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三个基于柔性 4-取代双三唑配体锌配位聚合物的合成、晶体结构

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摘要:以 1,2-二(4*H*-1,2,4-三唑)乙烷(btre)和 3 个二元羧酸 1,3-金刚烷二酸(H_2adc)、对苯二甲酸(1,4-H_2bdc)和邻苯二甲酸(1,2-H_2bdc)为配体,在室温下合成了 3 个锌配位聚合物{[Zn(μ_2-btre)(μ_2-adc)]H_2O}$_n$ (**1**·H_2O)、[Zn_2(μ_2-btre)(μ_2-1,4-bdc)$_2$(H_2O)$_2$]$_n$ (**2**)和[Zn(μ_2-btre)(μ_2-1,2-bdc)]$_n$ (**3**)。测试了 3 个配合物的晶体结构,并用红外光谱、元素分析和粉末衍射对其进行表征。晶体结构测试表明,**1** 为 2D (4,4)网格结构,π-π 作用将相邻的 2D 网格连接成 3D 结构。配合物 **2** 和 **3** 分别是 3D 和 2D(4,4)网格结构。另外,研究了 3 个配合物的热稳定性和室温下的固体荧光。

关键词:1,2-二(4*H*-1,2,4-三唑)乙烷;π-π 作用;(4,4)网格;荧光
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Syntheses, Structures of Three Zn(Ⅱ) Coordination Polymers Based on Flexible 4-Substituted Bis(1,2,4-triazole) Ligand

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Abstract: Three new coordination polymers, {[Zn(μ_2-btre)(μ_2-adc)]·H_2O}$_n$ (**1**·H_2O), [Zn_2(μ_2-btre)(μ_2-1,4-bdc)$_2$(H_2O)$_2$]$_n$ (**2**) and [Zn(μ_2-btre)(μ_2-1,2-bdc)]$_n$ (**3**) were synthesized at room temperature condition and characterized by IR spectra, elemental analyses, single-crystal and powder X-ray diffractions (btre=1,2-bis(1,2,4-triazol-4-yl)ethane, adc=1,3-adamantanedicarboxylate, 1,4-bdc=1,4-benzenedicarboxylate, 1,2-bdc=1,2-benzenedicarboxylate). Structural analyses reveal that complex **1** exhibits a 2D (4,4) network, and the adjacent 2D (4,4) networks are connected into 3D network by strong π-π interactions. The structure of **2** and **3** are 3D and 2D (4,4) network, respectively. Thermal stabilities and the solid-state luminescence at room temperature of **1**, **2** and **3** were investigated. CCDC: 1848223, **1**; 1848224, **2**; 1848225, **3**.

Keywords: 1,2-bis(1,2,4-triazol-4-yl)ethane; π-π interaction; (4,4) network; luminescence

0 Introduction

In recent years, the synthesis and characterization of coordination polymers (CPs) or metal-organic frameworks (MOFs) have attracted widely attention not only due to their structural diversity but also many physical properties with potential applications in many areas, such as ion exchange or absorption[1-2], cation/small molecule solvent recognition[3-5], catalysis[6-7], gas absorption, storage and separation[8-9], luminescence[10]. Although more and more coordination polymers have been synthesized, the controlled synthesis of complexes is still a great challenge, since many factors affect the structures and properties of coor-

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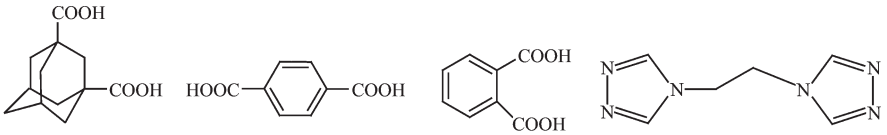
dination polymers. Of all factors, a judicious selection of organic bridging ligands is very fruitful in the crystal engineering[11-12]. Because of the diversity of the coordination modes and high-connected nods, polycarboxylate ligands are used to construct MOFs or CPs[13-16]. On the other hand, N-donor ligands also play an important role in synthesizing CPs or MOFs. More and more new flexible or rigid N-donor ligands have been synthesized and used in the synthesis of metal-organic frameworks. Especially, in recent years, the 4-substituted-bis(1,2,4-triazole) derivatives ligands have attracted much more attention of many researchers. We have synthesized some coordination polymers based on rigid 4-substituted-bis(1,2,4-triazole) ligand 1,4-bis-(1,2,4-triazol-4-yl)benzene (btx)[17-18], flexible ligand 1, 4-bis(1,2,4-triazol-4-ylmethyl)benzene (btrb)[19] and 1, 2-bis(1,2,4-triazol-4-yl)ethane (btre)[20-21]. With four possible coordination sites, btre has different coordination modes, such as bis-monodentate, tridentate and quadridentate mode. Ligand btre can adopt *cis* or *trans* conformation according to different coordination environments or different metal ions because of its flexibility. Meanwhile, the weak supramolecular interactions such as hydrogen bond, π-π stacking are as important as coordination bond in crystal engineering. These covalent interactions can improve the stability of the network and increase dimensionality[22-24].

Herein, three new coordination polymers $\{[Zn(\mu_2\text{-btre})(\mu_2\text{-adc})]\cdot H_2O\}_n$ (**1**·H_2O), $[Zn_2(\mu_2\text{-btre})(\mu_2\text{-1,4-bdc})_2(H_2O)_2]_n$ (**2**) and $[Zn(\mu_2\text{-btre})(\mu_2\text{-1,2-bdc})]_n$ (**3**) were synthesized based on three kinds of dicarboxylate (btre=1,2-bis (1,2,4-triazol-4-yl)ethane, adc=1,3-adamantanedicarboxylate, 1,4-bdc=1,4-benzenedicarboxylate, 1,2-bdc=1,2-benzenedicarboxylate) (Scheme 1). **1** and **3** show two-dimensional (4,4) networks. **2** exhibits 3D network. The thermal stabilities of complexs **1**~**3** were investigated.



H_2adc 1,4-H_2bdc 1,2-H_2bdc btre

Scheme 1 Structures of ligands H_2adc, 1,4-H_2bdc, 1,2-H_2bdc and btre

1 Experimental

1.1 Materials and measurement

Ligand btre was synthesized according to the literature method[25]. All other reagents are of analytical grade and used without further purification. Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C analyzer. The IR spectra were obtained using KBr pellets on a Nicolet iS10 spectrophotometer in the 4000~400 cm^{-1} region. Powder X-ray diffraction (PXRD) were performed on a D/MAX-3C diffractometer with the Cu $K\alpha$ radiation (λ=0.154 06 nm, U=40 kV, I=40 mA) over the 2θ range of 5°~50° 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. TGA was carried out using a Thermal Analyst 2100 TA Instrument and SDT 2960 Simultaneous TGA-DTA Instrument in flowing dinitrogen at a heating rate of 10 ℃·min^{-1}.

1.2 Syntheses of the complexes

1.2.1 Synthesis of $\{[Zn(\mu_2\text{-btre})(\mu_2\text{-adc})]\cdot H_2O\}_n$ (**1**·H_2O)

A solution of H_2adc (0.2 mmol) in 10 mL of H_2O was adjusted to pH=6 with 1.0 mol·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 **1**·H_2O (0.033 g, Yield: 35% based on btre). Anal. Calcd. for $C_{18}H_{24}N_6O_5Zn$(%): C, 46.02; H, 5.15; N, 17.89; Found(%): C, 46.05; H, 5.11; N, 17.80. IR (cm^{-1}): 3 434s, 3 113s, 2 937s, 2 906s, 2 855m, 1 578s, 1 458m, 1 383s, 1 308s, 1 207m, 1 201m, 1 075m, 1 031w, 974w, 892w, 810w, 697m, 641s.

1.2.2　Synthesis of $[Zn_2(\mu_2\text{-btre})(\mu_2\text{-1,4-bdc})_2(H_2O)_2]_n$ (**2**)

The synthesis of **2** was similar with that of **1** using 1,4-H_2bdc (0.2 mmol) in stead of H_2adc. Yield: 0.045 g, 28.43% based on Zn. Anal. Calcd. for $C_{22}H_{20}N_6O_{10}Zn_2$(%): C, 40.08; H, 3.06; N, 12.75; Found(%): C, 40.03; H, 3.10; N, 12.79. IR (cm^{-1}): 3 233s, 3 101s, 1 609s, 1 603s, 1 565m, 1 383s, 1 352s, 1 270s, 1 201 m, 1 144w, 1 075m, 1 081m, 892m, 842s, 748s, 635s, 540m, 489w.

1.2.3　Synthesis of $[Zn(\mu_2\text{-btre})(\mu_2\text{-1,2-bdc})]_n$ (**3**)

The synthesis of **3** was similar with that of **1** using 1,2-H_2bdc (0.2 mmol) in stead of H_2adc. Yield: 0.033 g, 42% yield based on Zn. Anal. Calcd. for $C_{14}H_{12}N_6O_4Zn$(%): C, 42.71; H, 3.07; N, 21.35; Found (%): C, 42.73; H, 3.10; N, 21.39. IR (cm^{-1}): 3 436w, 3 109s, 3 012w, 1 627s, 1 530s, 1 390s, 1 360s, 1 214m, 1 087m, 1 032s, 898m, 832m, 771m, 716m, 643s, 582w, 491w.

1.2.4　X-ray crystallography

The diffraction data of **1** and **2** were collected on the Xcalibur, Atlas, Gemini, **3** on Rigaku Mercury CCD diffractometer with graphite monochromated Mo $K\alpha$ (λ=0.071 073 nm for **1** and **2**, 0.071 070 nm for **3**) radiation. Intensities were collected by the ω scan technique. The structures were solved and refined by the SHELXTL package[26-27]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were determined with theoretical calculations and refined isotropically. The lattice water of **1**·H_2O is highly disordered and could not be modeled properly and was removed by the SQUEEZE routine in PLATON[28]. The number of lattice water molecules for **1**·H_2O was deduced from the TGA and elemental analysis. The parameters of the crystal data collection and refinement of **1~3** are given in Tables 1. Selected bond lengths and bond angles of **1~3** are listed in Table 2.

CCDC: 1848223, **1**; 1848224, **2**; 1848225, **3**.

Table 1　Crystallographic collection and refinement parameters of 1~3

Complex	**1**	**2**	**3**
Formula	$C_{18}H_{22}N_6O_4Zn$	$C_{22}H_{20}N_6O_{10}Zn_2$	$C_{14}H_{12}N_6O_4Zn$
Formula weight	451.78	659.18	393.67
T / K	295.31	223.00(10)	293.15
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1$
a / nm	0.663 65(8)	1.033 30(8)	0.699 56(17)
b / nm	0.967 03(13)	1.161 85(9)	1.210 1(3)
c / nm	1.507 39(10)	1.164 93(9)	0.925 4(2)
α / (°)	97.678(8)	65.017(8)	
β / (°)	91.960(7)	77.424(7)	105.009(4)
γ / (°)	92.400(10)	75.557(7)	
V / nm^3	0.957 10(18)	1.217 52(18)	0.756 6(3)
F(000)	468	668	400
Z	2	2	2
D_c / (g·cm^{-3})	1.568	1.798	1.728
μ / mm^{-1}	1.322	2.042	1.659
Reflection collected	7 194	8 821	7 268
Unique reflection	3 350 (R_{int}=0.057 9)	4 276 (R_{int}=0.041 2)	2 644 (R_{int}=0.022 3)
Parameter	262	377	227
Flack parameter			–0.005(13)
GOF on F^2	1.016	1.034	0.989
R_1, wR_2 [I>2σ(I)]	0.054 5, 0.129 7	0.037 0, 0.079 7	0.021 2, 0.042 9
R_1, wR_2 (all data)	0.066 9, 0.137 8	0.049 6, 0.085 9	0.023 3, 0.043 9
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ / (e·nm^{-3})	1890, –480	590, –410	350, –240

Table 2 Selected bond lengths (nm) and angles (°) for 1~3

Complex **1**					
Zn(1)-O(1)	0.195 0(4)	Zn(1)-O(3)A	0.201 4(3)	Zn(1)-N(1)	0.209 5(4)
Zn(1)-N(4)	0.202 2(3)				
O(1)-Zn(1)-O(3)A	109.31(15)	O(1)-Zn(1)-N(1)	102.58(15)	O(1)-Zn(1)-N(4)	124.54(15)
O(3)A-Zn(1)-N(1)	97.04(14)	O(3)A-Zn(1)-N(4)	116.57(16)	N(1)-Zn(1)-N(4)	101.04(15)
Complex **2**					
Zn(1)-O(1)	0.191 2(2)	Zn(1)-O(3)	0.195 6(2)	Zn(1)-O(9)	0.196 6(3)
Zn(1)-N(1)	0.199 8(3)	Zn(2)-O(5)	0.198 7(3)	Zn(2)-O(7)	0.194 8(2)
Zn(2)-O(10)	0.200 3(3)	Zn(1)-N(4)	0.200 1(3)		
O(1)-Zn(1)-O(3)	107.91(1)	O(1)-Zn(1)-O(9)	118.56(1)	O(1)-Zn(1)-N(1)	117.11(1)
O(3)-Zn(1)-O(9)	105.10(1)	O(3)-Zn(1)-N(1)	105.96(1)	O(9)-Zn(1)-N(1)	100.97(1)
O(5)-Zn(2)-O(10)	97.58(1)	O(5)-Zn(2)-N(4)	122.88(1)	O(7)-Zn(2)-O(5)	105.27(1)
O(7)-Zn(2)-O(10)	108.28(1)	O(7)-Zn(2)-N(4)	121.18(1)	O(10)-Zn(2)-N(4)	97.46(1)
Complex **3**					
Zn(1)-O(1)	0.193 5(2)	Zn(1)-O(4)A	0.195 1(2)	Zn(1)-N(1)	0.202 3(3)
Zn(1)-N(4)B	0.203 5(3)				
O(1)-Zn(1)-O(4)A	120.47(11)	O(1)-Zn(1)-N(1)	103.70(11)	O(4)A-Zn(1)-N(1)	116.18(10)
O(1)-Zn(1)-N(4)B	102.12(11)	O(4)A-Zn(1)-N(4)B	106.92(11)	N(1)-Zn(1)-N(4)B	105.75(11)

Symmetry codes: A: x, $-1+y$, z; B: x, $1+y$, z; C $-x$, $2-y$, $2-z$; D: $-x$, $2-y$, $1-z$ for **1**; A: $1-x$, $-y$, $1-z$; B: $2-x$, $1-y$, $1-z$; C: $2-x$, $-y$, $1-z$; D: $1-x$, $-y$, $-z$ for **2**; A: $2-x$, $y+1/2$, $-z+1$; B: $2-x$, $y+1/2$, $-z$; C: $2-x$, $y-1/2$, $-z+1$; D: $2-x$, $y-1/2$, $-z$ for **3**.

2 Results and discussion

2.1 Crystal structures of the complexes

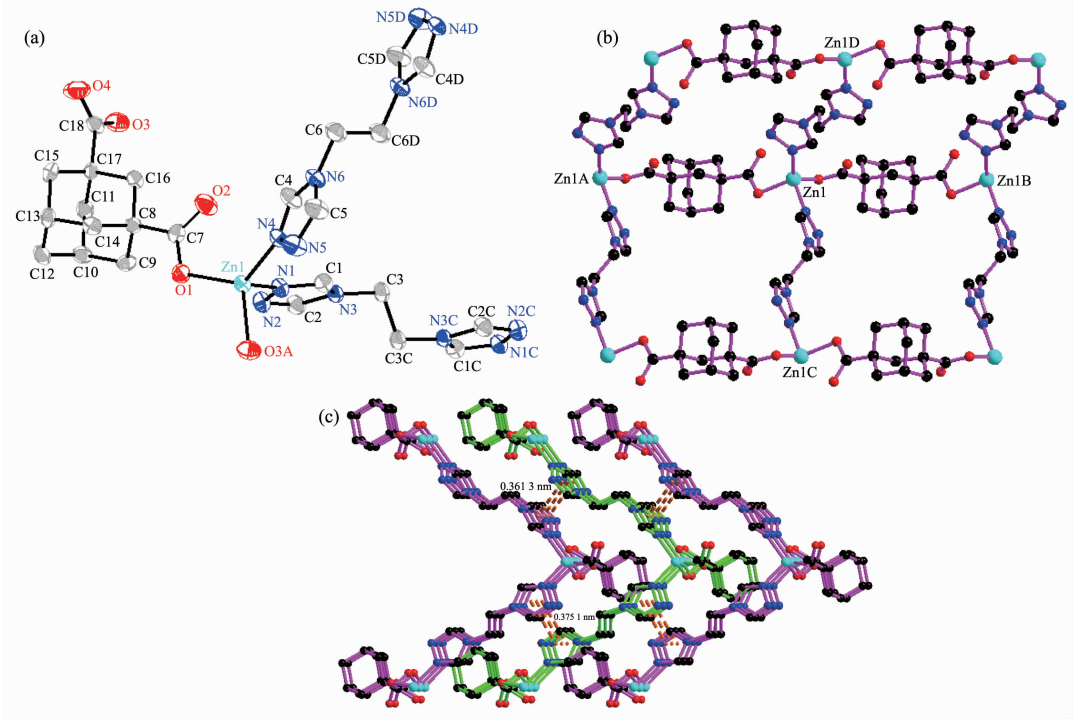
2.1.1 Crystal structure of $\{[Zn(\mu_2\text{-btre})(\mu_2\text{-adc})]\cdot H_2O\}_n$ ($\mathbf{1}\cdot H_2O$)

Single-crystal X-ray analysis shows that **1** crystallizes in the triclinic system with $P\bar{1}$ space group. The asymmetric unit of **1** consists of one Zn(Ⅱ) ion, two half μ_2-btre ligands and one μ_2-adc ligand. Two carboxyl oxygen atoms (O(1), O(3)A) from two μ_2-adc ligands, two nitrogen atoms (N(1), N(4)) from two μ_2-btre ligands are coordinated to Zn(Ⅱ) forming a distorted tetrahedron geometry $[ZnO_2N_2]$. The bond lengths of Zn-O/N are in the range of 0.195 0~0.209 5 nm (Fig. 1a). In **1**, ligand μ_2-adc shows bis-monodentate coordination mode and connects two Zn(Ⅱ) with the distance of 0.960 3 nm. Ligand btre adopts *trans*-conformation and coordinated to two Zn(Ⅱ) with the Zn…Zn distance of 1.186 02 nm. Each Zn(Ⅱ) links two adc and two btre ligands and expands to a waved 2D (4,4) network (Fig.1b). The adjacent 2D (4,4) nets were connected to give a 3D net by strong π-π interactions between triazole rings[29]. The centroid-to-centroid, perpendicular distances and dihedral angle between two Cg(3) are 0.375 1 nm, 0.361 3 nm and 0°, where Cg(3) represents the triazole ring N1-N2-C2-N3-C1. The centroid-to-centroid, perpendicular distances and dihedral angle between two Cg(4) are 0.361 6 nm, 0.339 42 nm and 0°, where Cg(4) represents the triazole ring N4-N5-C5-N6-C4. In addition, the p-π interactions are found between C9-(H9B) of adc ligand and Cg(3). The distances of C9 and H9B to centroid of Cg(3) are 0.393 7 nm and 0.299 nm (Fig.1c).

2.1.2 Crystal structure of $[Zn_2(\mu_2\text{-btre})(\mu_2\text{-1,4-bdc})_2(H_2O)_2]_n$ (**2**)

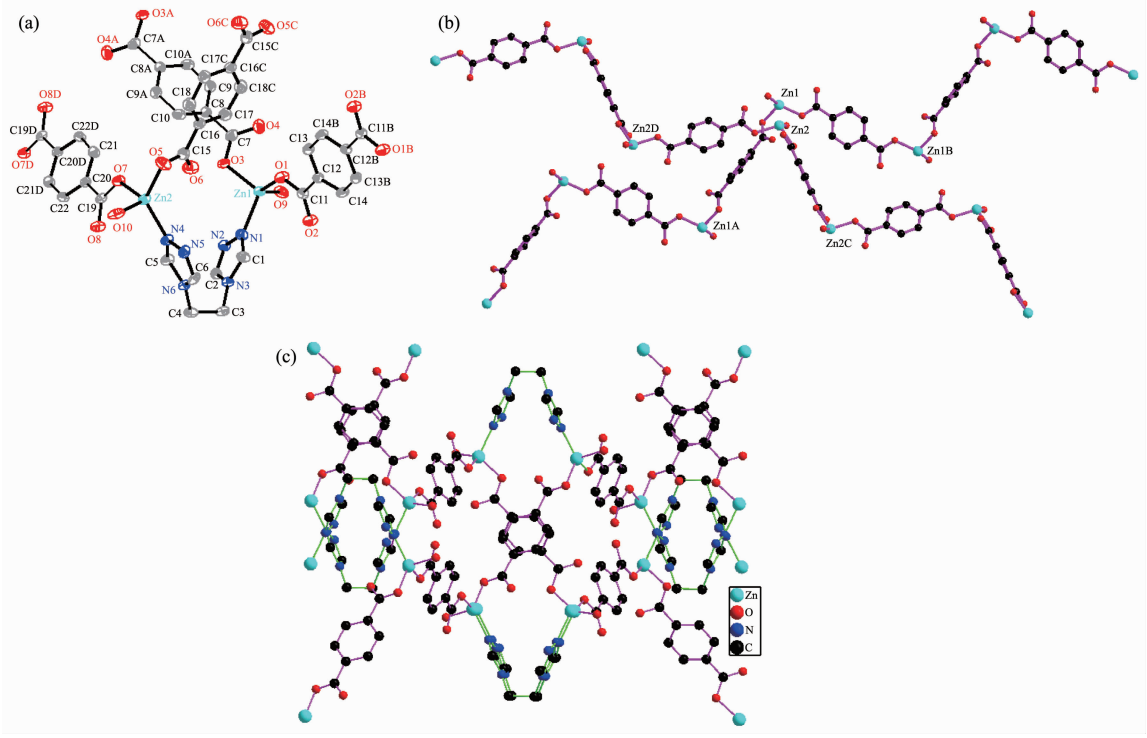
Complex **2** crystallizes in the triclinic system with $P\bar{1}$ space group. The asymmetric unit of **2** consists of two Zn(Ⅱ) ions, four half 1,4-bdc ligands, one btre ligand and two coordinated water molecules. There are two crystallographically independent Zn(Ⅱ)

(Zn(1) and Zn(2)) in **2**. The Zn(1)/Zn(2) are surrounded by two carboxyl oxygen atoms (O(1), O(3))/(O(5), O(7)) from two 1,4-bdc ligands, one nitrogen atom (N(1)/(N(4)) from btre ligand and one coordinated water molecule (O(9)/O(10)) to give a distorted tetrahedron geometry [ZnO_3N], respectively (Fig.2a). The bond



All H atoms are omitted for clarity; 50% thermal ellipsoids; Symmetry codes: A: x, $-1+y$, z; B: x, $1+y$, z; C: $-x$, $2-y$, $2-z$; D: $-x$, $2-y$, $1-z$

Fig.1　(a) Coordination environment of **1**; (b) 2D (4,4) network of **1**; (c) 3D network of **1**



All H atoms are omitted for clarity; 50% thermal ellipsoids; Symmetry codes: A: $1-x$, $-y$, $1-z$; B: $2-x$, $1-y$, $1-z$; C: $2-x$, $-y$, $1-z$; D: $1-x$, $-y$, $-z$

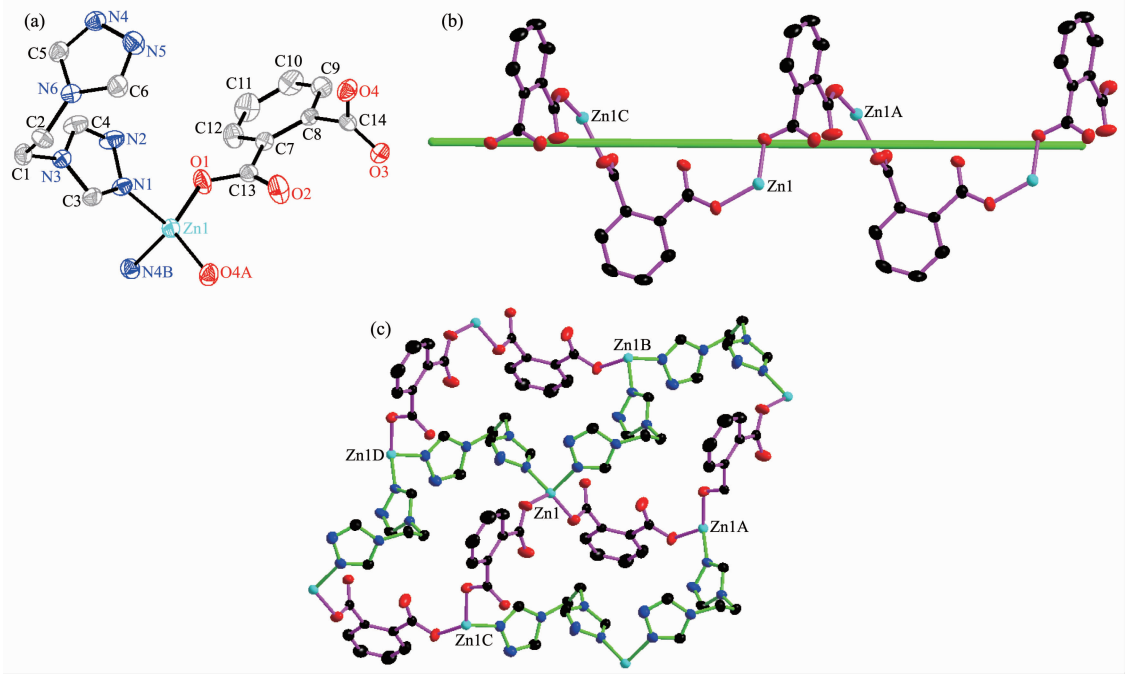
Fig.2　(a) Coordination environment of **2**; (b) Two zigzag chains of **2**; (c) 3D network of **2**

lengths of Zn-O/N are in the range of 0.191 2~0.200 3 nm, and the bond angles around Zn(Ⅱ) are in the range of 97.46°~122.88°. Ligand 1,4-bdc shows bis-monodentate coordination mode and connects two Zn(Ⅱ). Zn(1) atoms and Zn(2) atoms are connected by 1,4-bdc to form two interwoven zigzag chains with the distances Zn(1)…Zn(1) and Zn(2)…Zn(2) of 1.100 24, 1.101 04 and 0.110 93, 1.090 083 nm, respectively (Fig.2b). Ligand btre connects Zn(1) and Zn(2) of interwoven zigzag chains in bis-monodentate coordination mode to form a three-dimensional network and the distance of Zn(1)…Zn(2) is 0.613 80 nm (Fig.2c). Habib and co-worker synthesized 3D network $[Zn_2(\mu_2\text{-}1,4\text{-bdc})_2(\mu_4\text{-btre})]_n$ by hydrothermal reaction based on the same ligands and same ion. But, btre ligands show quadridentate, and there is no coordinated water molecule in $[Zn_2(\mu_2\text{-}1,4\text{-bdc})_2(\mu_4\text{-btre})]_n$[30].

2.1.3 Crystal structure of $[Zn(\mu_2\text{-btre})(\mu_2\text{-}1,2\text{-bdc})]_n$ (**3**)

Single-crystal X-ray analysis shows that **3** crystallizes in the monoclinic system with $P2_1$ space group. The asymmetric unit of **3** consists of one Zn(Ⅱ) ion, one btre ligand and one 1,2-bdc ligand. The Zn(1) atom is four-coordinated and surrounded by two oxygen atoms (O(1), O(4)A) from two 1,2-bdc ligands, two triazole nitrogen atom (N(1), N(4)B) from two btre ligands in a distorted tetrahedron geometry $[ZnO_2N_2]$. The bond length of Zn-O/N is in the range of 0.193 5~0.203 5 nm (Fig.3a). In **3**, each btre ligand acts as a gauche-conformation and connects two Zn(Ⅱ) with the distance of 0.808 02 nm. Each 1,2-bdc ligand adopts bis-monodentate coordination mode and bridges two Zn(Ⅱ) and forms a $[Zn(1,2\text{-bdc})]_n$ left-hand helix with a Zn…Zn distance of 0.739 37 nm (Fig.3b). Each Zn(Ⅱ) connects two btre and two 1,2-bdc ligands and expands to a waved 2D (4,4) network (Fig.3c).

Ligand btre shows *trans*-conformation in **1**, and gauche-conformation in **2** and **3**. The dihedral angle between two triazole rings of btre is 0.00° in **1**, 45.713° and 61.370° in **2** and **3**. The torsion angles of N3-C3-C3C-N3C/N6-C6-C6D-N6D, N3-C3-C4-N6, N3-C1-C2-N6 of btre are 180.00°/−180.00°, −54.083° and 53.758° in **1**, **2** and **3**, respectively. In the three complexes, Zn(Ⅱ) atoms are all four-coordinated and located at center of distorted tetrahedron geometry. The bond lengths of Zn-O/N and bond angles of O-Zn-



All H atoms are omitted for clarity; 50% thermal ellipsoids; Symmetry codes: A: 2−*x*, 1/2+*y*, 1−*z*; B: 2−*x*, 1/2+*y*, −*z*; C: 2−*x*, −1/2+*y*, 1−*z*; D: 2−*x*, −1/2+*y*, −*z*

Fig.3 (a) Coordination environment of **3**; (b) Left-hand helix of **3**; (c) 2D (4,4) network of **3**

N, O-Zn-O, N-Zn-N are in the normal range, which are comparable to the values in others zinc (Ⅱ) polymers based on btre ligand[20-21].

2.2 PXRD patterns and thermogravimetric analyses of 1~3

In order to characterize the purity of complexes **1~3**, and 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 are in good agreement with the simulated patterns, indicating the purity of the samples. The thermal stabilities of **1~3** were examined by thermogravimetric analyses. As shown in Fig.5, **1** is stable before 134 ℃, and the lattice water lost from 134 to 167 ℃ (Calcd. 3.83%, Obsd. 3.91%). The framework of **1** was thermally stable upon 297 ℃. Then the decomposition happened quickly until 540 ℃. The main residue should be ZnO (Calcd. 17.32%, Obsd. 18.13%). The TG curve of **2** showed that the coordinated water lost from 173 to 213 ℃ (Calcd. 5.46%, Obsd. 5.40%). The framework of **2** is very stable from 213 to 400 ℃. Then the weight decreased quickly and did not end until 528 ℃. The main residue should be ZnO (Calcd. 24.69%, Obsd. 25.09%). Before 302 ℃, the weight of **3** decreased very slowly. Then the weight decreased quickly until 800 ℃, The main residue should be ZnO (Calcd. 20.67%, Obsd. 20.92%).

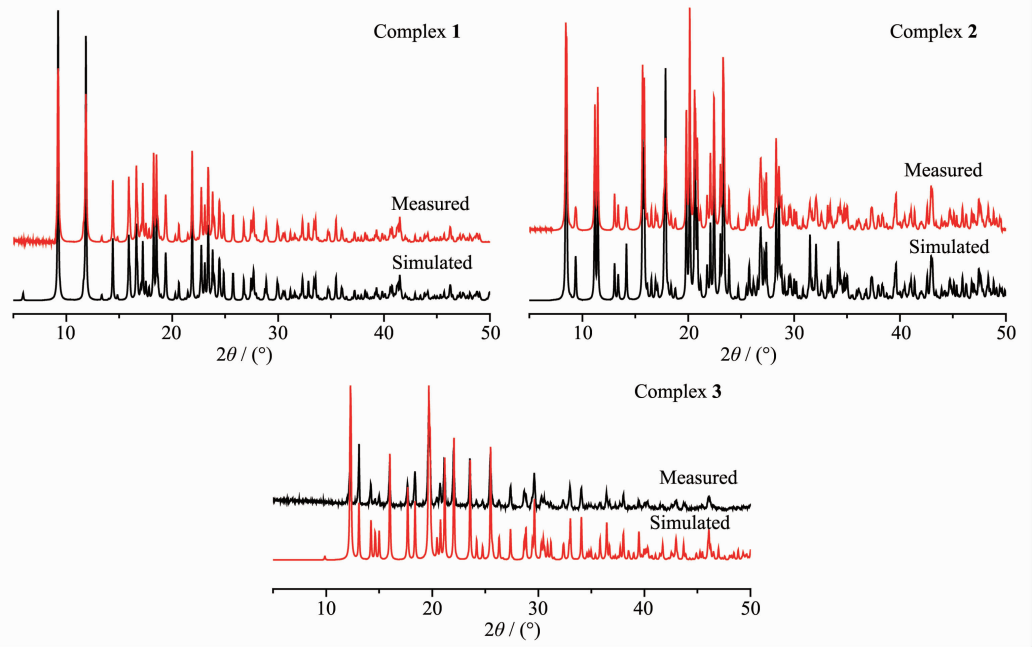


Fig.4　Measured and simulated PXRD patterns of complexes **1~3**

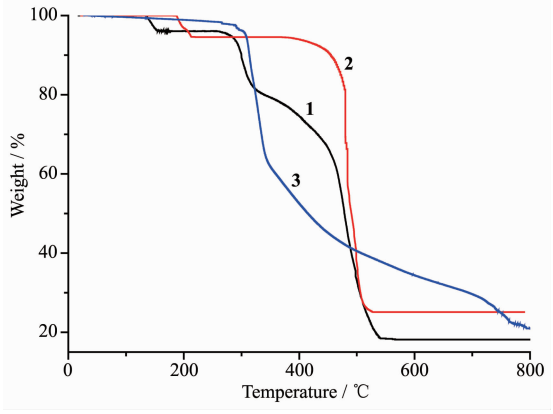


Fig.5　TG curves of **1~3**

2.3 Photoluminescence properties of 1~3

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. So, the solid state luminescence spectra of **1~3** 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 the literature[31]. The btre luminescence is possibly quenched by the

thermal intra-ligand rotations around the C-C and C-N bonds[32-33]. Complex **1** exhibits the emission at 442 and 471 nm (λ_{ex}=370 nm). Complexes **2** and **3** show strong emission band maxima at 436 and 384 nm upon excitation at 320 and 309 nm, respectively. The strong emission of **2** is blue-shift for 9 nm compared with $[Zn_2(\mu_2\text{-}1,4\text{-bdc})_2(\mu_4\text{-btre})]_n$[30]. The free H_2adc has no obvious emission at the same condition[34]. The free 1,4-H_2bdc and 1,2-H_2bdc exhibit the emissions at 390 and 375 nm, respectively[35]. Due to the d^{10} configuration, Zn(Ⅱ) ion is difficult to oxidize or reduce, the emissions are neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT). The emissions of **1**~**3** may be attributed to the intra-ligand and ligand-to-ligand charge transition (LLCT)[30,36].

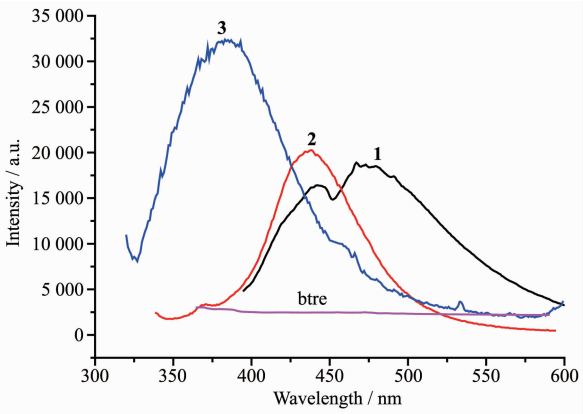


Fig.6 Solid-state emission spectra of the complexes and btre

3 Conclusions

Three zinc(Ⅱ) coordination polymers based on different dicarboxylate ligands and flexible 4-substituted bis(1,2,4-triazole) ligand were successfully synthesized and characterized. Complex **1** is a 2D (4,4) network, and the adjacent 2D networks are connected by strong π-π interactions to form a 3D supramolecular architecture. The structure of **2** and **3** are 3D and 2D (4,4) network, respectively. Thermogravimetric analysis showed that the framework of **2** and **3** have better thermal stability. In addition, the photoluminescence investigation shows that three complexes may have potential application as luminescent materials.

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