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Two- and Three-dimensional Frameworks with (6,3) and (10,3)-a Topology from Self-assembly of Three-connecting Organic Ligands with Cadmium(II) and Silver(I) Salts

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Two- and Three-dimensional Frameworks with (6,3) and (10,3)-a Topology from Self-assembly of Three-connecting Organic Ligands with Cadmium(II) and Silver(I) Salts

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Assembly of three-connecting ligands 1,3,5-tris(1-imidazolyl)benzene (tib) and 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene (titmb) with cadmium(II) and silver(I) salts provide new metal-organic frameworks, $[Cd(tib)_2](NO_3)_2 \cdot 4H_2O$ (1), $[Ag(tib)(PPh_3)](CF_3SO_3)$ (2) and $[Ag(titmb)(PPh_3)](CF_3SO_3) \cdot 1.5H_2O$ (3) (PPh_3 = triphenylphosphine). Single-crystal X-ray diffraction studies reveal that complexes 1 and 3 are two-dimensional honeycomb networks, while complex 2 is a noninterpenetrated three-dimensional architecture with (10,3)-a topology. The results indicate that the nature (structure and flexibility) of the organic ligands and the bulky auxiliary ligand have great impact on the assembly and structure of metal-organic frameworks. The photoluminescent properties of the synthesized complexes were studied in the solid state at room temperature.

Keywords: Crystal structure; 2D network; (10,3)-a topology; Cadmium(II) complex; Ag(I) complex

INTRODUCTION

The construction of supramolecular architectures for developing new functional materials and molecular devices has attracted increasing attention in recent years [1–6]. Metal-organic frameworks with novel structures and interesting properties have been obtained by assembly reactions of three-connecting ligands with metal ions having definite coordination geometry [7–11]. For example, assembly of 2,4,6-tris(4-pyridyl)-1,3,5-triazine with $Pd(en)(NO_3)_2$ (en = ethylenediamine) generates an M_6L_4 cage-like complex that has interesting properties such as inclusion of guest molecules, promotion of stereoselective [2 + 2] photodimerization of olefins and stabilization of labile silanol oligomers [7], and reaction of 1,3,5-tricyanobenzene with CF_3SO_3Ag gives a two-dimensional (2D) honeycomb network with exchange properties of guest molecules [10,11]. However, the assembly process is complicated and can be influenced by factors such as solvents, auxiliary ligands, counter anions, etc. [12]. In our previous works, we synthesized several imidazole-containing ligands and obtained various metal-organic frameworks with specific topologies and properties [13–16]. For example, reactions of 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene (titmb, Scheme 1) with silver(I) salts afforded a series of M_3L_2 cage-like complexes, in which the silver(I) atom has two-coordinated linear geometry [14], while reactions of titmb with six-coordinated metal ions, e.g. Zn(II), Mn(II) and Cd(II), gave 2D network frameworks with honeycomb and stepwise structures [15,16]. In addition, 1,3,5-tris(1-imidazolyl)benzene (tib) was synthesized to elucidate the influence of the structure of organic ligands on the structure of assemblies and, most recently, 2D networks have been obtained by reactions of tib with metal salts, and the resulting frameworks show anion exchange properties [17,18].

In this paper we report three new coordination polymers, $[Cd(tib)_2](NO_3)_2 \cdot 4H_2O$ (**1**), $[Ag(tib)(PPh_3)](CF_3SO_3)$ (**2**) and $[Ag(titmb)(PPh_3)]$–$(CF_3SO_3) \cdot 1.5H_2O$ (**3**) (PPh_3 = triphenylphosphine), constructed from assembly of tib and titmb with the corresponding cadmium(II) and silver(I) salts. The impact of the metal atoms, structure of organic ligands and auxiliary ligands is discussed.

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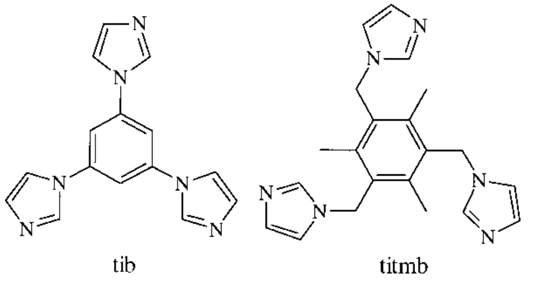

SCHEME 1 Tripodal ligands tib and titmb.

EXPERIMENTAL

The ligands titmb and tib were prepared according to the procedures reported previously [14,17,18]. All commercially available chemicals are reagent grade and used as received without further purification. Elemental analyses of C, H and N were taken on a Perkin-Elmer 240C elemental analyzer at the Center of Materials Analysis, Nanjing University. The luminescent spectra for the powdered solid samples were recorded at room temperature (25°C) on an Aminco Bowman Series 2 spectrofluorometer with a xenon arc lamp as the light source.

Preparation of [Cd(tib)$_2$](NO$_3$)$_2$·4H$_2$O (1)

The title complex was synthesized by the layering method. A solution of tib (8.3 mg, 0.03 mmol) in methanol (5 mL) was carefully placed on a solution of $Cd(NO_3)_2\cdot4H_2O$(7.1 mg, 0.023 mmol) in water (3 mL). Colorless crystals of **1** were obtained after several days. Yield: 50% (based on tib). Found: C, 41.85; H, 3.75; N, 22.77. Calcd. for $C_{30}H_{32}CdN_{14}O_{10}$: C, 41.93; H, 3.79; N, 22.57%.

Preparation of [Ag(tib)(PPh$_3$)](CF$_3$SO$_3$) (2)

All procedures for synthesis and measurements of silver(I) complexes were carried out in the dark. A solution of triphenylphosphine (8.7 mg, 0.03 mmol) in methanol (4 mL) was added dropwise into a solution of $AgCF_3SO_3$ (7.7 mg, 0.03 mmol) in methanol (4 mL). After stirring for 5 h, a solution of tib (8.3 mg, 0.03 mmol) was added dropwise and stirred for another 2 h. The solution was then filtered and colorless single crystals were obtained from the filtrate after standing for several days at room temperature. Yield: 42%.

Preparation of [Ag(titmb)(PPh$_3$)](CF$_3$SO$_3$)·1.5H$_2$O (3)

The compound was obtained by a method similar to that described for complex **2** using ligand titmb (10.8 mg, 0.03 mmol) instead of tib. Yield: 60%. Found: C, 53.04; H, 4.54; N, 9.07; Calcd. for $C_{40}H_{42}AgF_3N_6O_{4.5}PS$: C, 52.99; H, 4.67; N, 9.27%.

Crystallography

X-ray diffraction measurements for complex **1** were carried out on a Rigaku RAXIS-RAPID imaging plate diffractometer at 200 K, using graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). The structure was solved by direct methods using SIR92 [19], and expanded using Fourier techniques [20]. The data collection for complexes **2** and **3** were made on a Bruker Smart Apex CCD with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K. The structures were solved by direct methods with SHELXTS-97 and expanded using Fourier techniques [21]. All nonhydrogen atoms were refined anisotropically by the full-matrix least-squares method on F^2 using SHELXL-97 [22]. The hydrogen atoms, except for those of the water molecules, were generated geometrically. Calculations were performed with the Siemens SHELXTL program package.[†,‡] The nitrate anion and one crystal water molecule in **1** are disordered in two positions, each with site occupancy factors of 0.50, respectively. Details of the crystal parameters, data collection and refinements for complexes **1**, **2** and **3** are summarized in Table I, and selected bond distances and angles are listed in Table II. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center, as CCDC nos 225425 (**1**), 225426 (**2**) and 225427 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Description of Crystal Structures

Complex [Cd(tib)$_2$](NO$_3$)$_2$·4H$_2$O (1)

X-ray crystallographic analysis revealed that compound **1** crystallizes in the monoclinic space group $C2/c$. The coordination environment around the cadmium(II) center in complex **1** is shown in Fig. 1 with the atom numbering scheme, where the metal atom sits on the crystallographic inversion center. Each Cd(II) atom is coordinated by six N atoms of imidazole from six different tib ligands. The Cd—N bond distances range from 2.338(2) to 2.365(2) Å, and the N—Cd—N coordination angles are 180° or close to 90° (Table II). Thus the coordination geometry of

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[†] XSCANS, Version 2.1, Siemens Analytical X-ray Instruments (Madison, WI, USA, 1994).
[‡] SHELEXTL, Version 5.0 (Siemens Industrial Automation, Analytical Instruments, Madison, WI, USA, 1995).

TABLE I Crystallographic data for $[Cd(tib)_2](NO_3)_2{\cdot}4H_2O$ (**1**), $[Ag(tib)(PPh_3)](CF_3SO_3)$ (**2**) and $[Ag(titmb)(PPh_3)](CF_3SO_3){\cdot}1.5H_2O$ (**3**)

Compound	1	2	3
Formula	$C_{30}H_{32}CdN_{14}O_{10}$	$C_{34}H_{27}AgF_3N_6O_3PS$	$C_{40}H_{42}AgF_3N_6O_{4.5}PS$
Formula weight	861.10	795.52	906.70
Crystal system	Monoclinic	Cubic	Trigonal
Space group	$C2/c$	$P2_13$	$P\text{-}3c1$
Flack parameter		−0.01(3)	
a, Å	11.706(3)	15.6597(16)	12.082(1)
b, Å	20.565(5)	15.6597(16)	12.082(1)
c, Å	14.685(4)	15.6597(16)	31.900(3)
β, °	99.699(18)	90.00	90.00
V, Å^3	3484.7(15)	3840.2(7)	4032.5(6)
Z	4	4	4
μ, cm^{-1}	7.05	6.75	6.55
Reflections collected	17078	23116	20114
Unique reflections	4008	3091	2652
R_{int}	0.0591	0.0719	0.0263
$R1[I > 2\sigma(I)]$	0.0327	0.0378	0.0315
$wR2\ [I > 2\sigma(I)]$	0.0704*	0.0778†	0.0902‡

$^*w = 1/[\sigma^2(F_0)^2 + (0.0393P)^2]$, $^\dagger w = 1/[\sigma^2(F_0)^2 + (0.0398P)^2]$, $^\ddagger w = 1/[\sigma^2(F_0)^2 + (0.0400P)^2]$, where $P = (F_0^2 + 2F_c^2)/3$.

the Cd(II) atom in **1** is a slightly distorted octahedron. Each tib ligand connects three Cd(II) atoms to form an equilateral triangle, Cd1A, Cd1B and Cd1H in Fig. 2a. This triangle extends in the *ab* plane to generate an infinite 2D network structure based on the honeycomb motif (Fig. 2a). This can be seen more clearly from the schematic drawing (Fig. 2b) of the 2D honeycomb network in which the tib ligands are represented by three spokes radiating from a point (i.e. the centroid of the benzene ring) and the cadmium centers are represented by circles. The solid and dashed lines refer to the tib units above and below the plane formed by the cadmium atoms, respectively. In each tib ligand, the dihedral angles between the central benzene ring plane and each imidazole ring plane are 31.6, 32.1 and 37.8°, respectively. The three N atoms coordinated with the metal atoms of each tib ligand are located at the same side of the central benzene plane, and the benzene planes of the tib ligands in the 2D network are located above and below the plane formed by Cd(II) atoms alternately. The thickness of the 2D layer, namely the distance between the upper and lower benzene ring planes, is 3.73 Å as illustrated in Fig. 3. For the 2D networks of Cd(II), Zn(II) and Mn(II) with a flexible titmb ligand, the thickness of the 2D layer (8.40–8.90 Å) is much larger than that of **1** because of the presence of methylene groups between the imidazole and central benzene ring group in the titmb ligand [15,16].

TABLE II Selected bond distances (Å) and angles (°) for **1**, **2** and **3**

$Cd(tib)_2(NO_3)_2{\cdot}4H_2O$ (**1**)			
Cd1–N32	2.338(2)	Cd1–N12	2.344(2)
Cd1–N52$^{\text{i}}$	2.365(2)		
N32–Cd1–N32$^{\text{ii}}$	180.00	N32–Cd1–N12	91.09(8)
N12–Cd1–N12$^{\text{ii}}$	180.00	N32–Cd1–N52$^{\text{i}}$	92.50(8)
N12–Cd1–N52$^{\text{i}}$	91.92(8)	N52–Cd1–52$^{\text{i}}$	180.00
$[Ag(tib)(PPh_3)](CF_3SO_3)$ (**2**)			
Ag1–N12	2.323(3)	Ag1–P1	2.4373(14)
N12–Ag1–N12$^{\text{iii}}$	108.48(7)	N12–Ag1–P1$^{\text{iii}}$	110.45(6)
$[Ag(titmb)(PPh_3)](CF_3SO_3){\cdot}1.5H_2O$ (**3**)			
Ag1–N1	2.337(2)	Ag1–P1	2.4063(14)
N1–Ag1–N1$^{\text{iv}}$	97.40(8)	N1–Ag1–P1	119.84(6)

Symmetry transformations used to generate equivalent atoms: (i) $x - (1/2)$, $y - (1/2)$, z; (ii) $-x$, $-y$, $-z + 1$; (iii) $-z + (3/2)$, $-x + 1$, $y + (1/2)$; (iv) $-x + y$, $-x + 1$, z.

It is noteworthy that reaction of $Zn(NO_3)_2{\cdot}6H_2O$ with the same tib ligand afforded a 2D network of $[Zn(tib)_2(H_2O)_2](NO_3)_2$ (**4**) with a different structure and topology compared with **1** [9a]. Although both Cd(II) in **1** and Zn(II) in **4** are six-coordinated with the octahedral geometry, the Zn(II) atom in **4** has an N_4O_2 binding set, rather than the N_6 one in **1**. The four equatorial N atoms in **4** are from four distinct tib ligands and two axial coordination sites of the Zn(II) atom are occupied by two O atoms of two water molecules, while the six sites of Cd(II) atom in **1** are all occupied by N atoms from six tib ligands. In addition, only two of the three imidazole N atoms in each tib ligand participate in coordination with the Zn(II) atoms in **4**, while in **1**, all of three imidazole N atoms in each tib ligand take part in coordination with the Cd(II) atoms. Therefore, the tib ligand acts as a two-connecting (bridging) ligand in **4** and as a three-connecting ligand in **1**. As a result of such different coordination modes, complex **4** is a 2D network with (4,4) topology [17], while complex **1** can be regarded as two 2D sheets (shown in Fig. 2b by solid and dashed lines, respectively) each with (6,3) topology formed by sharing the metal atoms, in which both the metal center and centroid of the benzene ring of the tib ligand are considered as nodes.

The different topology and structure of complexes **1** and **4** show that the metal atom plays a crucial role in this reaction system. There is a clear difference between the bond lengths of Cd—N [2.338(2)–2.365(2) Å] in **1** (Table II) and

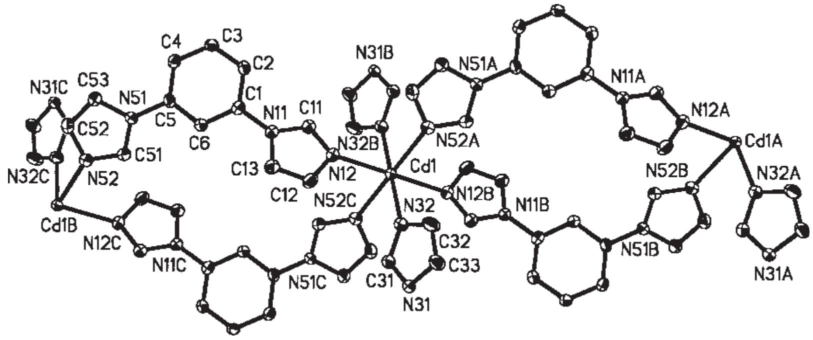

FIGURE 1 The coordination environment of Cd(II) atom in **1**. Thermal ellipsoids are drawn at 50% probability. The hydrogen atoms and anions are omitted for clarity.

Zn—N [2.1375(14)–2.1491(14) Å] in **4** [17]. Thus it is probably difficult for each Zn(II) atom to be coordinated by six N atoms from six different tib ligands because of the steric hindrance of the rigid tib ligand. Similar 2D networks with the same (4,4) topology as complex **4** have been obtained by reactions of the tib ligand with metal salts in the first transition series, such as those of Cu(II), Ni(II) and Mn(II) [17,18]. The results provide a good example that the structure and topology of metal complexes is influenced by the subtle difference of the metal atoms. Such a difference could not be observed in

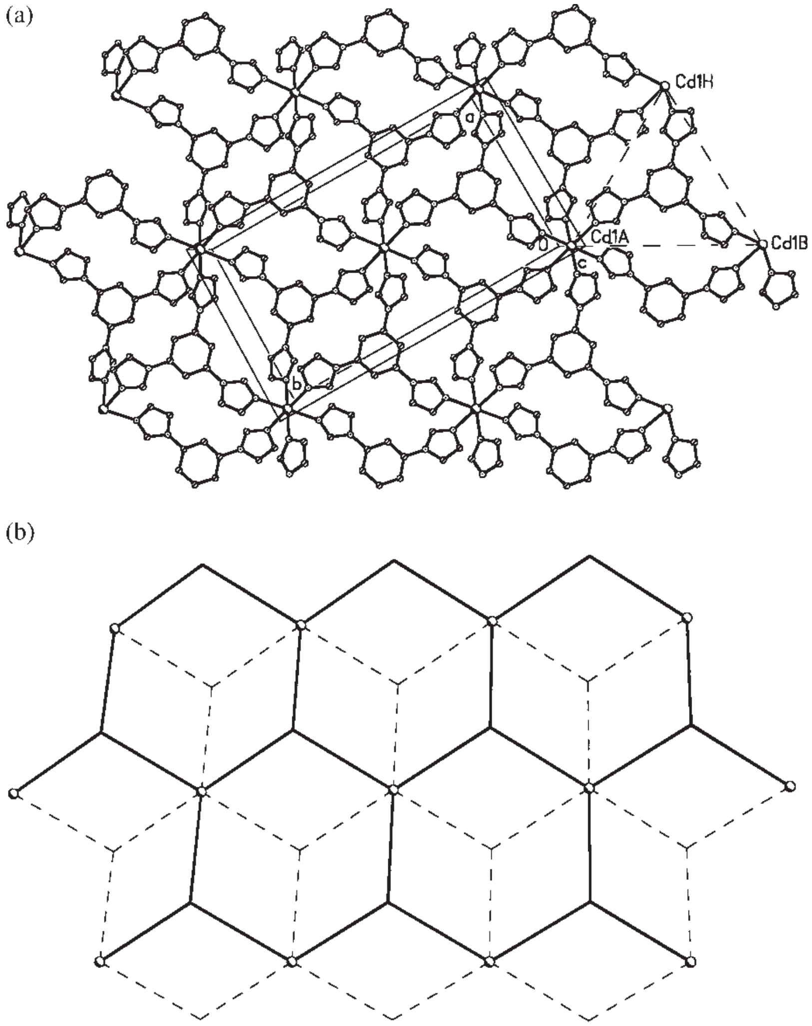

FIGURE 2 (a) Perspective view of the 2D cationic layer with the honeycomb structure of **1**. (b) Schematic drawing of 2D honeycomb network in which the tib units are represented by three spokes radiating from a point and cadmium centers are represented by circles. The solid and dashed lines refer to tib units above and below the plane formed by the cadmium atoms.

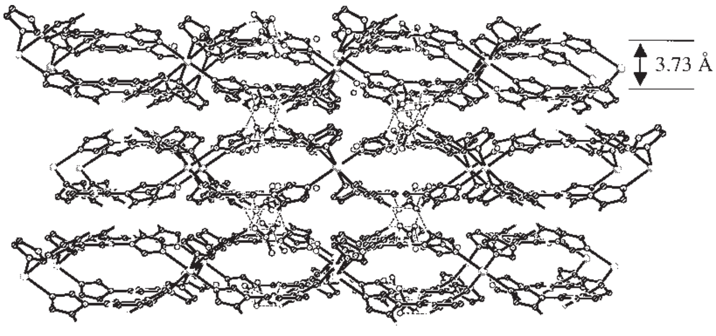

FIGURE 3 Crystal packing diagram of **1**. The two adjacent independent layers are connected by nitrate anions through hydrogen-bonding interactions.

the Cd(II) and Zn(II) complexes with the flexible titmb ligand [15,16], as the flexible titmb ligand can meet the coordination requirements of different metal atoms by adjustment its conformation. Thus the Cd(II) and Zn(II) complexes of titmb have the same framework structures [15,16].

The crystal packing diagram of complex **1** is shown in Fig. 3. The nitrate anions and water molecules are located in the voids formed between two adjacent cationic layers. The 2D networks in **1** are further linked through (water molecules) O—H···O (nitrate anions) and C—H···O (water molecules and nitrate anions) hydrogen-bonding interactions to form a three-dimensional (3D) structure [23]. The hydrogen bonding data for complexes **1**, **2** and **3** are summarized in Table III.

Complex [Ag(tib)(PPh$_3$)](CF$_3$SO$_3$) (2)

Complex **2** was obtained by reaction of the tib ligand with AgCF$_3$SO$_3$ in the presence of triphenylphosphine. This compound crystallizes in cubic space group $P2_13$ with very high symmetry and its asymmetric unit of contains one-third of a molecule of [Ag(tib)(PPh$_3$)](CF$_3$SO$_3$). A perspective view of the silver(I) center of complex **2** is shown in Fig. 4, where the Ag1, P1, S1 and C10 atoms lie on the threefold axis. Each Ag(I) atom is four-coordinated by three N atoms of imidazole groups derived from three different tib ligands and one P atom of triphenylphosphine. The coordination geometry of the Ag(I) center can be regarded as a tetrahedron with the N—Ag—N and N—Ag—P coordination angles ranging from 108.48(7) to 110.45(6)° (Table II), close to the ideal tetrahedral angle of 109.5°. The Ag—N and Ag—P bond lengths (Table II) are similar to those of a previously reported Ag(I) complex with triphenylphosphine and a benzimidazole-containing ligand [24].

TABLE III Hydrogen bond data for complexes **1**, **2** and **3**

D–H···A	D···A (Å)	H···A (Å)	D–H–A (°)
Cd(tib)$_2$(NO$_3$)$_2$·4H$_2$O (**1**)			
O1–H14···O21^{i}	2.660(6)	1.9080	157
C4–H2···O22^{ii}	3.408(6)	2.5598	149
C13–H6···O22^{iii}	3.043(6)	2.4230	123
C13–H6···O21^{iv}	3.235(6)	2.5282	131
C53–H12···O21^{v}	3.427(6)	2.4903	168
C2–H1···O13	3.244(5)	2.3600	155
C6–H3···O1^{iv}	3.383(4)	2.4546	166
C33–H9···O13^{vi}	3.246(6)	2.2963	179
[Ag(tib)(PPh$_3$)] (CF$_3$SO$_3$) (**2**)			
C2–H2A···O1^{vii}	3.459(4)	2.5304	176
C11–H11A···O1	3.374(4)	2.5143	154
[Ag(titmb)(PPh$_3$)](CF$_3$SO$_3$)·1.5H$_2$O (**3**)			
O2–H2C···O1^{viii}	2.793(4)	2.2424	123

Symmetry transformations used to generate equivalent atoms: (i) $-1+x, -y, -(1/2)+z$; (ii) $1(1/2)+x, (1/2)-y, (1/2)+z$; (iii) $-(1/2)-x, (1/2)-y, 1-z$; (iv) $(1/2)+x, (1/2)-y, (1/2)+z$; (v) $(1/2)-x, (1/2)-y, 1-z$; (vi) $-x, y, 1(1/2)-z$; (vii) $1-z, -(1/2)+x, (1/2)-y$; (viii) $x-y+1, -y, -z+(1/2)$.

In complex **2** each tib ligand in turn connects three silver(I) atoms using its three imidazole N atoms. However, it does not result in a 2D honeycomb network structure like **1** and the previously reported silver(I) complexes with the same tib ligand without the triphenylphosphine auxiliary ligand, [Ag$_2$(tib)$_2$][$p-$C$_6$H$_4$(COO)$_2$]·H$_2$O(**5**) and [Ag(tib)]ClO$_4$(**6**) [17]. Instead, in complex **2** five tib ligands, each using two of its three arms, connect five Ag(I) atoms to form an M$_5$L$_5$ (L refers to the tib ligand) decagon, the shortest closed circuit as shown in Fig. 5a. The three dihedral angles between

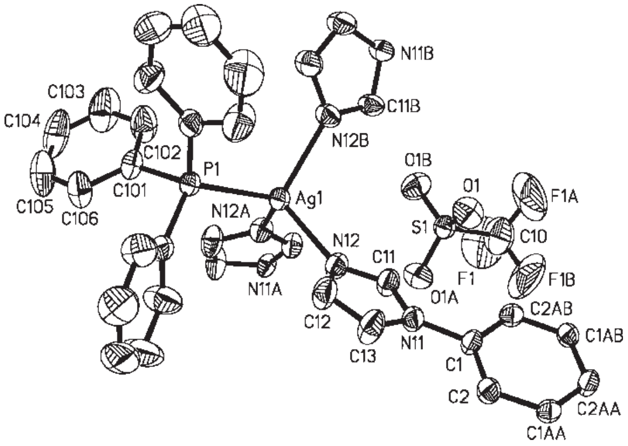

FIGURE 4 Molecular structure of **2**. Thermal ellipsoids are drawn at 50% probability. The hydrogen atoms are omitted for clarity.

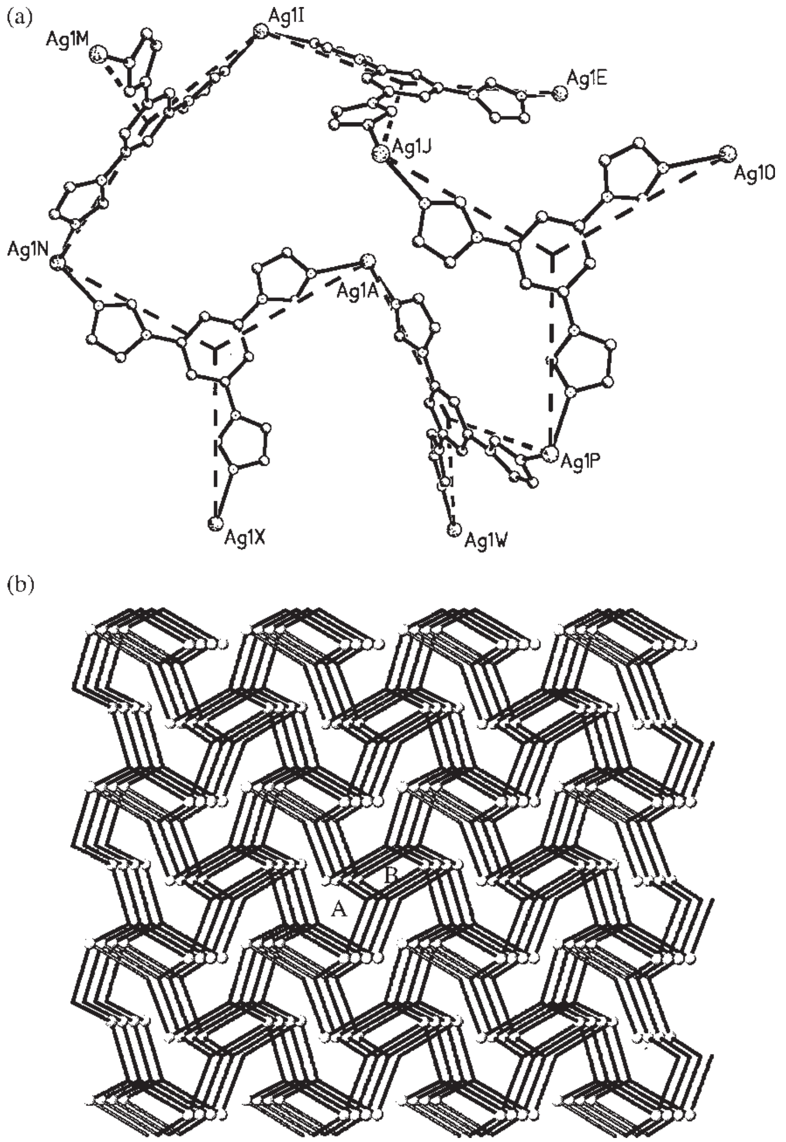

FIGURE 5 (a) View of an M_5L_5 macrocyclic ring of **2** in which the triphenylphosphine groups are omitted for clarity. (b) Schematic drawing of the 3D (10,3)-a framework of **2**, in which the tib ligands are represented by three spokes radiating from a point and Ag centers are represented by circles. The triphenylphosphine groups were omitted for clarity.

the central benzene ring plane and each imidazole ring plane in each tib ligand in **2** are all 19.3°, that is smaller than the angles observed in **1** as mentioned earlier. This means that the imidazole ring of tib in **2** lies in a plane that is closer to the plane in which the central benzene ring lies than that in **1**. The different structures between **2** and **5** as well as **6** suggest that the auxiliary ligand can affect the construction and structure of supramolecular architectures.

The remarkable structural feature of complex **2** is that the M_5L_5 macrocyclic motifs have non-planar geometry and extend in space to form a 3D framework. It can be seen clearly that the 3D framework of **2** has (10,3)-a topology by considering both the metal center and the centroid of the benzene ring of the ligand as nodes [25–34]. The schematic drawing of **2** is shown in Fig. 5b, in which the tib ligands are represented by three spokes radiating from a point (i.e. the center of the benzene ring plane) and Ag centers by circles, and triphenylphosphine groups were omitted for clarity. There are two types of channels (A and B) in the complex and the larger one (A) is filled with the coordinated PPh_3 groups and the $CF_3SO_3^-$ anions held there via two C—H···O hydrogen bonds [23], as listed in Table III.

Construction of (10,3)-a nets has attracted great attention because of their inherent chirality, as suggested by Wells [35,36]. In order to get chiral crystals, interpenetration of (10,3)-a nets should be avoided, as a meso structure may be obtained in the case of a net interpenetrating one with an opposite handedness [37]. In complex **2**, the bulky auxiliary

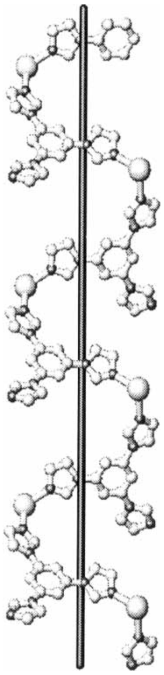

FIGURE 6 Side view of the helix in complex **2**.

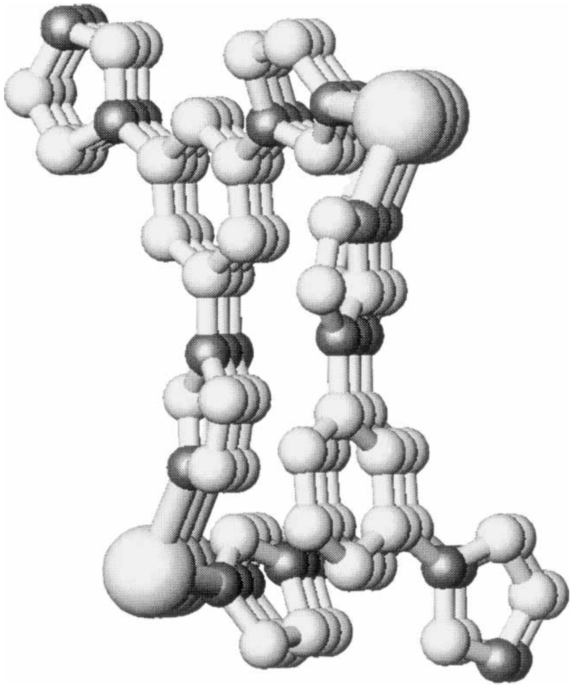

FIGURE S1 Top view of the helix in complex **2**.

ligand of triphenylphosphine and anions occupy the voids and accordingly prevent the interpenetration of the (10,3)-a net. Complex **2** is therefore a chiral crystal with a Flack parameter of $-0.01(3)$ (Table I) from the reaction of achiral components [38], although the bulk phase of **2** is a mixture of enantiomorphic crystals of both hands [39–41]. The individual crystals are randomly one-handed or the opposite, as illustrated in Fig. 6 (see also the top view of the helix in Fig. S1), there is only a one-handed helix in the crystal of **2** selected for study. Two tib ligands and two Ag(I) atoms complete a turn of the helix with a pitch length of 15.7 Å. In addition to the bulky triphenylphosphine ligand, the rigidity of the tib ligand may also contribute to the formation of the (10,3)-a net and the one-handed helix in **2**. Complex **3** with a 2D network structure was obtained by reaction of the flexible titmb ligand and triphenylphosphine with the same silver(I) salt (vide infra). In contrast to most examples of an interpenetrated (10,3)-a net reported [25–33], the present study provides an example of a noninterpenetrated (10,3)-a net and also an efficient pathway for construction of a (10,3)-a net by using a bulky auxiliary ligand to avoid possible interpenetration [34].

Complex [Ag(titmb)(PPh$_3$)](CF$_3$SO$_3$)·1.5H$_2$O (3)

Reaction using the flexible ligand titmb, instead of the rigid tib, with $AgCF_3SO_3$ in the presence of triphenylphosphine was carried out to investigate the impact of an organic ligand on the structure of assembly, and complex **3** was isolated. The results of the X-ray crystallographic analysis indicate that **3** crystallizes in trigonal space group $P\text{-}3c1$, rather than cubic $P2_13$ space group, like **2**. The Ag1, P1, S1 and C14 atoms lie on the threefold axis and the O atom of the crystal water molecule has crystallographically twofold symmetry. As shown in Fig. 7, the Ag(I) atom in **3** is coordinated by one P atom from the triphenylphosphine and three N atoms of imidazole from three distinct titmb ligands with a similar coordination environment to that in **2**. The P—Ag—N and N—Ag—N coordination angles in **3** are 119.84(6) and 97.40(8)° (Table II), respectively, and have a larger deviation from the ideal tetrahedral angle of 109.5° than those in complex **2**.

On the other hand, each ligand titmb in **3** connects three Ag(I) atoms with the Ag···Ag distance of 12.08 Å (e.g. Ag1A–Ag1B = Ag1B–Ag1E = Ag1A–Ag1E in Fig. 8). Even though complexes **2** and **3** have similar coordination modes, as described above, namely each Ag(I) atom links three ligands and each ligand in turn connects three metal atoms, the network structures of **2** and **3** are very different. In contrast to the 3D structure with (10,3)-a topology of **2**, it is clear that **3** is a 2D honeycomb network with (6,3) topology. The structural and topological differences between complexes **2** and **3** are attributed to the different structure and flexibility of the ligands tib and titmb. There are M_3L_3 macrocyclic motifs in **3**, rather than the M_5L_5 ones in **2**. The formation of the M_3L_3 macrocyclic motifs in **2** may be prohibited

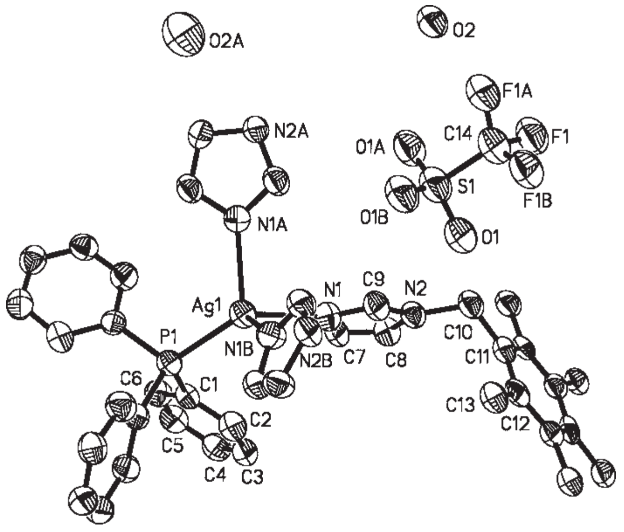

FIGURE 7 The crystal structure of **3**. Thermal ellipsoids are drawn at 50% probability. The hydrogen atoms are omitted for clarity.

by the steric hindrance and rigidity of the tib ligand [42,43]. The different structure and topology of **2** and **3** indicate that the nature of organic ligands has great influence on the assembly and structure of metal-organic frameworks.

From the side view of the 2D network of **3** as shown in Fig. S2, it can be seen that the triphenylphosphine ligands act as appending groups, like the azide anions in the complex [Ag(titmb)N_3]·H_2O (**7**) obtained by the reaction of titmb with $Ag(NH_3)_2N_3$ [44]. However, no interpenetration occurred in complex **3** because of the existence of the bulk-appending groups of triphenylphosphine. Therefore, complex **3** is a noninterpenetrated (6,3) 2D network, while complex **7** has a 2D polycatenated structure [44]. From the crystal packing diagram of **3** (Fig. 9), it is clear that the two 2D layers are packed together with face-to-face orientation form a double layer and the uncoordinated $CF_3SO_3^-$ anions and crystal water molecules are sandwiched between the two adjacent double layers through O−H···O hydrogen-bonding interactions (Table III).

Photoluminescence Properties of Complexes 1, 2 and 3

The photoluminescence properties of complexes **1**, **2** and **3** were studied in the solid state at room temperature and the spectra are shown in Fig. 10. Complex **1** showed photoluminescence with an emission maximum at 423 nm upon photoexcitation at 360 nm. The observed emission in **1** can probably be assigned to the intraligand fluorescence as a similar emission at 405 nm was observed for the free tib ligand. The red-shift observed in the emission spectra of **1** is considered to be caused by coordination of the tib ligand to the metal atoms. A previously reported Cd(II) complex $Cd(bimb)_2Cl_2$ [bimb = 4,4′-bis(imidazol-l-ylmethyl)biphenyl] exhibited similar photoluminescence with emission at 420 nm upon photoexcitation at 360 nm [45].

It is rare that silver(I) complexes can emit photoluminescence at room temperature, although they may show weak photoluminescence at low temperature [5,46,47]. However, complex **2** showed

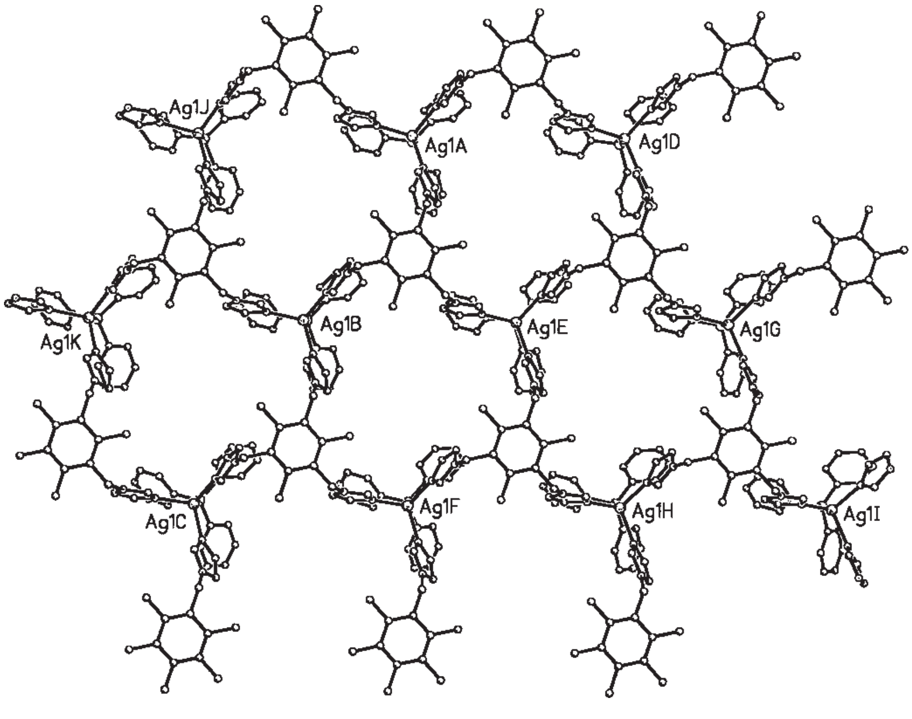

FIGURE 8 Perspective view of the 2D cationic layer with the (6,3) honeycomb structure of **3**.

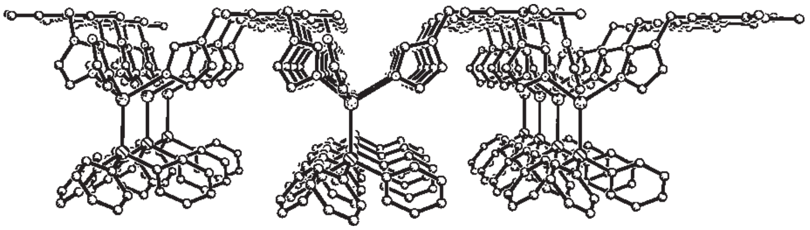

FIGURE S2 Side view of the 2D cationic layer with the (6,3) honeycomb structure of **3**.

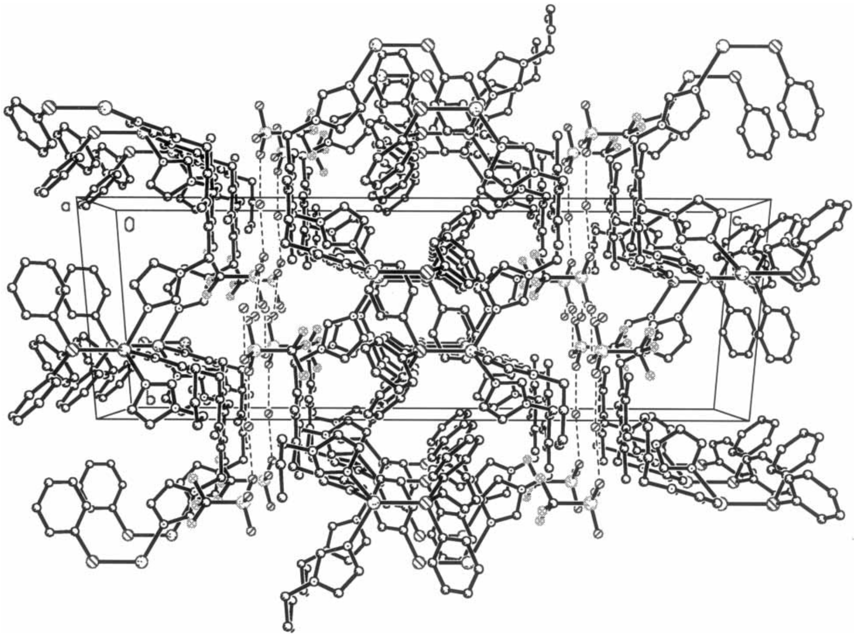

FIGURE 9 Crystal packing diagram of **3** with hydrogen bonds indicated by dashed lines.

photoluminescence with emission at 421 nm upon photoexcitation at 360 nm, which is very similar to that of **1** and can also be tentatively assigned to the intraligand fluorescence. Similar emissions observed in complexes **1** and **2** imply that the coordination of triphenylphosphine to the Ag(I) atom in **2** has no remarkable influence on the photoluminescence properties of the complex.

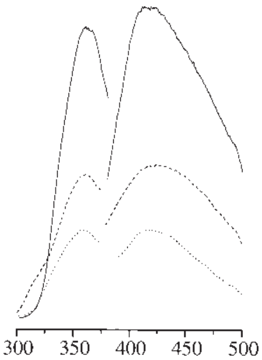

FIGURE 10 Excitation (left) and emission (right) spectra of **1** (dashed line), **2** (solid line) and **3** (dotted line).

Complex **3** also shows intense photoluminescence with an emission maximum at 414 nm upon excitation at 358 nm.

CONCLUSION

In conclusion, three new metal-organic architectures were obtained from assembly of rigid tib and flexible titmb tripodal ligands with Cd(II) and Ag(I)/PPh_3 metal salts. The results of present and our previous studies indicate that the structure and topology of assemblies with the rigid tib ligand are mainly controlled by the coordination geometry of metal ions, but are not influenced greatly by the anions. In addition, introduction of a bulky auxiliary ligand leads to the formation of a noninterpenetrated 3D framework with a (10,3)-a net.

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