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Isomeric luminescent Zn(II) coordination polymers based on pyridinecarboxylate and 5-methyl-1H-tetrazole ligands

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HIGHLIGHTS

- Two new coordination polymers have been obtained through varying position-isomer ligands.
- Compound **1** and **2** have the same molecular formula but have different topological framework.
- These two compounds emit strong luminescence at room temperature.

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ABSTRACT

Two new metal–organic frameworks, namely $[Zn(nic)(mtz)]_n$ (**1**) and $[Zn(isonic)(mtz)]_n$ (**2**) (Hnic = nicotinic acid, Hisonic = isonicotinic acid, Hmtz = 5-methyl-1H-tetrazole), have been obtained through the solvothermal reactions of $Zn(NO_3)_2$, Htmz and Hnic or Hisonic. Single crystal X-ray diffraction analysis reveals that compound **1** features a 2D layered structure with **sql** topology, which is further extended into a 3D supramolecular framework *via* weak CH…π interactions, and compound **2** is 2-fold interpenetrated 3D framework with **dia** topology. Luminescent investigation shows that both of them emit blue luminescence at room temperature.

1. Introduction

In recent years, much attention has been paid to the design and construction of metal–organic frameworks (MOFs) not only because of their intriguing topological frameworks but also because of their potential applications in various areas of luminescence, catalysis, magnetism, gas storage and so on [1–4]. Up to now, considerable progress has been achieved in the field of crystal engineering [5,6], and some successful synthetic strategies have also been well established [7,8]. Since the first tetrazole-based complex was discovered by Bladin [9], tetrazole and its derivatives as organic building blocks have attracted researchers' attention owing to its multiple N-donor atoms and various coordination modes. Against this background, numerous coordination polymers assembled from tetrazole and their derivatives have been extensively investigated, which display extraordinary structure diversities and facile accessibilities of functionalized materials [10–12]. In these complexes, the tetrazole-based ligands were obtained from in situ hydrothermal reactions of cyanide class, sodium azide and metal salts as catalyst [13–16]. To the best of our knowledge, directly using tetrazole and its derivatives as raw materials for construction of complexes was rarely reported [10].

Mixed-ligand self-assemble strategy is one of the most effective methods to prepare new crystalline materials with predictable structures and unique properties. Therefore, in this work, we introduced nicotinic acid or isonicotinic acid into the tetrazole–metal system as the second ligand based on the following considerations: (i) nicotinic acid and isonicotinic acid are position isomers and have been proven to be good building blocks for construction of novel frameworks. (ii) nicotinic acid and isonicotinic acid possess different binding orientation, which can significantly affect the crystal structures and physical properties of the coordination polymers [17]. Herein, we report a comparative investigation of two coordination polymers, namely $[Zn(nic)(mtz)]_n$ (**1**) and $[Zn(isonic)(mtz)]_n$ (**2**) (Hnic = nicotinic acid, Hisonic = isonicotinic acid, Hmtz = 5-methyl-1H-tetrazole), whose topological structures are effectively determined by position isomeric nic and isonic.

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2. Experimental

2.1. Materials and equipments

All chemicals were obtained from commercial sources and used without further purification. Element analyses (C, H and N) were determined with an elemental Vairo EL III analyzer. Infrared spectra using the KBr pellets were measured on a Nicolet Magna 750 FT-IR spectrometer in the range of 400–4000 cm^{-1}. Powder X-ray diffraction data were collected using PANalytical X'Pert Pro powder diffractometer with Cu Kα radiation and $5° \leqslant 2\theta \leqslant 50°$. Thermogravimetric analyses were carried out on a NetzschSTA499C integration thermal analyzer under a nitrogen atmosphere from 30 to 900 °C at a heating rate of 10 °C/min. Fluorescence spectra of the solid samples were performed on an Edinburgh Analytical instrument FLS920. Single crystal X-ray diffraction was carried out on Oxford Xcalibur E diffractometer.

2.2. Synthesis of compounds **1**–**2**

2.2.1. Synthesis of $[Zn(nic)(mtz)]_n$ **1**

A mixture of $Zn(NO_3)_2{\cdot}6H_2O$ (0.2 mmol, 0.060 g), Hnic (0.024 g, 0.2 mmol), Hmtz (0.017 g, 0.2 mmol), H_2O (2 mL) and DMF (2 mL) was placed in a small vial. Then the vessel was sealed and heated to 110 °C, and hold for 60 h. Then the reactant mixture was cooled at a rate of 0.5 °C/min to lead to the formation of crystal **1**. Yield: 47% based on $Zn(NO_3)_2{\cdot}6H_2O$. Elemental analyses for $C_8H_7N_5O_2Zn$ (270.58): C, 35.48; H, 2.59; N, 25.87%. Found: C, 35.50; H, 2.56; N, 25.90%. IR (KBr, cm^{-1}): 3038 (m), 2924 (w), 2862 (w), 1605 (vs), 1562 (m), 1508 (m), 1403 (s), 1246 (vs), 1170 (s), 1107 (m), 1033 (m), 851 (m), 783 (m), 750 (m).

2.2.2. Synthesis of $[Zn(isonic)(mtz)]_n$ **2**

Synthesis of **2** was similar to that of **1**, but with Hisonic (0.024 g, 0.2 mmol) in place of Hnic. Colorless crystals of **2** were obtained in 34% yield based on $Zn(NO_3)_2{\cdot}6H_2O$. Elemental analyses for $C_8H_7N_5O_2Zn$ (270.58): C, 35.48; H, 2.59; N, 25.87%. Found: C, 35.47; H, 2.54; N, 25.86%. IR (KBr, cm^{-1}): 3037 (m), 2923 (w), 2862 (w), 1608 (vs), 1563 (m), 1504 (m), 1401 (s), 1245 (vs), 1170 (s), 1102 (m), 1032 (m), 852 (m), 782 (m), 746 (m).

Table 1
Crystallographic data for **1** and **2**.

	1	2
Formula	$C_8H_7N_5O_2Zn$	$C_8H_7N_5O_2Zn$
Fw	270.58	270.58
Crystal system	Monoclinic	Monoclinic
Space group	$P\,2_1/c$	$C\,2/c$
a (Å)	7.8273(7)	17.2027(8)
b (Å)	10.1323(12)	16.6803(5)
c (Å)	19.155(3)	10.0443(5)
α (°)	90	90
β (°)	96.535(9)	120.267(6)
γ (°)	90	90
Volume (Å^3)	1509.3(3)	2489.29(19)
Z	4	8
Density (calculated)	1.191	1.444
Abs. coeff. (mm^{-1})	1.622	1.967
Total reflections	6541	4568
Unique reflections	3414 (R_{int} = 0.0281)	2195(R_{int} = 0.0267)
Goodness-of-fit on F^2	1.121	0.946
Final R indices [$I > 2$ sigma ($I2$)]	R = 0.0415, wR_2 = 0.1238	R = 0.0332, wR_2 = 0.1021
R (all data)	R = 0.0560, wR_2 = 0.1315	R = 0.0403, wR_2 = 0.1067

Table 2
Selected bond lengths (Å) and angles (°) for **1**.

Zn(1)–O(1)^a	1.974(3)	Zn(1)–N(2)	2.007(3)
Zn(1)–N(5)^b	2.012(3)	Zn(1)–N(1)	2.062(3)
O(1)^a–Zn(1)–N(2)	123.79(12)	O(1)^a–Zn(1)–N(5)^b	114.24(11)
N(2)–Zn(1)–N(5)^b	110.62(12)	O(1)^a–Zn(1)–N(1)	99.86(11)
N(2)–Zn(1)–N(1)	101.35(11)	N(5)^b–Zn(1)–N(1)	102.93(11)

Symmetry codes: (a) $x - 1, y, z$; (b) $x, -y + 3/2, z + 1/2$.

Table 3
Selected bond lengths (Å) and angles (°) for **2**.

Zn(1)–O(1)^a	1.943(2)	Zn(1)–N(1)	1.997(2)
Zn(1)–N(4)^b	2.008(3)	Zn(1)–N(5)	2.063(2)
O(1)^a–Zn(1)–N(1)	122.34(10)	O(1)^a–Zn(1)–N(4)^b	116.62(10)
N(1)–Zn(1)–N(4)^b	108.64(10)	O(1)^a–Zn(1)–N(5)	96.53(10)
N(1)–Zn(1)–N(5)	104.44(10)	N(4)^b–Zn(1)–N(5)	105.10(10)

Symmetry codes: (a) $x + 1/2, -y + 1/2, z + 1/2$; (b) $x, -y, z + 1/2$.

2.3. X-ray crystallography

Single crystal X-ray structure analysis of **1**–**2** was performed on Oxford Xcalibur E diffractometer (Mo Kα radiation, λ = 0.71073 Å, graphite monochromator) at 293(2) K. Empirical absorption corrections were applied to the data using the SADABS program [18]. The structures were solved by the direct method and refined by the full-matrix least-squares on F^2 using the SHELXL-97 program [19]. All of the non-hydrogen atoms were refined anisotropically, and the hydrogen atoms attached to carbon atoms were located at their ideal positions. Experimental details for the structure determination are presented in Table 1. Selected bond lengths and angles for compounds **1**–**2** are listed in Tables 2 and 3.

3. Result and discussion

3.1. Description of the structure **1**

Single-crystal X-ray analysis reveals that **1** crystallizes in monoclinic $P\,2_1/c$ space group with the asymmetric unit containing one Zn(II) ion, one nic ligand, and one mtz ligand. As shown in Fig. 1, the Zn1 is tetrahedrally coordinated by three nitrogen atoms from two mtz ligands and one nic ligand, one carboxylate oxygen atom from another nic ligand. The Zn–N distances locate in the range of 2.007(3)–2.062(3) Å, and the Zn–O distance is 1.974(4) Å, which are comparable to those of the related Zn(II) compounds [14]. The nic and mtz ligand adopt μ_2-bridge coordination mode, bridging the Zn(II) ions with the separation of Zn…Zn of 7.8273(1) and 6.1154(9) Å, respectively. These two kinds of ligands bridged the Zn(II) ions together, forming a 2D layer extending along crystallographical *ac* plane (Fig. 1b), which can be simplified into a 4-connected **sql** topological net by viewing Zn(II) ions as 4-connected nodes and nic and mtz ligands as linear linkers. These adjacent 2D sheets further packed into a 3D supramolecular framework *via* weak intermolecular CH…π interactions (CH…π = 3.5829(4) Å, ∠CH…π = 74.523(3)°) (Fig. 1c), which are well within the accepted rang of CH…π interaction [20].

3.2. Description of the structure **2**

Single crystal X-ray analysis reveals that **2** crystallizes in monoclinic $C\,2/c$ space group with the asymmetric unit containing one Zn(II) ion, one isonic ligand and one mtz ligand. As shown in Fig. 2a, the coordination environment of Zn1 ion is similar to that in compound **1**, where the four-coordinated Zn ion adopts a