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Syntheses, structures and properties of silver(I) complexes with flexible 1,3,5-tris(pyridylmethoxyl)benzene ligands

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ABSTRACT

Five new silver(I) complexes $[\text{Ag}_2(\text{L}_2)_2](\text{BF}_4)_2 \cdot \text{CH}_3\text{CN} \cdot \text{CH}_3\text{OH}$ (**1**), $[\text{Ag}(\text{L}_2)(\text{CF}_3\text{SO}_3)]$ (**2**), $[\text{Ag}(\text{L}_3)]\text{ClO}_4 \cdot \text{CH}_3\text{OH}$ (**3**), $[\text{Ag}_2(\text{L}_3)_2](\text{CF}_3\text{SO}_3)_2 \cdot \text{CH}_3\text{CN} \cdot \text{CH}_3\text{OH} \cdot \text{H}_2\text{O}$ (**4**) and $[\text{Ag}(\text{L}_3)]\text{PF}_6 \cdot 2\text{CH}_3\text{CN}$ (**5**) [$\text{L}_2 = 1,3,5$ -tris(2-pyridylmethoxyl)benzene, $\text{L}_3 = 1,3,5$ -tris(3-pyridylmethoxyl)benzene] were synthesized and characterized by single crystal X-ray diffraction analyses. In complexes **1–5**, ligands L_2 and L_3 show different conformations and act as three-connectors, while the Ag(I) atom serves as three-connecting node to result in the formation of 2D and 3D frameworks. Complexes **1** and **2** with different counteranions have similar 2D network structure with the same (4,8²) topology. Complex **3** has a 3D structure with (10,3)-a topology while complexes **4** and **5** have the same 2D (6,3) topological structure. The results showed that the structure of organic ligands and counteranions play subtle but important role in determining the structure of the complexes. In addition, the photoluminescence and anion-exchange properties of the complexes were investigated in the solid state at room temperature.

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1. Introduction

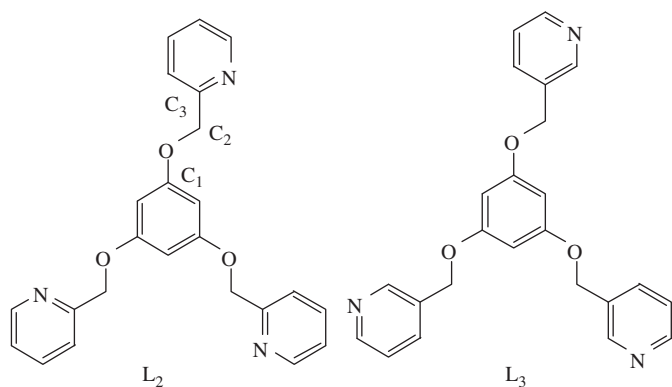
The assembly of building blocks into chains, networks and other supramolecular architectures with specific structures and topologies via coordination interactions is a major area of current research [1,2]. Architectures with specific structural motifs can be achieved by careful selection of organic ligands with suitable coordinating groups, metal centers with definite coordination geometry and reaction conditions [1b,3]. Such approach is using coordination interactions to generate primary framework which can be further organized into supramolecular architectures through weak non-covalent interactions, such as hydrogen bonding, C–H... π and π – π interactions [4]. This strategy has been proved to be an efficient and reliable method for preparation of organic–inorganic hybrid materials [5]. Up to date, various metal complexes with one- (1D), two- (2D), or three-dimensional (3D) structures have been obtained by using this strategy [6]. However, the exploration of synthetic routes is a long-term challenge since the assembly reactions can be affected by factors like the nature of organic ligands, solvents, templates, counterions and so on [7]. Thus further research is required to

achieve information for controlling and predicting the relevant structures as well as to establish the relationship between structures and properties.

On the other hand, crystal engineering of coordination frameworks based on multidentate ligands represents growing area of coordination and supramolecular chemistry. In particular, metal-organic architectures with flexible ligands attract more and more attention from chemists, since the flexible ligands can adopt varied conformation upon the different geometric requirement of the metal ions and lead to form diverse structures [8]. We focus our attention on the assembly of varied metal salts with flexible imidazole-containing tripodal ligands, for example 1,3,5-tris(imidazole-1-ylmethyl)-2,4,6-trimethylbenzene (TITMB), 1,3,5-tris(imidazole-1-ylmethyl)benzene (TIB), and metal complexes with various structures and properties have been obtained [9–13]. As an extension of our work, we synthesized flexible tripodal ligands with pyridyl groups, namely 1,3,5-tris(2-pyridylmethoxyl)benzene (L_2) and 1,3,5-tris(3-pyridylmethoxyl)benzene (L_3) as shown in Scheme 1 [8]. Herein we report five new metal complexes $[\text{Ag}_2(\text{L}_2)_2](\text{BF}_4)_2 \cdot \text{CH}_3\text{CN} \cdot \text{CH}_3\text{OH}$ (**1**), $[\text{Ag}(\text{L}_2)(\text{CF}_3\text{SO}_3)]$ (**2**), $[\text{Ag}(\text{L}_3)]\text{ClO}_4 \cdot \text{CH}_3\text{OH}$ (**3**), $[\text{Ag}_2(\text{L}_3)_2](\text{CF}_3\text{SO}_3)_2 \cdot \text{CH}_3\text{CN} \cdot \text{CH}_3\text{OH} \cdot \text{H}_2\text{O}$ (**4**) and $[\text{Ag}(\text{L}_3)]\text{PF}_6 \cdot 2\text{CH}_3\text{CN}$ (**5**) synthesized by reactions of L_2 or L_3 with the corresponding Ag(I) salts, respectively. The complexes were characterized by single crystal X-ray diffraction analyses, and their photoluminescence and anion-exchange properties were investigated.

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Scheme 1. Schematic structure of ligands L_2 and L_3 .

2. Experimental section

2.1. Materials and measurements

All commercially available chemicals are of reagent grade and were used as received without further purification. Ligands L_2 and L_3 were prepared as reported previously [8]. Solvents of methanol (CH_3OH), acetonitrile (CH_3CN), etc. were purified according to the standard methods. All procedures for synthesis of Ag(I) complexes were carried out in the dark. C, H, N elemental analyses were performed on a Perkin-Elmer 240C Elemental Analyzer at the Analysis Center of Nanjing University. Infrared (IR) spectra were recorded on a Bruker Vector22 FT-IR Spectrophotometer by using KBr pellets. The photoluminescent spectra for the powdered solid samples were recorded at room temperature on an Aminco Bowman Series 2 Spectrofluorometer with a xenon arc lamp as the light source and all the measurements were carried out under the same conditions.

2.2. Syntheses

2.2.1. $[\text{Ag}_2(L_2)_2](\text{BF}_4)_2 \cdot \text{CH}_3\text{CN} \cdot \text{CH}_3\text{OH}$ (**1**)

A methanolic solution (10 mL) of L_2 (24.0 mg, 0.06 mmol) was slowly added with stirring to an acetonitrile solution (10 mL) of AgBF_4 (11.7 mg, 0.06 mmol). The mixture was stirred for 15 min and was filtrated out. The clear filtrate stood at ambient temperature for several weeks, and single crystals suitable for X-ray diffraction analyses were obtained by slow evaporation of the filtrate. Yield: 48%. Anal. calcd. for $\text{C}_{51}\text{H}_{49}\text{B}_2\text{Ag}_2\text{F}_8\text{N}_7\text{O}_7$: C, 48.56; H, 3.92; N, 7.77%. Found: C, 48.64; H, 3.84; N, 7.69%. FT-IR (KBr: cm^{-1}): 1600(s), 1572(m), 1484(m), 1437(m), 1172(s), 1152(s), 1058(s), 1008(m), 818(m), 806(m), 766(m).

2.2.2. $[\text{Ag}(L_2)(\text{CF}_3\text{SO}_3)]$ (**2**)

The procedure for preparation of complex **2** is the same as that for **1** except for AgBF_4 replaced by AgCF_3SO_3 (15.4 mg, 0.06 mmol). Yield: 38%. Anal. calcd. for $\text{C}_{25}\text{H}_{21}\text{AgF}_3\text{N}_3\text{O}_6\text{S}$: C, 45.75; H, 3.23; N, 6.40%. Found: C, 45.68; H, 3.14; N, 6.31%. FT-IR (KBr: cm^{-1}): 1602(s), 1479(m), 1438(m), 1376(m), 1251(s), 1169(s), 1069(m), 1035(m), 816(m), 760(m), 706(m).

2.2.3. $[\text{Ag}(L_3)]\text{ClO}_4 \cdot \text{CH}_3\text{OH}$ (**3**)

The title complex was also prepared by the same method as that for preparation of complex **1** using L_3 (24.0 mg, 0.06 mmol) in methanol solution (10 mL) and AgClO_4 (13.1 mg, 0.06 mmol) in acetonitrile solution (10 mL). Block crystals were obtained by slow evaporation of the filtrate in 49% yield. Anal. calcd. for $\text{C}_{25}\text{H}_{25}\text{AgClN}_3\text{O}_8$: C 47.01; H 3.95; N 6.58%. Found: C 47.08; H

3.99; N 6.48%. FT-IR (KBr: cm^{-1}): 1608(s), 1586(m), 1483(m), 1431(m), 1165(s), 1117(m), 1078(s), 806(m), 709(m).

2.2.4. $[\text{Ag}_2(L_3)_2](\text{CF}_3\text{SO}_3)_2 \cdot \text{CH}_3\text{CN} \cdot \text{CH}_3\text{OH} \cdot \text{H}_2\text{O}$ (**4**)

The same method was used to prepare complex **4** using L_3 (24.0 mg, 0.06 mmol) in methanol solution (10 mL) and AgCF_3SO_3 (15.4 mg, 0.06 mmol) in acetonitrile solution (10 mL). Yield: 44%. Anal. calcd. for $\text{C}_{53}\text{H}_{51}\text{Ag}_2\text{F}_6\text{N}_7\text{O}_{14}\text{S}_2$: C, 45.35; H, 3.66; N, 6.98%. Found: C, 45.42; H, 3.70; N, 6.91%. FT-IR (KBr: cm^{-1}): 1603(s), 1458(m), 1431(m), 1264(s), 1166(s), 1071(m), 1032(m), 796(m), 706(m).

2.2.5. $[\text{Ag}(L_3)]\text{PF}_6 \cdot 2\text{CH}_3\text{CN}$ (**5**)

When AgNO_3 (10.2 mg, 0.06 mmol) and KPF_6 (10.4 mg, 0.06 mmol) were used instead of AgCF_3SO_3 (15.4 mg, 0.06 mmol) in preparation of **4**, colorless block crystals were obtained after about 2 weeks. Yield: 61%. Anal. calcd. for $\text{C}_{28}\text{H}_{27}\text{AgF}_6\text{N}_5\text{O}_3\text{P}$: C 45.79; H 3.71; N 9.54%. Found: C 45.88; H 3.78; N 9.48%. IR (KBr, cm^{-1}): 1604(s), 1434(m), 1158(s), 1051(m), 843(s), 704(m).

Safety note: Perchlorate salts of metal complex with organic ligands are potentially explosive and should be handled with care.

2.3. Crystal structure determination

The crystallographic data collections for complexes **1–5** were carried out on a Rigaku RAXIS-RAPID Imaging Plate diffractometer at 200 K, using graphite-monochromated Mo- $K\alpha$ radiation ($\lambda=0.71075 \text{ \AA}$). The structures were solved by direct methods with SIR92 [14], and expanded using Fourier technique [15]. All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method. The hydrogen atoms except for those of water molecules were generated geometrically and the ones of water molecule in **4** were located directly. All calculations were carried out on SGI workstation using the teXsan crystallographic software package of Molecular Structure Corporation [16]. In complex **1**, the F1, F2, F3, F4 atoms disordered into two positions with site occupation factors of 0.54(2) and 0.46(2), while the F8 and B2 atoms disordered into two positions with site occupation factors of 0.741(4) and 0.259(4), respectively. In complex **4**, S1, F3, O13, C10 disordered into two positions with site occupation factors of 0.606(6) and 0.394(6) and S2, F4, F5, F6, O21, O22, O23 and C20 disordered into two positions with site occupation factors of 0.501(5) and 0.499(5), respectively. Details of the crystal parameters, data collection and refinements for complexes **1–5** are summarized in Table 1, and selected bond lengths and angles with their estimated standard deviations are listed in Table 2. Hydrogen bonding data of the complexes are summarized in Table 3.

2.4. Anion-exchange of complexes **3** and **5**

The powder sample (50.0 mg) of **3** or **5** was suspended in water (10 mL), and then NaNO_3 (1.0 g) was added. The mixture was stirred for 36 h at ambient temperature, then was filtered, washed with deionized water three times, and dried to give the exchanged product of **3A** and **5A**, respectively. Elemental analysis for **3A**: C, 49.01; H, 4.05; N, 9.37%; calcd. for $[\text{Ag}(L_3)]\text{NO}_3 \cdot \text{H}_2\text{O}$ ($\text{C}_{24}\text{H}_{23}\text{N}_4\text{O}_7\text{Ag}$): C, 49.08; H, 3.95; N, 9.54%; for **5A**: C, 49.11; H, 3.97; N, 9.45%; calcd. for $[\text{Ag}(L_3)]\text{NO}_3 \cdot \text{H}_2\text{O}$ ($\text{C}_{24}\text{H}_{23}\text{N}_4\text{O}_7\text{Ag}$): C, 49.08; H, 3.95; N, 9.54%. The powder sample of **3A** (50.0 mg) was suspended in water (10 mL), and then NaClO_4 (1.0 g) was added. The mixture was stirred for 36 h at ambient temperature, then filtered, washed with deionized water three times, and dried to give the exchanged product of **3B**. Elemental analysis for **3B**: C, 46.17; H, 3.73; N, 6.89%; calcd. for $[\text{Ag}(L_3)]\text{ClO}_4 \cdot \text{H}_2\text{O}$ ($\text{C}_{24}\text{H}_{23}\text{N}_3\text{O}_8\text{ClAg}$): C,

Table 1
Crystallographic data for complexes **1–5**.

	1	2
Empirical formula	C ₅₁ H ₄₉ B ₂ Ag ₂ F ₈ N ₇ O ₇	C ₂₅ H ₂₁ AgF ₃ N ₃ O ₆ S
Formula weight	1261.33	656.38
Temperature (K)	200	200
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
Crystal size (mm)	0.20 × 0.20 × 0.01	0.30 × 0.30 × 0.04
<i>a</i> (Å)	14.3728(3)	15.230(9)
<i>b</i> (Å)	12.9250(3)	9.091(7)
<i>c</i> (Å)	30.3665(5)	18.952(10)
β (°)	106.688(1)	101.841(17)
<i>V</i> (Å ³)	5403.55(19)	2568(3)
<i>Z</i>	4	4
λ (Å)	0.71075	0.71075
<i>D_c</i> (g cm ⁻³)	1.550	1.698
μ (Mo <i>K</i> α) (cm ⁻¹)	0.809	0.935
Independent reflns.	12331	5849
<i>R</i> _{int}	0.0748	0.0406
Observed reflns.	4642	3830
<i>R</i> ₁ ^a (<i>I</i> > 2 σ (<i>I</i>))	0.0406	0.0275
<i>wR</i> ₂ ^b (<i>I</i> > 2 σ (<i>I</i>))	0.0394	0.0419

	3	4	5
Empirical formula	C ₂₅ H ₂₅ AgClN ₃ O ₈	C _{26.5} H _{25.5} AgF ₃ N _{3.5} O ₇ S	C ₂₈ H ₂₇ AgF ₆ N ₅ O ₃ P
Formula weight	638.80	701.93	734.39
Temperature (K)	200	200	200
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	<i>Pna</i> 2 ₁	<i>Cc</i>	<i>Pna</i> 2 ₁
Crystal size (mm)	0.15 × 0.15 × 0.15	0.30 × 0.10 × 0.07	0.25 × 0.15 × 0.10
<i>a</i> (Å)	22.258(15)	27.999(3)	7.0461(11)
<i>b</i> (Å)	11.154(9)	15.9739(14)	26.607(4)
<i>c</i> (Å)	10.409(9)	14.4213(16)	16.224(2)
β (°)	90.00	115.391(7)	90.00
<i>V</i> (Å ³)	2584(3)	5826.9(10)	3041.5(7)
<i>Z</i>	4	8	4
λ (Å)	0.71075	0.71075	0.71075
<i>D_c</i> (g cm ⁻³)	1.642	1.600	1.604
μ (Mo <i>K</i> α) (cm ⁻¹)	0.938	0.832	0.791
Independent reflns.	5865	11835	6929
<i>R</i> _{int}	0.0508	0.0559	0.0897
Observed reflns	3374	6787	3455
<i>R</i> ₁ ^a (<i>I</i> > 2 σ (<i>I</i>))	0.0351	0.0450	0.0422
<i>wR</i> ₂ ^b (<i>I</i> > 2 σ (<i>I</i>))	0.0636	0.0829	0.0481

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$^b wR_2 = \frac{\sum w(|F_o|^2 - |F_c|^2)^2}{\sum w(F_o)^2}^{1/2}, \quad \text{where } w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$$

$$P = (F_o^2 + 2F_c^2)/3$$

46.14; H, 3.71; N, 6.73%. The powder sample of **5A** (50.0 mg) was suspended in water (10 mL), and then NaPF₆ (1.0 g) was added. The mixture was stirred for 36 h at ambient temperature, then filtered, washed with deionized water three times, and dried to give the exchanged product of **5B**. Elemental analysis for **5B**: C, 42.97; H, 3.43; N, 6.39%; calcd. for [Ag(L₃)]PF₆ · H₂O (C₂₄H₂₃N₃O₄PF₆Ag): C, 43.01; H, 3.46; N, 6.27%.

3. Results and discussion

3.1. Crystal structure of complexes **1** and **2**

The results of crystallographic analysis indicate that complexes **1** and **2** have similar framework structure, accordingly only

Table 2
Selected bond lengths (Å) and bond angles (°) for complexes **1–5**.^a

1			
Ag1–N151	2.267(3)	Ag1–N11	2.286(3)
Ag1–N31#1	2.303(3)	Ag2–N131#2	2.20(3)
Ag2–N51	2.284(3)	Ag2–N111	2.291(3)
N151–Ag1–N11	125.64(11)	N151–Ag1–N31#1	121.53(10)
N11–Ag1–N31#1	112.52(11)	N131#2–Ag2–N51	121.18(10)
N131#2–Ag2–N111	116.27(10)	N51–Ag2–N111	122.55(11)
2			
Ag1–N51#3	2.287(2)	Ag1–N11	2.3300(17)
Ag1–N31#4	2.345(2)	Ag1–O11	2.5436(18)
N51#3–Ag1–N11	126.21(6)	N51#3–Ag1–N31#4	119.24(6)
N11–Ag1–N31#4	98.40(6)	N51#3–Ag1–O11	100.98(5)
N11–Ag1–O11	103.22(7)	N31#4–Ag1–O11	106.70(6)
3			
Ag1–N11	2.199(4)	Ag1–N31#5	2.206(4)
Ag1–N51#6	2.334(4)		
N11–Ag1–N31#5	139.42(14)	N11–Ag1–N51#6	108.99(15)
N31#5–Ag1–N51#6	109.36(16)		
4			
Ag1–N51#7	2.274(6)	Ag1–N31	2.299(4)
Ag1–N11	2.292(6)	Ag2–N151#8	2.266(5)
Ag2–N131#9	2.266(5)	Ag2–N111	2.302(5)
N51#7–Ag1–N31	118.8(2)	N51#7–Ag1–N11	118.90(18)
N31–Ag1–N11	118.0(2)	N151#8–Ag2–N131#9	118.00(19)
N111–Ag2–N151#8	117.8(2)	N131#9–Ag2–N111	118.16(19)
5			
Ag1–N51#10	2.234(4)	Ag1–N31#11	2.259(3)
Ag1–N11	2.267(3)		
N51#10–Ag1–N31#11	123.09(14)	N51#10–Ag1–N11	119.82(14)
N31#11–Ag1–N11	114.98(14)		

^a Symmetry transformations used to generate equivalent atoms: #1: $-x, y-1/2, -z+3/2$; #2: $-x+1, y+1/2, -z+3/2$; #3: $x, -y+1/2, z+1/2$; #4: $-x+2, y+1/2, -z+3/2$; #5: $-x+3/2, y-1/2, z-3/2$; #6: $x-1/2, -y+1/2, z-1$; #7: $x+1/2, y-1/2, z$; #8: $x-1/2, y+1/2, z$; #9: $x-1/2, y-1/2, z$; #10: $-x+3/2, y-1/2, z-1/2$; #11: $-x+3/2, y-1/2, z+1/2$.

Table 3
Hydrogen bonding data for complexes **1**, **4** and **5**.

D–H...A	D...A (Å)	D–H–A (deg.)
1		
C11–H5...F4#1	3.355(14)	142
O201–H49...F2#1	3.10(2)	163
C34–H13...F4	3.053(12)	126
C35–H14...F7#2	3.322(5)	149
C51–H17...O103#3	3.239(4)	150
C53–H18...F6#3	3.330(4)	155
C56–H21...F7	3.436(4)	160
C111–H25...F6	3.482(4)	158
C131–H31...N1	3.427(5)	145
C156–H42...F3#1	3.294(12)	135
C151–H37...O3#4	3.285(4)	148
4		
O201–H49...O12#5	2.829(11)	171
O202–H50...O201	2.930(15)	167(11)
O202–H51...O22#6	2.611(16)	177(16)
C51–H17...O21#5	3.439(16)	152
C56–H21...O11#7	3.348(9)	138
C102–H22...O21#6	3.373(15)	156
C116–H30...O12#8	3.288(10)	141
C203–H48...F4#9	3.237(18)	143
5		
C16–H9...F2	3.248(6)	159

Symmetry transformations used to generate equivalent atoms: #1: $x, 1/2+y, 3/2-z$; #2: $-1+x, y, z$; #3: $1-x, 1/2+y, 3/2-z$; #4: $-x, -1/2+y, 3/2-z$; #5: $-1/2+x, 1/2+y, z$; #6: $x, 1-y, 1/2+z$; #7: $-1/2+x, 3/2-y, 1/2+z$; #8: $-1/2+x, 1/2-y, 1/2+z$; #9: $x, -y, 1/2+z$.

the structure of **1** is described here in detail, while the one of **2** is provided in supporting information (Fig. S1). In the cationic part of complex **1**, there are two independent Ag(I) and two L_2 ligands as shown in Fig. 1a. The Ag1 and Ag2 have similar coordination geometry and each Ag(I) atom is coordinated by three nitrogen atoms from three different L_2 ligands with Ag–N bond length varying from 2.267(3) to 2.303(3) Å and N–Ag–N bond angles ranging from 112.52(11) to 125.64(11)° as listed in Table 2. Thus the coordination geometry of each Ag(I) center in **1** can be regarded as triangle with N3 donor set. On the other hand, each L_2 acts as a three-connector linking three Ag(I) atoms to form a 2D network (Fig. 1b). It is noteworthy that there are two macrocycles in the 2D network, one is 24-membered $Ag_2(L_2)_2$ macrocyclic motif (A) with Ag...Ag separation of 10.37 Å and the other one is 48-membered $Ag_4(L_2)_4$ macrocycle (B) as shown in Fig. 1b. There are π – π interactions within the macrocycle A since the centroid-to-centroid separation is 3.79 Å and the dihedral angle between the two benzene ring planes is 0.8° (Fig. 1b) [17]. Each A ring is surrounded by four B rings, and in turn each B is surrounded by four A and four B rings. Therefore, the 2D network of **1** has 4.8^2 topology as schematically shown in Fig. 1c, in which the L_2 ligand

is represented by spoke radiating from a point (i.e. the centroid of benzene ring plane) and the Ag(I) center is represented by three-connecting node.

The crystal-packing diagram of **1** is shown in Fig. 1d. Tetrafluoroborate anions locate in the voids and are connected to the 2D layer through C–H...F hydrogen bonds with the C...F distances in the range from 3.053(12) to 3.482(4) Å, and the C–H–F angles varying from 126 to 160° as listed in Table 3. The solvent acetonitrile molecules are also held to the 2D layer by C131–H31...N1 hydrogen bond with a C...N distance of 3.427(5) Å. In addition, there are C–H... π interactions in complex **1** between the two pyridine rings from two adjacent layers [17], since the distance between the hydrogen atom bound to the carbon of a pyridine ring and the centroid of the other pyridine group in the adjacent layer is 2.97 Å (the distance between the carbon atom of the pyridine ring and the centroid of the other pyridine group in the adjacent layer is 3.70 Å), and the C–H–centroid angle is 135°. The 2D layers are held together by such C–H... π interactions to give a 3D structure (Fig. 1d).

In contrast to the three-coordinated Ag(I) in **1**, the Ag(I) in **2** is four-coordinated by three nitrogen atoms from three different L_2

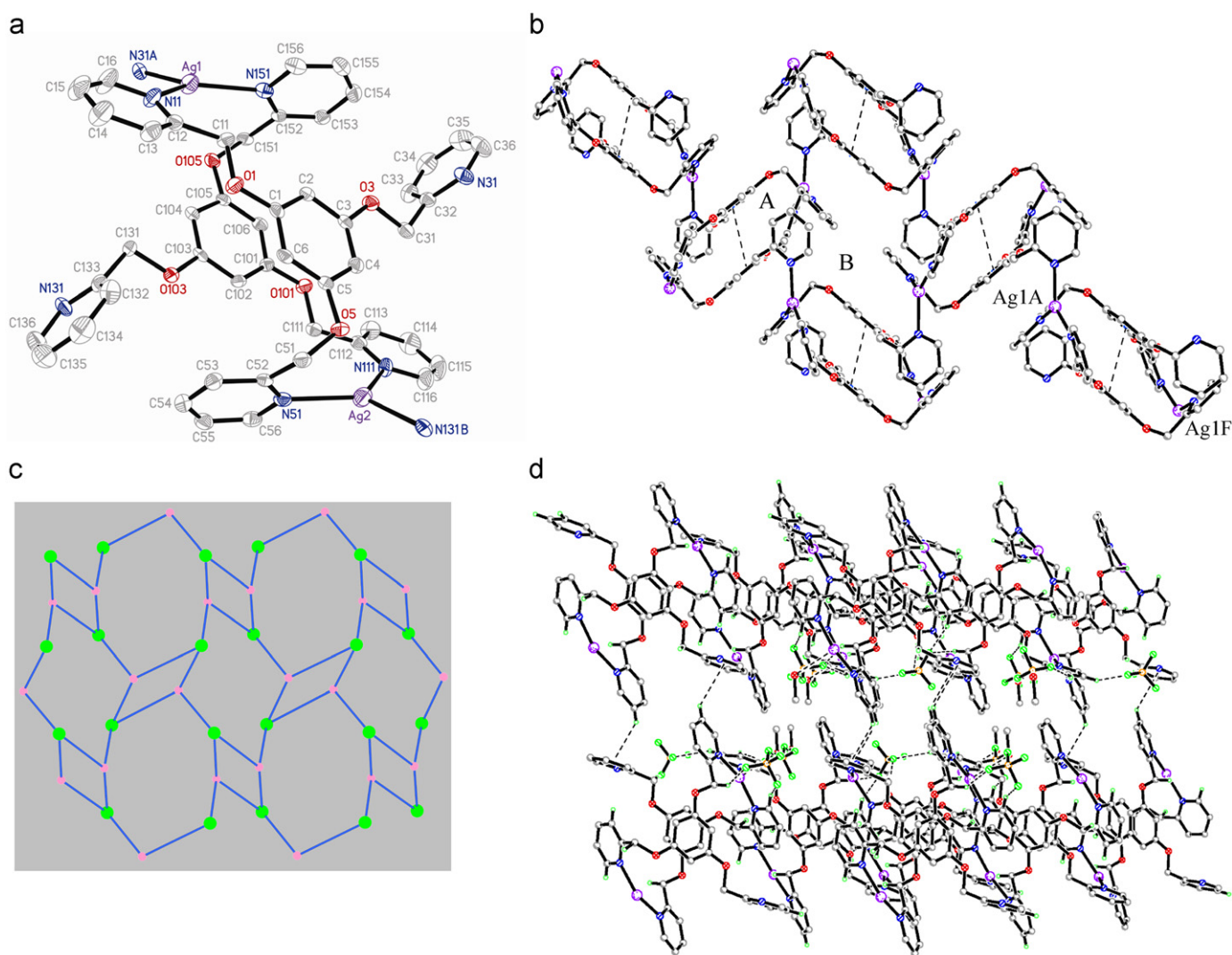


Fig. 1. (a) The coordination environment around the Ag(I) atoms in **1** with the ellipsoids drawn at 50% probability level, the CH₃CN, CH₃OH molecules, BF₄⁻ anions and hydrogen atoms are omitted for clarity. (b) 2D network structure of **1** with π – π interactions indicated by dashed lines. (c) Simplified 4.8^2 topology of **1**, the small balls (pink) represent the centroids of the central benzene ring of L_2 , the large ones (green) represent Ag(I) atoms. (d) Crystal-packing diagram of **1**, in which the hydrogen bonds and C–H... π interactions are indicated by dashed lines, CH₃CN molecules are omitted for clarity (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

ligands and one oxygen atom from CF_3SO_3^- anion (Fig. S1a). A distance of 2.5436(18) Å between the Ag1 and O11 suggests the existence of Ag–O coordination [18,19]. The N–Ag–N angles are ranging from $98.40(6)^\circ$ to $126.21(6)^\circ$, and the N–Ag–O ones are varying from $100.98(5)^\circ$ to $106.70(6)^\circ$ as listed in Table 2. Therefore, each Ag(I) atom in **2** has distorted tetrahedral coordination geometry. Nevertheless, complex **2** also has 2D network structure with 4.8^2 topology (Fig. S1).

3.2. Crystal structure of complex **3**

When ligand L_3 , instead of L_2 , was used to react with different Ag(I) salts, complexes **3–5** were isolated. The X-ray crystallographic analysis revealed that complex **3** contains one silver(I), one ligand L_3 , one perchlorate anion and one methanol molecule. The coordination environment of Ag(I) in complex **3** is displayed in Fig. 2a along with the atom-numbering scheme. It can be clearly seen that each Ag(I) atom in **3** is coordinated by three nitrogen atoms from three different L_3 ligands which is similar to the Ag(I) in **1**. Furthermore, each L_3 ligand also links three Ag(I) atoms like the L_2 in **1**, however, to generate a 3D structure with

open channels occupied by non-coordinated ClO_4^- anions and methanol molecules (Fig. 2b), rather than the 2D network observed in **1** as well as **2** (Figs. 1b and S1b).

The 3D framework of **3** can be regarded as a non-interpenetrated (10,3)-a net (Fig. 2c) by considering the metal center as three-connected node and the ligand as three-connector [18]. Five Ag(I) atoms and five L_3 ligands form a circuit of the (10,3)-a net (Fig. 2d) and helical unit in the (10,3)-a net can be found (Fig. 2e). It should be noticed that the most of previously reported (10,3)-a topological structures are interpenetrating nets [14]. Li et al. reported a non-interpenetrating (10,3)-a net by using bulky auxiliary triphenylphosphine ligand to avoid possible interpenetration [18]. Complex **3** provides an example of non-interpenetrated (10,3)-a topological net without bulky auxiliary ligand.

3.3. Crystal structure of complexes **4** and **5**

It is interesting to note that in contrast to the 3D structure of **3** with ClO_4^- anion, complex **4** with CF_3SO_3^- and **5** with PF_6^- have similar 2D network structure. The coordination environment of Ag(I) atoms in **4** is shown in Fig. 3a with atom-numbering scheme.

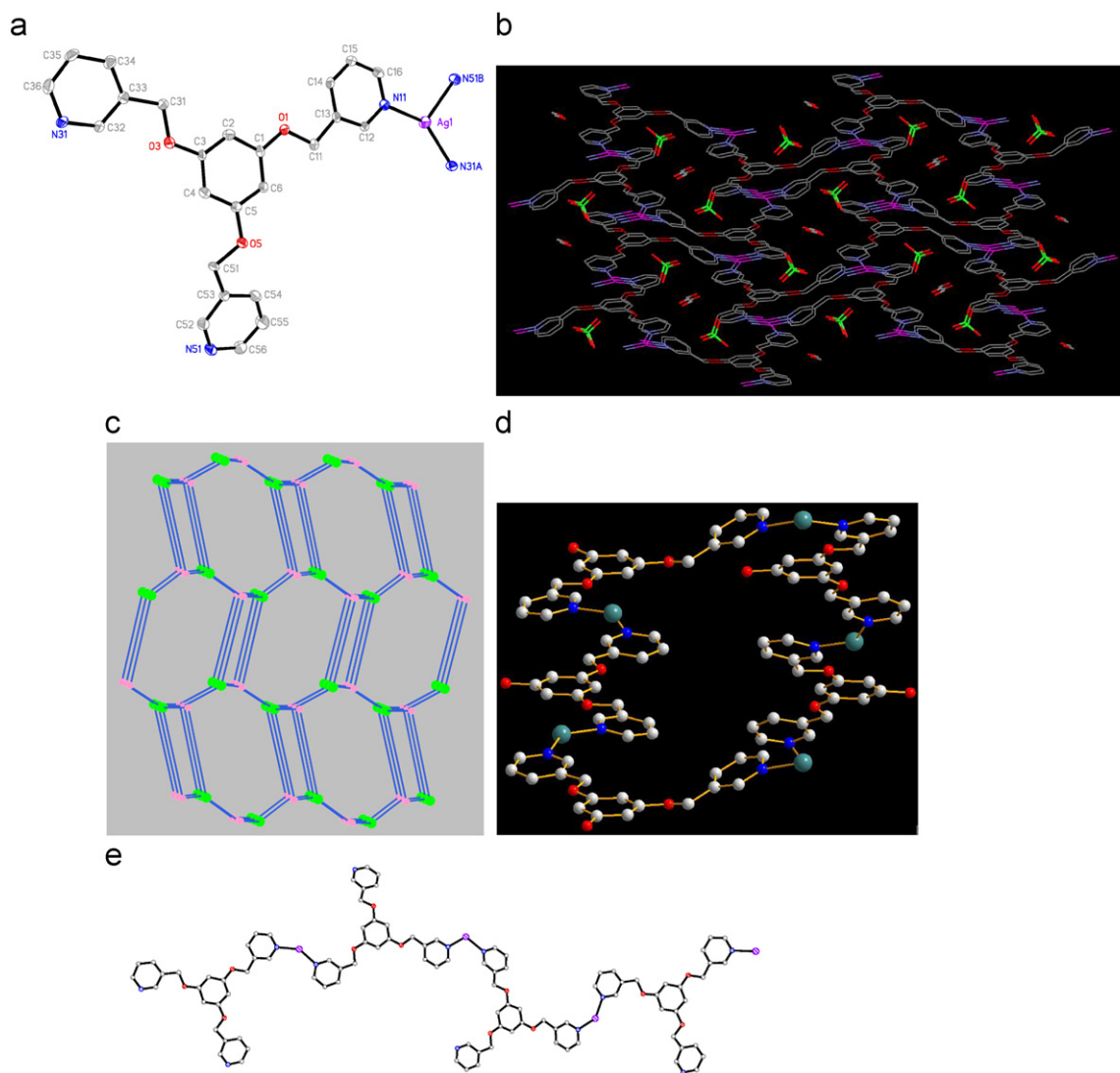


Fig. 2. (a) The coordination environment around the Ag(I) atom in **3** with the ellipsoids drawn at 50% probability level, the ClO_4^- , CH_3OH molecule and hydrogen atoms are omitted for clarity. (b) 3D structure of complex **3**. (c) Simplified (10,3)-a topology of **3**, the small balls (pink) represent the centroids of the central benzene ring of L_3 , the large ones (green) represent Ag(I) atoms. (d) A M_3L_3 macrocyclic ring in **3**. (e) Side view of the helix in **3** (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

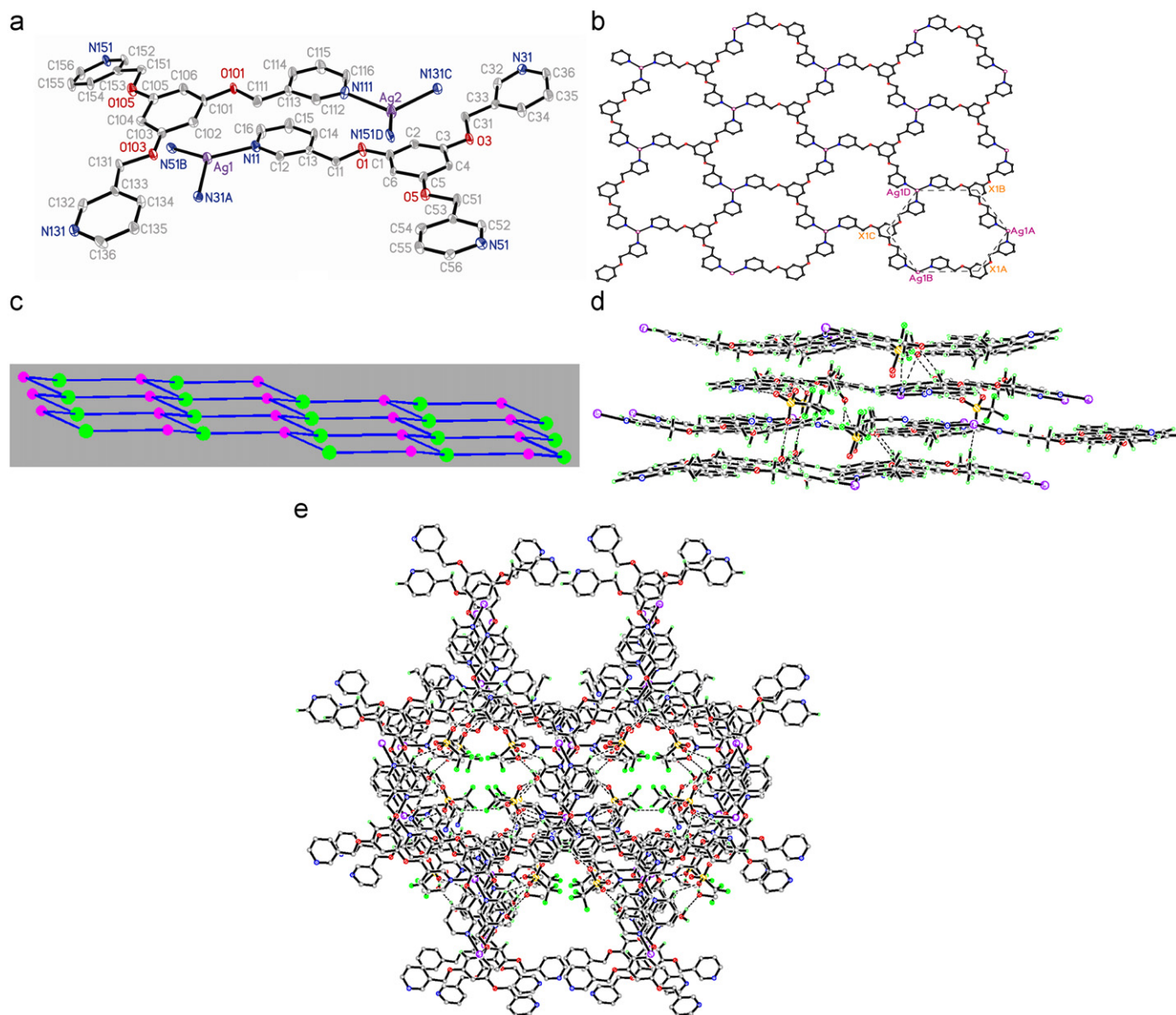
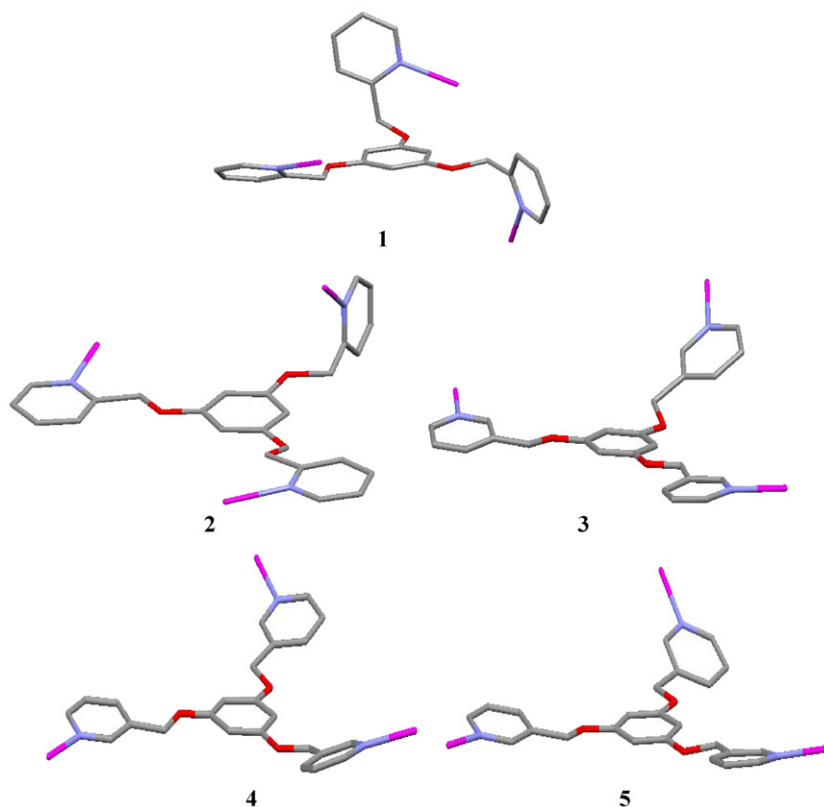


Fig. 3. (a) The coordination environment around the Ag(I) atoms in **4** with the ellipsoids drawn at 50% probability level, the CF_3SO_3^- anion, CH_3CN , CH_3OH , water molecules and hydrogen atoms are omitted for clarity. (b) 2D network of **4** with Ag1 atoms. (c) Simplified (6,3) 2D network structure of **4**, the small balls (pink) represent the centroids of the central benzene ring of L_3 , the large ones (green) represent Ag(I) atoms. Side (d) and top (e) views of crystal-packing diagram of **4**, hydrogen bonds are indicated by dashed lines (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

There are two crystallographically independent cationic units each with one Ag(I) atom and one L_3 ligand. Each Ag(I) atom acts as a three-connected node and is coordinated by three nitrogen atoms from three individual L_3 ligands. On the other hand, each L_3 serves as a three-connector coordinating to three Ag(I) atoms. Each ligand L_3 using two of its three pyridyl groups connects two Ag(I) atoms to form a 42-membered $\text{M}_3(\text{L}_3)_3$ macrometallo-cyclic ring through Ag–N coordination bonds. The remarkable structural feature of complex **4** is that the $\text{M}_3(\text{L}_3)_3$ macrocyclic motifs extend to form a 2D network with (6,3) topology which can be clearly seen from Fig. 3b and c with centroid of benzene ring–Ag(I) separations of 9.35 (Ag1D \cdots X1C=Ag1A \cdots X1A), 9.29 (X1B \cdots Ag1D=X1A \cdots Ag1B), 9.34 Å (Ag1A \cdots X1B=Ag1B \cdots X1C) (Fig. 3b showing the Ag1– L_3 layer), while the corresponding ones in Ag2– L_3 network are 9.36, 9.28, 9.33 Å, respectively. It should be noticed that the CF_3SO_3^- anion did not coordinate to the Ag(I) atom in **4**, which is different from that in **2**.

Fig. 3d and e shows the crystal-packing diagrams of complex **4**. It can be seen that there are open channels occupied by CF_3SO_3^- anions and solvent molecules. The CF_3SO_3^- anions link two 2D layers together through the C–H \cdots O hydrogen bonds. There are O–H \cdots O hydrogen bonds between the methanol and water molecules and also between the water molecule and the CF_3SO_3^- anion (Table 3, Fig. 3d). In addition, there are π – π interactions between two pyridine ring planes of adjacent layers with a centroid-to-centroid separation of 3.97 Å and a dihedral angle of 2.7°, and between the pyridine ring and benzene ring with a centroid-to-centroid distance of 3.65 Å and a dihedral angle of 16.9°. Therefore, the hydrogen bonding and π – π interactions play important role in the stabilizing the structure of complex **4**.

The asymmetric unit of complex **5** contains one L_3 ligand, one Ag(I), one PF_6^- and two CH_3CN molecules. In the cationic part of **5**, each Ag(I) links three L_3 ligands and each L_3 ligand in turn



Scheme 2. Typical conformations of ligands in complexes **1–5** (only one of two similar conformations is shown for **1** and **4**).

Table 4
Conformational parameters for complexes **1–5**.

Complex	$\varphi 1$ (deg.) ^a	$\varphi 1$ (deg.)	$\varphi 1$ (deg.)	$\varphi 2$ (deg.) ^b	$\varphi 2$ (deg.)	$\varphi 2$ (deg.)
1	33.5	77.9	86.6	9.4	6.7	73.1
1	28.7	78.9	86.1	8.3	6.8	73.8
2	2.5	94.8	2.5	0.3	12.3	9.6
3	6.0	7.9	24.5	2.2	1.7	30.4
4	4.3	19.8	13.8	12.8	14.9	2.0
4	5.5	18.6	6.4	3.3	14.5	5.1
5	21.8	10.0	6.3	5.8	9.0	5.8

^a $\varphi 1$ refers to the dihedral angle between the pyridyl ring and central benzene ring planes.

^b $\varphi 2$ refers to the torsion angle defined by C1–O–C2–C3, where C1, C2 and C3 are labeled in Scheme 1.

connects three Ag(I) atoms to give 2D network structure with (6,3) topology (Fig. S2), which is similar to that in **4**. The 2D layers repeat in an ...ABAB... stacking sequence with open channels occupied by PF_6^- anions, which link the framework through C16–H9...F2 hydrogen bond together with π – π interactions to form 3D framework structure of **5** (Fig. S2).

3.4. Comparison of the structures

Complexes **1** and **2** with L_2 ligand show similar 2D network structure with the same 4.8^2 topology, indicating that the counteranions are not relevant to the framework structure of the complexes. However, in the case of complexes with L_3 ligand, **3** with perchlorate anion has 3D structure with (10,3)-a topology while **4** with CF_3SO_3^- and **5** with PF_6^- are 2D networks with (6,3)

topology. The results imply that the counteranions are subtle in the assembly of metal complexes. The difference between **1–2** and **3–5** are apparently caused by the different structure of ligands L_2 and L_3 .

It is noteworthy that the connection modes of Ag(I) and ligands are the same in complexes **1–5**, namely each Ag(I) coordinates with three ligands and each ligand connects three Ag(I) atoms, however, the flexible ligands L_2 and L_3 show different conformations in these complexes as illustrated in Scheme 2. To elucidate the conformation of each ligand, dihedral angles between the pyridyl ring and central benzene ring plane ($\varphi 1$) and the torsion angles of C1–O–C2–C3 ($\varphi 2$) as labeled in Scheme 1 are defined and the calculated values are listed in Table 4. A value of $\varphi 1$ close to zero or 180° implies that the pyridyl ring is close to parallel with the central benzene ring plane, and a near 90° value of $\varphi 1$ indicates the near perpendicular relationship between the pyridyl ring and the central benzene ring. On the other hand, when the value of $\varphi 2$ is close to zero or 180° , it means that the flexible arm is extended to the central benzene ring plane, otherwise, when the value of $\varphi 2$ is close to 90° , the arm locates above or below the central benzene ring plane [14]. According to the $\varphi 1$ and $\varphi 2$ values listed in Table 4, it is clear that the flexible ligands L_2 and L_3 adopt different conformations in complexes **1–5** (Scheme 2). In **1** the Ag(I) is three-coordinated, while in **2** the Ag(I) is four-coordinated and the ligand L_2 has different conformation from that in **1**. The results show that the flexible ligand can adjust its conformation to meet the geometric requirement of the metal ion. In the case of complexes **3–5**, all the small values of $\varphi 1$ and $\varphi 2$ of ligand L_3 indicate that the ligands in these complexes have extended conformation, however, their subtle difference in conformation is responsible for the formation of 3D structure of **3** and 2D network structures of **4** and **5**.

3.5. Luminescence properties of the complexes

The inorganic–organic hybrid coordination polymers with d^{10} metal have been investigated for photoluminescence properties and potential applications as light-emitting diodes [20]. The photoluminescent properties of complexes **1–5** were studied in the solid state at room temperature. The emission spectra of **1–5** under the same excitation wavelength of 352 nm are shown in Fig. 4. Ligands L_2 and L_3 showed broad emission around 425 and 420 nm under the same excitation wavelength, respectively [8]. The maximum emission wavelengths of complexes **1** and **2** are 428 and 422 nm, respectively, which are close to that of ligand L_2 . While the emissions observed in complexes **3, 4, 5** are at 390, 410, 394 nm with 10–30 nm blue-shifts compared with that of ligand L_3 . The emissions observed in the complexes **1–5** may be tentatively assigned to the $\pi-\pi^*$ intraligand photoluminescence due to their resemblance of the emission bands as discussed previously, and the observed shifts of the emission maximum between the Ag(I) complexes and the corresponding ligand are considered to mainly originate from the coordination interactions between the metal atoms and the ligands [8,21–25]. In addition, in contrast to the weak or unobservable luminescence of silver(I) complexes at room temperature [7a], complexes **1–5** show

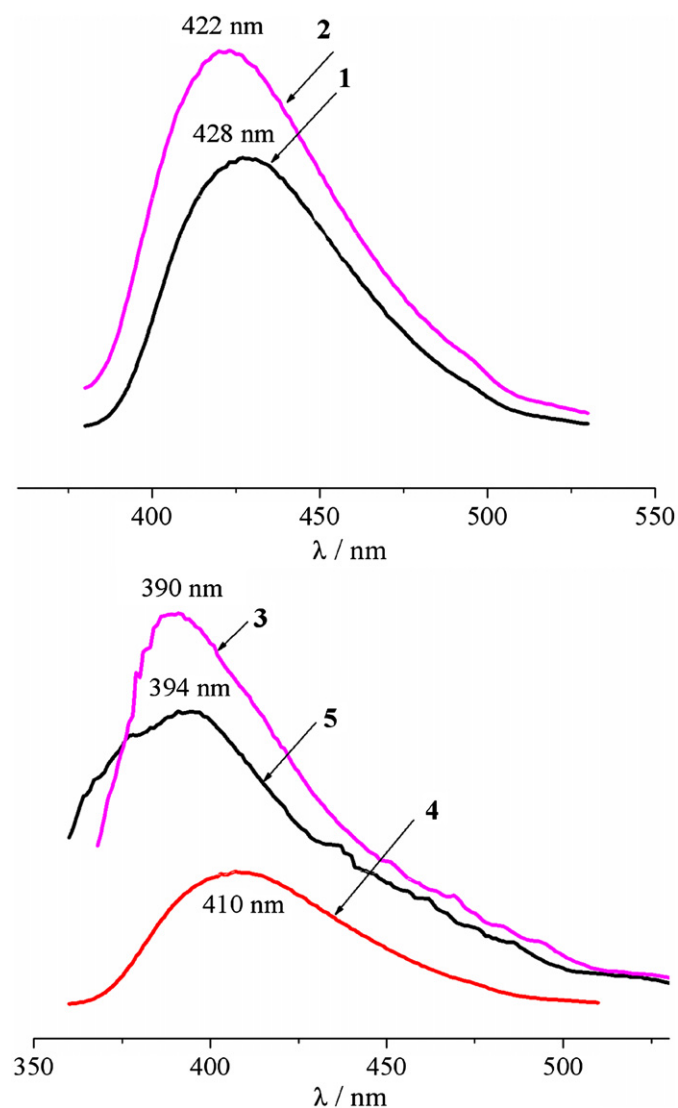


Fig. 4. Photoluminescent emission spectra of complexes **1–5** in the solid state.

apparent photoluminescence at ambient temperature implying that they may be good candidates for potential photoactive material.

3.6. Anion-exchange properties of complexes **3** and **5**

As revealed by the crystal structure analysis of the complexes, the anions locate within the channels of framework and held there through hydrogen bonding interactions except for complex **2** where the $CF_3SO_3^-$ anions coordinate to the Ag(I) atoms. The complexes are insoluble in water, and the anion-exchange properties of **3** with 3D structure and **5** with 2D layer structure were investigated. The FT-IR spectra of the exchanged solid **3A** and the as-synthesized **3** are shown in Fig. 5a and b, respectively. Intense band at 1384 cm^{-1} appeared, which is from the NO_3^- vibration, while the intense bands from 1120 to 1091 cm^{-1} of the ClO_4^- anion disappeared in the spectrum of **3A** (Fig. 5b). Furthermore, the results of elemental analysis of the anion exchanged product **3A** (see experimental section) also suggest the complete anion exchange.

To investigate the reversibility of this anion-exchange process, the excess $NaClO_4$ was added to the suspension mixture of the **3A**

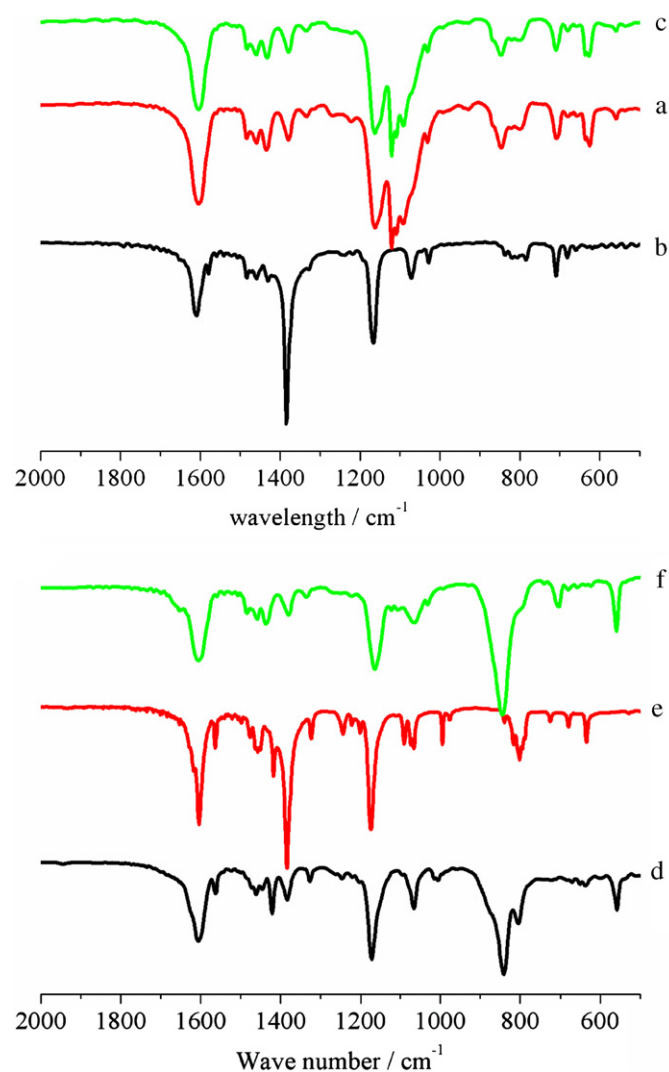


Fig. 5. FT-IR spectra of (a) complex **3**, (b) complex **3A**, (c) complex **3B**. FT-IR spectra of (d) complex **5**, (e) complex **5A**, (f) complex **5B**.

in water and the FT-IR spectrum of the exchanged solid **3B** shows that the intense band of NO_3^- disappeared while the intense bands of ClO_4^- appeared (Fig. 5c), implying the complete anion exchange, which is also supported by the results of elemental analysis. The results indicate that complex **3** has reversible anion-exchange property.

The anions exchange properties of complex **5** are also explored. The IR spectral (Fig. 5d–f) and elemental data reveal that the PF_6^- anions in complex **5** can be exchanged reversibly by NO_3^- .

The results indicate that the anions hydrogen bonded to the 3D framework in **3** and to the 2D network in **5** can be exchanged reversibly as previously reported for the 2D and 3D frameworks with imidazole-containing ligands [7f,7g,26]. It is worthy to note that such anion exchange is also an anion recognition process as reported for the complex $[\text{Zn}(\text{bib})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ [bib = 1-bromo-3,5-bis(imidazol-1-ylmethyl)benzene] [26a]. The anion exchanges occurred reversibly between NO_3^- and ClO_4^- in **3** and between NO_3^- and PF_6^- in **5** indicate that the vacancies in the frameworks **3** and **5** are large enough to allow the anions exchanged reversibly in these complexes.

4. Conclusions

Flexible tripodal ligands with 2- and 3-pyridyl groups were used to react with different Ag(I) salts and complexes with 2D and 3D structures and (4,8²), (10,3)-a and (6,3) topologies were obtained. The results show that the flexible ligand can have different conformation to meet geometric requirement of metal atom. The present study further suggests that the ligands as well as the counteranions have subtle but important influence on the structure of the complexes.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2010.07.036.

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