-D network (figure 2c). The four Ag units constructed by Ag(1)–Ag(2) and Ag(2)–Ag(2)^{iii} bonds and pztc^{4-} ligands are considered as 6-connected nodes, while bpy and Ag3 ions are simplified as lines; **2** can be simplified as a 6,6-connected *pcu* framework with Schlafli symbol 4^{12}.6^{3}, as shown in figure 2(d).

The asymmetric unit of **3** consists of two Ag(I) ions, one H$_2$pdtc^{2-}, two bpy molecules, and three lattice water molecules. The molecular structure and coordination environments of metal centers in **3** are shown in figure 3(a). Ag1 adopts a distorted T-shaped geometry, coordinated by N1 and N4 from different bpy molecules and O6 from a weakly coordinated H$_2$pdtc^{2-}. Ag2 adopts a distorted linear geometry, coordinated by N2 and N3A from two bpy molecules. The weakly coordinated H$_2$pdtc^{2-} connect Ag ions using its 3-position carboxyl with Ag–O distances of 2.711 Å, similar with

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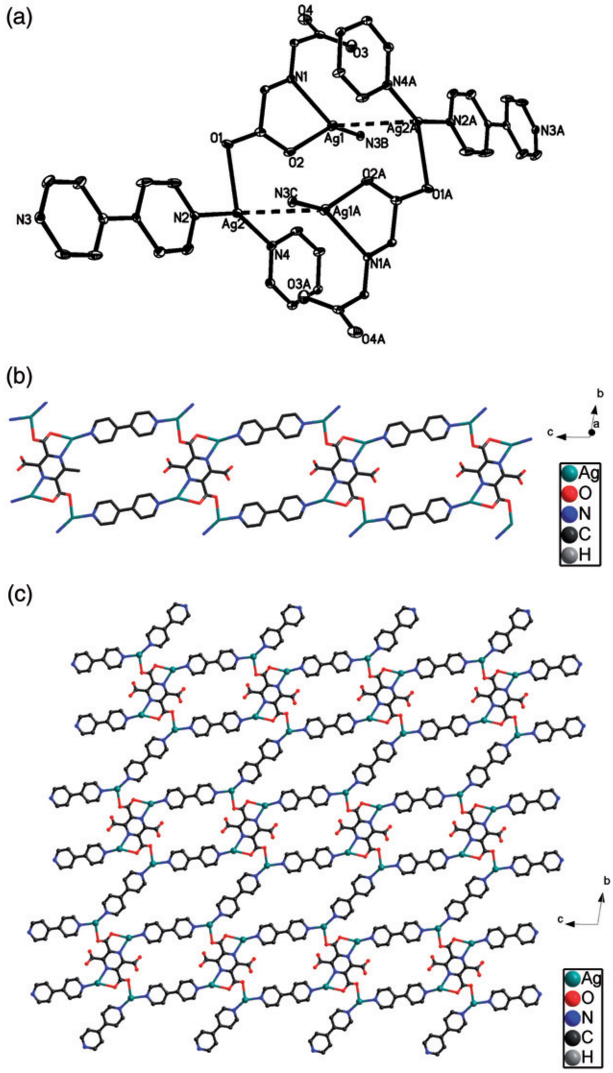

Figure 1. (a) ORTEP of **1** showing the molecular structure with 30% probability thermal ellipsoids. Symmetry transformations used to generate equivalent atoms: (A): $-x+1$, $-y+1$, $-z+1$; (B): x, y, $z-1$; (C): $-x+1$, $-y+1$, $-z+2$. (b) The infinite 1-D stair-like chain of **1**. (c) The 2-D grid structure of **1** connected by parallel bpy molecules. (d) The 3-D network of **1** *via* Ag···Ag ligand-unsupported interaction (viewed along the *c*-axis). (e) The 3-D network of **1** viewed along the *a*-axis. (f) The 3,4,4-connected framework of **1**. Hydrogen atoms are not shown for clarity.

Ag3···O1F in **2**. The Ag–N, Ag···O as well as ligand-unsupported Ag···Ag bonds construct an infinite 1-D chain (figure 3b, Ag2–Ag2A = 3.2196(9) Å). As shown in figure 3(c), H_2pdtc^{2-} are connected by O4–H4a···O8A (H4a···O8A = 1.64(3) Å, ∠OHO = 161(9)°) hydrogen bonds to construct a 1-D hydrogen-bonding chain. The 1-D hydrogen-bonding chain and N–Ag–N interactions further construct a 2-D layer (figure 3d).

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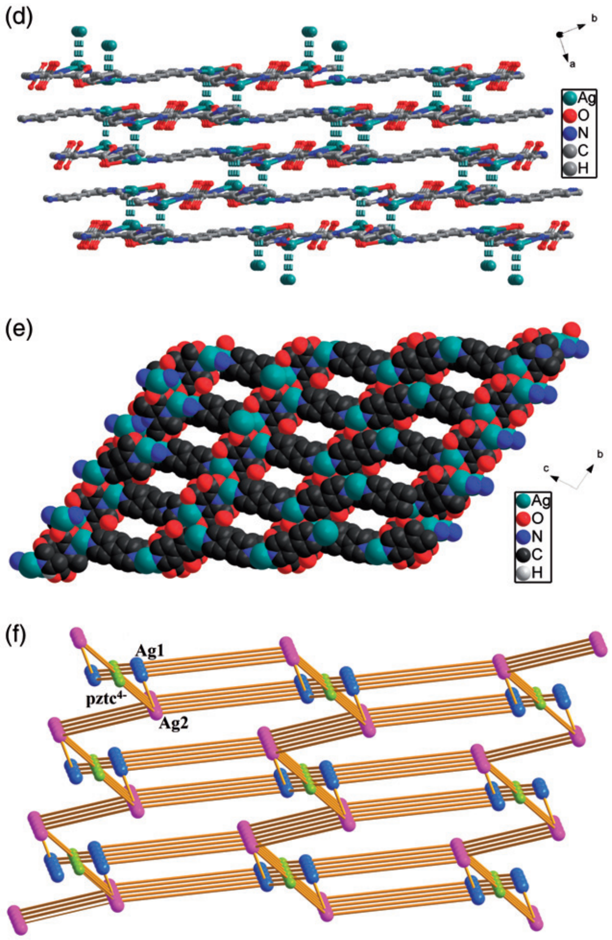

Figure 1. Continued.

3.2. *IR spectra*

The IR spectra of **1** and **2** are similar; strong absorptions at 1603, 1438, and 1407 cm^{-1} for **1**, 1620, 1439, and 1415 cm^{-1} for **2** are attributed to asymmetric and symmetric stretching vibrations of coordinated carboxylates. The broad absorption of **2** at 3420 cm^{-1} is assigned to $\nu_{\text{O–H}}$ of lattice water molecules and the weak absorption of **2** at 2140 cm^{-1} is assigned to $\nu_{\text{C≡N}}$. Characteristic bands of bpy in **1** and **2** are at 806 cm^{-1} and 808 cm^{-1}, respectively. The IR spectrum of **3** shows an absorption at 1709 cm^{-1}, indicating incomplete deprotonation of H_4pdtc. The asymmetric and symmetric stretching vibrations of carboxylate are at 1603 and 1416 cm^{-1}, lattice water bands appear near 3440 cm^{-1} and may be attributed to asymmetric and symmetric OH stretches; characteristic band of bpy is at 812 cm^{-1}. IR spectra of **1**–**3** agree with crystal structures and charge balance considerations.

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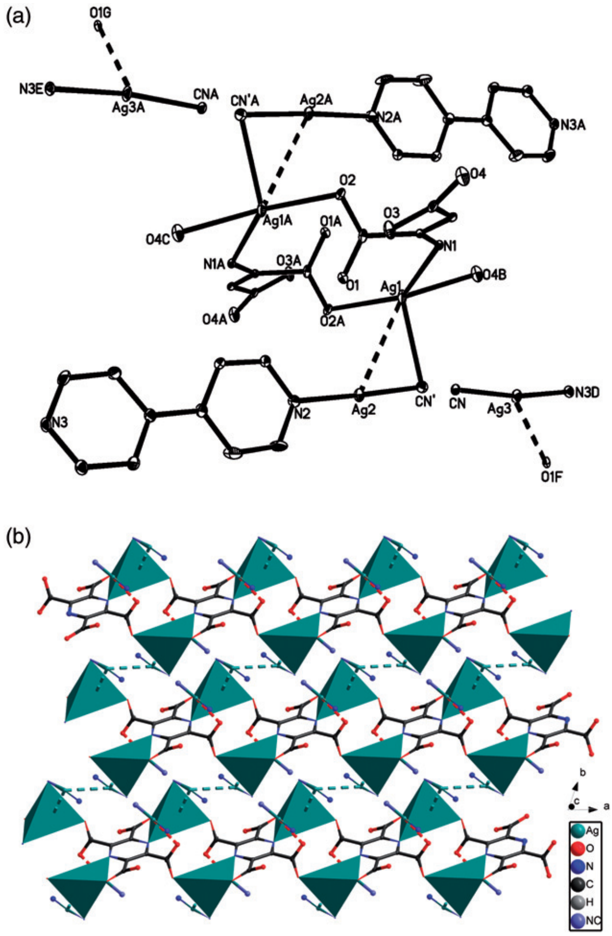

Figure 2. (a) ORTEP of **2** showing the molecular structure with 30% probability thermal ellipsoids. Symmetry transformations used to generate equivalent atoms: (A): $-x+1$, $-y+1$, $-z+1$; (B): $-x$, $-y+1$, $-z+1$; (C): $x+1$, y, z; (D): $x-1$, $y+1$, $z-1$; (E): $-x+2$, $-y$, $-z+2$; (F): $-x$, $-y+2$, $-z+1$; (G): $x+1$, $y-1$, z. (b) The 2-D layer structure of **2** connected by pztc^{4-} and Ag···Ag interactions. (c) The 3-D network structure of **2** connected by parallel bpy. (d) The 6,6-connected *pcu* framework of **2**. Lattice waters and hydrogen atoms are not shown for clarity.

3.3. *Thermogravimetric analyses*

TGA were carried out for **1**–**3** from 30°C to 800°C under N_2 with heating rate of 10°C min^{-1}. The TGA curve of **1** shows degradation of bpy and pztc^{4-} occur from 145°C to 600°C. The remaining mass of 40.80% is presumably Ag_2O, in agreement with the calculated value of 40.23%. All water molecules in **2** are uncoordinated and easily lost; partial water loss of **2** takes place when placed in air. TGA shows weight loss of 1.8% within 82°C corresponding to complete loss of residual water. From 80°C to 233°C, there is almost no mass change, above 233°C, the complex continued to decompose. The mass loss of **3** from 25°C to 187°C is 5.6% from loss of lattice water (calculated: 5.7%). When the temperature was further increased, **3** began to decompose.

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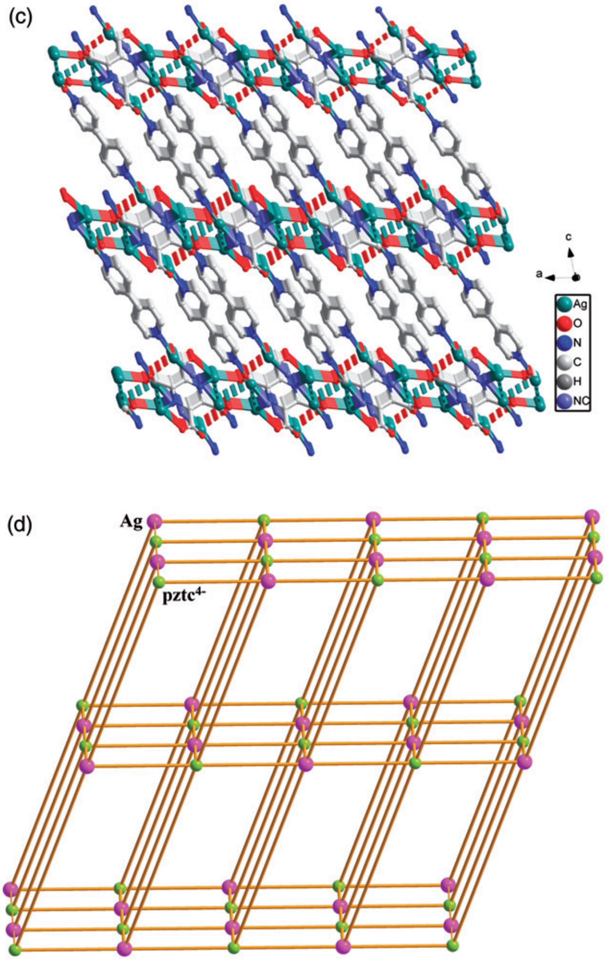

Figure 2. Continued.

3.4. *The UV spectra and fluorescent properties*

UV-Vis spectra of **1**–**3** similarly display three absorptions at 203, 238, and 289 nm; 202, 237, and 288 nm; 203, 236, and 279 nm, respectively, indicating π–π* and *n*–π* electronic transitions originating from pyrazinyl and pyridinyl groups.

Fluorescent emission spectra of **1**–**3** (figure 4) in the solid state at room temperature display blue/green emissions at 441, 494, and 531 nm for **1** ($\lambda_{ex} = 340$ nm), 506 nm for **2** ($\lambda_{ex} = 320$ nm) and 429, 474, and 549 nm for **3** ($\lambda_{ex} = 340$ nm). The maximum emissions occur at 494 nm and 531 nm for **1**, 506 nm for **2**, and 549 nm for **3**, similar to those of the corresponding ligands. Since Ag^+ is difficult to oxidize or reduce due to d^{10} configuration, emissions of **1**–**3** are neither ligand-to-metal charge transfer bands nor metal-to-ligand charge transfer bands, but may be attributed to fluorescent emissions from an intraligand excited state [30]. Enhancement of luminescence is attributed to ligands coordinated to the metal center, effectively increasing the rigidity of the ligands reducing the loss of energy by radiationless decay.

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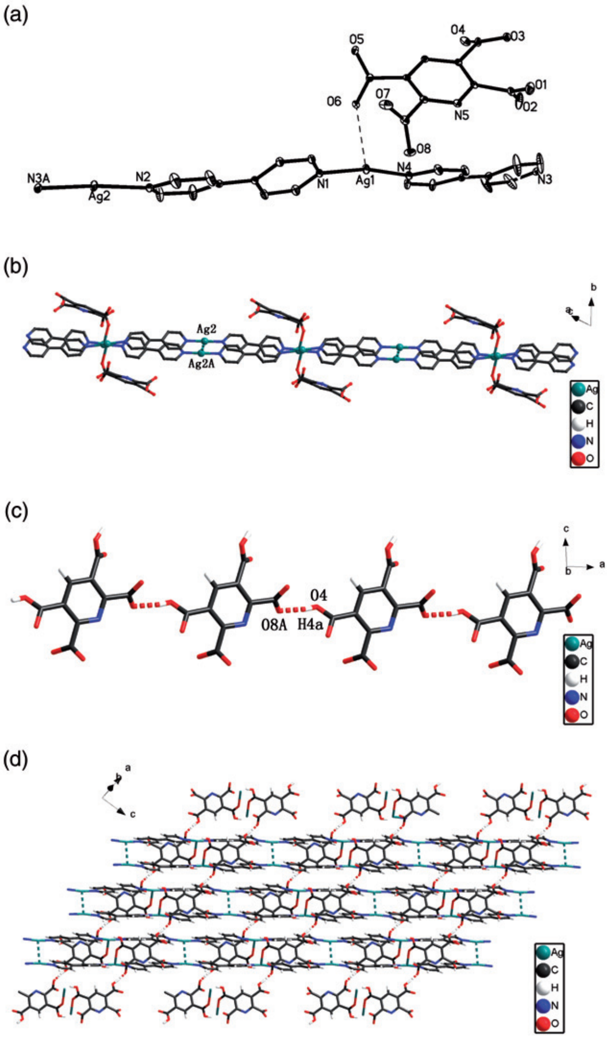

Figure 3. (a) ORTEP of **3** showing the molecular structure with 30% probability thermal ellipsoids. Lattice water molecules and hydrogen atoms are not shown for clarity. (b) The infinite 1-D chain of **3**. (c) The infinite 1-D hydrogen-bonding chain of **3**. (d) The 2-D layer structure of **3** connected by H_2pdtc^{2-}, bpy, and hydrogen-bonding. Symmetry transformations used to generate equivalent atoms (a), (A): $x+2$, $y-1$, $z+1$; (b), A: $-x+3$, $-y-1$, $-z+2$; (c), A: $x-1$, y, z.

4. Conclusion

We have synthesized three silver(I) coordination polymers constructed from H_4pztc or H_4pdtc and bridging bpy at room temperature avoiding light. H_4pztc possesses different coordination modes in **1** and **2** and the auxiliary bpy exerts significant influence on the final structures. The $pztc^{4-}$ and bpy in **1** are alternately coordinated to silver forming 2-D grid layers. Ag···Ag ligand-unsupported interactions between these layers form 3-D networks, which show channels of $6.4 \times 3.1\,Å^2$ along the *a*-axis. All Ag ions in **2** are connected by $pztc^{4-}$ and different Ag···Ag interactions to construct 2-D layers.

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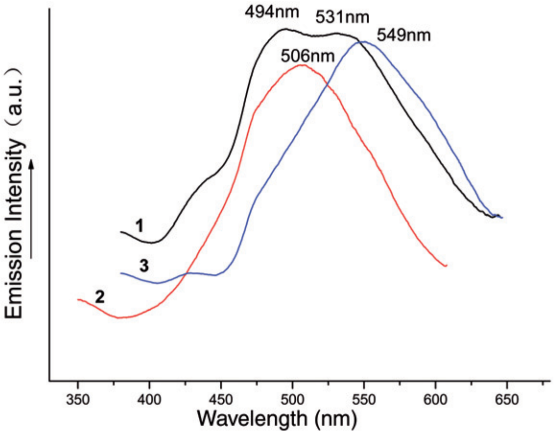

Figure 4. The luminescence spectra of **1–3** in the solid state at room temperature.

Parallel bpy molecules further link these layers to construct 3-D networks. Complex **1** is simplified as a 3,4,4-connected framework with *Schläfli* symbol $\{4\cdot6^2\cdot8^3\}_2\{4\cdot6^2\}_2\{6^4\cdot10^2\}$ and **2** can be simplified as a 6,6-connected *pcu* framework with *Schläfli* symbol $4^{12}\cdot6^3$. The structural characteristics of **1** and **2** are unusual among silver coordination polymers constructed from multicarboxylic acid ligands [22, 31–34] or N-heterocyclic ligands [35–39]. Complexes **1**–**3** show intense emission bonds, which render them potentially useful as fluorescent materials. These syntheses provide new opportunities for preparing other 3-D self-assembled silver coordination polymers.

Supplementary material

CCDC-872846 for **1**, CCDC-872847 for **2**, and CCDC-872848 for **3** contain the supplementary crystallographic data for this article. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: (+44) 1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk).

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