

溶剂对柔性配体 1,3,5-三(三氮唑-1-甲基)-2,4,6-三甲苯的银配合物的影响

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摘要: 通过在不同溶剂中硝酸银与 1,3,5-三(1,2,4-三氮唑-1-甲基)-2,4,6-三甲苯(ttmb)的反应,合成了 2 种新型的银配合物: $[\text{Ag}(\text{ttmb})(\text{H}_2\text{O})\text{NO}_3]_n$ (**1**)、 $[\text{Ag}(\text{ttmb})\text{NO}_3 \cdot \text{H}_2\text{O}]_n$ (**2**)。研究了室温条件下,2 个配合物与相关 ttmb 配体的固态荧光性质。通过元素分析、粉末和单晶 X 射线衍射分析、红外光谱分析等对其结构进行表征,结果表明化合物 **1** 包含一个高度起伏的二维网状结构,化合物 **2** 具有一个二维的(6,3)网状结构。

关键词: 晶体结构; 银配合物; 三氮唑配体; 配位聚合物

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Influence of Solvents on the Formation of Silver(I) Complexes with the Flexible 1,3,5-Tris(triazol-1-ylmethyl)-2,4,6-trimethylbenzene

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Abstract: Two novel silver complexes $[\text{Ag}(\text{ttmb})(\text{H}_2\text{O})\text{NO}_3]_n$ (**1**) and $[\text{Ag}(\text{ttmb})\text{NO}_3 \cdot \text{H}_2\text{O}]_n$ (**2**) were synthesized by the reaction of AgNO_3 with 1,3,5-tri(1,2,4-triazol-1-ylmethyl)-2,4,6-trimethylbenzene (ttmb) in different solvents. The solid-state fluorescent properties of these two complexes and related ligand ttmb were then investigated at room temperature. Structural characterizations by elemental analysis, powder and single-crystal X-ray diffraction analysis and infrared spectra shows that complex **1** contains a highly undulated 2D network while complex **2** carries a 2D (6,3) network. CCDC: 878517, **1**; 878518, **2**.

Keywords: crystal structure; silver complex; triazole ligand; coordination polymers

0 Introduction

In recent years, metal-organic frameworks (MOFs) have been rapidly developed and subjected to great attention, not only for their fantastic structures-cage, honeycomb, grid, ladder, multidimensional framework,

polyrotaxane and polycatenane^[1-5], but also for their potential applications to functional materials in magnetism, catalysis and gaseous storage, ionic/molecular recognition, ion-exchange and selective guest inclusion^[6-11]. Tripodal ligands with arene core have been found to be one of the most useful organic

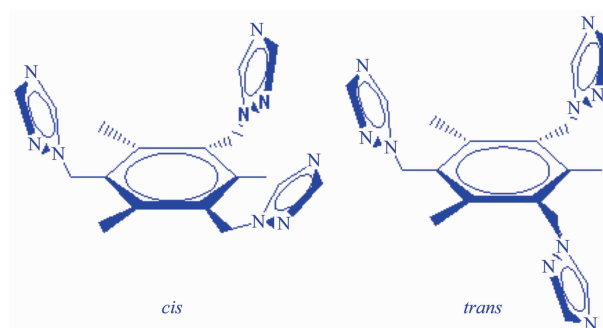
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building blocks for constructing novel coordination frameworks^[12-17]. Complexes with specific structures and interesting properties have been obtained by reactions of suitable metal salts with rigid exo-tridentate ligands, such as 2,4,6-tris(4-pyridyl)-1,3,5-triazine^[18-20], 1,3,5-tricyanobenzene^[21-22] and 1,3,5-benzenetribenzoate^[23-24]. Among them, the rigid ligands have minimal conformational changes upon reacting with metal salts^[25]. Based on the variable geometric requirements by the metal ions, flexible ligands can adopt a number of conformations and coordination modes, which may offer MOFs with unique structures and useful properties^[26]. To further investigate the nature of flexible ligands and their coordination polymers, a triazolyl group containing, not the reported pyridyl and imidazol groups, namely 1,3,5-tris(triazol-1-ylmethyl)-2,4,6-trimethylbenzene (ttmb, Scheme 1), was synthesized. Due to the presence of methylene group between the triazole and benzene ring groups, ttmb is considered as a flexible divergent ligand exhibiting the *cis*- and *trans*-configurations.

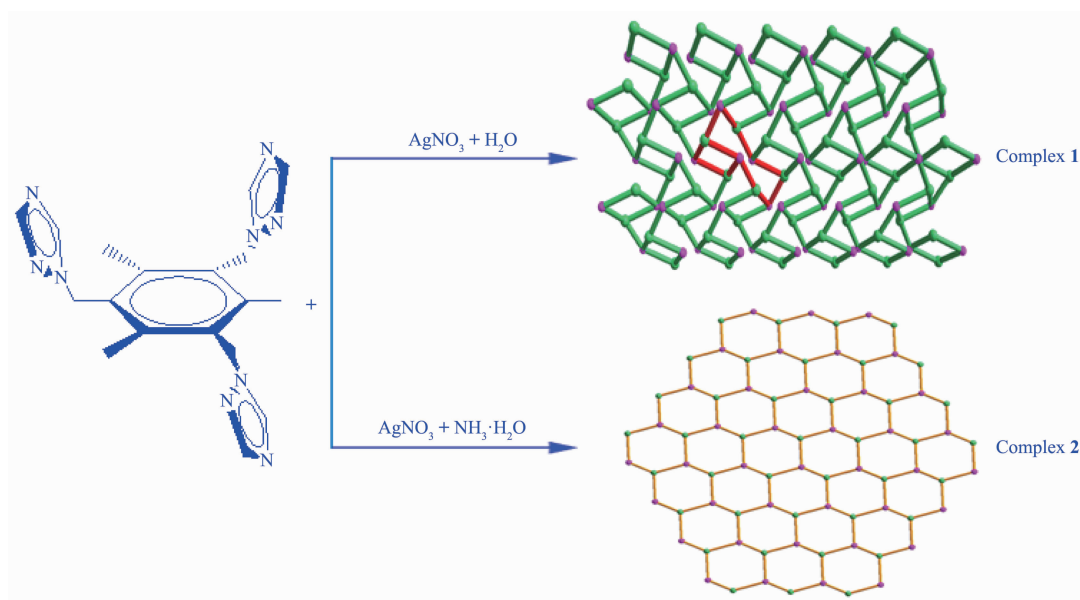
As well known, it is very important to control the reaction conditions using flexible ligands during the synthesis of the resulted complexes, such as the counter anions, the ratio of ligand to metal ion, temperature^[27-30], because there is a methylene group



Scheme 1 *Cis*- and *trans*-conformations of the flexible tripodal ligand ttmb

between the central benzene ring and terminal triazol group which may change configuration depending on solvents and counter ions. Hence, systematic studies on the relationship between MOF structure and reaction solvents is crucial in understanding MOFs and exploring their applications.

In the present work, two new polymers $\{[Ag(ttmb)(H_2O)]NO_3\}_n$ (**1**) and $\{[Ag(ttmb)]NO_3 \cdot H_2O\}_n$ (**2**) were assembled from flexible tripodal 1,3,5-tris(triazol-1-ylmethyl)-2,4,6-trimethylbenzene (ttmb) and silver nitrate under different conditions. Solvent significantly influences the structures of the coordination polymers (Scheme 2). As a whole, the synthesis, crystal structures as well as fluorescence properties of the two polymers are reported.



Red and green balls are metal ions and ligands, respectively

Scheme 2 Solvent control in the synthesis of coordination polymers **1** and **2**

1 Experimental

All chemicals were of reagent-grade quality, obtained from commercial sources, and used as received without further purification. Solvents were purified by standard methods prior to usage. 1,3,5-tris-(bromomethyl)-2,4,6-trimethylbenzene was synthesized according to the reported procedures^[28]. Elemental analyses were determined using a Vario EL III elemental analyzer. The IR spectra were recorded in the 400~4 000 cm^{-1} region using KBr pellets and a Nicolet AVATAR-370 spectrometer. Excitation and emission spectra were recorded on a Shimadzu F-4500 fluorescence spectrophotometer using slit width of 3.0 nm both for excitation and emission at room temperature for the solid samples. Thermogravimetric (TG) analysis data were collected on a Netzsch STA-409PC under air in the temperature range from 20 to 800 $^{\circ}\text{C}$ with a heating rate of 10 $^{\circ}\text{C}\cdot\text{min}^{-1}$. Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku D/max-2550 X-ray diffractometer with graphite mono-chromatic $\text{Cu } K\alpha$ ($\lambda=0.154\,056\text{ nm}$) radiation at 40 kV and 250 mA and 2θ ranging from 5° to 60° at room temperature.

1.1 Synthesis of $\{[\text{Ag}(\text{L})(\text{H}_2\text{O})]\text{NO}_3\}_n$ (1)

An aqueous solution (5 mL) of AgNO_3 (17.0 mg, 0.1 mmol) was added slowly to a solution of ttmb (36.3 mg, 0.1 mmol) in methanol (10 mL) to give a clear solution. It was stirred for 10 min at room temperature. Colorless block crystals for X-ray diffraction were obtained upon slow evaporation of the solvent after two weeks. Yield: 43% based on Ag. Anal. Calcd. for $\text{C}_{18}\text{H}_{23}\text{AgN}_{10}\text{O}_4(\%)$: C 39.21; H 4.20; N 25.40. Found (%): C 39.42; H 4.23; N 25.32. IR (KBr pellet, cm^{-1}):

3 451br, 3 110m, 1 517s, 1 383s, 1 274s, 1 202w, 1 135s, 1 011s, 987w, 676s, 643m.

1.2 Synthesis of $\{[\text{Ag}(\text{L})]\text{NO}_3\cdot\text{H}_2\text{O}\}_n$ (2)

An aqueous solution of ammonia (0.5 $\text{mmol}\cdot\text{mL}^{-1}$, 2 mL) was dropped to a stirred aqueous solution (5 mL) of AgNO_3 (17.0 mg, 0.1 mmol). The resulting solution was continuously stirred for 30 min and then a solution of ttmb (36.3 mg, 0.1 mmol) in methanol (10 mL) was added. Well-shaped colorless block crystals were obtained by slow evaporation at room temperature for one week. They were collected by filtration, washed with a small amount of distilled water and dried in air. Yield: 57% based on Ag. Anal. Calcd. for $\text{C}_{18}\text{H}_{23}\text{AgN}_{10}\text{O}_4(\%)$: C 39.21; H 4.20; N 25.40. Found(%): C 39.05; H 4.55; N 25.23. IR (KBr pellet, cm^{-1}): 3 448br, 3 111m, 1 514s, 1 363s, 1 335s, 1 274s, 1 208m, 1 137s, 1 009s, 979w, 675s, 643m.

1.3 X-ray structure determination

Single crystal diffraction data for complexes **1** and **2** were collected on a Bruker Smart Apex-II CCD diffractometer with graphite monochromatic $\text{Mo } K\alpha$ radiation ($\lambda=0.071\,073\text{ nm}$) at 296(2) K. Empirical absorption corrections were performed using SADABS program^[31]. The structures were extracted by a direct method with SHELXS-97 program^[32] and refined by full-matrix least squares on F^2 with SHELXL-97 program^[33]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed geometrically. Molecular graphics were drawn by using XP, and Diamond software. The crystal data and refinement results are given in Table 1. The selected bond distances and angles are listed in Table 2.

CCDC: 878517, **1**; 878518, **2**.

Table 1 Crystallographic data for complexes **1** and **2**

Complex	1	2
Empirical formula	$\text{C}_{18}\text{H}_{23}\text{AgN}_{10}\text{O}_4$	$\text{C}_{18}\text{H}_{25}\text{AgN}_{10}\text{O}_5$
Formula weight	551.32	551.32
Crystal size / mm	0.32×0.20×0.20	0.30×0.30×0.21
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a / nm	1.172 9(2)	0.892 95(19)
b / nm	1.258 7(2)	1.092 2(2)

Continued Table 1

c / nm	1.594 0(3)	1.245 7(4)
$\alpha / (^{\circ})$	90	107.055(4)
$\beta / (^{\circ})$	110.421(2)	102.727(4)
$\gamma / (^{\circ})$	90	102.461(3)
V / nm^3	2.205 3(7)	1.080 5(5)
Z	4	2
$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.658	1.695
μ / mm^{-1}	0.963	0.982
$F(000)$	1 116	560
R_{int}	0.015 9	0.019 4
GOF on F^2	1.047	1.076
$R_1 [I > 2\sigma(I)]$	0.066 7	0.071 7
wR_2	0.181 1	0.205 9
$(\Delta\rho)_{\text{max}}, (\Delta\rho)_{\text{min}} / (\text{e} \cdot \text{nm}^{-3})$	1 876, -991	1 747, -1 197

Table 2 Bond lengths (nm) and angles ($^{\circ}$) for 1 and 2

Complex 1					
Ag(1)-N(1)	0.219 1(5)	Ag(1)-N(7)#2	0.220 7(5)	Ag(1)-N(4)#1	0.247 5(7)
Ag(1)-O(4)	0.251 8(9)				
N(1)-Ag(1)-N(7)#2	151.6(2)	N(1)-Ag(1)-N(4)#1	105.6(3)	N(7)#2-Ag(1)-N(4)#1	95.0(2)
N(1)-Ag(1)-O(4)	101.4(2)	N(7)#2-Ag(1)-O(4)	87.0(2)	N(4)#1-Ag(1)-O(4)	115.0(4)
Complex 2					
Ag(1)-N(9)#1	0.220 2(6)	Ag(1)-N(1)	0.222 5(6)	Ag(1)-N(6)#2	0.236 9(6)
N(9)#1-Ag(1)-N(1)	144.8(2)	N(9)#1-Ag(1)-N(6)#2	109.4(2)	N(1)-Ag(1)-N(6)#2	104.7(2)

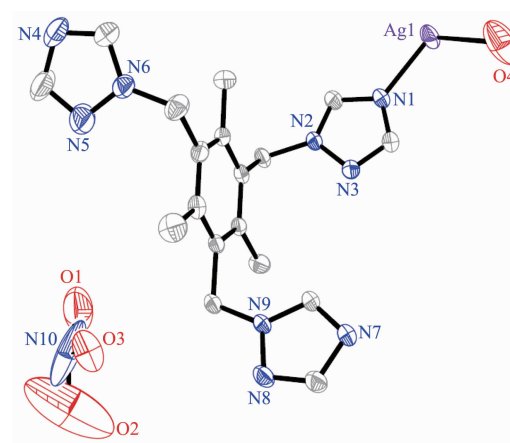
Symmetry codes: #1: $-x, -y, -z$; #2: $x-1/2, -y-1/2, z-1/2$; #3: $x+1/2, -y-1/2, z+1/2$ for **1**; #1: $x-1, y-1, z-1$; #2: $x, y, z-1$; #3: $x, y, z+1$; #4: $x+1, y+1, z+1$ for **2**.

2 Results and discussion

2.1 Crystal structure description

The crystal structure of complex **1** is shown in Fig.1 with the atom numbering scheme. Complex **1** crystallizes in the Monoclinic form with $P2_1/n$ space group. Each asymmetric unit of complex **1** contains one Ag(I) center, one ttmb, one water molecule and one nitrate anion. The silver(I) ion is coordinated by three nitrogen atoms from three individual ttmb ligands and one oxygen atom from a water molecule (Fig.1) to form tetrahedral environment. The Ag-N bond lengths are in the range of 0.219 1 (5)~0.247 5(7) nm, and Ag-O bond lengths are 0.251 8(9) nm, which are longer than the Ag-N distances. They are in conformity with those found in reported corresponding

silver complexes^[34]. Coordination geometry around Ag(I) in complex **1** can be judged as a distorted tetrahedron



Hydrogen atoms omitted for clarity

Fig.1 ORTEP drawing of complex **1** with 30% thermal ellipsoids probability

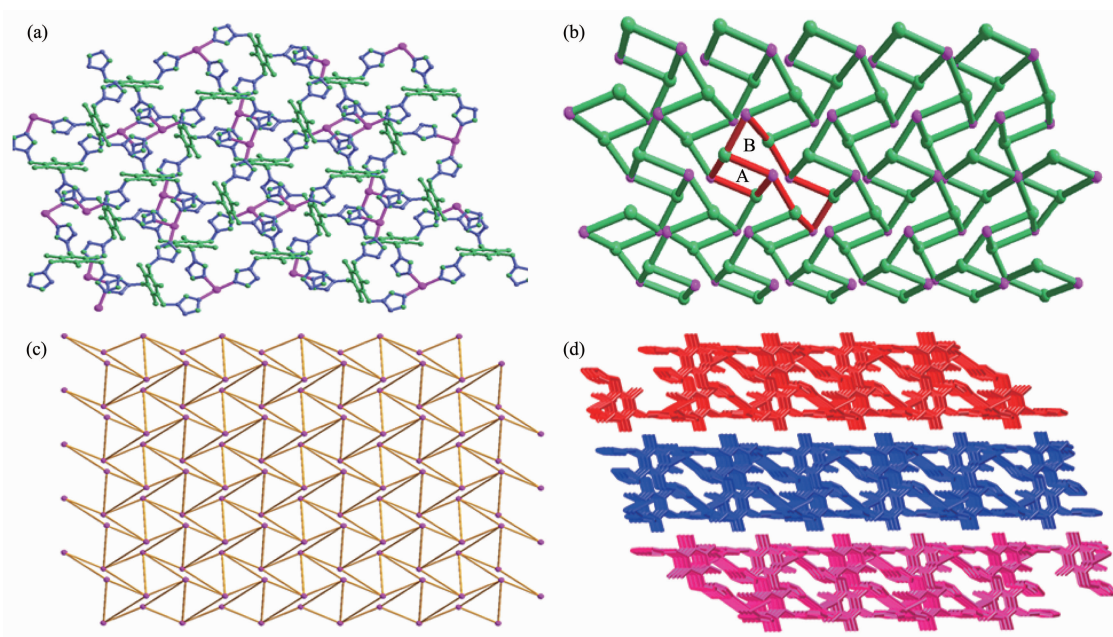


Fig.2 (a) 2D network of **1**; (b) Simplified structure of the 2D network; (c) Two-dimensional sheet consisting of the four-membered and three membered rings where only the silver(I) atoms are present; (d) Crystal packing diagram viewed from the *b*-axis

with a N_3O donor set.

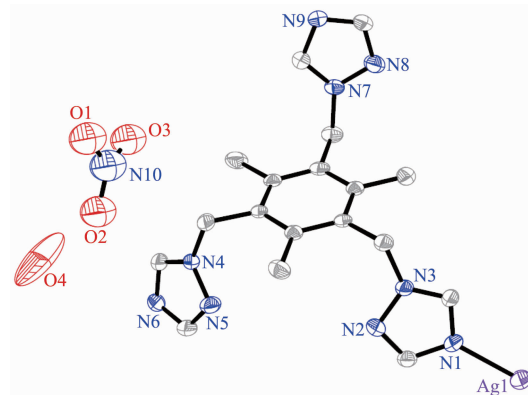
Each ttmb shows trans-conformation as tri-monodentate linking three different silver(I) atoms. The distances between the N1, N4, N7 atoms and the central benzene ring plane are 0.301, 0.294 and 0.350 nm, respectively. The dihedral angles between each triazole group and the central benzene ring plane are 78.33° , 79.35° and 82.20° , respectively. Three ligands link three Ag(I) ions using their three flexible arms to generate an infinite 2D undulated network^[35] (Fig.2a).

The combination of the flexible ttmb ligands and four-coordinated Ag(I) ions leads to the formation of a 2D network with two different macrocycles as illustrated in Fig.2b. In macrocyclic ring A, two ttmb ligands, each using two of its three flexible arms, link two Ag(I) ions to form a 24-membered ring with a $\text{Ag} \cdots \text{Ag}$ distance of 1.192 nm, while in ring B, four ttmb ligands are connected by four Ag(I) ions to generate a 48-membered ring with intermetallic separations of $d_{\text{Ag} \cdots \text{Ag}} = 2.224, 0.689$ nm.

The crystal packing diagram of **1** is displayed in Fig.2d. The 2D networks are further linked together via the interlayer $\text{C}-\text{H} \cdots \text{O}$ (nitrate anion) hydrogen bonds and $\pi-\pi$ stacking interactions to generate a 3D framework; the uncoordinated nitrate anions and

coordinated water molecules are located in the voids between the two adjacent layers.

The coordination environment around the Ag(I) ion in complex **2** was shown in Fig.3. The X-ray crystallographic analysis indicates that complex **2** crystallizes in the triclinic form with $P\bar{1}$ space group. Complex **2** consists of one Ag(I) center, one ttmb, one nitrate anion and two uncoordinated water molecules. The Ag(I) ion is surrounded by three tridentate bridging ligands, coordinated with three N atoms (N1, N6 and N9) from three different ligands with a N-Ag-N bond angle ranging from $104.7(2)^\circ$ to $144.8(2)^\circ$ and Ag-N



Hydrogen atoms omitted for clarity

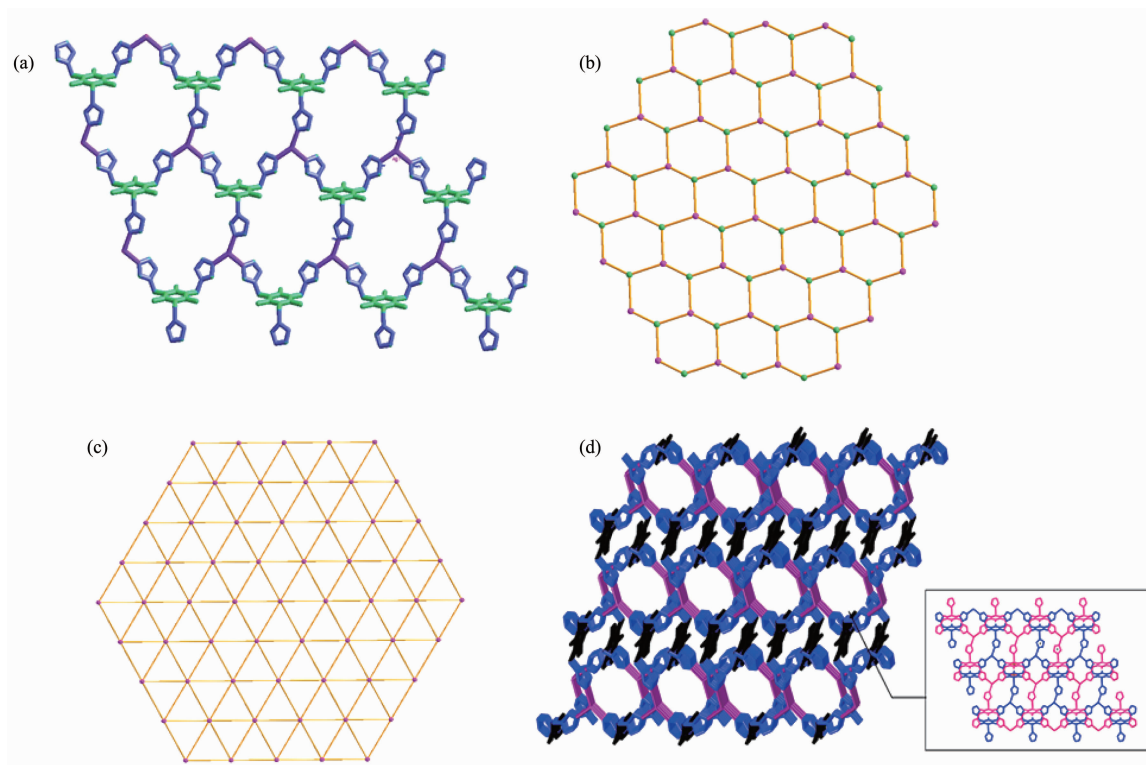
Fig.3 ORTEP drawing of complex **2** with 30% thermal ellipsoids probability

bond distance ranging from 0.220 2(6) to 0.236 9(6) nm, respectively, which is comparable with those of the reported Ag(I) complexes^[36]. The complex displays a distorted planar triangle geometry around the Ag centre (Table 1) with a N₃ donor set(N3, N6 and N9).

Ligands in complex **2** adopt a *cis*-, *trans*-, *trans*-conformation and act as a tridentate linker using its three triazole groups to coordinate with three Ag(I) ions (Fig.3). The two triazole groups within each ttmb are located in the same side and inclined to the central benzene ring plane with dihedral angles of 10.93°, 44.89°, and 72.98°, respectively, and the distances between the coordinated N atoms and central benzene ring plane are 0.422, 0.452, and 0.568 nm, respectively. The polymeric structure of complex **2**, generated by such coordination mode and conformation of ligand, is an infinite two-dimensional (2D) stepwise layered network as shown in Fig.4a. Then, a schematic drawing is shown in Fig.4b^[37]. Fig. 4c shows the two dimensional sheet where only the

Ag(I) ions are presented. This is a (6,3) sheet-like network consisting of the Ag₃ unit where the distance between two adjacent Ag(I) ions are 0.892, 1.192 and 1.384 nm, respectively. These 2D layers are further linked by partial π - π stacking interactions involving the triazol rings to generate a 3D honeycomb network structure in Fig.4d.

Although the complexes **1** and **2** were synthesized by the reaction of AgNO₃ with ttmb, the structures are actually influenced by the solvent. When the reactant AgNO₃ was only resolved in H₂O, we obtained complex {[Ag(ttmb)(H₂O)]NO₃}_n (**1**), in which the Ag(I) adopts a distorted tetrahedron geometry with a N₃O donor set and the coordinated O is from solvent water. When NH₃·H₂O was added to the aqueous solution of AgNO₃, we obtained complex {[Ag(ttmb)]NO₃·H₂O}_n (**2**), in which the Ag(I) results in a planar triangle geometry with a N₃ donor set and the uncoordinated solvent water. So, it suggests that since the coordination ability of NH₃ is stronger than H₂O, when NH₃ was



Nitrate anions and water molecules were omitted for clarity in (a); Red and green balls are metal ion and ligands in (b), respectively

Fig.4 (a) View of the stepwise 2D layered network of **2** in which the; (b) Simplified structure of the 2D coordination polymer; (c) Two-dimensional sheet consisting of the three membered rings where only the silver(I) atoms are presented; (d) 3D honeycomb network structure by partial π - π stacking interactions involving the triazol rings

added to AgNO_3 , NH_3 occupies the coordination site prior to H_2O to form $[\text{Ag}(\text{NH}_3)_2]^+$ firstly, then the N atom of the added ligand ttmb coordinated to $\text{Ag}(\text{I})$ replaces NH_3 . As a consequence, the solvent water is unable to coordinate to $\text{Ag}(\text{I})$, leading to more crystalline water in complex **2** than that in **1**.

Overall, it can be concluded that the structure of the complexes are related to the reaction condition and that the solvent plays an important role. The structural difference of the two complexes may lead to the different properties associated with the complexes, as described below.

2.2 PXRD, IR, thermal analysis and fluorescent spectra

In order to confirm the phase purity of the bulk materials, PXRD was carried out for complexes **1** and **2**. The diffraction peaks of simulated (Sim.) and experimental (Exp.) match well in peak positions, indicating that the phase purities of the complexes **1** and **2** are good (Fig.5). The difference in reflection intensities between Sim. and Exp. is due to the different orientation of the crystals in the powder samples.

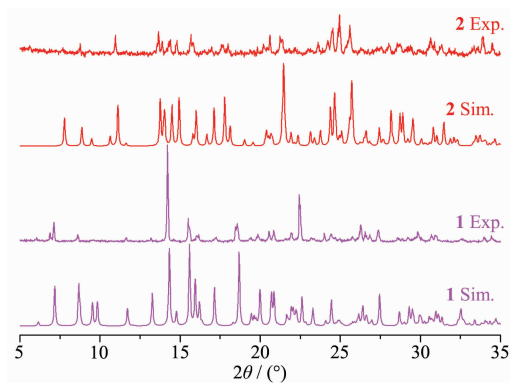


Fig.5 PXRD simulated and experimental patterns for complexes **1** and **2**

The IR spectra of the free ligand ttmb and complexes **1** and **2** are shown in Fig.6. Compared with free ttmb, the strong absorption band of the triazole ring at $1\,507\text{ cm}^{-1}$ is shifted to $1\,520$ and $1\,510\text{ cm}^{-1}$ in complexes **1** and **2**, respectively. The $1\,275\text{ cm}^{-1}$ absorption band in ttmb is red-shifted slightly ($1\,270\text{ cm}^{-1}$ in **1** and **2**, Fig.6). The absorption band for the free NO_3^- anion is both observed at $1\,380\text{ cm}^{-1}$ in

complexes **1** and **2**. The IR data of the complexes agree with their crystal structures.

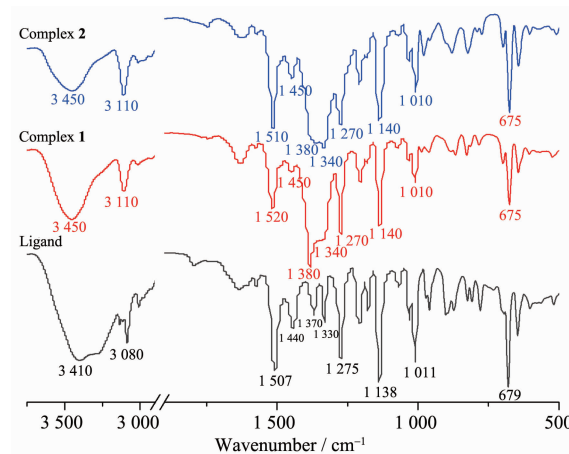


Fig.6 IR spectra of free ttmb ligand and complexes **1** and **2**

The thermal stabilities of **1** and **2** were investigated by thermogravimetric analysis (Fig.7). The analysis shows that complex **1** is stable up to $149\text{ }^\circ\text{C}$, and subsequently loses one coordinated water molecules (Found 3.38% , Calcd. 3.26%) from 149 to $178\text{ }^\circ\text{C}$. The complex begins to decompose at $371\text{ }^\circ\text{C}$. Complex **2** loses one lattice water molecule (Found 3.53% , Calcd. 3.26%) from 26 to $93\text{ }^\circ\text{C}$. It suggests that complex **1** is more stable. This can be explained by the fact that the coordinated water and high compactness of the crystal lattice can stabilize complex **1**.

Organic-inorganic coordination polymers, especially those with d^{10} metal centers, have been investigated for their fluorescent properties and potential applications as fluorescent-emitting materials, such as

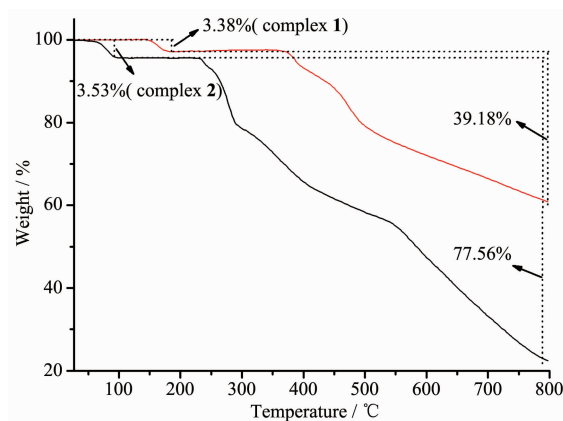


Fig.7 TG curves of complexes **1** and **2**

light-emitting diodes^[38]. Therefore, the emission spectra of complexes **1** and **2** and the free ligand in solid state at room temperature were investigated. Excitation at 360 nm leads to broad fluorescence signals with emission maxima at 388 and 428 nm for free ttmb ligand. Complex **1** and **2** exhibited emission peaks at 386 and 432 nm, 387 and 450 nm upon excitation at 360 nm, respectively (Fig.8). In contrast to that of the free ligand ttmb, the emission wavelengths of **1** and **2** are red-shifted by 4 and 22 nm, respectively. The spectrum shapes of **1** and **2** resemble the free ligand ttmb. Probably, the emission either complex **1** or complex **2** is mainly due to a ligand-centered emission-significant charge transfer character induced by the polar cation as reported for Hg(II) or other d^{10} metal complexes^[39-40] with N-donor ligands based on the position and shape of the emission bands. The difference of red-shifted wavelength can be explained by the fact that the extent of π - π conjugation in **2** is more dramatic than that in **1**.

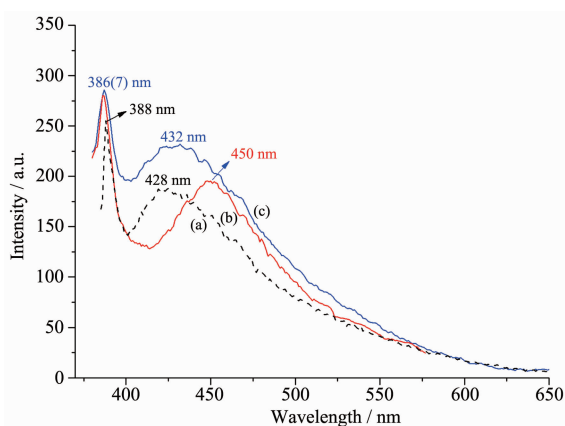


Fig.8 Fluorescence spectra of ligand (a), complex **1** (c), complex **2** (b) in solid state excited at 360 nm

3 Conclusions

The self-assembly reactions of ttmb with AgNO_3 yield two 2D network silver(I) coordination polymers $[\text{Ag}(\text{ttmb})(\text{H}_2\text{O})]\text{NO}_3$ (**1**) in $\text{CH}_3\text{OH}-\text{H}_2\text{O}$ and $[\text{Ag}(\text{ttmb})]\text{NO}_3 \cdot \text{H}_2\text{O}$ (**2**) in $\text{CH}_3\text{OH}-\text{NH}_3 \cdot \text{H}_2\text{O}$. Complex **1** contains a highly undulated 2D network with Ag(I) having a distorted tetrahedron geometry with a N_3O donor set and O is from the coordinated solvent H_2O . While **2** has a 2D (6,3) network where Ag(I) adopts a planar triangle geometry with a N_3 donor set, and

more crystalline water are present than in complex **1**. The structure and characterization of the two complexes are influenced by the reaction solvent. Both complexes **1** and **2** show ligand centered emissions but shifted to longer wavelength compared with free ligand. With less crystalline water molecules, the stability of framework of complex **1** is much higher than that of complex **2**. In short, two new MOFs clearly demonstrate the subtle interplay of ligand geometry, metal coordination preferences, and solvent control in the formation of framework materials. The structure-function relationships of such components are expected to further guide the synthetic methodologies.

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