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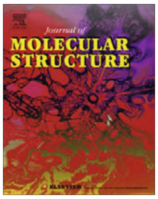

Syntheses, structures and fluorescence properties of three new polymers based on a flexible tripodal ligand

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ABSTRACT

Three new polymers, namely, $\{[Cd(TTTMB)(bdic^{2-})(H_2O)]\cdot H_2O\}_n$ (**1**), $\{[Cd(TTTMB)(Hbtrc^{2-})(H_2O)]\cdot 2H_2O\}_n$ (**2**) and $[Zn(TTTMB)(Hbtrc^{2-})(H_2O)]_n$ (**3**) based on a flexible tripodal ligand 1,3,5-tris(triazol-1-ylmethyl)-2,4,6-trimethylbenzene (TTTMB) have been synthesized by choosing H_2bdic and H_3btrc as auxiliary ligands under hydrothermal reaction (H_2bdic = 1,3-benzenedicarboxylic acid and H_3btrc = 1,3,5-benzenetricarboxylic acid). The structures of the polymers were determined by single-crystal X-ray diffraction analyses, and the results reveal that **1** and **2** exhibits a two-dimensional (4,4) network. While the crystal structure of **3** shows one-dimensional zigzag chain. Additionally, the solid-state fluorescent properties of these three polymers and ligand TTTMB were investigated at room temperature.

1. Introduction

The design and construction of metal–organic frameworks (MOFs) have attracted much attention in the fields of supramolecular chemistry and crystal engineering in recent years due to their versatile intriguing architectures and their potential applications in optical, electronic, magnetic and biomimetic materials [1–6]. Generally, the diversity in the framework structures of such MOFs depends on many factors, such as the selection of metal centers, organic ligands and the reaction pathways [7]. Among these factors, the design and selection of organic ligands with suitable binding groups are especially crucial [8]. Flexible tripodal ligands with an arene core have been found to be one of the most useful organic building blocks in construction of MOFs, such as 1,3,5-tris(4-pyridylmethyl)benzene [9], 1,3,5-tris(pyrazol-1-ylmethyl)-2,4,6-triethylbenzene [10], 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene [11–14], 1,3,5-tris(benzimidazole-1-ylmethyl)-2,4,6-trimethylbenzene [15]. These flexible tripodal ligands can adopt different conformations and coordination modes according to the geometric requirements of different metal ions, so they are helpful to construct intriguing architectures and topologies.

Considerable progress has been made on the design and construction of MOFs using this kind of flexible tripodal ligands [9–15]. However, using the aromatic acids as auxiliary ligands, the study on the structures of coordination complexes containing flexible tripodal ligands is extremely rare [16,17]. In addition, the 1,3-benzenedicarboxylic acid (H_2bdic) and 1,3,5-benzenetricarboxylic acid (H_3btrc) are good organic building blocks in constructing metal–organic frameworks [7]. H_2bdic and H_3btrc have two or three carboxyl groups, which can be completely or partially deprotonated, and they may serve as potential anion groups. This makes it very appealing for the design of MOFs with interesting structures and properties. Hence, our group started on a program aimed at constructing new MOFs by rational utilization of flexible tripodal ligands and selection of aromatic acids H_2bdic and H_3btrc as auxiliary ligands.

In the present work, we selected a novel flexible tripodal compound with aromatic core 1,3,5-tris(triazol-1-ylmethyl)-2,4,6-trimethylbenzene (TTTMB) [8,17] as a functional ligand, and three polymers $\{[Cd(TTTMB)(bdic^{2-})(H_2O)]\cdot H_2O\}_n$ (**1**), $\{[Cd(TTTMB)(Hbtrc^{2-})(H_2O)]\cdot 2H_2O\}_n$ (**2**) and $[Zn(TTTMB)(Hbtrc^{2-})(H_2O)]_n$ (**3**) were obtained by choosing H_2bdic and H_3btrc as auxiliary ligands under hydrothermal reaction. Herein, we report the syntheses, crystal structures as well as fluorescence properties of these polymers.

2. Experimental

2.1. Materials and physical techniques

1,3,5-Tris(triazol-1-ylmethyl)-2,4,6-trimethylbenzene (TTTMB) was prepared according to literature method [18]. All other staring materials were of reagent-grade quality and were obtained from commercial sources and used without further purification.

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Elemental analyses (C, H and N) were carried out on a FLASH EA 1112 elemental analyzer. Infrared spectra data were recorded on a Bruker TENSOR 27 spectrophotometer with KBr pellets in the 400–4000 cm^{-1} region.

*2.2. Preparation of polymer {[Cd(TTTMB)(bdic^{2-})(H_2O)]·H_2O}$_n$ (**1**)*

A mixture of TTTMB (0.037 g, 0.1 mmol), $Cd(NO_3)_2·4H_2O$ (0.031 g, 0.1 mmol) and H_2bdic (0.017 g, 0.1 mmol) in H_2O (10 mL) was kept in a Teflon-lined autoclave at 130 °C for 3 days. After the mixture was cooled to room temperature, colorless crystals suitable for X-ray diffraction were obtained. Yield: 78%. Anal. Calcd for $C_{52}H_{58}Cd_2N_{18}O_{12}$ (%): C, 46.19; H, 4.32; N, 18.65. Found: C, 46.27; H, 4.35; N, 18.57. IR (KBr, cm^{-1}): 3427(m), 3123(w), 2364(w), 1693(w), 1605(s), 1548(s), 1479(w), 1443(s), 1386(s), 1276(s), 1216(w), 1134(s), 1076(m), 1010(w), 750(m), 726(m), 675(m), 642(w).

*2.3. Preparation of polymer {[Cd(TTTMB)(Hbtrc^{2-})(H_2O)]·$2H_2O$}$_n$ (**2**)*

A mixture of TTTMB (0.037 g, 0.1 mmol), $3CdSO_4·8H_2O$ (0.026 g, 0.03 mmol) and H_3btrc (0.021 g, 0.1 mmol) in H_2O (10 mL) was kept in a Teflon-lined autoclave at 120 °C for 3 days. Then the reaction system was cooled to room temperature slowly, and colorless crystals of **2** were obtained. The crystals were collected and were further used for single-crystal analysis and physical measurements. Yield: 67%. Anal. Calcd for $C_{54}H_{62}Cd_2N_{18}O_{18}$ (%): C, 43.94; H, 4.23; N, 17.08. Found: C, 43.37; H, 4.20; N, 17.35. IR (KBr, cm^{-1}): 3430(m), 3128(w), 2364(w), 1712(s), 1614(s), 1566(s), 1439(s), 1371(s), 1279(m), 1226(w), 1136(s), 1012(w), 986(w), 879(w), 759(w), 731(m), 675(s), 641(w), 527(w).

*2.4. Preparation of polymer [Zn(TTTMB)(Hbtrc^{2-})(H_2O)]$_n$ (**3**)*

The synthesis was the same as that for **2**, except using $Zn(NO_3)_2·4H_2O$ (0.030 g, 0.1 mmol) instead of and $3CdSO_4·8H_2O$. Yield: 79%. Anal. Calcd for $C_{27}H_{27}ZnN_9O_7$ (%): C, 49.51; H, 4.16; N, 19.25. Found: C, 49.77; H, 4.20; N, 19.07. IR (KBr, cm^{-1}): 3428(m), 3138(w), 2964(m), 2367(w), 1720(s), 1620(s), 1582(m), 1542(s), 1439(m), 1352(s), 1281(m), 1211(s), 1161(s), 1138(s), 997(m), 893(w), 760(m), 720(m), 671(s), 641(m), 551(w).

2.5. X-ray crystallographic study

Single crystals of **1**, **2** and **3** were selected for indexing and intensity data collection on a Rigaku Saturn 724 CCD diffractometer using graphite-monochromated Mo Kα X-radiation ($\lambda = 0.71073$ Å) at room temperature. A single crystal suitable for X-ray diffraction was mounted on a glass fiber. The data were integrated using the Siemens SAINT program [19]. Absorption corrections were applied. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares using SHELXTL [20]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located at geometrically calculated positions and refined with isotropic thermal parameters. Crystallographic and refinement details are listed in Table 1, with selected bond lengths and angles in Table 2.

2.6. Determination of fluorescent properties

The fluorescent spectra were measured on powder samples at room temperature using a F-4500 HITACHI Fluorescence Spectrophotometer. The excitation slit was 5 nm and the emission slit was 5 nm too, the response time was 2 s. The different concentration of TTTMB and polymers **1**–**3** were obtained by adding the KBr, because the KBr does not show any fluorescence upon excitation at 284 nm.

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

Polymers	**1**	**2**	**3**
Formula	$C_{52}H_{58}Cd_2N_{18}O_{12}$	$C_{54}H_{62}Cd_2N_{18}O_{18}$	$C_{27}H_{27}ZnN_9O_7$
Formula weight	1351.96	1476.02	654.95
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2(1)/n$
a (Å)	10.158(2)	10.388(2)	8.6070(17)
b (Å)	10.654(2)	11.619(2)	20.393(4)
c (Å)	15.477(3)	14.162(3)	15.481(3)
α (°)	106.43(3)	67.89(3)	90
β (°)	91.56(3)	86.21(3)	91.28(3)
γ (°)	115.34(3)	70.39(3)	90
V (Å^3)	1430.6(5)	1488.2(5)	2716.6(9)
Z	1	1	4
D_c (g/cm^3)	1.569	1.647	1.601
Reflections collected	15,712	16,238	29,623
Unique reflections	5610	5843	5368
R_{int}	0.0326	0.0271	0.0824
Data/restraints/ parameters	5610/24/398	5843/0/439	5368/0/406
GOF	1.024	1.072	1.004
R_1[a] [$I > 2\sigma(I)$]	0.0442	0.0448	0.0884
wR_2[b] [$I > 2\sigma(I)$]	0.1061	0.1079	0.2044
R_1[a] (all data)	0.0511	0.0489	0.1119
wR_2[b] (all data)	0.1114	0.1111	0.2230

[a] $R_1 = ||F_o| - |F_c||/|F_o|$.

[b] $wR_2 = [w(|F_o^2| - |F_c^2|)^2/w|F_o^2|^2]^{1/2}$, $w = 1/[\sigma^2(F_o)^2 + 0.0297P^2 + 27.5680P]$, where $P = (F_o^2 + 2F_c^2)/3$.

Table 2
Selected bond lengths (Å) and bond angles (°) for polymers **1**–**3**.

*Polymer **1***			
Cd(1)–N(1)	2.279(3)	Cd(1)–N(6)#1	2.299(3)
Cd(1)–O(2)	2.306(3)	Cd(1)–O(4)#2	2.340(3)
Cd(1)–O(5)	2.356(3)	Cd(1)–O(3)#2	2.485(3)
Cd(1)–O(1)	2.596(3)	N(1)–Cd(1)–N(6)#1	168.97(13)
N(1)–Cd(1)–O(2)	95.46(12)	N(6)#1–Cd(1)–O(2)	90.79(12)
N(1)–Cd(1)–O(4)#2	93.51(12)	N(6)#1–Cd(1)–O(4)#2	96.36(13)
O(2)–Cd(1)–O(4)#2	81.98(10)	N(1)–Cd(1)–O(5)	88.04(13)
N(6)#1–Cd(1)–O(5)	81.18(14)	O(2)–Cd(1)–O(5)	136.48(12)
O(4)#2–Cd(1)–O(5)	141.22(12)	N(1)–Cd(1)–O(3)#2	90.36(11)
N(6)#1–Cd(1)–O(3)#2	91.47(12)	O(2)–Cd(1)–O(3)#2	135.83(10)
O(4)#2–Cd(1)–O(3)#2	53.93(9)	O(5)–Cd(1)–O(3)#2	87.34(12)
N(1)–Cd(1)–O(1)	87.98(12)	N(6)#1–Cd(1)–O(1)	88.61(12)
O(2)–Cd(1)–O(1)	52.67(9)	O(4)#2–Cd(1)–O(1)	134.50(9)
O(5)–Cd(1)–O(1)	84.26(12)	O(3)#2–Cd(1)–O(1)	171.49(9)
*Polymer **2***			
Cd(1)–N(1)	2.251(3)	Cd(1)–O(1)	2.267(3)
Cd(1)–O(5)#1	2.300(3)	Cd(1)–O(7)	2.339(3)
Cd(1)–N(6)#2	2.374(3)	N(1)–Cd(1)–O(1)	132.85(11)
N(1)–Cd(1)–O(5)#1	136.29(11)	O(1)–Cd(1)–O(5)#1	90.84(10)
N(1)–Cd(1)–O(7)	94.22(14)	O(1)–Cd(1)–O(7)	90.68(12)
O(5)#1–Cd(1)–O(7)	85.19(13)	N(1)–Cd(1)–N(6)#2	94.63(13)
O(1)–Cd(1)–N(6)#2	88.11(12)	O(5)#1–Cd(1)–N(6)#2	83.88(12)
O(7)–Cd(1)–N(6)#2	168.98(13)		
*Polymer **3***			
Zn(1)–N(1)	2.019(5)	Zn(1)–O(1)	1.965(4)
Zn(1)–O(7)	1.971(5)	Zn(1)–N(6)#2	2.023(5)
O(1)–Zn(1)–O(7)	102.73(18)	O(1)–Zn(1)–N(1)	113.22(19)
O(7)–Zn(1)–N(1)	114.5(2)	O(1)–Zn(1)–N(6)#2	118.36(19)
O(7)–Zn(1)–N(6)#2	100.3(2)	N(1)–Zn(1)–N(6)#2	107.2(2)

Symmetry transformations used to generate equivalent atoms. Polymer **1**: #1 $x, y, z + 1$; #2 $x + 1, y, z$; #3 $x, y, z - 1$; #4 $x - 1, y, z$. Polymer **2**: #1 $x + 1, y, z$; #2 $x, y - 1, z$; #3 $x, y + 1, z$; #4 $x - 1, y, z$. Polymer **3**: #1 $x + 1/2, -y + 3/2, z - 1/2$; #2 $x - 1/2, -y + 3/2, z + 1/2$.

3. Results and discussion

3.1. Syntheses

As far as we know, hydrothermal synthesis at mild temperature (100–200 °C) under autogenous pressure was proven to be a powerful approach in the preparation of low-soluble organic–inorganic hybrid materials [21–23]. The ligands H_2bdic, H_3btrc and TTTMB suit for hydrothermal reactions due to the high structural stability. Thus, we believe that the new structures of metal–organic frameworks could be obtained using these mixed-ligands under hydrothermal reaction. As anticipated, treatment of TTTMB as functional ligand with $Cd(NO_3)_2{\cdot}4H_2O$, H_2bdic as auxiliary ligand yielded polymer **1** at 130 °C hydrothermal reactions. Polymer **2** and **3** was obtained successfully by using TTTMB, H_3btrc and introducing $3CdSO_4{\cdot}8H_2O$ or $Zn(NO_3)_2{\cdot}4H_2O$ at 120 °C hydrothermal reactions.

3.2. Description of crystal structures

3.2.1. Crystal structure of polymer $\{[Cd(TTTMB)(bdic^{2-})(H_2O)]{\cdot}H_2O\}_n$ (**1**)

X-ray diffraction analysis reveals that polymer **1** crystallizes in the triclinic space group $P\bar{1}$. Each Cd(II) ion is seven-coordinated by one oxygen atom from a water molecule, four oxygen atoms from two $bdic^{2-}$ groups and two nitrogen donors arising from two TTTMB ligands (Fig. 1a). The equatorial position is occupied by O1AA, O2AA, O3AC, O4AC and O5AA (the mean deviation is 0.0538 Å) and N1AA, N6AB are in axial position. So the local coordination environment of Cd(II) can be described as a distorted pentagonal bipyramid (Fig. 1b). The Cd–N bond lengths are 2.279 and 2.299 Å, and Cd–O bond lengths are in the range of 2.306–2.596 Å. They are in conformity with those found in reported corresponding cadmium complexes [24–27]. The ligand TTTMB is the *cis,trans,trans*-conformation (Scheme 1) and each TTTMB

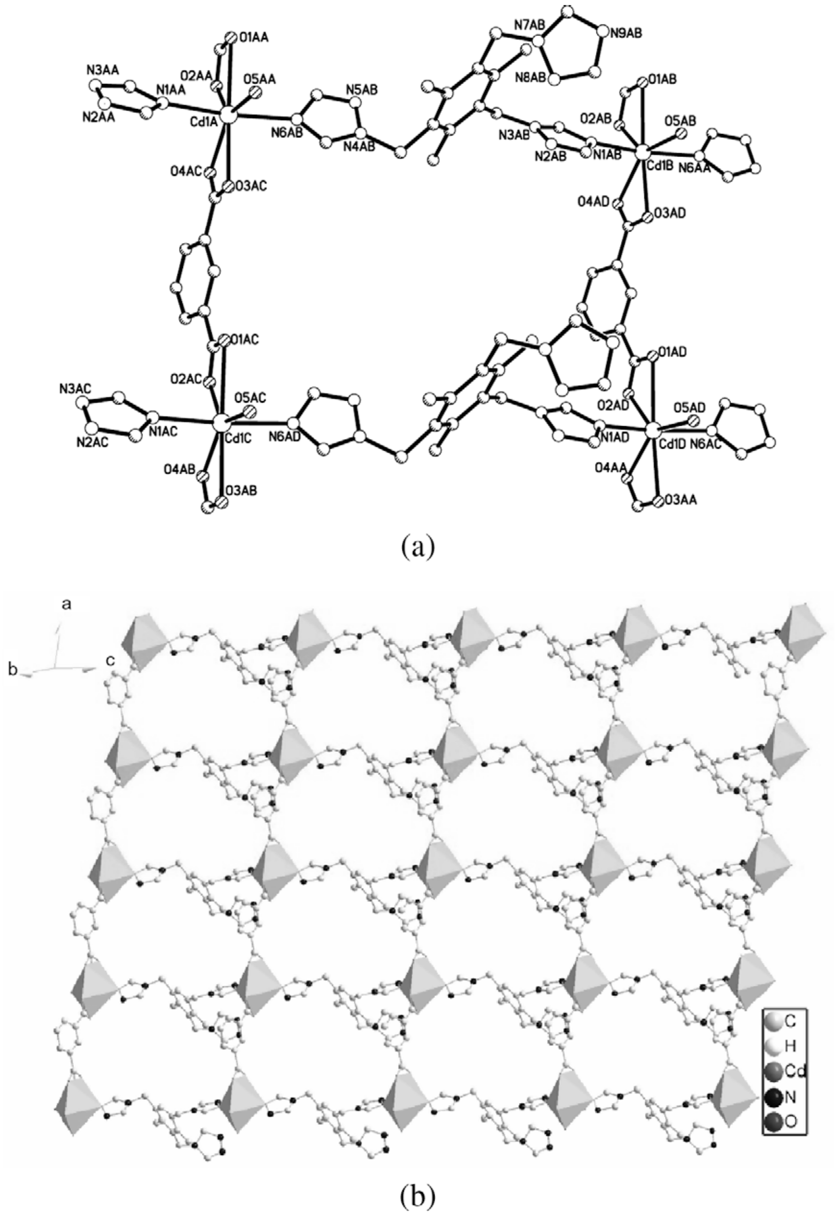
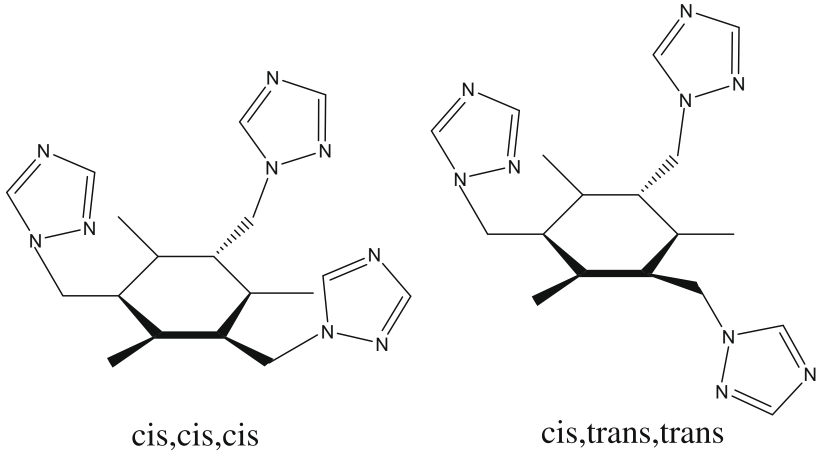


Fig. 1. (a) The coordination environment of Cd(II) in polymer **1**. (b) Perspective view of the (4,4) coordination layer of **1** with the Cd(II) centers highlighted as grey polyhedron. The lattice water molecules and H atoms are omitted for clarity in (a) and (b).



Scheme 1. Schematic drawing for tripodal ligand TTTMB with *cis,cis,cis*- and *cis,trans,trans*-conformation.

molecule coordinates to two Cd(II) ions as a bidentate ligand rather than a tridentate ligand that connects three metal ions. The ligand TTTMB adopts similar coordination mode to the other tripodal ligands of the reported complexes [28]. Each bdic^{2-} group as the bidentate ligand also links two Cd(II) ions. Such coordination modes of TTTMB and bdic^{2-} groups result in the formation of an infinite two-dimensional network structure as shown in Fig. 1b. Four Cd(II) ions, two bdic^{2-} groups and two TTTMB units form a 40-membered ring (Fig. 1a). Thus the framework of polymer **1** can be regarded as a (4,4) network. The distance between Cd1A and Cd1B is 15.477 Å, whereas the distance between Cd1A and Cd1C is 10.158 Å. All the Cd(II) ions in one layer of **1** are in the same plane, and the layers are parallel (Fig. 2). The benzene ring planes of TTTMB and bdic^{2-} are deflected from the Cd(II) ions plane with the dihedral angles of 65.1° and 77.3°, respectively.

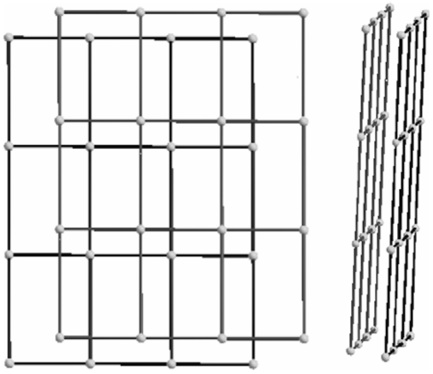


Fig. 2. Schematic representation of the layer stacking in **1**.

Additionally, the adjacent layers are linked together through hydrogen bonds between coordinated oxygen atoms of the bdic^{2-} groups and coordinated water molecules, $O_{(carboxylate)}$ and solvent H_2O molecules resulting in a three-dimensional network (Fig. 3). The benzene rings of bdic^{2-} groups and triazole rings in adjacent layers are parallel with the average interplanar distance of 3.623, and 3.571 Å, respectively. These distances are slightly longer than the π–π stacking distances of 3.33–3.53 Å reported elsewhere [29], thus π–π interactions between adjacent layers in this complex are very weak [30,31].

*3.2.2. Crystal structure of polymer {[Cd(TTTMB)(Hbtrc^{2-})(H_2O)]·$2H_2O$}$_n$ (**2**)*

Single-crystal structural determination reveals that polymer **2** has the same space group as polymer **1**. As shown in Fig. 4a.

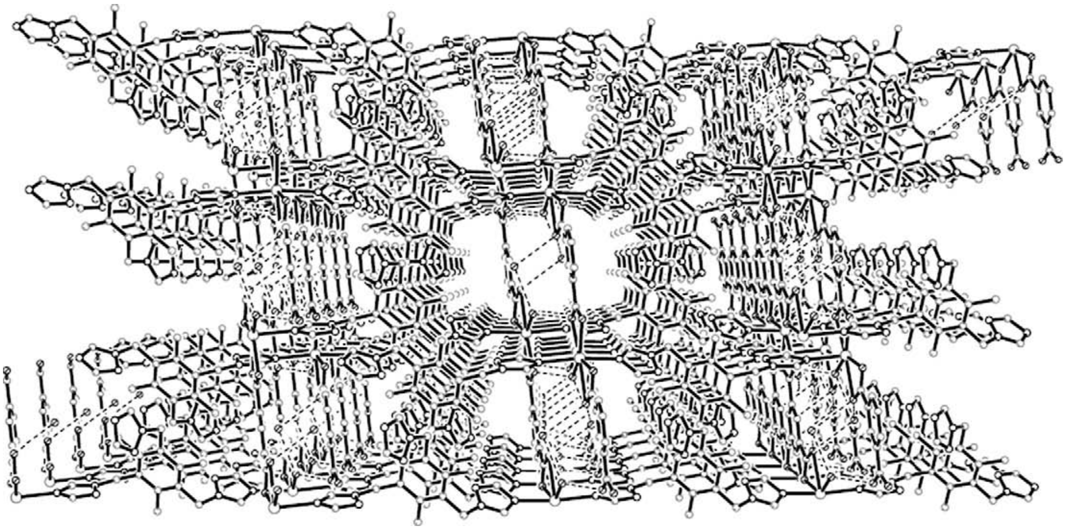


Fig. 3. View of the infinite three-dimensional supramolecular structure of polymer **1**, generated through extensive hydrogen bonding. Hydrogen atoms are omitted for clarity.

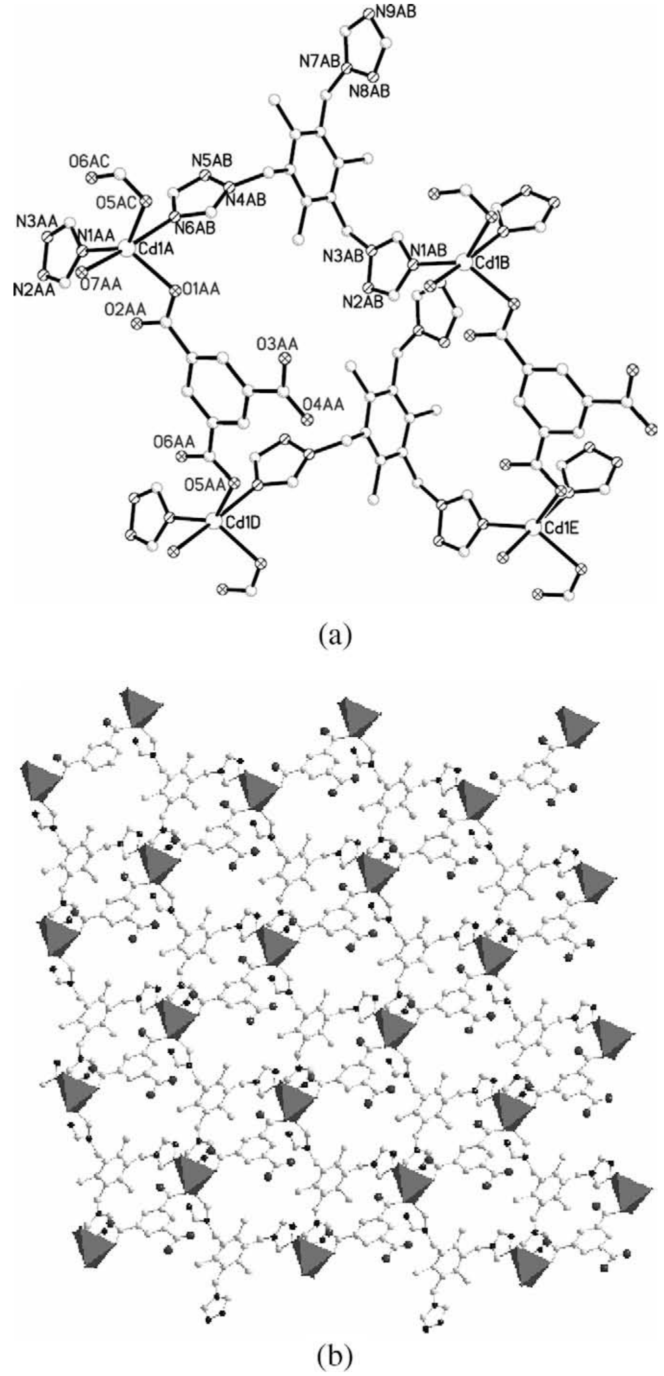


Fig. 4. (a) The coordination environment of Cd(II) in polymer **2**. (b) Perspective view of the two-dimensional layer of **2** with the Cd(II) centers highlighted as grey polyhedron. The lattice water molecules and H atoms are omitted for clarity in (a) and (b).

Cd1A is five-coordinated in a slightly distorted trigonal bipyramid environment by binding two O atoms (O1AA and O5AB) from two $Hbtrc^{2-}$ groups, one O atom (O7AA) from a water molecule and two nitrogen donors (N1AA and N6AB) arising from two TTTMB ligands. The Cd–N bond lengths are 2.251 and 2.374 Å. The Cd–O bond lengths are in the range of 2.267–2.340 Å, and these distances are slightly shorter than those of **1**. The distance of Cd1···O2 (2.691 Å) is longer than the common $Cd–O_{(carboxyl)}$ bond length. In other words, the O2 atom coordinates to the Cd(II) ion very weakly. The coordination mode of ligand TTTMB in **2** is in conformity with that in polymer **1**. Two carboxyl groups of H_3btrc are deprotonated and coordinated to two Cd(II) ions in a monodentate mode. Thus the framework of polymer **2** is the same as **1** exhibiting a two-dimensional network (Fig. 4b). The distances of Cd1A···Cd1B and Cd1A···Cd1C are 11.619 and 10.388 Å, respectively. Moreover, the triazole rings are parallel between the adjacent layers (Fig. 5). The adjacent layers are linked through hydrogen bonds between uncoordinated oxygen atoms of the $Hbtrc^{2-}$ groups and coordinated H_2O molecules, solvent H_2O molecules and oxygen atoms of the $Hbtrc^{2-}$ groups resulting in a three-dimensional network. Although the hydrogen bonds are weak, they are important in the molecular assembly.

*3.2.3. Crystal structure of polymer $[Zn(TTTMB)(Hbtrc^{2-})(H_2O)]_n$ (**3**)*

The crystal structure of **3** is significantly different from **2**: it exhibits one-dimensional zigzag chain as shown in Fig. 6, and this complex crystallizes in the monoclinic space group *P2(1)/n*. Each Zn(II) ion is four-coordinated in a distorted tetrahedron geometry with one oxygen atom from a terminal $Hbtrc^{2-}$ group, one oxygen atom from a water molecule and two nitrogen donors from two TTTMB molecules. The Zn–N bond lengths are 2.019 and 2.023 Å, and Zn–O bond lengths (1.965 and 1.971 Å) compare well with the distances found in the reported zinc complexes [32]. The bond angles around each Zn(II) ion range from 100.3° to 118.4°. Hence, average bond angle at Zn(1) is 109.3°, which is slightly smaller than 109.5° for an ideal tetrahedron. Two carboxyl groups of H_3btrc are deprotonated, but only one carboxyl group coordinated to a Zn(II) ion in a monodentate mode. The coordination mode of ligand TTTMB in **3** is in conformity with those in polymers **1** and **2**. Each ligand TTTMB coordinates to two Zn(II) ions as a bidentate ligand forming one-dimensional chain, and between the adjacent chains, the triazole rings are parallel with the average interplanar distance of 3.494 Å. Similarly, π–π interaction exists in the benzene rings of $Hbtrc^{2-}$ groups and benzene rings of TTTMB ligands with the average interplanar distance of 3.537 Å. So, the adjacent layers

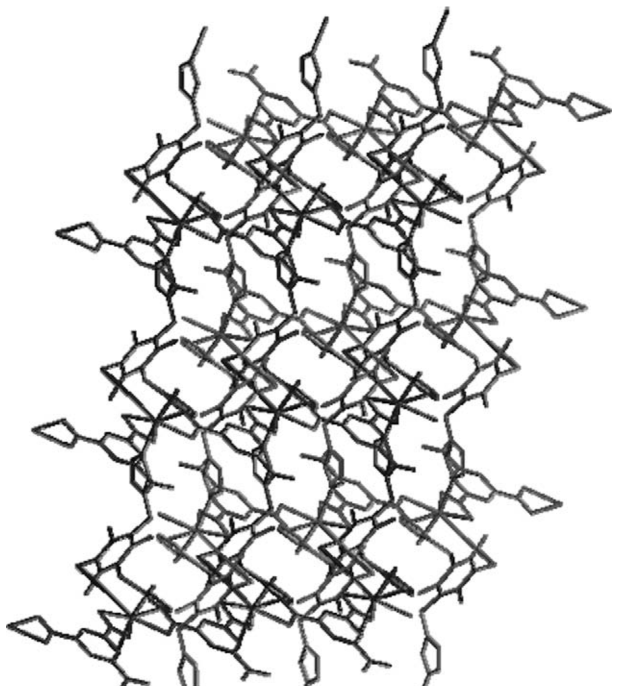


Fig. 5. Two layers of the structure of **2**. The lattice water molecules and H atoms are omitted for clarity.

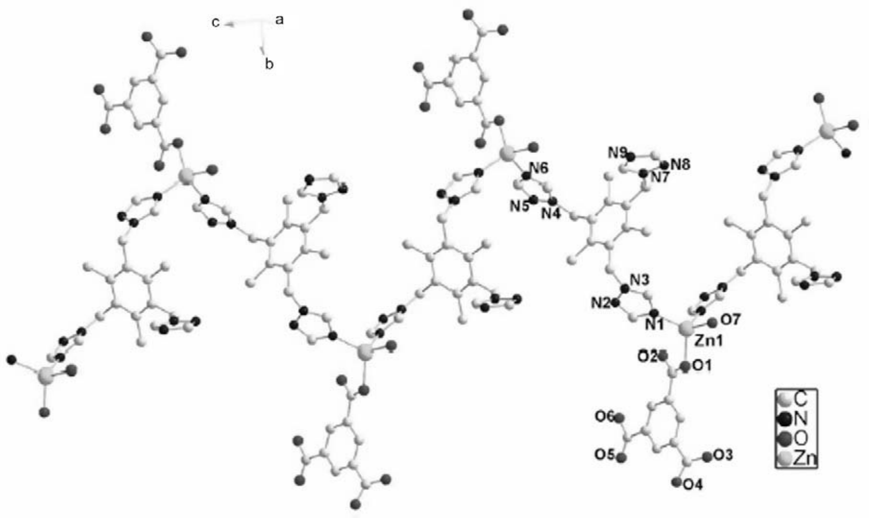


Fig. 6. One-dimensional zigzag chain structure of polymer **3**. Hydrogen atoms are omitted for clarity.

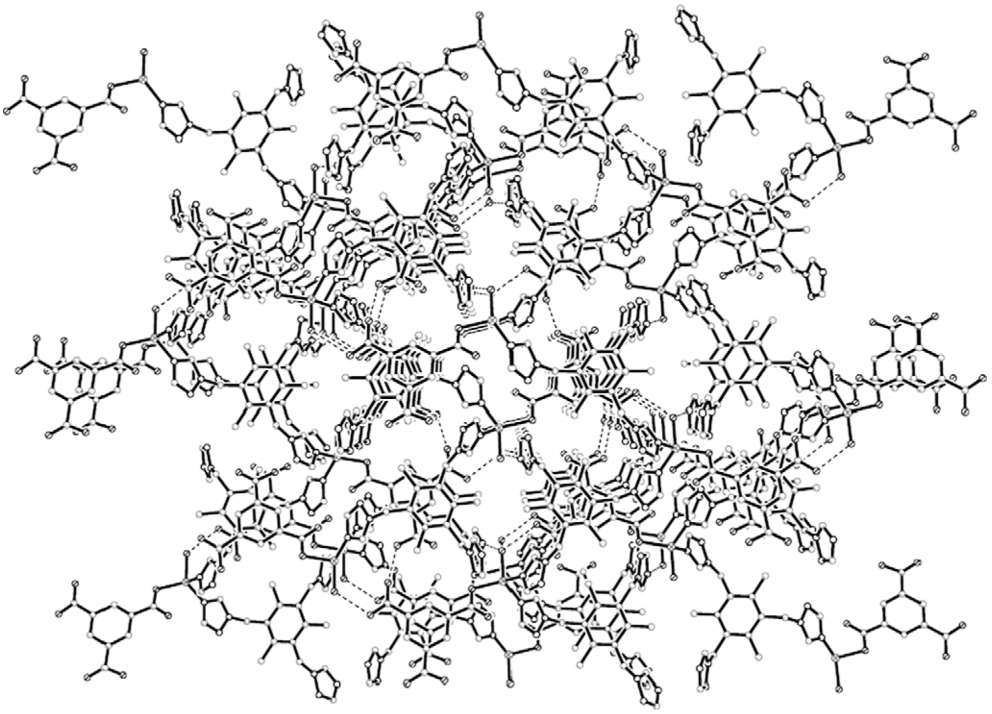


Fig. 7. View of the infinite three-dimensional supramolecular structure of polymer **3**, generated through extensive hydrogen bonding. Hydrogen atoms are omitted for clarity.

are linked through hydrogen bonds and π–π interactions resulting in a three-dimensional network (Fig. 7).

In polymers **1**, **2** and **3**, the ligand TTTMB is the *cis,trans,trans*-conformation and each TTTMB molecule coordinates to two Cd(II) ions as a bidentate ligand rather than a tridentate ligand that connects three metal ions. Additionally, $bdic^{2-}$ and $Hbtrc^{2-}$ as bidentate bridging ligand or monodentate ligand coordinates to metal ions, and they all serve as anion groups to keep the equilibrium of charges in these three polymers.

3.3. Fluorescence properties

The solid-state fluorescent spectra of **1**–**3** and TTTMB at room temperature are shown in Fig. 8. The free TTTMB ligand is fluorescent with a main emission band at 301 nm upon excitation at 284 nm. Polymers **2** and **3** give broad strong fluorescence center at 308 and 318 nm under the same experimental conditions, respectively. However, polymer **1** gives two peaks at 312 and 381 nm upon excitation at 284 nm. The peak at 381 nm which can be attributed to the auxiliary ligand H_2bdic since the ligand H_2bdic shows one strong emission band at 380 nm. In addition, we investigated the solid-state fluorescent spectra of TTTMB and polymers under the different concentration [33]. The result shows the main emission bands of the TTTMB and polymers **1**–**3** with different concentration do not change, and the fluorescence intensities of TTTMB and polymers **1**–**3** are falling along with reduction of the concentration (such as Fig. 9). The fluorescent spectra of all polymers exhibit slight red-shift in contrast to free ligands,

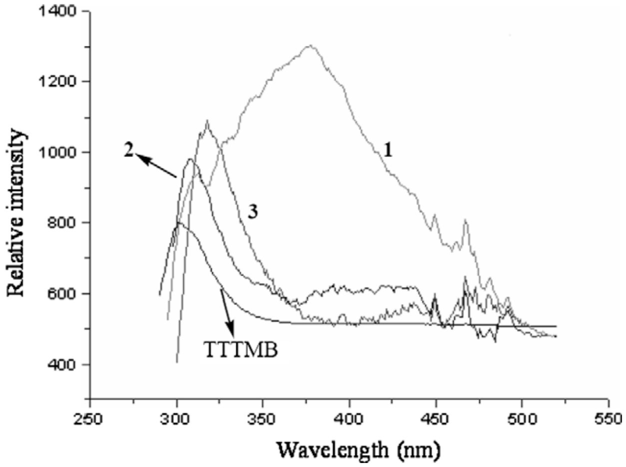


Fig. 8. Solid-state photoluminescence spectra of the ligand TTTMB and polymers **1**, **2** and **3** at ambient temperature.

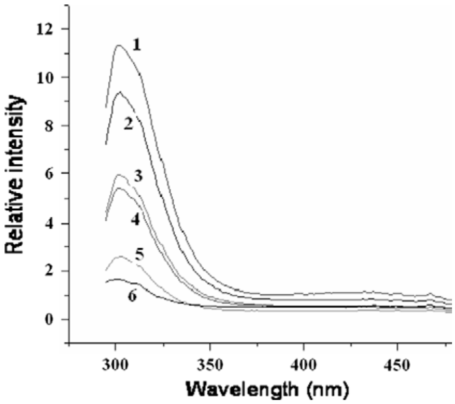


Fig. 9. Solid-state photoluminescence spectra of the ligand TTTMB under the different concentration at ambient temperature (1, TTTMB; 2, 20% TTTMB; 3, 10% TTTMB; 4, 5% TTTMB; 5, 2% TTTMB; 6, 1% TTTMB).

which implies that the fluorescence emissions of **1**–**3** are ruled by ligands [34,35]. It is worth noting that the fluorescence intensities of polymers **1**–**3** are higher than those of TTTMB. It may be attributed to the incorporation of metal cations, which effectively increases the conformational rigidity of ligand and reduces the loss of energy via vibration motions [36].

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Appendix A. Supplementary data

CCDC numbers 711653, 711654 and 711655 contain the supplementary crystallographic data for **1**, **2** and **3**, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2009.09.024.

References

[1] B. Moulton, M.J. Zaworotko, Chem. Rev. 101 (2001) 1629.
[2] J.J. Perry, G.J. McManus, M.J. Zaworotko, Chem. Commun. (2004) 2534.
[3] M. Eddaoudi, H. Li, O.M. Yaghi, J. Am. Chem. Soc. 122 (2000) 1391.
[4] L. Carlucci, G. Ciani, D.M. Proserpio, Coord. Chem. Rev. 246 (2003) 247.
[5] V.V. Smirnov, J.P. Roth, J. Am. Chem. Soc. 128 (2006) 3683.
[6] S.R. Batten, R. Robson, Angew. Chem. Int. Ed. 37 (1998) 1460.
[7] M. Du, X.J. Jiang, X.J. Zhao, Inorg. Chem. 45 (2006) 3998.
[8] H.K. Liu, W.Y. Sun, H.L. Zhu, K.B. Yu, W.X. Tang, Inorg. Chim. Acta 295 (1999) 129.
[9] M. Fujita, S. Nagao, K. Ogura, J. Am. Chem. Soc. 117 (1995) 1649.
[10] C.M. Hartshorn, P.J. Steel, Chem. Commun. (1997) 541.
[11] W.Y. Sun, J. Fan, T. Okamura, J. Xie, K.B. Yu, N. Ueyama, Chem. Eur. J. 7 (2001) 2557.
[12] H.K. Liu, W.Y. Sun, W.X. Tang, T. Yamamoto, N. Ueyama, Inorg. Chem. 38 (1999) 6313.
[13] J. Fan, H.F. Zhu, T. Okamura, W.Y. Sun, W.X. Tang, N. Ueyama, Inorg. Chem. 42 (2003) 158.
[14] W. Zhao, Y. Song, T. Okamura, J. Fan, W.Y. Sun, N. Ueyama, Inorg. Chem. 44 (2005) 3330.
[15] C.Y. Su, Y.P. Cai, C.L. Chen, F. Lissner, B.S. Kang, W. Kaim, Angew. Chem. Int. Ed. 41 (2002) 3371.
[16] J. Fan, B. Sui, T. Okamura, W.Y. Sun, W.X. Tang, N. Ueyamab, J. Chem. Soc.: Dalton Trans. (2002) 3868.
[17] J.L. Du, T.L. Hu, S.M. Zhang, Y.F. Zeng, X.H. Bu, Cryst. Eng. Commun. 10 (2008) 1866.
[18] B.L. Schottel, H.T. Chifotides, M. Shatruk, A. Chouai, L.M. Perez, J. Bacsa, K.R. Dunbar, J. Am. Chem. Soc. 128 (2006) 5895.
[19] SAINT, Program for Data Extraction and Reduction, version 6.01, Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1995.
[20] G.M. Sheldrick, SHELXTL, Program for Refinement of Crystal Structures, version 6.10, Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1997.
[21] J. Tao, M.L. Tong, F.X. Shi, X.M. Chen, S.W. Ng, Chem. Commun. (2000) 2043.
[22] S. Feng, R. Xu, Acc. Chem. Res. 34 (2001) 239.
[23] J.Y. Lu, Coord. Chem. Rev. 246 (2003) 327.
[24] X.R. Meng, Y.L. Song, H.W. Hou, H.Y. Han, B. Xiao, Y.T. Fan, Y. Zhu, Inorg. Chem. 43 (2004) 3528.
[25] Z.Y. Wang, R.G. Xiong, B.M. Foxman, S.R. Wilson, W.B. Lin, Inorg. Chem. 38 (1999) 1523.
[26] M.J. Plater, M.R.S.J. Foreman, T. Gelbrich, S.J. Coles, J. Chem. Soc.: Dalton Trans. (2000) 3065.
[27] J. Tao, M.L. Tong, X.M. Chen, J. Chem. Soc.: Dalton Trans. 20 (2000) 3669.
[28] J. Fan, L. Gan, H. Kawaguchi, W.Y. Sun, K.B. Yu, W.X. Tang, Chem. Eur. J. 9 (2003) 3965.
[29] S.L. Zheng, J.H. Yang, X.L. Yu, X.M. Chen, W.T. Wong, Inorg. Chem. 43 (2004) 830.
[30] B.H. Ye, M.L. Tong, X.M. Chen, Coord. Chem. Rev. 249 (2005) 545.
[31] M.X. Li, Z.X. Miao, M. Shao, S.W. Liang, S.R. Zhu, Inorg. Chem. 47 (2008) 4481.
[32] G. Li, B.Y. Chen, L. Kell, H.W. Hou, Y. Zhu, Y.T. Fan, J. Coord. Chem. 56 (2003) 877.
[33] H.M. Li, Y.D. Chen, C.Y. Yan, Y.Z. Hu, Acta Phys. Chim. Sin. 23 (2007) 1454.
[34] V.T. Yilmaz, S. Hamamci, S. Gumus, Chem. Phys. Lett. 425 (2006) 361.
[35] L.P. Wang, X.R. Meng, E.P. Zhang, H.W. Hou, Y.T. Fan, J. Organomet. Chem. 692 (2007) 4367.
[36] H. Xu, Z.Y. Chao, Y.L. Sang, H.W. Hou, Y.T. Fan, Inorg. Chem. Commun. 11 (2008) 1436.