Wuhan University
Journal of Natural Sciences

2019, Vol.24 No.1, 008-014

Article ID 1007-1202(2019)01-0008-07
DOI https://doi.org/10.1007/s11859-019-1362-1

Syntheses, Crystal Structures, and Fluorescence Properties of Two 2D→2D Coordination Polymers Based on the Flexible 4-Substituted Bis(1,2,4-triazole) Ligand

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Abstract: Two new 2D → 2D zinc(II) coordination polymers, $[Zn(btre)_{0.5}(nbdc)(H_2O)]_n$ (**1**) and $\{[Zn(btre)_{0.5}(MeOip)(H_2O)_2]\cdot H_2O\}_n$ (**2**) (btre = 1,2-bis(1,2,4-triazol-4-yl)ethane, nbdc=3-nitro-1, 2-benzenedicarboxylate, MeOip=4-methoxybenzene-1, 3-dicarboxylate) were synthesized at room temperature condition and characterized by IR spectra, elemental analyses, single-crystal and powder X-ray diffractions. Three sets of equivalent 2D (6, 3) networks parallel polycatenated with each other to give a 2D → 2D network in **1** and **2**. There are strong π-π interactions and hydrogen bonding interactions between adjacent parallel polycatenated 2D (6, 3) network in **1**. Only hydrogen bonding interactions exist in **2**. Thermal stabilities and luminescence of **1** and **2** were investigated.

Key words: 3-fold interpenetration; 1,2-bis(1,2,4-triazol-4-yl) ethane; 2D (6, 3) network; luminescence
CLC number: O 614.24+1

Received date: 2018-06-12
Foundation item: Supported by the National Natural Science Foundation of China (21271035), the Natural Science Foundation of Anhui Province (KJ2016A512), and the Key Projects of Anhui Province University Outstanding Youth Talent Support Program (gxyqZD2016372)

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0 Introduction

The intriguing variety of architectures and topologies of coordination polymers (CPs) or metal-organic framework (MOF) have always been a hot research issue, due to their potential application as functional materials in crystal engineering[1-3]. Among them, the most investigated types of entanglement are self-interpenetration and interpenetration. Self-interpenetration is single nets with the peculiarity that the shortest circuits within the network are catenated by other rings or rods belonging to the same net. Interpenetration can be described as two, three, four or more same individual nets participating in interpenetration with each other[4-7]. Interpenetration can prevent formation of large channels. Sometimes interpenetration can increase the dimensionality, such as, 1D+1D→2D[8], 1D+2D→3D[9-11], 2D+2D+1D→3D[12], 2D+2D→3D[13, 14]. However, in many cases, parallel inclined interpenetration cannot increase structure dimensionality resulting 2D+2D→2D[15, 16].

Judicious selection of organic ligands is very crucial for obtaining frameworks with fascinating structure in the crystal engineering. The flexible 4-subsituted bis (triazole) ligand with four potential coordination sites can adopt different conformation according different coordination environment. In previous work, we synthesized some coordination polymers based on 1,2-bis(4H-1, 2,4-yl) ethane (btre)[17-19], 1,4-bis(1,2,4-triazol-4-yl) benzene (btx)[20], 1,4-bis(1,2,4-triazol-4-ylmethyl) benzene (btrb)[21], bis(4-(1,2,4-triazol-4-yl) phenyl) methane (btpm)[22]. For example, $\{[Zn(btx)(1,4\text{-}bdc)]\cdot 3H_2O\}_n$ (1,4-bdc=1,4-benzenedicarboxylate) shows a 5-fold interpenetrated three-dimensional diamondoid network. $[Zn(btx)_{0.5}(fum)(H_2O)]_n$ (fum=fumarate) displays a 2D →3D inclined polycatenation motif consisting of two sets of equivalent 2D (6,3) layers.

With this background information, two new coordination polymers, $[Zn(btre)_{0.5}(nbdc)(H_2O)]_n$ (**1**) and $\{[Zn(btre)_{0.5}(MeOip)(H_2O)_2]\cdot H_2O\}_n$ (**2**), were synthesized based on 1,2-bis(1,2,4-triazol-4-yl)ethane (btre), 3-nitro-1,2-benzenedicarboxylate (nbdc) and 4-Methoxybenzene-1,3-dicarboxylate (MeOip). The structures of **1** and **2** are all two-dimensional (6,3) networks and display 2D→2D parallel polycatenation motif consisting of three sets of equivalent 2D (6,3) layers. The thermal stabilities of compound **1** and **2** were investigated. CCDC (The number of Cambridge Crystallographic Data Centre): 1832685 for **1**, 1832686 for **2.**

1 Experimental

1.1 Materials and Methods

The ligand btre was synthesized according to Ref. [23]. All other reagents (such as $Zn(NO_3)_2\cdot 6H_2O$, H_2MeOip, H_2nbdc) were of analytical grade and used without further purification. Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C analyser (PerkinElmer, America). The IR spectra were obtained using KBr pellets on a Nicolet *iS*10 spectrophotometer (Thermo Fisher, American) in the 4 000-400 cm^{-1} region. Powder X-ray diffraction (PXRD) were performed on a D/MAX-3C diffractometer (Rigaku) with the CuKa radiation (λ = 0.154 06 nm) at room temperature. The luminescence measurements were carried out in the solid state at room temperature and the spectra were collected with a Perkin-Elmer LS50B spectrofluorimeter (PerkinElmer, America). TGA was carried out using a Thermal Analyst 2100 TA Instrument and SDT 2960 Simultaneous TGA-DTA Instrument (American TA) in flowing dinitrogen at a heating rate of 10 ℃/min.

1.2 Synthesis of $[Zn(btre)_{0.5}(nbdc)(H_2O)]_n$ (1)

A solution of 3-nitro-1,2-benzenedicarboxylic acid (H_2nbdc, 0.2 mmol) in 10 mL of H_2O was adjusted to pH =6 with 1.0 $mol\cdot L^{-1}$ NaOH solution and $Zn(NO_3)_2\cdot 6H_2O$ (0.2 mmol) was added with stirring. Then 5 mL methanol solution of btre (0.2 mmol/L) was added and continuously stirred for 10 min. The mixture solution was filtered and stood for two weeks to give colorless single crystals of **1** (0.034 g, 45% yield based on Zn). Anal. Calcd. (%) for $C_{11}H_9N_4O_7Zn$ (374.59) **(1)**: C, 35.27; H, 2.42; N, 14.96; Found: C, 35.30; H, 2.41; N, 14.98. IR data (cm^{-1}): 3 428w, 3 113w, 1 710w, 1 615s, 1 528s, 1 465m, 1 383s, 1 352s, 1 257w, 1 213w, 1 069w, 1 006w, 792w, 754w, 716w, 641w.

1.3 Synthesis of $\{[Zn(btre)_{0.5}(MeOip)(H_2O)_2]H_2O\}_n$ (2)

A solution of 4-methoxybenzene-1,3-dicarboxylic acid (H_2MeOip, 0.2 mmol) in 10 mL of H_2O was adjusted to pH=6 with 1.0 $mol\cdot L^{-1}$ NaOH solution and $Zn(NO_3)_2\cdot 6H_2O$ (0.2 mmol) was added with stirring. Then 5 mL methanol solution of btre (0.2 mmol) was added and continuously stirred for 10 min. The mixture solution was filtered and stood for one week to give colorless single crystals of **2** (0.041 g, 52% yield based on Zn). Anal. Calcd. (%) for $C_{12}H_{16}N_3O_8Zn$ (395.65) (**2**): C, 36.43; H, 4.08; N, 10.62; Found: C, 36.45; H, 4.10; N, 10.59. IR data (cm^{-1}): 3 409m, 3 157w, 3 113m, 1 685w, 1 603s, 1 565m, 1 383s, 1 352s, 1 270s, 1 201m, 1 075m, 1 018m, 905m, 848w, 798m, 691m, 628s.

1.4 X-Ray Crystallography

The diffraction data of **1** and **2** were collected on the Rigaku Saturn 724 CCD diffractometer with graphite monochromated MoKa radiation (λ = 0.071 075 nm) at 293.15 K. The intensities were collected by ω-scan and reduced on the CrystalClear (Rigaku Inc., 2007), and a multi-scan absorption correction was applied. All non-hydrogen atoms were refined anisotropically on F^2 by full-matrix least-squares techniques using SHELXL crystallographic package[24,25]. All the hydrogen atoms were determined with theoretical calculations and refined isotropically. The parameters of the crystal data collection and refinement of **1** and **2** are given in Table 1. The selected bond lengths and bond angles of **1** and **2** are listed in Tables 2 and 3.

2 Results and Discussion

2.1 Crystal Structure of 1

Single-crystal X-ray analysis shows that **1** crystallizes in the monoclinic system with P2₁/a space group. The asymmetric unit of **1** consists of one Zn(Ⅱ) atom, half a btre, one nbdc and one coordination water molecule. The Zn(1) atom is four-coordinated and surrounded by two oxygen atoms (O(1), O(3)#1) from

Table 1 Crystallographic collection and refinement parameters of 1 and 2

Item	1	2
Formula	$C_{11}H_9N_4O_7Zn$	$C_{12}H_{16}N_3O_8Zn$
M_r / g · mol^{-1}	374.59	395.65
T/K	293.15	293.15
Crystal system	monoclinic	monoclinic
Space group	$P2_1/a$	$P2_1/n$
a/nm	1.219 5(3)	1.036 9(3)
b/nm	0.6948 5(13)	0.843 4(2)
c/nm	1.554 5(3)	1.828 6(5)
α /(°)	90	90
β /(°)	91.260(4)	98.865(7)
γ /(°)	90	90
V/nm^3	1.316 8(4)	1.671 12(13)
F(000)	756	812
Z	4	4
D_c /g · cm^{-3}	1.889	1.663
μ/mm^{-1}	1.913	1.602
Reflections collected	6 229	7 844
Unique reflections	2 308[R_{int} = 0.102 1]	2 757[R_{int} = 0.037 0]
Parameter	216	228
GooF on F^2	1.035	1.008
R_1, wR_2*	0.046 3, 0.112 7	0.033 9, 0.089 5
R_1, wR_2**	0.059 6, 0.120 0	0.041 7, 0.093 1
$(\triangle\rho)_{max}$/eA^{-3}	0.56	0.63
$(\triangle\rho)_{min}$/eA^{-3}	−0.72	−0.36

$^*I>2\sigma(I)$; ** all data

Table 2 Selected bond lengths for 1 and 2

Compound	Bond	Bond length/nm
1	Zn(1)-O(1)	0.193 6(3)
	Zn(1)-O(7)	0.199 5(3)
2	Zn(1)-O(1)	0.200 9(2)
	Zn(1)-O(7)	0.213 8(2)
	Zn(1)-O(6)	0.210 5(2)
1	Zn(1)-N(1)	0.199 5(3)
	Zn(1)-O(3)#1	0.196 0(3)
2	Zn(1)-O(3)#1	0.220 7(2)
	Zn(1)-O(4)#1	0.219 4(2)
	Zn(1)-N(1)	0.209 1(3)

Symmetry codes: #1 −1/2+x, 1/2−y, +z for **1**; −1/2+x, 1/2−y, −1/2+ z for **2**

two nbdc ligands, one oxygen atom (O(7)) from coordination water, and one triazole nitrogen atom (N(1)) from btre ligand in a distorted tetrahedron geometry (ZnO_3N). The bond length of Zn-O/N is in the range of 0.193 6(3)-0.199 5(3) nm. Each nbdc ligand exhibits bis-monodentate bridging ligand and connects two Zn(Ⅱ) with the Zn···Zn distance of 0.639 43(1) nm (Fig. 1(a)). Each btre ligand acts as trans-conformation and bis-monodentate bridging ligand, and connects two Zn(Ⅱ) with the Zn···Zn distance of 1.143 15(1) nm. Each Zn(Ⅱ) connects three Zn(Ⅱ) atoms through one btre and two nbdc ligands and extends to form a 2D waved (6,3) network. Six Zn(Ⅱ) atoms are located at six vertexes and six edges are four nbdc and two btre ligands (Fig. 1(b)).

Table 3 Selected bond angles for 1 and 2

Compound	Bond	Bond angle/(°)	Compound	Bond	Bond angle/(°)
1	O(1)-Zn(1)-N(1)	106.83(1)	1	O(1)-Zn(1)-O(3)#1	124.52(1)
	O(3)#1-Zn(1)-O(7)	101.05(1)		O(3)#1-Zn(1)-N(1)	114.78(1)
	N(1)-Zn(1)-O(7)	102.91(1)		O(1)-Zn(1)-O(7)	103.69(1)
2	O(1)-Zn(1)-O(3)#1	148.59(8)	2	O(1)-Zn(1)-O(4)#1	89.39(8)
	O(1)-Zn(1)-O(7)	102.65(1)		O(1)-Zn(1)-N(1)	95.93(10)
	O(6)-Zn(1)-O(3)#1	119.14(9)		O(6)-Zn(1)-O(7)	87.00(1)
	O(7)-Zn(1)-O(3)#1	81.71(9)		N(1)-Zn(1)-O(7)	159.81(1)
	N(1)-Zn(1)-O(4)#1	98.83(9)		N(1)-Zn(1)-O(6)	84.42(1)
	O(1)-Zn(1)-O(6)	92.24(9)		O(7)-Zn(1)-O(4)#1	89.29(9)
	O(6)-Zn(1)-O(4)#1	176.20(1)		N(1)-Zn(1)-O(3)#1	86.56(9)

Symmetry codes: #1 −1/2+x, 1/2−y, +z for **1**; −1/2+x, 1/2−y, −1/2+ z for **2**

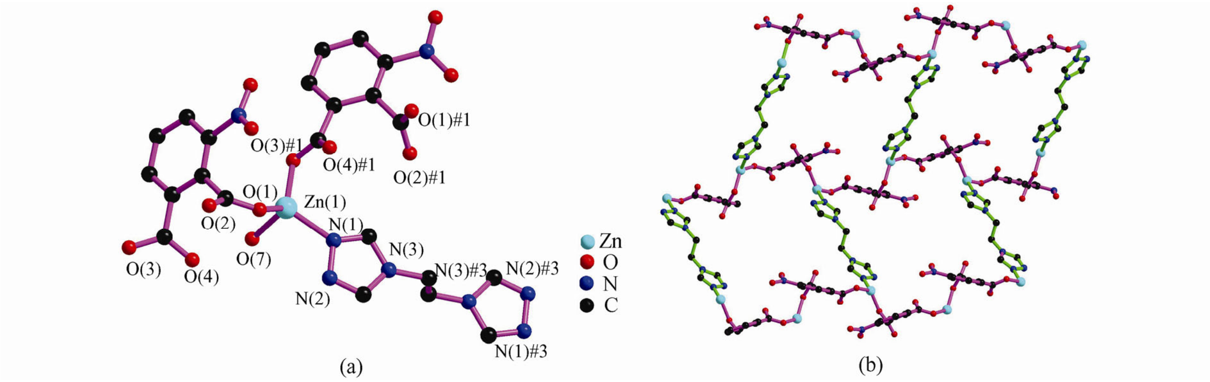

Fig. 1 **Coordination environment of the Zn(Ⅱ) atom (a) and the two-dimensional (6,3) network (b) in 1**

2.2 Crystal Structure of 2

2 crystallizes in the monoclinic system with $P2_1/n$ space group. The asymmetric unit of **2** consists of one Zn(Ⅱ) atom, half a btre, one MeOip, one coordination water and lattice water molecule. The Zn(1) atom is six-coordinated and surrounded by three oxygen atoms (O(1), O(3)#1, O(4)#1) from two MeOip ligands, two oxygen atom (O(6), O(7)) from coordination water and one triazole nitrogen atom (N(1)) from btre ligand with a distorted tetrahedron geometry [ZnO_5N]. The bond length of Zn-O/N is in the range of 0.200 9(2)-0.220 7(2) nm (Fig. 2(a)). Carboxyl groups (O(1), O(2)) and (O(3), O(4)) show monodentate and chelate mode, respectively, and bridge two Zn(Ⅱ) at the distance of 1.013 06(2) nm. Each btre ligand acts transconformation and bis-monodentate bridging ligand, and connects two Zn(Ⅱ) with the Zn···Zn distance of 1.176 44(2) nm. Each Zn(Ⅱ) connects three Zn(Ⅱ) atoms through one btre and two MeOip ligands and extends to form a 2D waved (6,3) network. Six Zn(Ⅱ) atoms lie six vertexes and six edges are four MeOip and two btre ligands. The edges of the rectangular windows of the layers are measured as 1.176 44 nm × 1.958 19 nm, as defined by Zn···Zn distance; these layers are nearly rectangular in shape, with Zn···Zn···Zn angles of 84.037° and 95.963° (Fig. 2(b)).

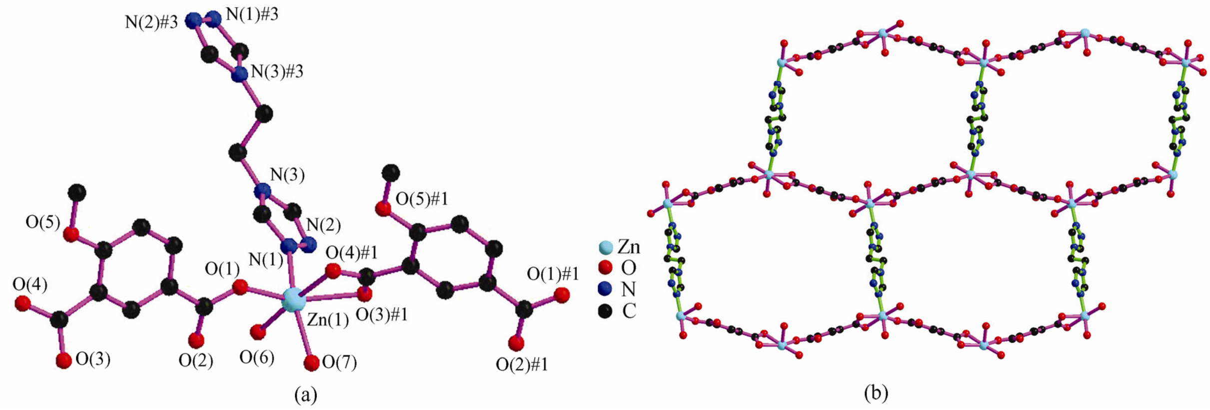

Fig. 2 **Coordination environment of the Zn(Ⅱ) atom (a) and the two-dimensional (6,3) network (b) in 2**

2.3 2D→2D Polycatenated Network of 1 and 2

The structures of **1** and **2** are all 2D undulated 2D (6,3) networks. The interpenetration between each other of three sets of 2D (6,3) networks to give a 2D→2D polycatenated networks is somewhat exceptional, although the 2D (6,3) networks is rather common. In compound **1**, the centroid-centroid, perpendicular distances and dihedral angle of the triazole ring of btre from one 2D network and triazole ring of btre from the polythreaded 2D network are 0.354 50(4) nm, 0.340 79 nm and 0°, respectively, showing the strong π-π interaction between triazole rings from adjacent polythreaded 2D networks (Fig. 3(a)).

There are hydrogen bond interactions between the coordinated water molecules and the carboxyl oxygen atoms of nbdc from adjacent 2D (6,3) networks (O(7)-H(7w)···O(2)#4 ($+x$, $-1+y$, $+z$) 0.266 5(4)). There is no π-π interactions in complex **2**. There are hydrogen bond interactions between the coordinated water molecules and the carboxyl oxygen atoms of MeOip and nitrogen of btre from adjacent 2D (6,3) networks in **2** (O(6)-H(6w)···O(3)#1 (1/2−*x*, 1/2+*y*, 3/2−*z*) 0.262 6(3); O(7)-H(7w)···N(2)#2 (1/2−*x*, 1/2+*y*, 3/2−*z*) (Fig. 3(b)). The hydrogen bond parameters are shown in Table 4. These hydrogen bonding interactions and π-π interactions improve the stability of the 2D→2D polythreaded network. The three-fold parallel interpenetration does not increase the dimension (Fig. 3(c)). Batten group has described the *n*-fold interpenetrated 2D structures with no increase in dimensionality[26].

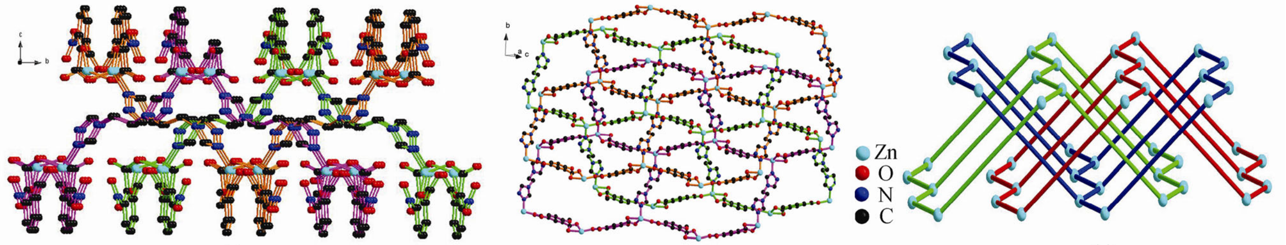
(a) (b) (c)

Fig. 3 Three-fold interpenetration 2D network of 1(a) and 2(b) and the schematic depiction(c)

The sticks in (c) represent the btre and nbdc for **1** or MeOip for **2**

Table 4 Hydrogen bonds for 1 and 2

Compound	D-H··· A	*d*(D-H)/nm	*d*(H··· A)/ nm	*d*(D··· A)/nm	∠(DHA)/(°)
1	O(7)-H(7W)··· O(2)#4	0.084(2)	0.183(2)	0.266 5(4)	171(8)
	O(7)-H(7W)··· O(4)	0.085(2)	0.203(3)	0.284 5(5)	159(5)
2	O(6)-H(6W)··· O(3)#1	0.087	0.183	0.262 6(3)	150.4
	O(7)-H(7W)··· N(2)#2	0.086	0.205	0.290 4(3)	170.9

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

2.4 PXRD Patterns and Thermogravimetric Analysis of 1 and 2

In order to characterize the purity of compound **1** and **2**, the as-synthesized samples were measured by X-ray powder diffraction at room temperature. As shown in Fig. 4, the peak position of the measured patterns is in good agreement with the simulated patterns, indicating the purity of the samples. The thermal stability of **1** and **2** was examined by thermogravimetric analyses. In the thermogravimetric (TG) curve of **1** (Fig. 5), 1 mol coordinated water lost from 87 to 100 ℃ (calcd.: 4.80%, found: 4.80%). The network was thermally stable upon 297 ℃. Then the decomposition happened quickly up to 688 ℃. The main residue should be ZnO (calcd.: 21.71%, found: 21.92%). The TG curve of **2**, 2 mol coordinated water and 1 mol lattice water lost from 57 to 185 ℃ (calcd.: 4.80%, found: 4.80%). The framework of **2** is very stable from 185 to 290 ℃. Then the weight decreased quickly and did not end until 680 ℃. The main residue should be ZnO (calcd.: 20.56%, found: 20.71%). TG analysis shows that the frameworks of complexes **1** and **2** have high stability after losing coordination water and lattice water molecule.

2.5 Photoluminescence Properties of 1 and 2

There is continuous interest in the study of photoluminescence coordination polymers with d^{10} electronic configuration because of their ability to shift, quench or enhance luminescent emission of organic ligands in coordination polymers. Therefore, the solid state luminescence spectra of **1**, **2** and free ligands H_2MeOip, H_2nbdc and btre were investigated at room temperature (Fig. 6). The free btre ligand does not show luminescence at room temperature which is the same as Refs.[17,19]. The btre luminescence is possibly quenched by the thermal intra-ligand rotations around the C—C and C—N bonds[27, 28]. No fluorescence emission was observed in the free ligand H_2nbdc and compound **1**. The free H_2MeOip ligand exhibits the strong emission at 367 nm and a weak emission at 464 nm upon excitation at 330 nm. **2** shows strong emission band maxima approximately at 418 nm and weak emission at 470 nm upon excitation at 320 nm. Due to the d^{10} configuration, Zn(Ⅱ) ion is difficult to be oxidized or reduced, and the emissions are neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT). Emission peaks at 418 and 470 nm of **2** may be attributed to the intra-ligand charge transition (ILCT)

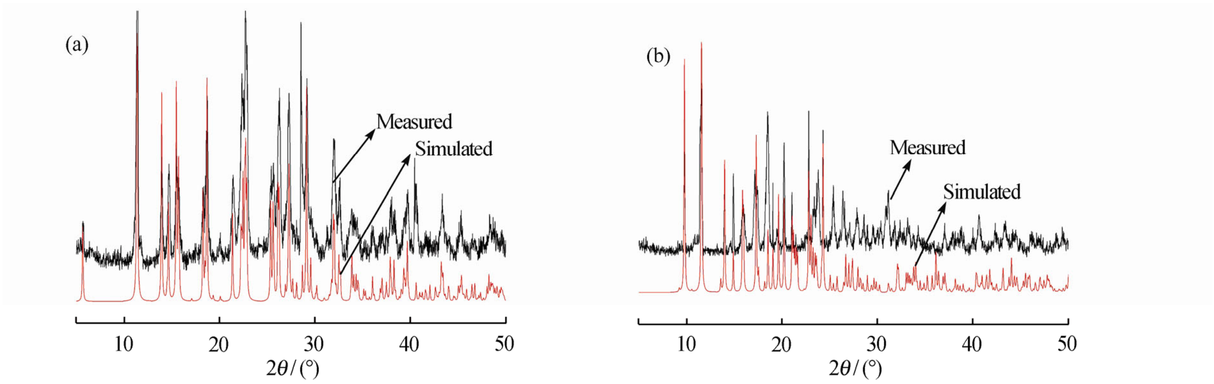

Fig. 4 PXRD patterns in compound 1(a) and 2(b)

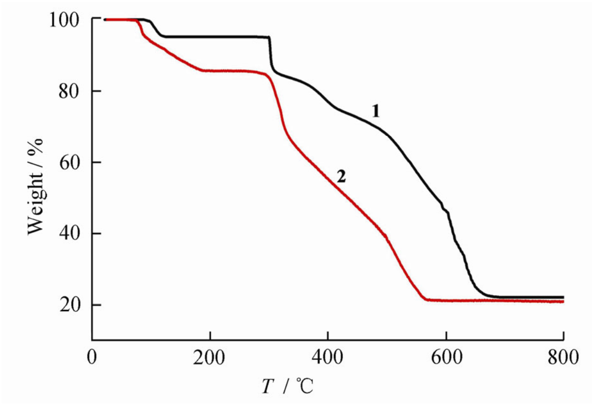

Fig. 5 TG of compounds 1 and 2

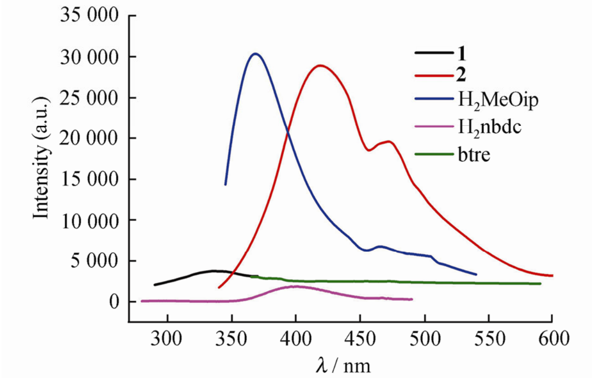

Fig. 6 Emission spectra of 1, 2, free ligands btre and H_2MeOip in solid state at room temperature

or ligand to ligand charge transition (LLCT) and the emission of ligand H2MeOip, respectively[29,30].

3 Conclusion

In summary, two new coordination polymers were synthesized successfully by reacting with the Zn(Ⅱ) salts, the flexible N-donor ligand btre and the auxiliary O-donor ligand 3-nitro-1,2-benzenedicarboxylate and 4-methoxybenzene-1,3-dicarboxylate at room temperature. **1** and **2** are all 2D (6,3) networks. Three sets of identical 2D (6,3) networks parallel polycatenated with each other to give a 2D→2D polythreaded network. These covalent interactions such as hydrogen bonds and π-π interactions improve the stability of the 3-fold polythreaded network.

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