



# Two new luminescent Zn(II) compounds constructed from guanazole and aromatic polycarboxylate ligands



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## ABSTRACT

Two new Zn(II) compounds, namely  $[(\text{CH}_3)_2\text{NH}_2]_{2n}[\text{Zn}_3(\text{bpt})_2(\text{datrz})_2]_n$  (**1**) and  $[(\text{CH}_3)_2\text{NH}_2]_n[\text{Zn}_2(\text{bptc})(\text{datrz})]_n \cdot n(\text{H}_2\text{O})$  (**2**) ( $\text{H}_3\text{bpt}$  = biphenyl-3,4',5-tricarboxylic acid,  $\text{H}_4\text{bptc}$  = biphenyl-3,3',5,5'-tetracarboxylic acid,  $\text{Hdatrz}$  = 3,5-diamino-1,2,4-triazole), have been obtained by the self-assemble reactions of  $\text{Zn}(\text{NO}_3)_2$ , 3,5-diamino-1,2,4-triazole, aromatic polycarboxylate ligands under solvothermal conditions. Single crystal X-ray structural analyses reveal that both compounds display three-dimensional (3D) frameworks. Compound **1** features a trinodal (3, 4, 6)-connected topological network with the point symbol of  $\{4.6^2\}_2\{4.6^4.8\}\{4^6.6^4.8^5\}$ . Compound **2** displays a binodal (4, 6)-connected topological network with the point symbol of  $\{3^2.6^2.7^2\}\{3^4.4^2.6^4.7^5\}$ . In addition, the thermal stabilities and luminescent properties of compounds **1** and **2** were also investigated in the solid state at room temperature.

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## 1. Introduction

Over the past few decades, metal-organic frameworks (MOFs) have been extensively studied for their intriguing topological frameworks and huge potential applications as functional materials in the realm of luminescence, catalysis, magnetism and gas separation [1–5]. One common method for the construction of MOFs is the hydrothermal or solvothermal self-assembly of metal ions and organic ligands. Through this method, numerous MOFs have been successfully obtained and structurally characterized [6–9]. However, it is still a great challenge in crystal engineering to obtain the MOFs with predictable frameworks and properties. It is well known that the structures and properties of MOFs greatly depend on the structure of the organic ligands, the coordination geometry and electronic characteristics of the metal ions [10–12]. Thus, selection of appropriate organic ligands and metal ions are the most important for the construction of desired MOFs with potential properties. In addition, the synthetic strategy is also a key factor for the design and construction of MOFs. Among the widely used strategies for the construction of MOFs, the mixed-ligand self-assemble strategy, which combines the N-containing and O-containing ligands

together, has been proven to be one of the most effective methods to synthesize MOFs [13–15]. The combination of two different kinds of ligands provides more possibilities to result in various 3D structures. 3,5-diamino-1,2,4-triazole ( $\text{Hdatrz}$ ) is a good multidentate N-containing organic ligands which can bridge metal ions in various coordination modes. O-containing polycarboxylate ligands have multiple bonding sites and high affinity to transition metal ions. The combination of polycarboxylate and  $\text{Hdatrz}$  ligands can result in various intriguing topological frameworks with promising potential properties. To date, only few examples of Zn(II) compounds constructed from  $\text{Hdatrz}$  and polycarboxylate ligands [16,17]. Compared with traditional hydrothermal conditions, the solvothermal conditions not only can greatly enhance the solubility of the organic ligands, but also the organic solvents can act as templates directing the synthesis of MOFs. On the basis of aforementioned points, herein, we selected  $\text{Hdatrz}$  and two different polycarboxylate ligands as the mixed ligands to constructed two new Zn(II) compounds, namely  $[(\text{CH}_3)_2\text{NH}_2]_{2n}[\text{Zn}_3(\text{bpt})_2(\text{datrz})_2]_n$  (**1**) and  $[(\text{CH}_3)_2\text{NH}_2]_n[\text{Zn}_2(\text{bptc})(\text{datrz})]_n \cdot n(\text{H}_2\text{O})$  (**2**) ( $\text{H}_3\text{bpt}$  = biphenyl-3,4',5-tricarboxylic acid,  $\text{H}_4\text{bptc}$  = biphenyl-3,3',5,5'-tetracarboxylic acid,  $\text{Hdatrz}$  = 3,5-diamino-1,2,4-triazole). Compound **1** features a 3D framework with trinodal (3, 4, 6)-connected topology, and compound **2** features a 3D framework with binodal (4,6)-connected topology.

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## 2. Experimental

### 2.1. Materials and instrumentation

All reagents and solvents employed in this work were commercially available and used without further purification. Elemental analyses (C, H and N) were determined with an elemental Vario EL III analyzer. Infrared spectrum using the KBr pellet was measured on a Nicolet Magna 750 FT-IR spectrometer in the range of 400–4000  $\text{cm}^{-1}$ . Powder X-ray diffraction (PXRD) analyses were recorded on a PANalytical X'Pert Pro powder diffractometer with  $\text{Cu}/\text{K}\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) with a step size of  $0.05^\circ$ . Thermal analyses were carried out on a NETSCH STA-449C thermoanalyzer with a heating rate of  $10^\circ\text{C}/\text{min}$  under a nitrogen atmosphere. Fluorescence spectra of the solid samples were performed on an Edinburgh Analytical instrument FLS920.

### 2.2. Synthesis of $[(\text{CH}_3)_2\text{NH}_2]_{2n}[\text{Zn}_3(\text{bpt})_2(\text{datrz})_2]_n$ (**1**)

A mixture of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.030 g, 0.1 mmol),  $\text{H}_3\text{bpt}$  (0.025 g, 0.1 mmol),  $\text{Hdatrz}$  (0.01 g, 0.1 mmol), DMF (3 mL) and  $\text{CH}_3\text{OH}$  (1 mL) was placed in a small vial at  $90^\circ\text{C}$  for 72 h and then cooled to room temperature slowly. Colorless block crystals were obtained in 42% yield based on  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . Anal. calcd. for  $\text{C}_{36}\text{H}_{29}\text{N}_{11}\text{O}_{12}\text{Zn}_3$  (1004.88): C, 42.99; H, 2.89; N, 15.33%. Found: C, 42.89; H, 2.85; N, 15.42%. IR ( $\text{cm}^{-1}$ ): 3422(w), 1712(m), 1675(s), 1587(m), 1509(m), 1389(m), 1378(m), 1109(w), 1025(w), 958(m), 893(m), 826(m), 778(w), 690(w), 674(w), 589(w), 562(w).

### 2.3. Synthesis of $[(\text{CH}_3)_2\text{NH}_2]_n[\text{Zn}_2(\text{bptc})(\text{datrz})]_n \cdot n(\text{H}_2\text{O})$ (**2**)

The synthesis of compound **2** was similar to that of **1**, but with  $\text{H}_4\text{bptc}$  (0.093 g, 0.1 mmol) in place of  $\text{H}_3\text{bpt}$ . Colorless crystals of **2** were obtained in 38% yield based on  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . Elemental analyses calcd. for  $\text{C}_{20}\text{H}_{18}\text{N}_6\text{O}_9\text{Zn}_2$  (617.18): C, 38.89; H, 2.92; N, 13.61%. Found: C, 38.86; H, 2.97; N, 13.67%. IR data (KBr pellet): 3450(s), 3179(m), 1652(m), 1626(m), 1550(s), 1478(s), 1431(m), 1182(s), 1135(m), 1034(m), 826(w), 807(m), 787(w), 610(m), 550(m), 519(m), 486(w).

### 2.4. X-ray crystallography

Suitable single crystals of **1** and **2** were carefully selected under an optical microscope and glued to thin glass fibers. Structural

measurements were performed with a computer-controlled Oxford Xcalibur E diffractometer with graphite-monochromated  $\text{Mo}-\text{K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at  $T = 293(2) \text{ K}$ . Absorption corrections were made using the SADABS program [18]. The structures were solved by direct methods and refined by full-matrix least-square methods on  $F^2$  by using the SHELXL-97 program package [19]. All non-hydrogen atoms were refined anisotropically. The H atoms attached to their parent atoms of organic ligands were geometrically placed and refined using a riding model. Crystal data, as well as details of data collection and refinements of **1** and **2** are summarized in Table 1, selected bond lengths and angles are given in Table 2.

## 3. Results and discussion

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

Single crystal X-ray diffraction analysis reveals that compound **1** crystallizes in the monoclinic  $C2/c$  space group and features a 3D framework with (3,4,6)-connected topology. There are one and a half  $\text{Zn}(\text{II})$  ions, one  $\text{bpt}^{3-}$  ligand, one  $\text{datrz}^-$  ligand and one dimethylamine cations. As shown in Fig. 1a, both  $\text{Zn1}$  and  $\text{Zn2}$  are four-coordinated with tetrahedral coordination geometries, which are defined by two carboxylate oxygen atoms and two nitrogen atoms. The  $\text{Zn}-\text{O}$  and  $\text{Zn}-\text{N}$  distances are in the range of 1.914(4)–1.936(3)  $\text{\AA}$ , 1.954(5)–1.994(4)  $\text{\AA}$ , respectively. Two symmetry-related  $\text{Zn2}$  ions are bridged by two  $\text{datrz}^-$  ligands into a dinuclear  $[\text{Zn}_2(\text{datrz})_2]$  unit with the  $\text{Zn} \dots \text{Zn}$  separation of 3.678  $\text{\AA}$  (Fig. 1b). These dinuclear  $[\text{Zn}_2(\text{datrz})_2]$  units and all  $\text{Zn1}$  ions are further connected together via the connection of  $\text{L}^{3-}$  and  $\text{datrz}^-$  ligands, affording a 3D framework of **1** (Fig. 1c). In **1**, each  $\text{datrz}^-$  ligand links three  $\text{Zn}(\text{II})$  ions in  $\mu_3\text{-N1, N2, N3}$  mode and each  $\text{bpt}^{3-}$  ligand links three  $\text{Zn}(\text{II})$  ions with its three carboxylate groups in uniform monodentate mode. From a topological viewpoint, each  $\text{bpt}^{3-}$  ligand links two dinuclear  $[\text{Zn}_2(\text{datrz})_2]$  units and one  $\text{Zn1}$  ion, and it can be considered as a 3-connected node. Each  $\text{Zn1}$  ion is surrounded by two dinuclear  $[\text{Zn}_2(\text{datrz})_2]$  units and two  $\text{Zn1}$  ions, and it can be reduced into a 4-connected node. Each dinuclear  $[\text{Zn}_2(\text{datrz})_2]$  unit is connected by two  $\text{Zn1}$  ions and four  $\text{bpt}^{3-}$  ligands, so it can be viewed as 6-connected node. The  $\text{datrz}^-$  ligands act as 2-connected spacers. As a result, the 3D framework of **1** can be simplified into a new trinodal (3,4,6)-connected topological network with the point symbol of  $\{4.6^2\}_2\{4.6^4.8\}\{4.6^4.8^5\}$  (Fig. 1d).

**Table 1**  
Crystal data and structure refinements for compounds **1** and **2**.

	<b>1</b>	<b>2</b>
Formula	$\text{C}_{36}\text{H}_{29}\text{N}_{11}\text{O}_{12}\text{Zn}_3$	$\text{C}_{20}\text{H}_{18}\text{N}_6\text{O}_9\text{Zn}_2$
Fw (g/mol)	1004.88	617.18
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/m$
$a$ ( $\text{\AA}$ )	28.3006(15)	18.8226(10)
$b$ ( $\text{\AA}$ )	20.085(3)	18.6427(8)
$c$ ( $\text{\AA}$ )	15.4335(12)	14.2485(5)
$\alpha$ ( $^\circ$ )	90.00	90.00
$\beta$ ( $^\circ$ )	92.498(5)	130.175(3)
$\gamma$ ( $^\circ$ )	90.00	90.00
Volume ( $\text{\AA}^3$ )	8764.4(16)	3820.3(3)
$Z$	4	4
Density ( $\text{cm}^3/\text{g}$ )	1.761	1.073
Abs. coeff. ( $\text{mm}^{-1}$ )	0.850	1.295
Total reflections	17271	7465
Unique reflections	8552 (Rint = 0.0721)	3464 (Rint = 0.0248)
Goodness of fit on $F^2$	0.952	1.026
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R = 0.0873$ , $wR_2 = 0.2117$	$R = 0.0598$ , $wR_2 = 0.1903$
$R$ (all data)	$R = 0.1301$ , $wR_2 = 0.2485$	$R = 0.0703$ , $wR_2 = 0.2033$

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