



# Three new three dimensional Zn(II)-benzenetetracarboxylate coordination polymers: Syntheses, crystal structures and luminescent properties



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## ABSTRACT

Three novel coordination polymers, namely,  $[\text{Zn}_2(\text{btec})(\text{L}_1)\text{H}(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$  (**1**),  $[\text{Zn}_2(\text{btec})(\text{L}_2)_2]$  (**2**) and  $[\text{Zn}_5(\text{btec})_2(\text{L}_3)_{1.5}(\text{OH})_2]\cdot 2\text{H}_2\text{O}$  (**3**) ( $\text{L}_1 = 3,5\text{-di}(1\text{H-imidazol-1-yl})\text{benzoate}$ ,  $\text{L}_2 = 1,3\text{-bis}((1\text{H-1,2,4-triazol-1-yl})\text{methyl})\text{benzene}$  and  $\text{L}_3 = 1,3\text{-di}(1\text{H-1,2,4-triazol-1-yl})\text{propane}$ ), have been hydrothermally synthesized. Compound **1** shows a three dimensional (3D) framework with *fsc-3,5-P4/mbm* topology. Compound **2** reveals a 3D pillar-layered framework with the presence of 3-fold left- and right-handed helical chains. Compound **3** also exhibits a 3D framework based on 1D zinc chains. In addition, the luminescent properties for **1–3** have also been investigated.

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## 1. Introduction

Coordination polymers (CPs) are attracting more and more interests in recent years, not only due to their intriguing architectures but also due to their wildly potential applications including gas storage, separation, magnetism and catalysis [1]. Although a great effort have been paid to prepare novel CPs, it is still difficult to prepare CPs with expected structures. Because the final structures can be affected by many kinds of factors, such as metal ions, organic ligands, pH value, solvents, reaction temperature, and so on [2]. Among the above mentioned factors, the organic ligand has been considered as one of the most important fact in the self-assembly system. The multi-carboxylate ligands as an important family of O-donor ligands are good choices in the construction of CPs with fascination architectures and properties [3]. In this regard, 1,2,4,5-Benzenetetracarboxylic acid ( $\text{H}_4\text{btec}$ ) have been widely used for their variety of coordination modes [4]. The four carboxylate groups of  $\text{H}_4\text{btec}$  are equally arranged around the benzene ring and can rotate along the C–C bond resulting in kinds of conformations. On the other hand, flexible N-donor ligands have been proved as excellent co-ligands for the construction of novel

networks [5]. In this work, we are prompted to construct novel CPs by utilizing  $\text{H}_4\text{btec}$  and flexible N-donor ligands under hydrothermal condition. Herein we report three Zn(II) CPs, namely,  $[\text{Zn}_2(\text{btec})(\text{L}_1)\text{H}(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$  (**1**),  $[\text{Zn}_2(\text{btec})(\text{L}_2)_2]$  (**2**) and  $[\text{Zn}_5(\text{btec})_2(\text{L}_3)_{1.5}(\text{OH})_2]\cdot 2\text{H}_2\text{O}$  (**3**) ( $\text{L}_1 = 3,5\text{-di}(1\text{H-imidazol-1-yl})\text{benzoate}$ ,  $\text{L}_2 = 1,3\text{-bis}((1\text{H-1,2,4-triazol-1-yl})\text{methyl})\text{benzene}$  and  $\text{L}_3 = 1,3\text{-di}(1\text{H-1,2,4-triazol-1-yl})\text{propane}$ ). All of the title compounds show three dimensional (3D) frameworks. Compound **1** represents a rare example of CP with *fsc-3,5-P4/mbm* topology. In addition, the luminescent properties for **1–3** have also been investigated.

## 2. Experimental section

### 2.1. Materials and general methods

All reagents and solvents were purchased from commercial sources and used without further purification. Powder X-ray diffraction (PXRD) patterns were collected on a Rigaku  $D_{\text{max}}$  2000 X-ray diffractometer with graphite monochromatized  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.154 \text{ nm}$ ) and  $2\theta$  ranging from  $5^\circ$  to  $50^\circ$  with an increment of  $0.02^\circ$  and a scanning rate of  $5^\circ/\text{min}$ . The FI-IR spectra were measured in KBr pellets in the range  $4000\text{--}400 \text{ cm}^{-1}$  on a Mattson Alpha-Centauri spectrometer. Elemental analysis (EA) for C, H and N was performed on a Perkin-Elmer 2400 Elemental

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Analyzer. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer Thermal Analyzer under nitrogen atmosphere at a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$ . The fluorescent property was measured on a FLS920 Edinburgh Luminescence Spectrometer with a light source of Xenon lamp. The wavelengths for the photoexcitation of each compound were set the maximum of the excitation spectra.

### 2.2. Preparation of $[\text{Zn}_2(\text{btec})(\text{L}_1)\text{H}(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$ (**1**)

The pH of the mixture of  $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$  (0.1 mmol, 30.0 mg),  $\text{H}_4\text{btec}$  (0.04 mmol, 10.0 mg), 3,5-Di(1H-imidazol-1-yl)benzotrile (0.04 mmol, 9.0 mg) and  $\text{H}_2\text{O}$  (10 ml) was adjusted to about 3.5 with HCl (aq. 0.1 M) and NaOH (aq. 0.1 M). The resulting mixture was transferred into a 23 ml Teflon-lined stainless steel autoclave reactor and then heated at  $160\text{ }^{\circ}\text{C}$  for 72 h. After cooled to room temperature at a rate of  $3\text{ }^{\circ}\text{C h}^{-1}$ , colorless crystals suitable for X-ray structural analysis were isolated by filtrating, washing with water several times, and drying in air. Yield: ca. 20% (based on Zn). Anal. calc. for  $\text{C}_{23}\text{H}_{18}\text{N}_4\text{O}_{13}\text{Zn}_2$ : C, 40.08; H, 2.63; N, 8.13. Found: C, 39.98; H, 2.59; N, 8.09%. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 3450$  (m), 3120 (m), 3070 (m), 1600 (s), 1520 (s), 1410 (m), 1350 (s), 1260 (s), 1130 (m), 1080 (s), 1010 (m), 949 (m), 812 (s), 732 (m), 667 (m), 611 (s), 503 (m).

### 2.3. Preparation of $[\text{Zn}_2(\text{btec})(\text{L}_2)_2]$ (**2**)

The preparation of **2** (colorless crystals) is similar to that of **1** except that  $\text{L}_2$  (0.04 mmol, 10.0 mg) was used instead of 3,5-Di(1H-imidazol-1-yl)benzotrile. Yield: ca. 35% (based on Zn). Anal. calc. for  $\text{C}_{17}\text{H}_{13}\text{N}_6\text{O}_4\text{Zn}$ : C, 47.41; H, 3.04; N, 19.51. Found: C, 47.38; H, 2.95; N, 19.46%. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 3150$  (m), 1620 (m), 1580 (m), 1530 (m), 1480 (s), 1417 (s), 1360 (s), 1310 (s), 1280 (m), 1140 (s), 1020 (m), 997 (s), 904 (m), 864 (s), 816 (s), 739 (s), 671 (s), 606 (s), 515(s).

### 2.4. Preparation of $[\text{Zn}_5(\text{btec})_2(\text{L}_3)_{1.5}(\text{OH})_2]\cdot 2\text{H}_2\text{O}$ (**3**)

The preparation of **3** (colorless crystals) is similar to that of **1** except that  $\text{L}_3$  (0.04 mmol, 7.0 mg) was used instead of 3,5-Di(1H-imidazol-1-yl)benzotrile and the pH of the mixture was adjusted to about 5.5. Yield: ca. 15% (based on Zn). Anal. calc. for  $\text{C}_{61}\text{H}_{42}\text{N}_{18}\text{O}_{40}\text{Zn}_{10}$ : C, 31.57; H, 1.82; N, 10.86. Found: C, 31.38; H, 1.79; N, 10.79%. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 3450$  (m), 3130 (m), 1620 (m), 1550 (m), 1510 (s), 1400 (s), 1340 (s), 1290 (s), 1250 (s), 1140 (m), 1020 (m), 925 (m), 890 (m), 858 (m), 795 (m), 756 (m), 710 (s), 638 (m), 563 (m), 501 (m).

### 2.5. Single-crystal X-ray crystallography

Crystallographic diffraction dates for **1** and **2** were performed on a Bruker Apex CCD diffractometer and those of compound **3** were recorded on an Oxford Diffraction Gemini R Ultra diffractometer at 293 K, using a graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ). All the structures were solved by Direct Method of SHELXS-97 and refined by full-matrix least-squares techniques using the SHELXL-97 program. [6] All non-hydrogen atoms were refined with anisotropic temperature parameters. All hydrogen atoms on organic ligands (except for C23A and C23B of **3**) were placed in geometrically idealized position as a riding mode. The water hydrogen atoms (except for O3WA and O3WB of **1**, O1W and O2W of **3**) were located from difference Fourier maps. The disordered atoms (O3WA and O3WB of **2**; C23A, C28A, C29A, C23B, C28B and C29B of **3**) were split over two sites with a total occupancy of 1 and restricted by SIMU and ISOR. The atoms with ADP

**Table 1**  
Crystal data and structure refinement for **1**, **2** and **3**.

	<b>1</b>	<b>2</b>	<b>3</b>
Formula	$\text{C}_{23}\text{H}_{18}\text{N}_4\text{O}_{13}\text{Zn}_2$	$\text{C}_{17}\text{H}_{13}\text{N}_6\text{O}_4\text{Zn}$	$\text{C}_{61}\text{H}_{42}\text{N}_{18}\text{O}_{40}\text{Zn}_{10}$
Formula weight	689.15	430.7	2320.83
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2(1)/n$	$P2(1)/c$	$P-1$
<i>a</i> (Å)	7.0878(10)	10.355(3)	11.9764(5)
<i>b</i> (Å)	34.978(5)	8.977(3)	12.2491(5)
<i>c</i> (Å)	11.9500(14)	18.237(6)	14.5512(6)
$\alpha$ (°)	90	90	68.795(4)
$\beta$ (°)	125.259(9)	100.548(4)	67.582(4)
$\gamma$ (°)	90	90	85.387(4)
<i>V</i> (Å <sup>3</sup> )	2419.1(6)	1666.6(9)	1835.63(13)
<i>Z</i>	4	4	1
$\mu$ (mm <sup>-1</sup> )	2.066	1.515	3.322
<i>F</i> (000)	1392	876	1154
Reflections collected	8242	8093	12916
Reflections unique	4208	2867	7706
<i>R</i> <sub>int</sub>	0.0767	0.0658	0.0286
Goodness-of-fit (GOF) on <i>F</i> <sup>2</sup>	1.089	1.08	1.07
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup>a</sup>	0.0795, 0.1869	0.0623, 0.1533	0.0452, 0.1088
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data) <sup>a</sup>	0.1040, 0.2040	0.0855, 0.1664	0.0654, 0.1207

$$^a R_1 = \sum |F_o| - |F_c| / \sum |F_o|, wR_2 = \{ \sum (wF_o^2 - F_c^2)^2 / \sum (wF_o^2)^2 \}^{1/2}.$$

(O1, O3 and C6 for **1**; C4 for **2**; C24 for **3**) were restricted by ISOR. The crystallographic data for **1–3** are summarized in Table 1.

## 3. Results and discussion

### 3.1. Crystal structure of **1**

Single crystal X-ray structural analysis reveals that **1** is crystalline in monoclinic  $P21/c$  space group. A proton has been added to the formula directly to balance the charge. The 3,5-Di(1H-imidazol-1-yl)benzotrile is hydrolyzed into  $\text{L}_1$  under hydrothermally condition. The asymmetric unit of **1** contains two  $\text{Zn}^{2+}$  ions, one  $\text{btec}^{4-}$  anions and one  $\text{L}_1$  ligands. As shown in Fig. 1a, Zn1 and Zn2 are both four-coordinated in  $\text{ZnO}_2\text{N}_2$  tetrahedral geometries, but with different coordination environments. Zn1 is coordinated by two carboxylate oxygen atoms (O1 and O7#1; #1  $x+1, y, z+1$ ), one nitrogen atom (N1) from  $\text{L}_1$  and one water oxygen atom (O1W). Zn2 is coordinated by three carboxylate oxygen atoms (O3, O6#1 and O9#3; #1  $x+1, y, z+1$ ; #3  $x, -y+3/2, z+1/2$ ) and one nitrogen atom (N3#2; #2  $-x+1, y-1/2, -z+1/2$ ) from  $\text{L}_1$ . The Zn–O and Zn–N bond lengths vary from 1.927(4) to 2.035(5) Å and from 1.979(5) to 1.986(5) Å, respectively. Zn1 and Zn2 ions are connected by  $\text{btec}^{4-}$  to form 1D chains, which are further connected by  $\text{L}_1$  ligands through Zn1–N1 and Zn2–N3 bonds to form 2D layered structure (Fig. 1b and c). Then,  $\text{L}_1$  ligands coordinated to  $\text{Zn}^{2+}$  ions through Zn2–O9 bonds to connect the 2D layers into a 3D framework (Fig. 1d). The remaining blank of the 3D structure is occupied by the lattice water molecules. Topologically, if Zn1 and Zn2 are considered as a bimetal center, it connects three  $\text{L}_1$  and two other bimetal centers can be regarded as a 5-connected node.  $\text{L}_1$  connect three bimetal centers can be regarded as a 3-connected node. Thereafter, the framework of **1** can be described as a bi-nodal (3,5)-connected framework with *fsc-3,5-P4/mbm* topology (Fig. 2b) [7]. As far as we know, the CPs with *fsc-3,5-P4/mbm* topology is still rare [8].

### 3.2. Crystal structure of **2**

Single crystal X-ray structural analysis reveals that **2** is crystalline in monoclinic  $P21/c$  space group. The asymmetric unit of

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