



# A three-dimensional highly stable Zn(II) coordination polymer based on 1,4-benzeneditetrazolate (H<sub>2</sub>BDT): Synthesis, crystal structure, and luminescent properties

Ji-Hua Deng<sup>\*</sup>, Xiao-Lin Yuan, Guang-Quan Mei<sup>\*</sup>

Key Laboratory of Jiangxi University for Applied Chemistry and Chemical Biology, College of Chemistry and Bio-engineering, Yichun University, Yichun 336000, China

## ARTICLE INFO

### Article history:

Received 12 July 2010

Accepted 21 September 2010

Available online 27 September 2010

### Keywords:

1,4-benzeneditetrazolate

Coordination polymer

Zinc(II)

Crystal structure

Luminescence

## ABSTRACT

1,4-benzeneditetrazolate [H<sub>2</sub>BDT] (**1**) and its 3D coordination polymer [Zn(BDT)]<sub>n</sub> (**2**), have been synthesized and structurally characterized by infrared spectroscopy (IR), thermal gravimetric analysis (TG), and single-crystal/powder X-ray diffraction. The result of the single-crystal X-ray diffraction analysis indicates that **1** is a 3D supramolecular structure stabilized by intermolecular hydrogen bonds and π...π stacking interactions. **2** is a 3D (4,4)-connected coordination polymer with the central metal Zn(II) ions linked together by BDT<sup>2-</sup> anions. Photoluminescent measurement for **2** in the solid state elucidates that **2** displays a strong photoluminescence at 469 nm, which suggests that **2** may be a potential blue-light material.

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In the past decade, considerable interests have been drawn to synthesis and design coordination polymers due to their fascinating architectures [1] and potential applications in catalysis [2], magnetism [3], gas storage and separation [4], and luminescent materials [5]. The use of varied organic linkers or the alteration of metal ions can lead to diverse frameworks with desirable functions. Initially, the ligands were mostly focused on carboxylic compounds (such as terephthalic acid) [6] or simple N-heterocyclic aromatic compounds (such as 4,4'-bipyridine) [7]. Recently, heterocyclic carboxylic acids were also used as building spacers [8]. Since the pioneering work of Sharpless and Demko [9], the synthesis and property studies of tetrazolyl compounds have been explored and developed rapidly [10]. Of interest to supramolecular chemists is the coordination ability of the tetrazolyl compound through the four nitrogen electron-donating atoms that allow the tetrazolyl ligand to serve as either a multidentate or a bridging building block in supramolecular assembly. The diverse coordination modes of a tetrazolyl ring enable a tetrazolyl compound to be endowed with rich coordination chemistry [11].

Recently, coordination polymers exhibited a good potential application prospect in the luminescent field [12], because the metal coordination action can adjust the emission wavelength of the organic moiety, and the resulting products have higher thermal stability than the pure organic ligands [13]. Therefore, the combination of metal centers and organic spacers is considered an efficient method for obtaining new types of luminescent materials for potential applica-

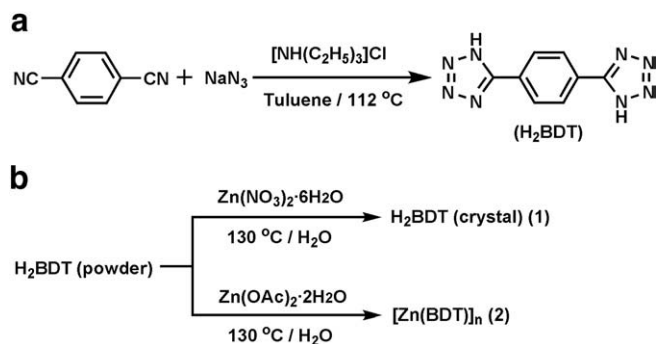
tions as light-emitting diodes (LEDs) [14]. To date, among the transition metal coordination polymers, those with good luminescent abilities are mostly assembled from Zn(II) or Cd(II) centers, as this two type of ions have filled, core-like *d*-orbitals and thus no *d-d* transitions are possible [15].

1,4-benzeneditetrazolate (H<sub>2</sub>BDT), containing two tetrazolyl rings at 1,4-position of benzene, can serve as multidentate chelating ligand or organic linking ligand for bridging inorganic moieties in solid materials. Recently, several coordination polymers based on H<sub>2</sub>BDT have been synthesized and characterized [16]. Herein, we report the synthesis, crystal structures, and luminescent properties of 1,4-benzeneditetrazolate (H<sub>2</sub>BDT; **1**) and its 3D coordination polymer [Zn(BDT)]<sub>n</sub> (**2**).

H<sub>2</sub>BDT was synthesized according to reference [16a]. Reaction of terephthalonitrile with NaN<sub>3</sub> and Et<sub>3</sub>N·HCl in toluene yields a crude powder of H<sub>2</sub>BDT. The crystal of H<sub>2</sub>BDT (**1**) suitable for single-crystal X-ray analysis was unexpectedly afforded by the hydrothermal reaction of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and powdered H<sub>2</sub>BDT in a molar ratio of 1:1 at 130 °C for six days [17] (Scheme 1). Anal. Calcd for C<sub>8</sub>H<sub>6</sub>N<sub>8</sub>: C, 44.86; H, 2.82; N, 52.32%. Found: C, 44.89; H, 2.80; N, 52.28%. Interestingly, by a similar procedure to that for **1**, when using Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O instead of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, the yellow block-shaped crystals of **2** were given [17] (Scheme 1). Anal. Calcd for C<sub>8</sub>H<sub>4</sub>N<sub>8</sub>Zn: C, 34.62; H, 1.45; N, 40.37%. Found: C, 34.69; H, 1.48; N, 40.28%. These results indicate that these reactions are anion-dependent. We speculate that this different result may be related with the alkali of OAc<sup>-</sup> and NO<sub>3</sub><sup>-</sup>. The OAc<sup>-</sup> anion, compared with NO<sub>3</sub><sup>-</sup>, has stronger alkali, which can deproton the H<sub>2</sub>BDT ligand, leading to the formation of the coordination polymer.

<sup>\*</sup> Corresponding authors.

E-mail addresses: [djhyuc\\_2006@yahoo.com.cn](mailto:djhyuc_2006@yahoo.com.cn) (J.-H. Deng), [yc\\_mgq@163.com](mailto:yc_mgq@163.com) (G.-Q. Mei).

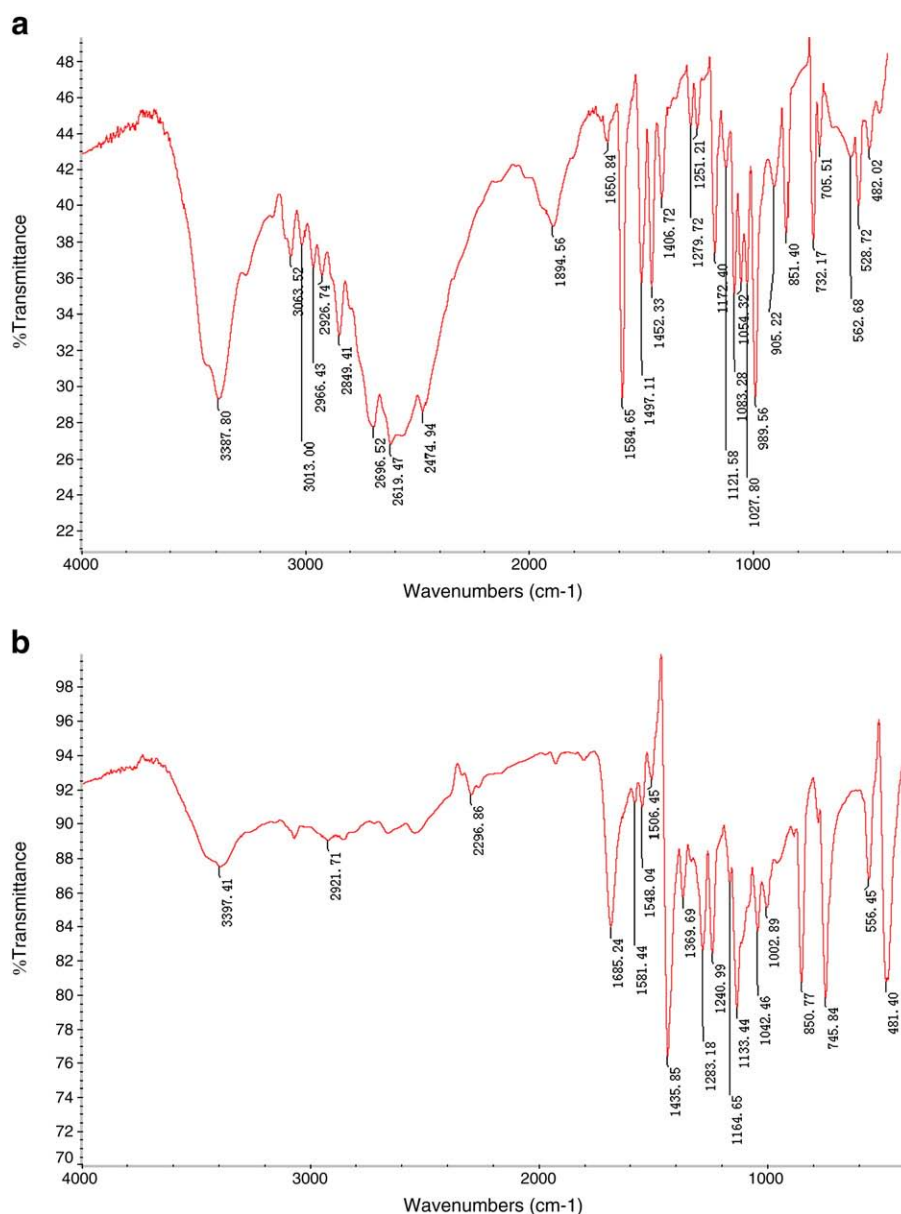


**Scheme 1.** The synthesis strategies for (a) H<sub>2</sub>BDT, (b) **1** and **2**.

**1** and **2** were firstly characterized by using infrared spectra (IR), which were recorded in the 4000 to 400 cm<sup>-1</sup> region using KBr pellets and a Bruker EQUINOX 55 spectrometer. As shown in Fig. 1, the IR spectrum of **1** shows that an intense peak at 3388 cm<sup>-1</sup> can be assigned to the stretching of the tetrazolyl ring N–H bonds. The peaks

at 1585 cm<sup>-1</sup>, 1406 cm<sup>-1</sup> can be attributed to the resonance of the aromatic ring skeleton, and the peak at 732 cm<sup>-1</sup> corresponds to the adsorption of C–H bond stretching of aromatic rings. The resonance adsorption peaks of the tetrazolyl ring skeleton locate at 1621 cm<sup>-1</sup>, 1497 cm<sup>-1</sup>, 1452 cm<sup>-1</sup> [16a]. The IR spectrum of **1** is similar to the one of **1**·2H<sub>2</sub>O except the peak at 3388 cm<sup>-1</sup> in **1** is narrower than the one in **1**·2H<sub>2</sub>O [16a], indicating the absence of crystal lattice water molecules in **1**. The IR spectrum of **2**, compared with the one of **1**, exhibit obvious change. The peak at 3388 that appeared in **1** has disappeared in **2**, implying that the tetrazolyl rings are deprotonated [16a,18]. In addition, due to the coordination with Zn(II), the adsorption peaks of the tetrazolate group at 1685 cm<sup>-1</sup> and 1434 cm<sup>-1</sup> become sharp and intense. These IR data preliminarily evidence the formation of **1** and **2**.

The single-crystal X-ray diffraction method was further used to characterize the structures of **1** and **2**. Both diffraction data were collected at 173 K on a Bruker Smart Apex CCD diffractometer with graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The result of the X-ray diffraction analysis indicated that **1** crystallized in monoclinic crystal system, *P*<sub>2</sub>/c space group (Table 1). As seen in



**Fig. 1.** The infrared spectra of **1** (a) and **2** (b).

**Table 1**  
Crystal data and structure refinement for **1** and **2**.

Compound	<b>1</b>	<b>2</b>
Formula	C <sub>8</sub> H <sub>6</sub> N <sub>8</sub>	C <sub>8</sub> H <sub>4</sub> N <sub>8</sub> Zn
F.w.	214.21	277.56
T (K)	173(2)	173(2)
Crystal system	Monoclinic	Orthorhombic
Space group	P2 <sub>1</sub> /c	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
a (Å)	4.5428(14)	8.1009(15)
b (Å)	9.862(3)	8.7376(16)
c (Å)	9.755(3)	12.991(3)
α (°)	90	90
β (°)	92.920(6)	90
γ (°)	90	90
V (Å <sup>3</sup> )	436.5(2)	919.6(3)
Z	2	4
D <sub>c</sub> (g cm <sup>-3</sup> )	1.630	2.005
μ (mm <sup>-1</sup> )	0.116	2.658
Data collected/uniq. (R <sub>int</sub> )	1342/747 (0.0159)	3396/1948 (0.0172)
R <sub>1</sub> , wR <sub>2</sub> [I > 2σ(I)]	R <sub>1</sub> = 0.0321, wR <sub>2</sub> = 0.0837	R <sub>1</sub> = 0.0173, wR <sub>2</sub> = 0.0429
R <sub>1</sub> , wR <sub>2</sub> (all data)	R <sub>1</sub> = 0.0375, wR <sub>2</sub> = 0.0902	R <sub>1</sub> = 0.0179, wR <sub>2</sub> = 0.0431
GOF	1.047	1.060
Residues (e Å <sup>-3</sup> )	0.160 and -0.181	0.311 and -0.255

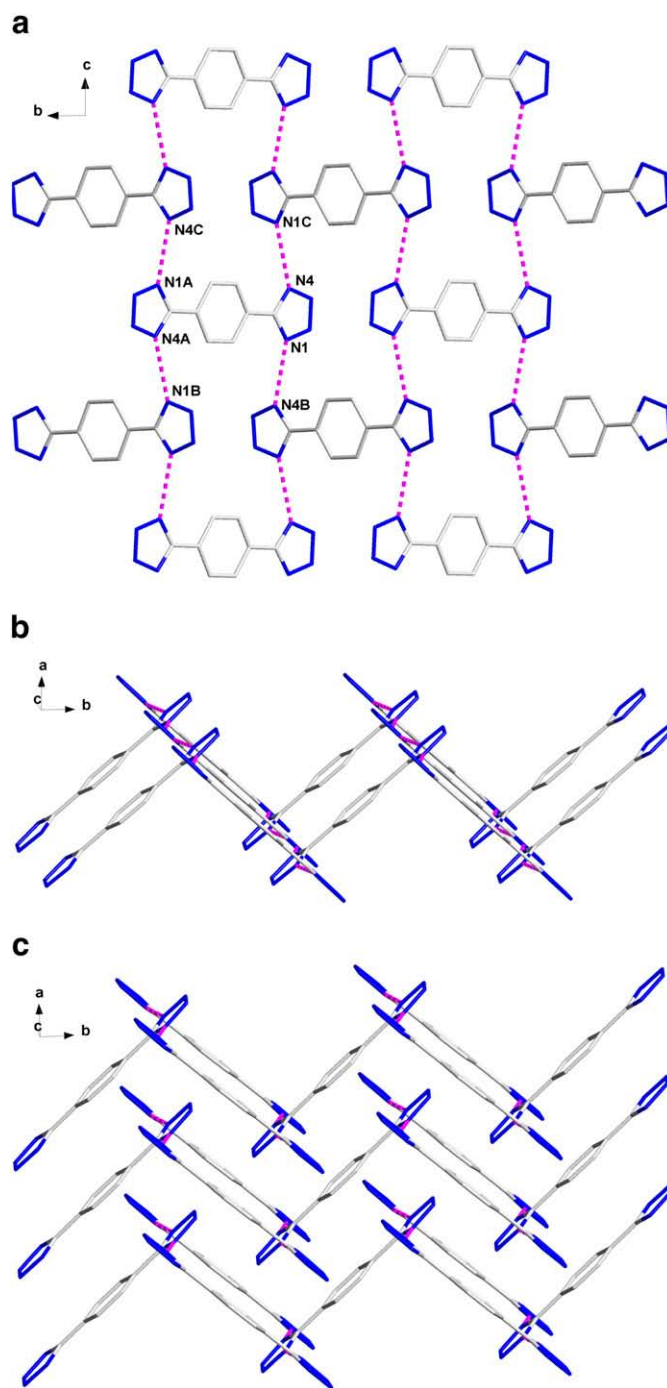
<sup>a</sup>R<sub>1</sub> = Σ||F<sub>o</sub> - |F<sub>c</sub>||/Σ|F<sub>o</sub>|. <sup>b</sup>wR<sub>2</sub> = [Σ[w(F<sub>o</sub><sup>2</sup> - F<sub>c</sub><sup>2</sup>)<sup>2</sup>]/Σw(F<sub>o</sub><sup>2</sup>)<sup>1/2</sup>. w = 1/[σ<sup>2</sup>(F<sub>o</sub>)<sup>2</sup> + (0.0054P)<sup>2</sup> + 0.00000P], where P = [(F<sub>o</sub><sup>2</sup>) + 2F<sub>c</sub><sup>2</sup>]/3.

Fig. 2a, each H<sub>2</sub>BDT molecule affords two hydrogen-bond donors (N1, N1A) and two hydrogen-bond acceptors (N4, N4A), forming four equivalent N-H...N (N...N separation of 2.7848(19) Å) hydrogen bonds. Through the strong hydrogen bonds, a 2-D zigzag layer is formed (Fig. 2b). The adjacent layers are further stacked by π...π interactions between tetrazolyl ring (N1 → N2 → N3 → N4 → C1) and phenyl ring (C(2) → C(3) → C(4)<sup>i</sup> → C(2)<sup>i</sup> → C(3)<sup>i</sup> → C(4), *i* = -x + 2, -y + 2, -z + 2), generating a 3-D supramolecular structure (Fig. 2c). The distance between ring centroids is 3.5101 Å and the dihedral angle between two planes is 2.52°. It should be noted that the crystal structure of **1**·2H<sub>2</sub>O, recrystallized from distilled water, has been reported in literature [16a]. Different from **1**, **1**·2H<sub>2</sub>O is stabilized by another two types of hydrogen bonds (N-H...O, O-H...N) involving H<sub>2</sub>BDT molecules and lattice water molecules, while no N-H...N hydrogen bond is observed between H<sub>2</sub>BDT molecules.

**2** is crystallized in an orthorhombic crystal system, P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> chiral space group (Table 1). The Flack parameter of 0.016(10) demonstrates the homochirality of the single crystal. As shown in Fig. 3a, the asymmetric unit in **2** consists of one Zn(II) ions and one BDT<sup>2-</sup> anion ligand. The Zn(II) ion coordinates with four N atoms from four individual BDT<sup>2-</sup> ligands, forming a tetrahedral coordination geometry. The BDT<sup>2-</sup> ligand, employing tetra-dentate bridging coordination mode, links with four Zn(II) ions by four N atoms of two tetrazolyl rings (C1 → N4, and C8 → N8) are not coplanar with the phenyl ring (C2 → C7), with the dihedral angles of 27.9° and 29.4° respectively. The Zn-N bond distances of 1.9931(18)–2.0340(16) Å are in good agreement with literature values in Zn-tetrazole complexes, and the C-C and C-N distances are unexceptional (Table 2) [19]. Through the bridging of the BDT<sup>2-</sup> anions, Zn(II) are connected together, forming a 3D network structure (Fig. 3b).

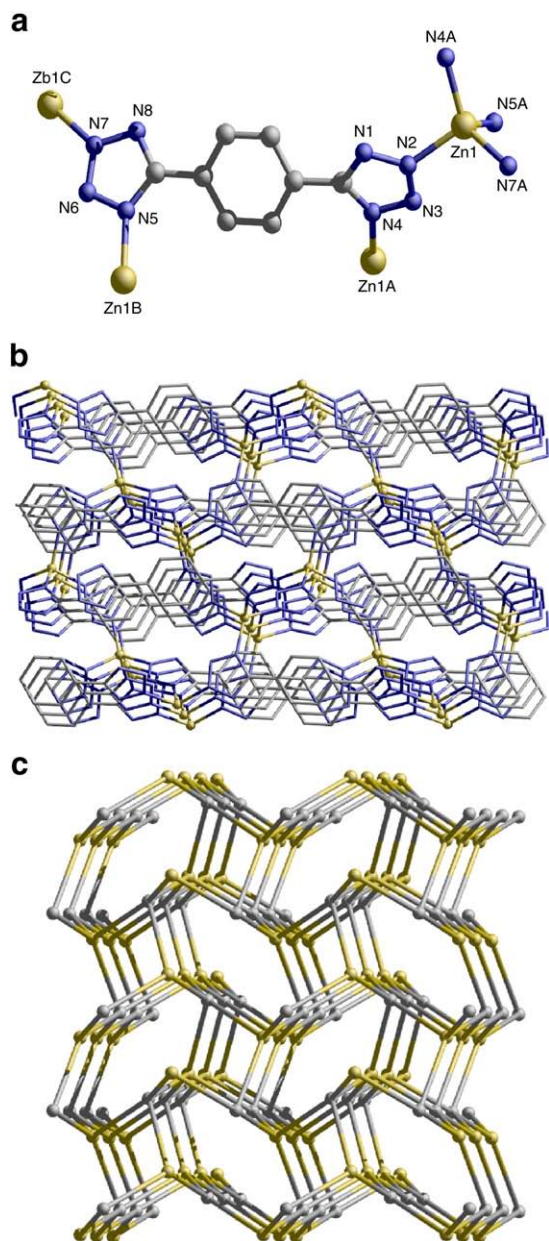
According to the regulation of the topology, each Zn(II) bonding to four BDT<sup>2-</sup> anions can be viewed as a four-connected node, and similarly, each BDT<sup>2-</sup> anion linking with four Zn(II) ions, can be considered as another four-connected node. Therefore, the 3D metal-organic framework of **2** belongs to a 4,4-c net, with the topological type of *unc* and Schläfli symbol of {6<sup>6</sup>} (Fig. 3c), which was also found in other reported coordination polymers [20].

It is worth noting that although the ligand BDT<sup>2-</sup> anion is achiral, **2** crystallized in the chiral space group. The chirality of the single crystal probably originated from the asymmetric coordination mode of the BDT<sup>2-</sup> ligand.



**Fig. 2.** (a) 2-D layer is generated by intermolecular hydrogen-bond interactions, viewed along *a* axis, the H atoms are omitted for clarity. (b) 2-D zigzag layer viewed along *c* axis. (c) Adjacent zigzag layers are stacked together through π...π interactions, resulting in 3-D supramolecular structure.

The bulk phase purity of **2** was examined by a powder X-ray diffraction method. A microcrystalline sample of **2** was gently ground in an agate mortar, then deposited in the hollow of an aluminum sample holder (equipped with a zero-background plate). Diffraction data were collected in the range of 5–50° 2θ on Bruker D8 ADVANCE Diffractometer (CuKα radiation, 40 kV, 40 mA) at room temperature. Fig. 4 shows the measured powder diffraction patterns of the as-synthesized **2** and the calculated patterns generated from the single-crystal X-ray diffraction data, respectively. The results elucidate that all the peak positions displayed in the measured patterns at room



**Fig. 3.** (a) The coordination environment of Zn(II) and the coordination mode of the ligand BDT<sup>2-</sup>, the H atoms are omitted for clarity. (b) The Zn(II) ions are bridged by BDT<sup>2-</sup> anions, generating a 3D network structure. (c) 4,4-connected *unc* net (the atoms in dark yellow and gray represent the Zn(II) ions and BDT<sup>2-</sup> anions, respectively).

temperature closely match to those in the simulated one, indicating that a single phase of **2** was formed [21].

To probe the thermal stability of **2**, the thermogravimetric (TG) test was performed on a NetzschTG-209 instrument under an air atmosphere in the temperature range from 30 to 600 °C. The TG curve of **2** was depicted in Fig. 5. The result showed that there was no noticeable weight loss before the temperature of 400 °C, and further heating led to the decomposing of the framework. This thermal behavior reveals that **2** is endowed with a high thermal stability. To the best of our knowledge, only a few coordination polymers showing such excellent thermal stabilities have been reported [22].

It is well known that Zn(II) is an ideal metal center for building coordination polymers with luminescent function, as Zn(II) has d<sup>10</sup> electronic configuration. To date, considerable coordination polymer solids constructed from Zn(II) and organic linkers exhibited good luminescent properties. For example, MOF-5, Zn<sub>4</sub>O(1,4-BDC)<sub>3</sub> (1,4-

**Table 2**  
Selected bond length (Å) and angle (°) for **1** and **2**.

<b>1</b>			
C(1)–N(1)	1.326(2)	C(1)–N(4)	1.3379(19)
C(1)–C(2)	1.464(2)	C(2)–C(3)	1.396(2)
C(2)–C(4)#1	1.400(2)	C(3)–C(4)	1.378(2)
C(4)–C(2)#1	1.400(2)	N(1)–N(2)	1.3617(19)
N(2)–N(3)	1.2930(19)	N(3)–N(4)	1.3452(19)
N(1)–C(1)–N(4)	107.24(13)	N(1)–C(1)–C(2)	126.53(13)
N(4)–C(1)–C(2)	126.21(13)	C(3)–C(2)–C(4)#1	119.02(15)
C(3)–C(2)–C(1)	121.31(13)	C(4)#1–C(2)–C(1)	119.67(13)
C(4)–C(3)–C(2)	120.63(14)	C(3)–C(4)–C(2)#1	120.35(14)
C(1)–N(1)–N(2)	106.75(12)	N(3)–N(2)–N(1)	110.10(12)
N(2)–N(3)–N(4)	106.56(12)	C(1)–N(4)–N(3)	109.34(13)
<b>2</b>			
Zn(1)–N(7)#1	1.9931(18)	Zn(1)–N(4)#2	1.9987(15)
Zn(1)–N(2)	2.0169(17)	Zn(1)–N(5)#3	2.0340(16)
N(7)#1–Zn(1)–N(4)#2	121.77(7)	N(7)#1–Zn(1)–N(2)	110.17(7)
N(4)#2–Zn(1)–N(2)	108.49(7)	N(7)#1–Zn(1)–N(5)#3	101.15(7)
N(4)#2–Zn(1)–N(5)#3	110.52(6)	N(2)–Zn(1)–N(5)#3	103.04(7)

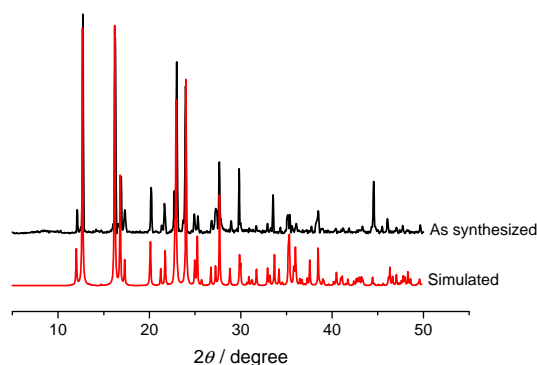
Symmetry transformations used to generate equivalent atoms: symmetry transformations used to generate equivalent atoms for **1**: #1 =  $-x + 2, -y + 2, -z + 2$ ; for **2**: #1 =  $x, y, z + 1$ ; #2 =  $-x + 2, y + 1/2, -z + 3/2$ ; #3 =  $x + 1/2, -y + 1/2, -z + 1$ .

H<sub>2</sub>BDC = 1,4-benzenedicarboxylic acid), consisting of basic zinc acetate units linked by benzene, are reported to be a type of potential blue material ( $\lambda_{em} = 525$  nm) [23]. Built from Zn(II) and a conjugated organic ligand, **2** may exhibit excellent luminescent behavior. Therefore, the photoluminescent property of **2** was investigated in the solid state at room temperature. As depicted in Fig. 6, it can be observed that **2** exhibits an emission maximum at 469 nm upon excitation at 340 nm. According to the reported literature, the free ligand exhibits a broad emission peak at 473 nm [16a]. Therefore, the photoluminescent emission for **2** can be tentatively ascribed to the ligand-to-ligand charge transfer (LLCT) [24].

In summary, the ligand 1,4-benzeneditetrazolate [H<sub>2</sub>BDT] (**1**) and its 3D coordination polymer [Zn(BDT)]<sub>n</sub> (**2**) have been synthesized and structurally characterized. The polymer **2** shows high thermal stability with the decomposed temperature over 400 °C, and displays a strong photoluminescence at 469 nm, suggesting **2** may be a potential blue-light material.

## Acknowledgments

The authors thank the Youth Foundation of Jiangxi Provincial Office of Education (GJJ09605), the Science Foundation of Jiangxi Provincial Office of Education (GJJ09637, GJJ09355), and the Natural Science Foundation of Jiangxi Province (2008GZH0063) for financial support.



**Fig. 4.** The powder X-ray diffraction patterns for **2**.

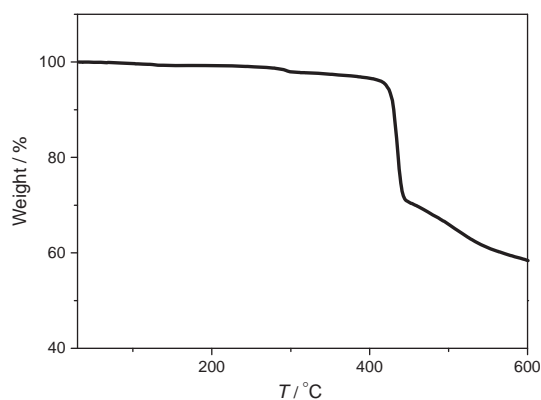


Fig. 5. The TG curve for **2**.

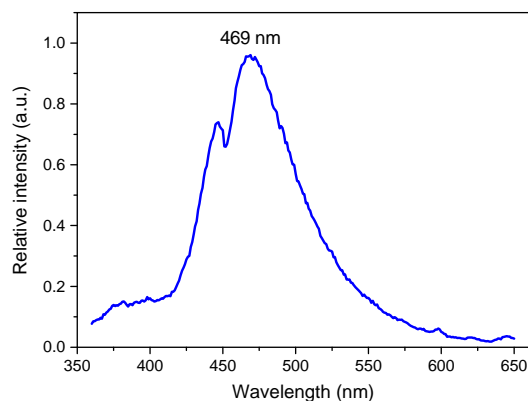


Fig. 6. Fluorescent emission spectra of **2** in the solid state at room temperature ( $\lambda_{\text{ex}} = 340 \text{ nm}$ ).

## Appendix A. Supplementary material

Supplementary material to this article can be found online at doi:10.1016/j.inoche.2010.09.023.

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