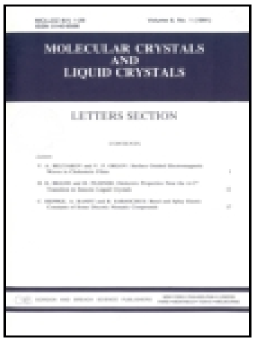

MOLECULAR CRYSTALS AND LIQUID CRYSTALS

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Ag(I) and Cu(II) Coordination Polymers of Pyridylmethyl-Benzimidazole Ligand: Syntheses, Crystal Structure, and Influence of Metal Ion

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*In our efforts to investigate the relationships between the metal ions and the structures of their complexes based on N-donor ligand, 1-(4-pyridylmethyl)-1*H*-benzimidazole (**L**), and their complexes* $[Ag(\mathbf{L})(ClO_4)]_n$ *(**1**),*$\{[Cu(\mathbf{L})_2(ClO_4)_2](H_2O)_2\}_n$ *(**2**) were synthesized and structurally characterized by elemental analyses, IR spectra and single-crystal X-ray diffraction analysis. Structural analyses show that **1** possess one-dimensional (1D) double helix chain structure, which further forms two-dimensional supramolecular framework connected by Ag···Ag and Ag···O weak interactions. When the metal ion was changed to Cu(II), **2** was obtained, which shows a two-fold interpenetrating three-dimensional diamond network. The results show that the metal ions and weak interactions play important roles in the construction of such coordination architectures. X-ray powder diffractions show that the bulk synthesized materials and the crystals used for diffraction are homogeneous. Meanwhile, the photoluminescent property of the complex **1** is investigated in the solid state at room temperature.*

Keywords 1-(4-pyridylmethyl)-1*H*-benzimidazole; crystal structure; metal ion effect; photoluminescent properties

Introduction

Coordination polymers have received considerable attention because of their intriguing topologies and potential applications as functional materials [1–5]. Many efforts have been devoted to the rational design of specific frameworks including one (1D), two (2D), and three-dimensional (3D) structures [6–9]. However, the coordination polymers with desired topologies and specific properties still remains a difficult challenge since there are a variety of factors influencing the formation of coordination networks, such as the coordination geometry and the oxidation state of the metal ions, nature of the ligands, metal-to-ligand ratio, solvent system, counteranions, even the reaction temperature and pH value [10–14].

Compared with rigid aromatic ligands, flexible N-donor linkers enable the formation of frameworks with uncommon or even novel topologies and special properties because of

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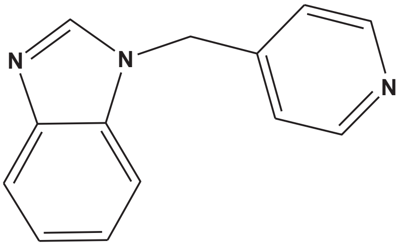
their flexibility and conformational diversity. Large numbers of coordination networks have been prepared by using various organic ligands, such as benzimidazoles, imidazoles, and pyridine derivatives. Many complexes with these ligands show unique structural topologies and interesting properties, such as 1D helical chains and 2D and 3D networks [15–20]. As our continuous focus on the synthesis, structure, and property of coordination frameworks with flexible organic ligands, flexible ligand 1-(4-pyridylmethyl)-1*H*-benzimidazole (**L**) (Scheme 1.) has been synthesized, and two new coordination polymers, $[Ag(\mathbf{L})(ClO_4)]_n$ (**1**) and $\{[Cu(\mathbf{L})_2(ClO_4)_2](H_2O)_2\}_n$ (**2**) have been obtained by reacting of **L** with $AgClO_4$ and $Cu(ClO_4)_2{\cdot}6H_2O$. They have been characterized by elemental analysis, IR, TGA, XRPD, and single crystal X-ray diffraction determination. In addition, the photoluminescent property of the complex **1** is investigated in the solid state at room temperature.



Scheme 1. Structure of the ligand L.

Experimental

Materials and Methods

All regents and solvents for synthesis were obtained from commercial sources and used as received. 1-(4-pyridylmethyl)-1*H*-benzimidazole (**L**) was synthesized according to the literature method [21]. Elemental analysis of C, H, and N was carried out with a Perkin-Elmer 240C analyzer. The IR spectra were recorded in the range 4000 to 400 cm^{-1} on a Nicolet Impact 410 FT-IR spectrometer with KBr pellets. The X-ray powder diffraction (XRPD) was recorded on a Bruker D8 ADVANCE X-ray diffractometer with Cu $K\alpha$ radiation. Simulation of the XRPD spectra was carried out by the single-crystal data and mercury (1.4.2) program. The luminescent spectra for the powdered solid samples were recorded at room temperature on an Edinburgh FLS 980 fluorescence spectrophotometer.

Synthesis of Complexes

$[Ag(\mathbf{L})(ClO_4)]_n$ (**1**) A buffer layer of methanol and distilled water (5 mL, v:v = 1:1) was carefully layered over a water (5 mL) solution of $AgClO_4$ (0.05 mmol). Then a solution of **L** (0.05 mmol) in methanol (5 mL) was layered on the buffer layer in a test tube. After 3 weeks in the dark at room temperature, colorless block crystals were obtained. Yield ~30% (based on **L**). Anal. Calcd for $C_{13}H_{11}ClN_3O_4Ag$ (%): C, 37.48; H, 2.66; N, 10.09. Found (%): C, 37.44; H, 2.81; N, 10.12. IR (KBr pellet, cm^{-1}): 3423 br, 3112 w, 1616 w, 1510 s, 1465 w, 1426 m, 1385 m, 1298 w, 1269 m, 1185 m, 1117 s, 1091 s, 1070 s, 788 w, 763 s, 750 s, 646 w, 624 s, and 429 w.

$\{[Cu(\mathbf{L})_2(ClO_4)_2](H_2O)_2\}_n$ (**2**) **2** was obtained by the similar method as described for **1**, excepted for using $Cu(ClO_4)_2{\cdot}6H_2O$ instead of $AgClO_4$. Yield: ~40% (based on **L**). Anal. Calcd for $C_{26}H_{26}Cl_2N_6O_{10}Cu$ (%): C, 43.56; H, 3.66; N, 11.72. Found (%): C, 43.61;

Table 1. Crystal data and structure refinement parameters for complexes **1** and **2**

	1	**2**
Formula	$C_{13}H_{11}N_3ClO_4Ag$	$C_{26}H_{26}N_6Cl_2O_{10}Cu$
Fw	416.57	716.94
Crystal system	Orthorhombic	Tetragonal
Space group	F d d 2	I 41/a
T/K	293(2)	293(2)
a (Å)	20.3566(7)	14.748(2)
b (Å)	27.8567(9)	14.748(2)
c (Å)	9.8803(3)	27.262(6)
α/deg	90	90
β/deg	90	90
γ/deg	90	90
V/Å^{-3}	5602.8(3)	5929.8(17)
Z	16	8
D/g cm^{-3}	1.975	1.597
μ/mm^{-1}	1.652	0.984
F(000)	3296	2904
R^a/wR^b	0.0147/0.0390	0.0968/0.2659
Total/unique/R_{int}	7004/2430/0.0147	25297/2618/0.0842
Goodness-of-fit on F^2	1.031	1.167

$^aR = \Sigma(||F_0|-|F_C||)/\Sigma|F_0|$, $^bwR = [\Sigma w(|F_0|^2-|F_C|^2)^2/\Sigma w(F_0{}^2)^2]^{1/2}$.

H, 3.61; N, 11.75. IR (KBr pellet, cm^{-1}): 3423 br, 3112 w, 1619 m, 1517 m, 1466 w, 1435 m, 1395 w, 1267 w, 1210 w, 1120 s, 1108 s, 747 m, 623 m, 506 w, and 485 w.

Caution! Perchlorate complexes of metal ions in the presence of organic ligand are potentially explosive. Only a small amount of material should be used and handled with care.

X-ray Crystallography

A suitable single crystal was selected for single-crystal X-ray diffraction analysis. Data were collected on a Bruker Smart Apex II CCD diffractometer with graphite monochromator Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) in the ω scanning mode at 293(2) K. The structure was solved by direct methods and refined by full-matrix least-squares procedure on F^2 by the SHELXL-97 program [22]. All nonhydrogen atoms were refined anisotropically, while the hydrogen atoms were located geometrically and refined isotropically except for the hydrogen atoms of coordinated water (H atoms of water molecules in complex **2** could not be correctly located in a difference Fourier map). Crystallographic data and collection parameters are listed in Tables 1 and 2.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 968584 and 968585. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union road, Cambridge, CB21EZ, UK (fax: +44 1223 336033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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

1			
Ag(1)-N(1)	2.127(2)	Ag(1)-N(3)$^{\#1}$	2.164(2)
Ag(1)-Ag(1)$^{\#2}$	3.2169(3)		
N(1)-Ag(1)-N(3)$^{\#1}$	166.97(7)	N(1)-Ag(1)-Ag(1)$^{\#2}$	88.09(5)
N(3)$^{\#1}$-Ag(1)-Ag(1)$^{\#2}$	78.99(5)		
2			
Cu(1)-N(1)	2.009(5)	Cu(1)-N(3)$^{\#2}$	2.016(5)
N(1)$^{\#1}$-Cu(1)-N(1)	91.4(3)	N(1)$^{\#1}$-Cu(1)-N(3)$^{\#2}$	175.0(2)
N(1)-Cu(1)-N(3)$^{\#2}$	89.4(2)	N(3)$^{\#2}$-Cu(1)-N(3)$^{\#3}$	90.1(3)

Symmetry code for **1**: #1 $-x + 2, -y, z - 1$; #2 $-x + 2, -y, z$; **2**: #1 $-x + 2, -y + 1/2, -z + 0$; #2: $-y + 1/4, x - 1/4, z - 1/4$; #3: $y + 3/4$; $-x + 3/4, z - 1/4$.

Results and Discussion

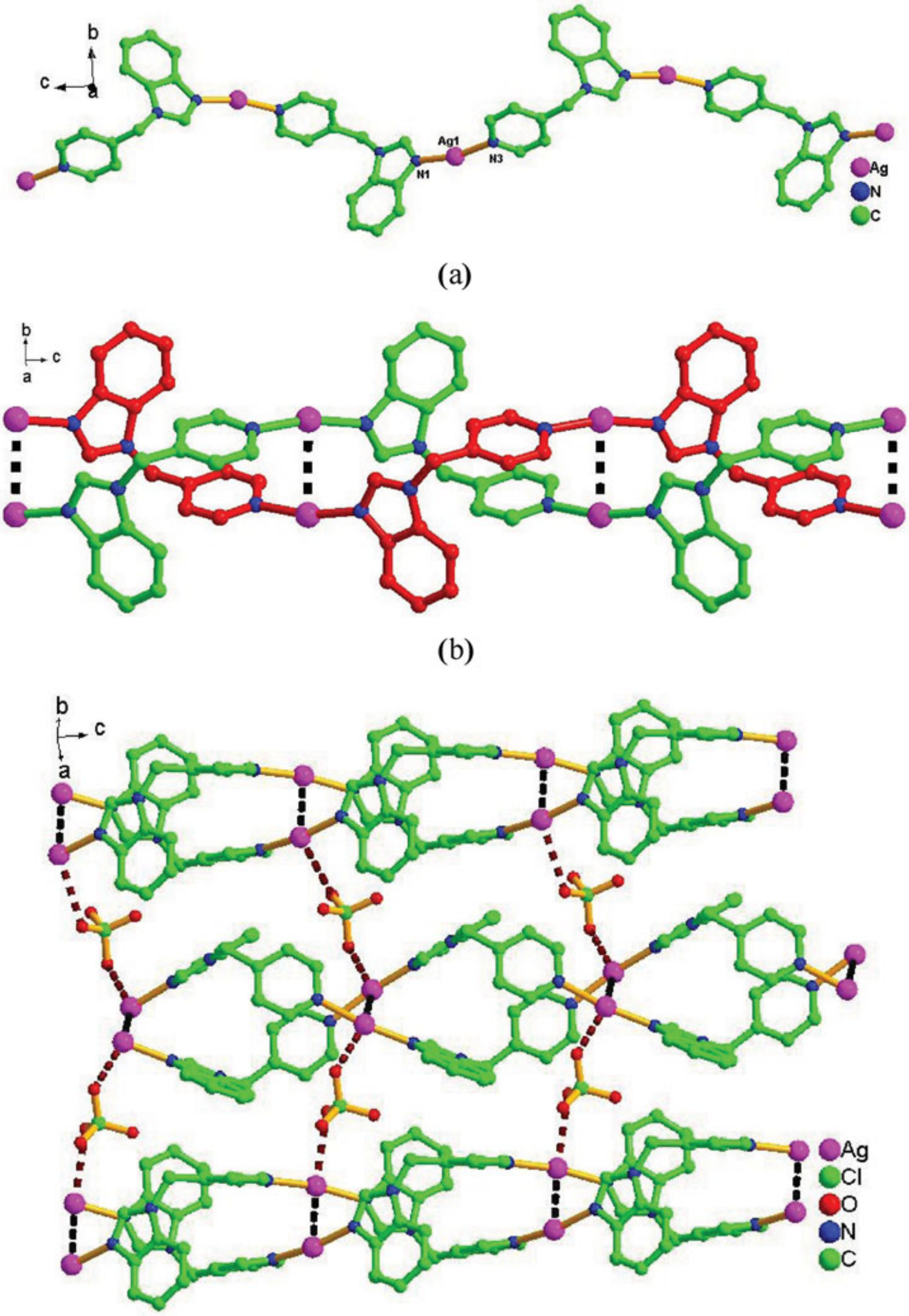
Synthesis and Characterization

In our efforts to investigate the relationships between the metal ions and the structures of their complexes based on N-donor ligand, 1-(4-pyridylmethyl)-1*H*-benzimidazole (**L**), and their complexes $[Ag(\mathbf{L})(ClO_4)]_n$ (**1**),$\{[Cu(\mathbf{L})_2(ClO_4)_2](H_2O)_2\}_n$ (**2**) were synthesized and structurally characterized by elemental analyses, IR spectra, and single-crystal X-ray diffraction analysis. The absorptions bands at *ca.* 1100 cm^{-1} in the infrared spectra of complexes indicate the existence of the ClO_4^- anions.

Structure Descriptions of Complexes

$[Ag(\mathbf{L})(ClO_4)]_n$ (**1**). Single crystal X-ray analyses reveal that **1** possesses a 1D double helix chain structure (Fig. 1a). Each Ag(I) ion in **1** is coordinated by two N donors from the benzimidazole ring and the pyridyl ring with Ag–N distance being 2.127(2) Å and 2.164(2) Å, the N(1)–Ag(1)–N(3)$^{\#1}$ (Symmetry code: #1 $-x + 2, -y, z - 1$) angle is 166.97(7)°. The coordination geometry of Ag(I) can be described as a dicoordinated linear fashion. In **1**, the dihedral angle between the benzimidazole ring and pyridyl ring is 77.768°. Each L acts as μ_2-bridging ligand to bridge two Ag$^+$ ions, the nearest Ag···Ag distance is 3.217(3). As shown in Fig. 1b, through the coordination mode and Ag···Ag weak interactions, a 1D double helix chain is formed. It should be noted that there are also Ag···O weak interactions in **1** (Ag(1)···O(4) = 2.698 Å). Thus, the adjacent double helix chains are arranged into 2D network through the Ag···O weak interactions (Fig. 1c).

$\{[Cu(\mathbf{L})_2(ClO_4)_2](H_2O)_2\}_n$ (**2**). In the similar reaction condition, when the metal ion was changed to Ag(I), **2** was obtained. The complex **2** crystallizes in Tetragonal, space group *I* 41/a. The asymmetric unit of **2** consists of one Cu^{2+} ion, two **L** ligands, two ClO_4^- counterions and two free water molecules. In **2**, each Cu(II) ion is four-coordinated by two N atoms from benzimidazole rings and two N atoms from pyridyl rings of four different **L** ligands (Fig. 2a). Due to Jahn-Teller effect, the Cu(II) ions display a plane four coordination with Cu(1)–N(1) bond distance of 2.009(5) Å, Cu(1)–N(3)$^{\#2}$ (Symmetry



(a)

(b)

(c)

Figure 1. View of (a) the 1D chain structure of **1**; (b) the 1D double helix chain structure of **1** formed by Ag···Ag weak interactions; and (c) the 2D coordination network of **1** formed by Ag···O weak interactions (Symmetry code: #1: $-x + 2, -y, z - 1$, H atoms were omitted for clarity in all and ClO_4^- were omitted for clarity in 1a and 1b).

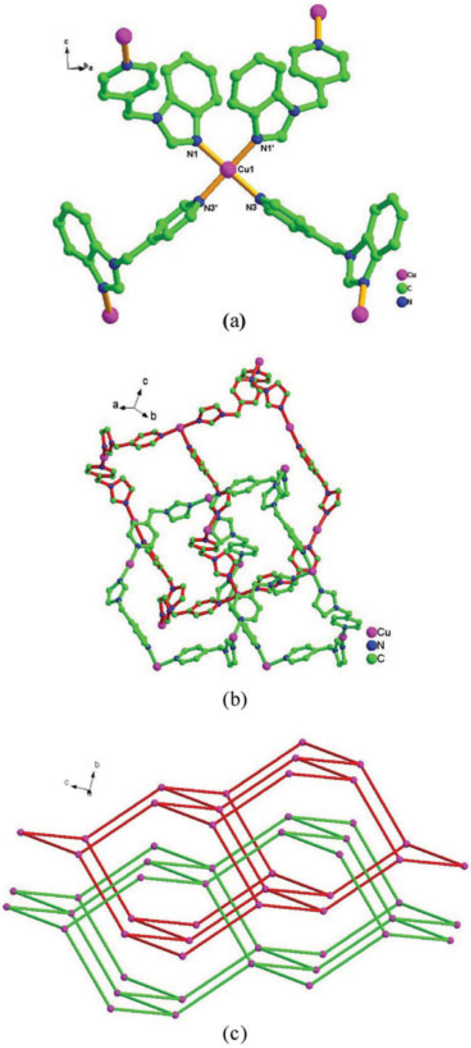


Figure 2. View of (a) the coordination environment of the $\mathrm{Cu^{II}}$ center in **2**; (b) twofold interpenetrated diamond like 3D structure of **2**; and (c) twofold interpenetrated diamond topology of **2** (Symmetry code: #1: $-x+1$, $-y$, $-z$, H atoms were omitted for clarity).

code: $-y+1/4, x-1/4, z-1/4$) bond distance of 2.016(5) Å, which are close to those reported in literature [23]. The N–Cu–N angles range from 89.4(2)° to 175.0(2)°. Each **L** ligand in **2** links two $\mathrm{Cu^{2+}}$ ions and shows dihedral angle of 73.742°, adopting a μ_2-coordination mode.

Thus each metal center is coordinated by four **L** ligands and each ligand in turn links two $\mathrm{Cu^{2+}}$ ions, which shows a four-connected net with diamondoid structure with the adjacent Cu···Cu distance of 10.041 Å and the Cu···Cu···Cu angles ranging from 94.508° to 117.432°, deviating significantly from the standard value of 109.5° for diamond network (Fig. 2b). Two set of such nets interpenetrate and form the structure of compound **2** (Fig. 2c).

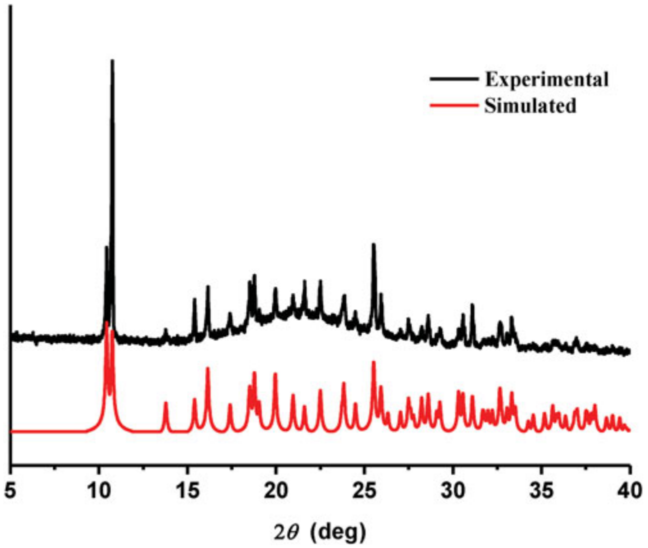


Figure 3. XRPD patterns for **1**.

XRPD Results and Photoluminescent Property

To confirm the phase purity of the bulk materials, X-ray powder diffraction (XRPD) experiments have been carried out for complexes **1** and **2**. The XRPD experimental and computer-simulated patterns of the corresponding complexes are shown in Figs. 3 and 4. Although the experimental patterns have a few un-indexed diffraction lines and some are slightly broadened in comparison with those simulated from the single-crystal models, it

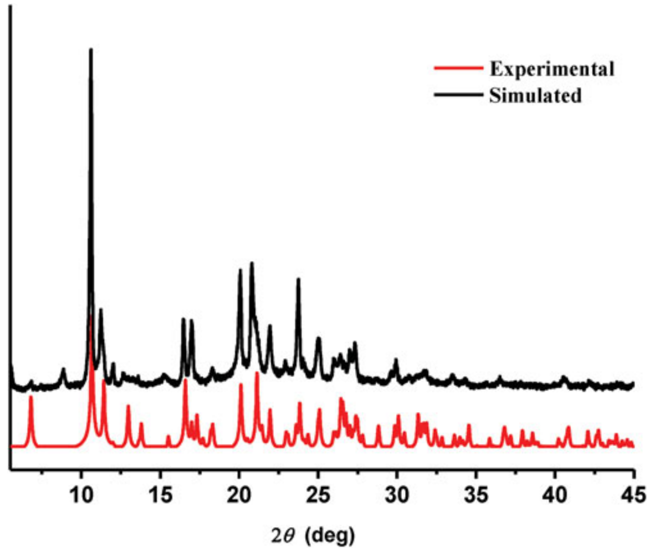


Figure 4. XRPD patterns for **2**.

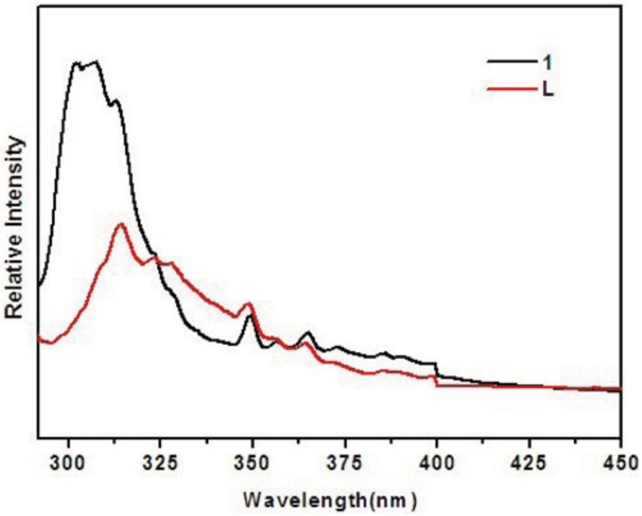


Figure 5. Emission spectra of complex **1** and ligand **L** in the solid state at room temperature.

still can be well considered that the bulk synthesized materials and the crystals used for diffraction are homogeneous.

Considering the excellent luminescent properties of coordination polymers with d^{10} metals [24–26], solid-state luminescence properties of complex **1** and the **L** ligand were investigated in the solid state at room temperature. The emission spectra are depicted in Fig. 5. Complex **1** shows an emission band at 314 nm upon the excitation at 280 nm. The emission is neither metal-to-ligand charge transfer nor ligand-to-metal charge transfer, which can probably be assigned to the intra-ligand (n–π^* or π–π^*) transition, because similar emission is observed at 312 nm for the free ligand **L** when excited at 280 nm. The results are in reasonable agreement with literature examples [27,28].

Conclusions

In summary, two new transition metal complexes based on 1-(4-pyridylmethyl)-1*H*-benzimidazole ligand were synthesized and structurally characterized. Single crystal structure analysis shows that **1** is 1D double helix chain structure, which form a 2D supramecular network through Ag···Ag and Ag···O weak interactions. **2** shows a twofold interpenetrating 3D diamond network. The results show that the metal ions and weak interactions play important roles in the construction of such coordination architectures. X-ray powder diffractions show that the bulk synthesized materials and the crystals are homogeneous. Meanwhile, the photoluminescent property of the complex **1** is investigated in the solid state at room temperature.

Acknowledgments

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