

## 基于双(1,2,4-三氮唑基)刚性配体和芳香羧酸的两个配位聚合物的合成、晶体结构及荧光性质

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**摘要:** 水热条件下, 合成了 2 个结构新颖的金属配位聚合物:  $[\text{Co}_{1.5}(\text{btb})_2(\text{nbt})_2(\text{H}_2\text{O})_2]_n$  (**1**),  $[\text{Cd}(\text{btb})_{0.5}(\text{nph})(\text{H}_2\text{O})]_n$  (**2**) (btb=4,4'-二(1,2,4-三氮唑-1-基)联苯,  $\text{H}_3\text{nbt}$ =5-硝基-1,2,3-苯三甲酸,  $\text{H}_2\text{nph}$ =3-硝基邻苯二甲酸)并对它们进行了元素分析, 红外光谱及 X-射线单晶衍射等表征。结构分析表明, 化合物 **1** 是一个二维(3,4)-连接 3,4L90 拓扑结构, 并进一步通过 O-H $\cdots$ O 氢键作用构筑成三维超分子结构。而配合物 **2** 是一个三维(3,4,4)-连接的 sqc69 网络, 它的拓扑符号为  $(4.8^2)_2(4^2.8^2.10^2)(8.10^4.12)$ 。此外, 还研究了这两个配合物的热重和荧光性质。

**关键词:** 双(三氮唑)配体; 晶体结构; 配位聚合物; 混合配体; 荧光

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## Syntheses, Crystal Structures and Fluorescence Properties of Two Metal-Organic Coordination Polymers Derived from Rigid Bis(1,2,4-triazolyl) and Aromatic Carboxylic Acid Ligands

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**Abstract:** Two metal-organic coordination polymers with novel structural based on a rigid bis(triazole) ligand, namely,  $[\text{Co}_{1.5}(\text{btb})_2(\text{nbt})_2(\text{H}_2\text{O})_2]_n$  (**1**), and  $[\text{Cd}(\text{btb})_{0.5}(\text{nph})(\text{H}_2\text{O})]_n$  (**2**) (btb=4,4'-bis(1,2,4-triazolyl-1-yl)-biphenyl,  $\text{H}_3\text{nbt}$ =5-nitro-1,2,3-benzenetricarboxylic acid,  $\text{H}_2\text{nph}$ =3-nitrophthalic acid) were synthesized hydrothermally and characterized by IR, elemental analysis, as well as single-crystal X-ray diffraction. Compound **1** features a 2D structure with a (3,4)-connected 3,4L90 topology, which ultimately is extended into a 3D supramolecular framework via O-H $\cdots$ O hydrogen bonding interactions. While complex **2** exhibits a 3D (3,4,4)-connected sqc69 network with the Schläfli symbol of  $(4.8^2)_2(4^2.8^2.10^2)(8.10^4.12)$ . Furthermore, the thermal stability and fluorescence properties of the complexes have been investigated. CCDC: 1055345, **1**; 1063802, **2**.

**Key words:** bis(triazole); crystal structure; coordination polymer; mixed-ligand; fluorescence

## 0 Introduction

The rational design and synthesis of novel metal-organic coordination polymers (MOCs) is currently

attracting considerable interest because of their intriguing structures and potential applications as functional materials in luminescence, conductivity, magnetism, porosity, and so on<sup>[1-4]</sup>. In recent years, a

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great number of MOCPs with miscellaneous topological architectures and promising applications have been successfully obtained through self-assembly strategy<sup>[5-8]</sup>. According to previously reported, judicious selection of multifunctional N-donor and polycarboxylate mixed ligands is crucial to direct the synthesis of desirable MOCPs. Triazole-containing ligands as good candidates for the construction of metal coordination polymers, have aroused a great deal of attention due to their diversities in coordination modes and conformations<sup>[9-11]</sup>. Specifically, the bis(1,2,4-triazole) ligands can donate four N-donor atoms, which can enhance their coordination ability with metal ions and consequently contribute the formation of complexes<sup>[12-14]</sup>. From the viewpoint of crystal engineering and supermolecular chemistry, 4,4'-bis(1,2,4-triazolyl-1-yl)-biphenyl(btb) rigid ligand could be introduced as an attractive building block owing to its strong coordinating ability and planar  $\pi$ -conjugated system. However, only a few examples of metal coordination polymers with btb ligand have been previously reported<sup>[15-18]</sup>.

Herein, in order to investigate the influence of organic carboxylate co-ligands and metal ions on the structures and properties of MOCPs derived from rigid btb ligand, two new coordination polymers were fortunately isolated and characterized, namely,  $[\text{Co}_{1.5}(\text{btb})_2(\text{nbta})(\text{H}_2\text{O})_2]_n$  (**1**), and  $[\text{Cd}(\text{btb})_{0.5}(\text{nph})(\text{H}_2\text{O})]_n$  (**2**) ( $\text{H}_3\text{nbta}$ =5-nitro-1,2,3-benzenetricarboxylic acid,  $\text{H}_2\text{nph}$ =3-nitrophthalic acid). Structural diversification and the related properties such as fluorescence, thermal stability of two MOCPs were also investigated.

## 1 Experimental

### 1.1 Materials and general methods

Reagents and solvents employed were commercially available and used as received without further purification. Ligand btb was prepared according to literature procedure<sup>[19]</sup>. Elemental analyses for C, H and N were performed on a Perkin-Elmer automatic analyzer. IR spectra were recorded from KBr pellets in the range of 4 000~400  $\text{cm}^{-1}$  on a Nicolet FTIR Avatar 360 spectrophotometer. Thermogravimetric

analysis for complexes **1** and **2** were determined on a NETZSCH TG 209 thermal analyzer from room temperature to 800  $^{\circ}\text{C}$  with a heating rate of 10  $^{\circ}\text{C}\cdot\text{min}^{-1}$  under  $\text{N}_2$  atmosphere. The solid samples for photoluminescent measurements were performed with a Hitachi F-7000 spectrophotometer at room temperature. Powder X-ray diffraction (PXRD) patterns were collected on a Rigaku D/Max-2500PC X-ray diffractometer using  $\text{Cu } K\alpha$  radiation ( $\lambda=0.154\ 2\ \text{nm}$ ) and  $\omega$ - $2\theta$  scan mode at 293 K.

### 1.2 Synthesis of the complex $[\text{Co}_{1.5}(\text{btb})_2(\text{nbta})(\text{H}_2\text{O})_2]_n$ (**1**)

A mixture of  $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$  (240 mg, 1 mmol), btb (290 mg, 1 mmol), NaOH (120 mg, 3 mmol),  $\text{H}_3\text{nbta}$  (760 mg, 3 mmol) and 10 mL water was heated at 140  $^{\circ}\text{C}$  for 3 days in a Teflon-lined vessel (25 mL). After the mixture cooled to room temperature at a rate of 5  $^{\circ}\text{C}\cdot\text{h}^{-1}$ . Purple block single crystals of **1**, suitable for X-ray diffraction, were collected by filtration, washed with distilled water, and dried at ambient temperature. Yield: 43% (based on  $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ ). Anal. Calcd. for  $\text{C}_{82}\text{H}_{60}\text{Co}_3\text{N}_{26}\text{O}_{20}$  (%): C, 51.66; H, 3.17; N, 19.10. Found(%): C, 51.88; H, 2.95; N, 19.36. IR (KBr,  $\text{cm}^{-1}$ ): 3 432(s), 3 124(m), 1 589(s), 1 506(s), 1 394(s), 1 357(m), 1 324(m), 1 217(w), 1 155(w), 967(m), 824(m), 725(s), 649(m), 574(w).

### 1.3 Synthesis of the complex $[\text{Cd}(\text{btb})_{0.5}(\text{nph})(\text{H}_2\text{O})]_n$ (**2**)

Complex **2** was prepared in the similar way to **1** except that  $\text{Cd}(\text{OAc})_2$  (799 mg, 3 mmol) and  $\text{H}_2\text{nph}$  (630 mg, 3 mmol) were used instead of  $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$  and  $\text{H}_3\text{nbta}$ . Crystals of **2** were obtained in 65% yield. Anal. Calcd. for  $\text{C}_{16}\text{H}_{11}\text{CdN}_4\text{O}_7$  (%): C, 39.73; H, 2.29; N, 11.58. Found (%): C, 39.49; H, 2.55; N, 11.36. IR (KBr,  $\text{cm}^{-1}$ ): 3 415(m), 3 134(w), 1 601(s), 1 520(s), 1 454(m), 1 387(s), 1 281(w), 1 154(w), 973(w), 826(m), 713(m), 513(w).

### 1.4 X-ray crystallography

Single crystal X-ray diffraction data for the title complexes were collected on a Bruker Smart 1000 CCD diffractometer with  $\text{Mo } K\alpha$  radiation ( $\lambda=0.071\ 073\ \text{nm}$ ) by using an  $\omega$  scan mode. An empirical absorption correction was applied to the collected reflections with

SADABS<sup>[20]</sup>. The structures were solved by direct methods using SHELXS-97 and were refined on  $F^2$  by the full-matrix least-squares technique using the program SHELXL-97 program package<sup>[21]</sup>. The hydrogen atoms of water molecule were added by difference

Fourier maps and refined with isotropic displacement parameters. Crystal data of **1** and **2** are summarized in Table 1. Selected bond distances and angles of the complexes are listed in Table 2.

CCDC: 1055345, **1**; 1063802, **2**.

**Table 1 Crystallographic data and structural refinement of complexes 1 and 2**

Complex	<b>1</b>	<b>2</b>
Empirical formula	C <sub>16</sub> H <sub>11</sub> CdN <sub>4</sub> O <sub>7</sub>	C <sub>82</sub> H <sub>60</sub> Co <sub>3</sub> N <sub>26</sub> O <sub>20</sub>
Formula weight	1 906.35	483.69
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
$a$ / nm	1.100 40(9)	0.753 8(4)
$b$ / nm	1.228 57(10)	0.765 3(4)
$c$ / nm	1.504 58(12)	1.469 3(8)
$\alpha$ / (°)	73.971(10)	98.110(7)
$\beta$ / (°)	89.373(10)	98.764(6)
$\gamma$ / (°)	84.088(10)	90.313(7)
$V$ / nm <sup>3</sup>	1.944 3(3)	0.829 0(8)
$Z$	1	2
$D_c$ / (g·cm <sup>-3</sup> )	1.628	1.938
$F(000)$	975	478
Crystal size / mm	0.19×0.19×0.17	0.17×0.16×0.14
$\theta$ range for data collection / (°)	2.31~27.41	1.42~25.02
Absorption coefficient $\mu$ / mm <sup>-1</sup>	0.729	1.370
Reflections collected / unique	17 906 / 8 717 ( $R_{int}=0.029$ 6)	3 917 / 2 827 ( $R_{int}=0.031$ 6)
Refinement method	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$
Data / restraints / parameters	8 717 / 389 / 681	2 827 / 3 / 264
Goodness-of-fit on $F^2$	1.000	1.070
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1=0.039$ 7, $wR_2=0.071$ 7	$R_1=0.054$ 4, $wR_2=0.161$ 1
Final $R$ indices (all data)	$R_1=0.058$ 5, $wR_2=0.078$ 7	$R_1=0.071$ 7, $wR_2=0.179$ 2
Largest diff. peak and hole / (e·nm <sup>-3</sup> )	316 and -453	1 927 and -2 395

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

<b>1</b>					
Co1-O8 <sup>i</sup>	0.205 09(15)	Co1-O6	0.209 40(14)	Co1-O1W	0.211 33(17)
Co1-N7	0.213 57(18)	Co1-O2W	0.215 08(18)	Co1-N8	0.217 83(18)
Co2-O3 <sup>ii</sup>	0.204 14(14)	Co2-O3	0.204 14(14)	Co2-O5	0.207 72(15)
Co2-O5 <sup>ii</sup>	0.207 72(15)	Co2-N2 <sup>iii</sup>	0.214 26(17)	Co2-N2 <sup>iv</sup>	0.214 26(17)
<b>2</b>					
O8 <sup>i</sup> -Co1-O6	162.90(7)	O8 <sup>i</sup> -Co1-O1W	89.53(6)	O6-Co1-O1W	105.88(6)
O8 <sup>i</sup> -Co1-N7	91.90(7)	O6-Co1-N7	95.31(6)	O1W-Co1-N7	90.30(7)
O8 <sup>i</sup> -Co1-O2W	80.13(6)	O6-Co1-O2W	84.17(6)	O1W-Co1-O2W	169.53(6)
N7-Co1-O2W	91.69(7)	O8 <sup>i</sup> -Co1-N8	88.84(7)	O6-Co1-N8	85.89(7)
O1W-Co1-N8	82.70(7)	N7-Co1-N8	172.96(8)	O2W-Co1-N8	95.33(7)
O3 <sup>ii</sup> -Co2-O3	180.00(8)	O3 <sup>ii</sup> -Co2-O5	91.71(6)	O3-Co2-O5	88.29(6)
O3 <sup>ii</sup> -Co2-O5 <sup>ii</sup>	88.28(6)	O3-Co2-O5 <sup>ii</sup>	91.72(6)	O5-Co2-O5 <sup>ii</sup>	180.0

Continued Table 1

O3 <sup>ii</sup> -Co2-N2 <sup>iii</sup>	88.92(6)	O3-Co2-N2 <sup>iii</sup>	91.08(6)	O5-Co2-N2 <sup>iii</sup>	86.76(7)
O5 <sup>ii</sup> -Co2-N2 <sup>ii</sup>	93.24(7)	O3 <sup>ii</sup> -Co2-N2 <sup>iv</sup>	91.08(6)	O3-Co2-N2 <sup>iv</sup>	88.92(6)
O5-Co2-N2 <sup>iv</sup>	93.23(7)	O5 <sup>ii</sup> -Co2-N2 <sup>iv</sup>	86.76(7)	N2 <sup>iii</sup> -Co2-N2 <sup>iv</sup>	180.0
<b>2</b>					
Cd1-O2	0.225 4(6)	Cd1-N3	0.229 0(6)	Cd1-O3	0.228 9(5)
Cd2-O1W	0.229 3(6)	Cd2-O4 <sup>iii</sup>	0.230 8(5)	Cd2-O1	0.231 2(5)
O2-Cd1-O2 <sup>i</sup>	180.0	O2-Cd1-N3	88.2(2)	O2i-Cd1-N3	91.8(2)
O2-Cd1-N3 <sup>i</sup>	91.8(2)	N3-Cd1-N3 <sup>i</sup>	180.0	O2-Cd1-O3i	93.8(2)
N3-Cd1-O3 <sup>i</sup>	92.6(2)	O2-Cd1-O3	86.2(2)	N3-Cd1-O3	87.4(2)
O3 <sup>i</sup> -Cd1-O3	180.0	O1W <sup>ii</sup> -Cd2-O1W	180.0	O1W <sup>ii</sup> -Cd2-O4 <sup>iii</sup>	89.7(2)
O1W-Cd2-O4 <sup>iii</sup>	90.3(2)	O1W-Cd2-O4 <sup>iv</sup>	89.7(2)	O4 <sup>iii</sup> -Cd2-O4 <sup>iv</sup>	179.999(1)
O1W-Cd2-O1 <sup>ii</sup>	86.58(19)	O4 <sup>iii</sup> -Cd2-O1 <sup>ii</sup>	93.3(2)	O1W <sup>ii</sup> -Cd2-O1	86.58(19)
O1W-Cd2-O1	93.42(19)	O4 <sup>iii</sup> -Cd2-O1	86.7(2)	O4 <sup>iv</sup> -Cd2-O1	93.3(2)
O1 <sup>ii</sup> -Cd2-O1	180.0(3)	O4 <sup>iii</sup> -Cd2-O1 <sup>ii</sup>	93.3(2)	O4 <sup>iv</sup> -Cd2-O1 <sup>ii</sup>	86.7(2)

Symmetry codes: <sup>i</sup>  $x-1, y, z$ ; <sup>ii</sup>  $-x+2, -y, -z$ ; <sup>iii</sup>  $-x+1, -y, -z-1$ ; <sup>iv</sup>  $x+1, y, z+1$  for **1**; <sup>i</sup>  $-x, -y+2, -z$ ; <sup>ii</sup>  $-x+1, -y+3, -z$ ; <sup>iii</sup>  $x, y+1, z$ ;

<sup>iv</sup>  $-x+1, -y+2, -z$  for **2**

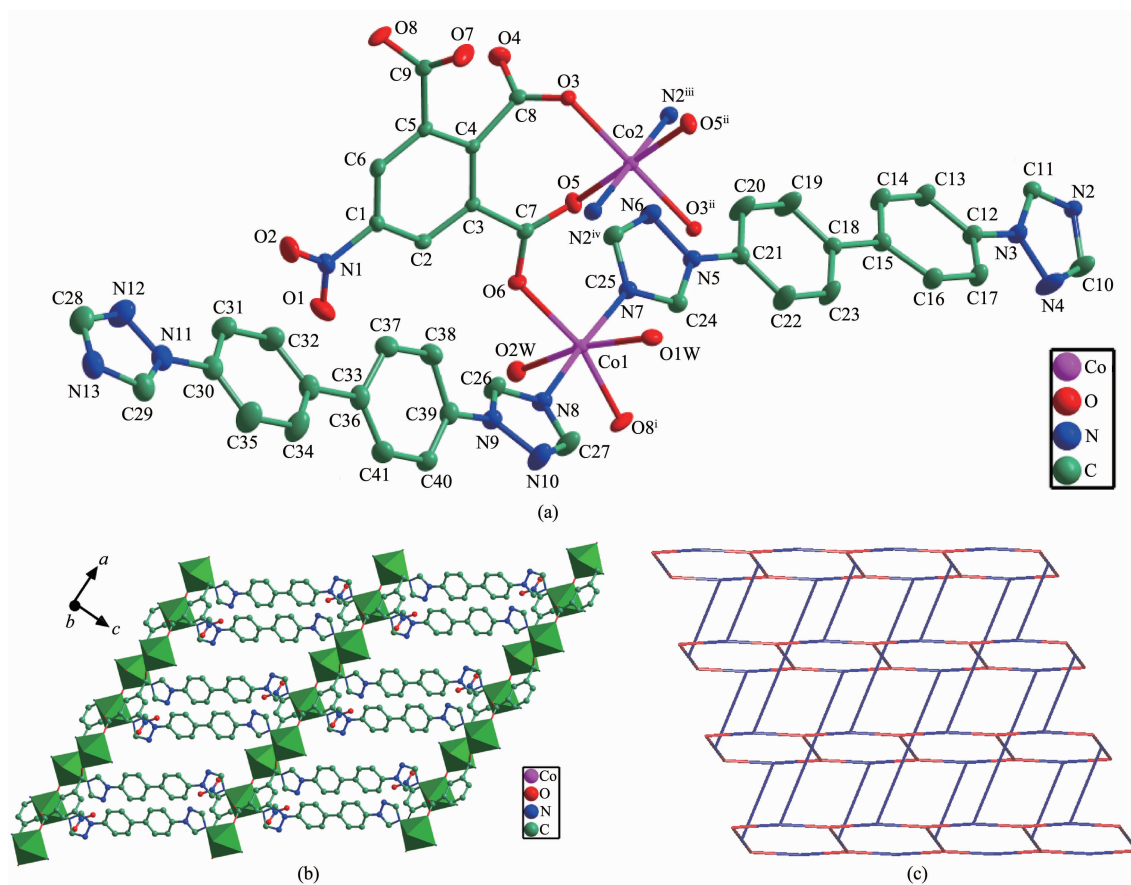
## 2 Results and discussion

### 2.1 Crystal structure of $[\text{Co}_{1.5}(\text{btb})_2(\text{nbtA})(\text{H}_2\text{O})_2]_n$ (**1**)

Structure analysis exhibits that complex **1** crystallizes in the triclinic space group  $P\bar{1}$ . The asymmetry unit contains one and half Co atoms (The Co2 atom lies on an inversion centre and therefore has an occupancy of 0.5), two btb ligands, one nbtA anion and two coordinated water molecules. As illustrated in Fig.1a, the two unique cobalt centres including Co1, Co2 exhibit octahedral coordination geometry. Co1 ion is in a distorted octahedron, in which two nitrogen atoms (N7, N8) from different btb ligands comprise the apical position, four oxygen atoms (O1W, O2W, O6, and O8<sup>i</sup>, Symmetry code: <sup>i</sup>  $x-1, y, z$ ) from two nbtA ligands and two coordinated water molecules occupy the equatorial plane. Co2 is coordinated by four carboxyl oxygen atoms (O3, O3<sup>ii</sup>, O5, O5<sup>ii</sup>, Symmetry code: <sup>ii</sup>  $-x+2, -y, -z$ ) from different nbtA<sup>3-</sup> anions, two nitrogen atoms (N2<sup>iii</sup> and N2<sup>iv</sup>, Symmetry code: <sup>iii</sup>  $-x+1, -y, -z-1$ ; <sup>iv</sup>  $x+1, y, z+1$ ) from two btb ligands to give a perfect octahedron geometry. The Co-N distances range from 0.213 57(18) to 0.217 83(18) nm, and the Co-O lengths are in the range of 0.204 14(14)~0.215 08(18) nm, which are all

comparable to those observed in related Co(II) coordination compounds<sup>[22]</sup>.

In the structure of **1**, each nbtA<sup>3-</sup> anion is completely deprotonated and displays  $\mu_3\text{-}\eta^2\text{:}\eta^1\text{:}\eta^1$  coordination mode connecting neighboring Co atoms to generate a 1D linear chain along the *a*-axis with a through-ligand Co...Co distances of 1.10 nm. It is noteworthy that the two crystallographically independent btb ligands exhibit distinct coordination behaviors when coordinated to cobalt atoms, one acts as a terminal ligand (N2-N7) and the other one acts as a linker (N8-N13). Each  $\mu_2$ -bridging btb ligand further extended neighboring 1D chains into a 2D sheet (Fig.1b). To better understand the nature of this network, a topological analysis was performed with the TOPOS 4.0 software<sup>[23]</sup>. If the Co1 and Co2 atoms are considered as 3-connected nodes and the nbtA ligands are considered as 4-connected nodes, the  $\mu_2$ -bridging btb ligands could act as connectors. Hence, the 2D structure of **1** can be represented to be a rarely (3,4)-connected 3,4L90 topology with the Schläfli symbol of  $(6^2.8^4)(6^2.8)4$  (Fig.1c). Moreover, the 2D layer is further extended by the classical O-H...O hydrogen bonding interactions (O2W-H2B...O2W<sup>v</sup>: 0.302 6(2) nm, 153(3)°, Symmetry code: <sup>v</sup>  $-x+1, -y+1, -z$ ) between coordinated water molecules to construct a 3D



Hydrogen atoms are omitted for clarity; Symmetry codes: <sup>i</sup>  $x-1, y, z$ ; <sup>ii</sup>  $-x+2, -y, -z$ ; <sup>iii</sup>  $-x+1, -y, -z-1$ ; <sup>iv</sup>  $x+1, y, z+1$

Fig.1 (a) Coordination environment of Co(II) ion in **1** (30% ellipsoid probability); (b) 2D layer for **1**; (c) (3,4)-connected 3,4L90 topology for **1**

Table 3 Hydrogen bond distances (nm) and angles ( $^{\circ}$ ) for complex **1**

D-H $\cdots$ A	$d(\text{D}\cdots\text{H})$	$d(\text{H}\cdots\text{A})$	$d(\text{D}\cdots\text{A})$	$\angle \text{DHA}$
O2W-H2B $\cdots$ O2W <sup>v</sup>	0.084(4)	0.226(4)	0.302 6(2)	153(3)

Symmetry code: <sup>v</sup>  $-x+1, -y+1, -z$

supramolecular framework. The related hydrogen bonding geometries are given in Table 3.

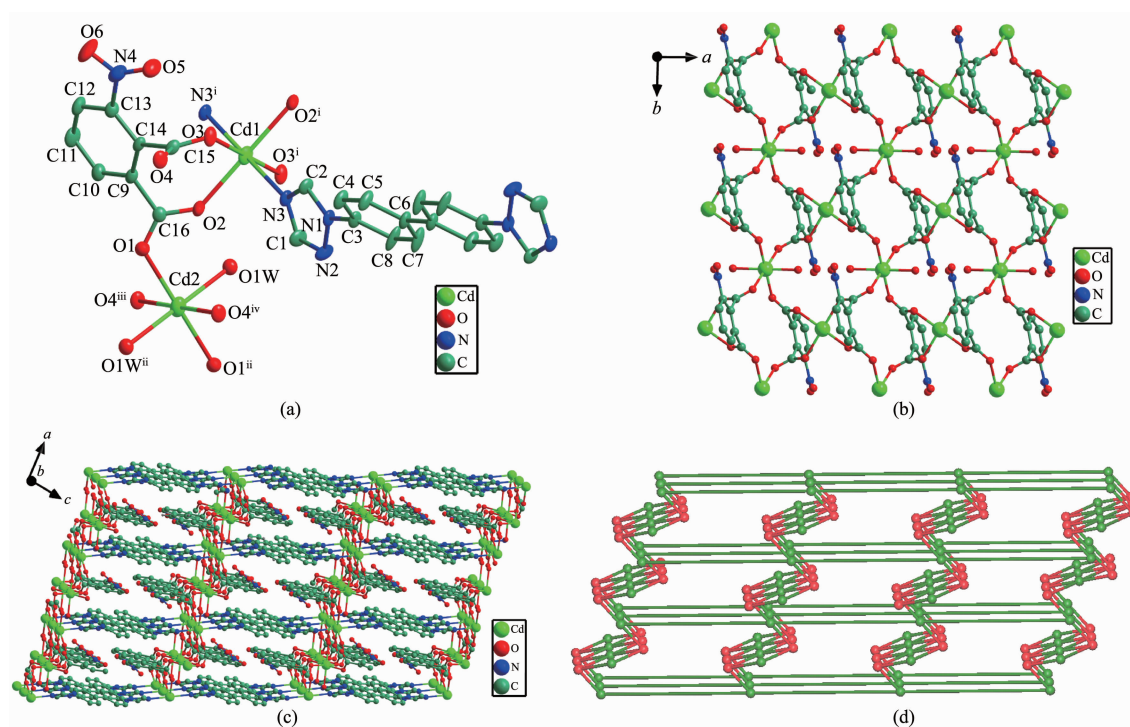
## 2.2 Crystal structure of $[\text{Cd}(\text{btb})_{0.5}(\text{nph})(\text{H}_2\text{O})]_n$ (**2**)

X-ray single crystal structure analysis reveals that **2** crystallizes in the triclinic space group  $P\bar{1}$ . Two coordination cadmium and C6 (from btb) atoms lie on centers of inversion. As shown in Fig.2a, both Cd1 and Cd2 ions take on distorted octahedron geometries. Cd1 is coordinated by four carboxyl oxygen atoms of two  $\text{nph}^{2-}$  ligands, two nitrogen atoms from different btb ligands. Cd2 binds with four carboxyl oxygen atoms from four  $\text{nph}^{2-}$  ligands, together with two oxygen atoms from two coordinated water molecules. The

distances of Cd-O bonds range from 0.225 4(6) to 0.231 2(5) nm and Cd-N length is 0.229 0(6) nm, respectively, both of which are in the normal range<sup>[8]</sup>.

The  $\text{nph}^{2-}$  ligands are completely deprotonated, whose two carboxylic groups exist in types of bridging bidentate and monodentate fashions, respectively. Each  $\text{nph}^{2-}$  ligand linking neighboring three Cd(II) ions (one Cd1 and two Cd2) with its two carboxylates to build a 2D layer (Fig.2b). The btb ligands exhibit the anti-conformation and acts as a  $\mu_2$ -mode bridging adjacent Cd1 atoms to pillar 2D layer into a 3D framework, in which the Cd $\cdots$ Cd distance through btb ligand is 1.816 nm (Fig.2c). In the topology view, each Cd1 atom is connected by two btb and two  $\text{nph}^{2-}$





Hydrogen atoms are omitted for clarity; Symmetry codes: <sup>i</sup>  $-x, -y+2, -z$ ; <sup>ii</sup>  $-x+1, -y+3, -z$ ; <sup>iii</sup>  $x, y+1, z$ ; <sup>iv</sup>  $-x+1, -y+2, -z$

Fig.2 (a) Coordination environment of Cd(II) ion in **2** (30% ellipsoid probability); (b) View of the 2D network assembled by Cd(II) and nph<sup>2-</sup> ligands for **2**; (c) 3D framework for **2**; (d) (3,4,4)-connected sqc69 network with the Schläfli symbol (4.8<sup>2</sup>)<sub>2</sub>(4<sup>2</sup>.8<sup>2</sup>.10<sup>2</sup>)(8.10<sup>4</sup>.12) for **2**

ligands in a tetrahedral geometry and can be regarded as a tetrahedral node; each Cd2 is linked to four nph<sup>2-</sup> ligands and can be considered as a four-connected node; each nph anion bridges three Cd(II) ions and thus can be regarded as a three-connected node. In such a case, the 3D framework of **2** can be described as a (3,4,4)-connected sqc69 network with the Schläfli symbol of (4.8<sup>2</sup>)<sub>2</sub>(4<sup>2</sup>.8<sup>2</sup>.10<sup>2</sup>)(8.10<sup>4</sup>.12) (Fig.2d). Further, the 3D structure was further reinforced by  $\pi$ - $\pi$  interactions between benzene rings from nph<sup>2-</sup> ligands and triazole rings from btb ligands with the Cg1 $\cdots$ Cg3<sup>i</sup> (Cg1 containing N1, N2, C1, N3, C2 atoms and Cg2 holding C9<sup>i</sup>, C10<sup>i</sup>, C11<sup>i</sup>, C12<sup>i</sup>, C13<sup>i</sup> and C14<sup>i</sup> atoms, Symmetry code: <sup>i</sup>  $-x, -y+2, -z$ . The  $x$ ,  $y$  and  $z$  coordinates of centroid of the specified atoms are (0.263 75, -0.019 14, 0.211 74) for Cg1, (-0.166 50, 2.075 35, 0.282 78) for Cg2, respectively.) center-to-center separation of 0.360 2(5) nm and the inter-planar angle  $\alpha$  of 14.5(4)°, slipping angles  $\beta$  ( $\gamma$ ) of 9.43° (5.78°).

### 2.3 IR spectroscopy

The IR spectra of the complexes show broad

bands at about 3 432 cm<sup>-1</sup> for **1**, 3 415 cm<sup>-1</sup> for **2**, which can be ascribed to the presence of water molecules. There is no band in the region of 1 690~1 730 cm<sup>-1</sup>, indicating complete deprotonation of the carboxyl groups<sup>[24]</sup>. The asymmetric and symmetric stretching vibrations of carboxyl groups are observed at 1 589 and 1 394 cm<sup>-1</sup> for **1**, 1 601, 1 454 and 1 387 cm<sup>-1</sup> for **2**, respectively. The separations ( $\Delta\nu[\nu_{as}(\text{COO}) - \nu_s(\text{COO})]$ ) between these bands indicate the presence of bridging (195 cm<sup>-1</sup> for **1**, 147 cm<sup>-1</sup> for **2**) and monodentate (214 cm<sup>-1</sup> for **2**) coordination modes of carboxyl groups<sup>[25]</sup>. The bands at 1 506 cm<sup>-1</sup> for **1**, 1 520 cm<sup>-1</sup> for **2** can be assigned to the  $\nu_{C=N}$  absorption of triazole ring of btb ligand.

### 2.4 Thermal analysis and PXRD results

The thermal stabilities were investigated as shown in Fig.3. The TGA curve of **1** shows a two-step weight loss process. The first weight loss of 4.5% occurs in the range of 80~135 °C corresponding to the loss of the coordinated water molecules (Calcd. 3.8%). The second weight loss may be assigned to the loss of

organic ligands, which begins at 205 °C and completes at 520 °C. The remaining weight (11.5%) corresponds to the percentage (11.8%) of Co and O components, indicating that the final residue is CoO. While for

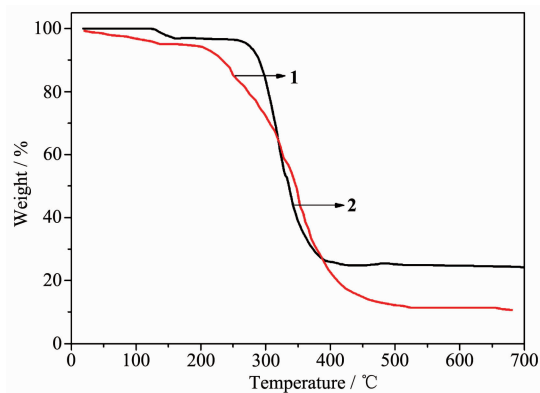


Fig.3 TGA curves of complexes **1** and **2**

complex **2**, the first weight loss step from 127 to 160 °C is attributed to the loss of the coordinated water molecule. The weight loss is about 3.1%, in correspondence with the calculated value of 3.7%. The second step with a weight-loss occurred in a temperature range from 256 to 435 °C for corresponding to the decomposition of the btb and  $\text{nph}^{2-}$  ligands. Finally, the residue weight of 25.6% for **2** is due to the Cd and O components in CdO (Calcd. 26.4%).

To confirm the phase purity of the new compounds, PXRD patterns have been carried out at room temperature (Fig.4). The peak positions of the experimental PXRD are well in agreement with the simulated data, demonstrating the phase purity of the bulk compounds.

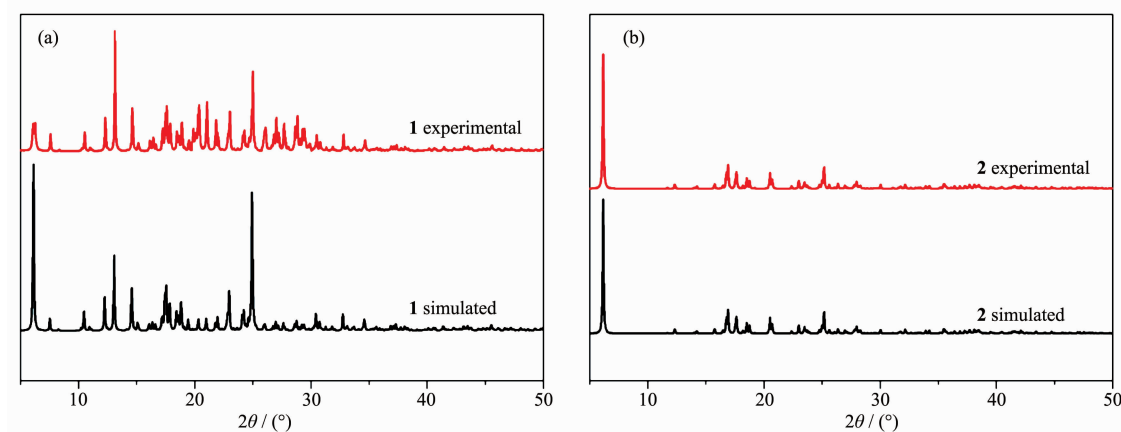


Fig.4 (a) X-ray powder diffraction patterns of **1**; (b) X-ray powder diffraction patterns of **2**

## 2.5 Fluorescence properties

The fluorescence properties of two complexes and the free btb ligand have been investigated in the solid state at room temperature. As shown in Fig.5, the free btb ligand exhibits fluorescent emission peaks at 439 nm ( $\lambda_{\text{ex}}=380$  nm), which may be assigned to the intraligand  $n \rightarrow \pi^*$  or  $\pi \rightarrow \pi^*$  transition<sup>[26]</sup>. Excitation of the as-synthesized **1** at 280 nm leads to the maximum emission peak at 328 nm. Upon excitation at 230 nm the maximum emission peaks of **2** are observed at 340 nm. On comparison with the free btb ligand, the maximum emission peak of **1** shows a blue shift of 111 nm and that of **2** shows a blue shift of 99 nm, which may tentatively be assigned to the ligand-to-metal charge transfer (LMCT). The emission discre-

pancy of these complexes is probably due to the differences of organic ligands and coordination environments of central metal ions, which have a close

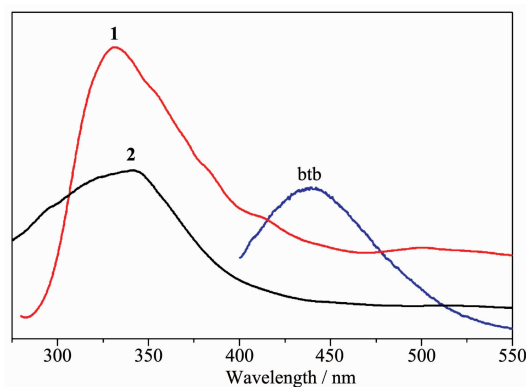


Fig.5 Emission spectra of the free btb ligand as well as complexes **1** and **2**

relationship to the photoluminescence behavior<sup>[27]</sup>.

### 3 Conclusions

In summary, two metal coordination polymers based on rigid btb ligand have been synthesized and characterized. The results of this work suggest that the metal centers and organic carboxylate ligands can greatly affect the construction of MOCPs with btb ligand. In addition, complexes **1** and **2** show intense fluorescence emission, signifying that the title MOCPs may be promising candidates for use as optical materials.

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