



Two new Zn(II) coordination polymers based on mixed pipemidic acid and flexible aromatic dicarboxylic acid ligands: Syntheses, crystal structures and luminescent properties

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ABSTRACT

Two new Zn(II) coordination polymers, namely $[\text{Zn}(4,4'\text{-sdb})(\text{HPPA})]_n$ (**1**) and $[\text{Zn}(2,2'\text{-bpdc})_{0.5}(\text{PPA})]_n$ (**2**) ($4,4'\text{-H}_2\text{sdb} = 4,4'\text{-sulfonyldibenzoate}$, $2,2'\text{-H}_2\text{bpdc} = 2,2'\text{-biphenyldicarboxylic acid}$, $\text{HPPA} = \text{pipemidic acid}$) were successfully obtained under hydrothermal conditions. These two compounds were further characterized by single-crystal X-ray diffraction analyses, elemental analyses, powder X-ray diffraction (PXRD) analyses and IR spectra. Compound **1** features a 1D chain structure, which further extended into a 3D supramolecular framework *via* intermolecular hydrogen bonds and weak van der Waals interactions, and compound **2** features a 3D framework with 6-connected α -Po-type topology. The structural regulation for these two compounds was successfully achieved by changing the flexible aromatic dicarboxylic acid ligand. Moreover, the thermal stabilities and luminescent properties for these two compounds were also investigated.

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1. Introduction

During the past few years, coordination polymers (CPs) have attracted more and more attention owing to their intriguing topological architectures and potential applications, such as luminescence, catalysis, gas storage, nonlinear optics and so on [1–4]. One of the most effective methods for the synthesis of CPs is hydrothermal self-assembly of multifunctional organic ligands and metal ions [5,6]. However, some unpredictable factors of the hydrothermal self-assemble reactions hinder us to predict the final structure of the obtained CPs [7–9]. In order to achieve the controllable synthesis at the molecular level, many effective synthetic strategies for the synthesis of CPs have been brought up such as the mixed-ligand approach, the building-block methodology, post-synthetic modification, the pillar-layer strategy, the reticular approach and so on [10–12]. In addition, selection of an appropriate organic ligand also plays an important role in the construction of CPs. Pipemidic acid (HPPA) is a bifunctional organic ligand and has not been used for the construction of CPs before. Under appropriate conditions, HPPA not only can act as a bridging ligand but also can

act as a terminal ligand. In viewing of its unique coordination mode, in this work, we selected HPPA as the main organic ligand and flexible aromatic dicarboxylic acid ($4,4'\text{-H}_2\text{sdb}$ or $2,2'\text{-H}_2\text{bpdc}$) as the auxiliary ligand to react with Zn(II) ions under hydrothermal conditions. By using this mixed-ligand strategy, we successfully obtained two new Zn(II) coordination polymers, namely $[\text{Zn}(4,4'\text{-sdb})(\text{HPPA})]_n$ (**1**) and $[\text{Zn}(2,2'\text{-bpdc})_{0.5}(\text{PPA})]_n$ (**2**) ($4,4'\text{-H}_2\text{sdb} = 4,4'\text{-sulfonyldibenzoate}$, $2,2'\text{-H}_2\text{bpdc} = 2,2'\text{-biphenyldicarboxylic acid}$, $\text{HPPA} = \text{pipemidic acid}$). Compound **1** features a 1D chain structure, which further extended into a 3D supramolecular framework *via* intermolecular hydrogen bonds and weak van der Waals interactions, and compound **2** features a 3D framework with 6-connected α -Po-type topology. Herein, we will report the syntheses, crystal structures and luminescent properties of these two compounds in this work.

2. Experimental

2.1. Materials and instrumentation

All reagents and solvents employed in this work were commercially available and used without further purification. FT-IR spectra were recorded with a Bruker Equinox 55 FT-IR

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spectrometer as a dry KBr pellet in the 400–4000 cm^{-1} range. Elemental analyses (C, H and N) were determined with an elemental Vario EL III analyzer. 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° . Thermal analyses for compound **1** and **2** were performed on a NETSCH STA-449C thermal analyzer at a heating rate of $10^\circ\text{C}/\text{min}$ in the temperature range $30\text{--}800^\circ\text{C}$ under nitrogen atmosphere. Fluorescence spectra of the compounds **1** and **2** were performed on an Edinburgh Analytical instrument FLS920.

2.2 Synthesis of $[\text{Zn}(4,4'\text{-sdb})(\text{HPPA})]_n$ (**1**)

A mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.06 g, 0.2 mmol), $4,4'\text{-H}_2\text{sdb}$ (0.061 g, 0.2 mmol), HPPA (0.061 g, 0.2 mmol), NaHCO_3 (0.026 g, 0.6 mmol) and H_2O (12 ml) was sealed in an 23 ml Teflon-lined stainless steel reactor under autogenous pressure at 150°C for 60 h, and then cooled to room temperature, giving rise the colorless block crystals (Yield: 42% based on $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$). Elemental Anal. Calcd. (%) for $\text{C}_{28}\text{H}_{24}\text{N}_5\text{O}_9\text{SZn}$ (671.97): C, 50.00; H, 3.57; N, 10.42. Found: C, 49.95; H, 3.62; N, 10.46. IR (cm^{-1} , KBr pellet): 3272 (w), 1612 (s), 1443 (m), 1352 (m), 1271 (s), 1147 (m), 1021 (s), 964 (s), 859 (s), 758 (m), 644 (m).

2.3 Synthesis of $[\text{Zn}(2,2'\text{-bpdc})_{0.5}(\text{PPA})]_n$ (**2**)

The synthesis of compound **2** was similar to that of **1** by using of $2,2'\text{-H}_2\text{bpdc}$ (0.04 g, 0.2 mmol) in place of $4,4'\text{-H}_2\text{sdb}$. The colorless block crystals of **2** were obtained (Yield: 28% based on $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$). Anal. Calcd. for $\text{C}_{21}\text{H}_{20}\text{N}_5\text{O}_5\text{Zn}$ (487.81): C, 51.66; H, 4.10; N, 14.35. Found: C, 51.73; H, 4.08; N, 14.42. IR/ cm^{-1} (KBr): 3142 (w), 1623 (m), 1568 (m), 1411 (m), 1356 (m), 1283 (m), 1067 (m), 947 (m), 853 (m), 733 (m), 658 (m).

2.4 X-ray crystallography

Single crystal X-ray diffraction analysis of **1–2** were carried out on 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 [13]. The structures were solved using direct methods and refined by full-matrix least-square methods on F^2 by using the SHELXL-97 program package [14]. 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 **1–2** 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** features a 1D chain structure with the asymmetric unit containing one Zn^{2+} ion, one $4,4'\text{-sdb}$ ligand and one HPPA ligand. As shown in Fig. 1a, the Zn1 ion is coordinated by three carboxylate O atoms (O2, O5 and O9a) and one carbonyl O atom (O1), displaying a distorted tetrahedron coordination geometry. The Zn–O distances locate in the range of $1.944(2)\text{--}2.003(2) \text{ \AA}$. Notably, the carboxylate group of the HPPA ligand are deprotonated, and the piperazine N atom are protonated which was to balance to the charge. The $4,4'\text{-sdb}$ ligand acts a bidentate ligands linking two Zn(II) ions with its two carboxylate groups in uniform bis-monodentate mode, and the HPPA ligand acts as a terminal ligand with its one carboxylate O atom and one carbonyl O atom in chelating mode. The Zn(II) ions are bridged together by the $4,4'\text{-sdb}$ ligands in to a 1D chain with the dangled terminal HPPA ligands (Fig. 1b). Adjacent 1D chains are further connected into a 2D supramolecular layer via intermolecular hydrogen bonding interactions (Fig. 1c). The detailed hydrogen parameters are listed in Table S1. Finally, these 2D supramolecular layers in –ABAB– sequence are hold together by weak van der Waals interactions, giving rise to a 3D supramolecular framework (Fig. 1d).

3.2. Crystal structure of compound **2**

When the $4,4'\text{-sdb}^{2-}$ ligand was instead by $2,2'\text{-bpdc}^{2-}$ ligand, compound **2** was successfully obtained, which was crystallized in monoclinic $C2/c$ space group with the asymmetric unit containing one Zn(II) ion, half of $2,2'\text{-bpdc}^{2-}$ ligand, one PPA^- ligand. As shown in Fig. 2a, the Zn(II) ion is coordinated by four carboxylate O atoms (O2, O2a, O4 and O5), one carbonyl O atom (O1) and one piperazine N atom (N5b), generating a slightly distorted octahedral coordination geometry. The Zn–O distances is in the range of $2.048(2)\text{--}2.358(3) \text{ \AA}$ and the Zn–N distance is $2.097(2) \text{ \AA}$. Notably, two symmetry-related Zn(II) ions are bridged by two PPA^- ligands,

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

	1	2
Formula	$\text{C}_{28}\text{H}_{24}\text{N}_5\text{O}_9\text{SZn}$	$\text{C}_{21}\text{H}_{20}\text{N}_5\text{O}_5\text{Zn}$
M_r	671.97	487.81
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$
a (\AA)	23.8120(16)	27.868(2)
b (\AA)	12.7900(7)	10.1238(12)
c (\AA)	21.2945(14)	16.2808(12)
β ($^\circ$)	94.865(7)	114.1790(10)
V (\AA^3)	6462.0(7)	4190.3(7)
Z	8	8
$F(000)$	2760	2704
μ (mm^{-1})	0.881	1.217
ρ (g cm^{-3})	1.381	1.546
R_{int}	0.0262	0.0335
$R [I > 2\sigma(I)]$	$R_1 = 0.0428, wR_2 = 0.1388$	$R_1 = 0.0385, wR_2 = 0.1164$
R (all data)	$R_1 = 0.0541, wR_2 = 0.1437$	$R_1 = 0.0495, wR_2 = 0.1259$
Gof	0.959	0.936

Table 2
Selected bond lengths (\AA) and angles ($^\circ$) for compounds **1** and **2**.

Compound 1			
Zn(1)–O(9) ^a	1.944 (2)	Zn(1)–O(5)	1.962 (2)
Zn(1)–O(2)	1.978 (2)	Zn(1)–O(1)	2.003 (2)
O(9) ^a –Zn(1)–O(5)	114.03 (10)	O(9) ^a –Zn(1)–O(2)	116.94 (11)
O(5)–Zn(1)–O(2)	101.62 (10)	O(9) ^a –Zn(1)–O(1)	100.03 (9)
O(5)–Zn(1)–O(1)	132.80 (10)	O(2)–Zn(1)–O(1)	90.01 (9)
Compound 2			
Zn(1)–O(2)	2.048 (2)	Zn(1)–N(5) ^b	2.097 (2)
Zn(1)–O(4)	2.109 (3)	Zn(1)–O(1)	2.143 (2)
Zn(1)–O(2) ^a	2.157 (2)	Zn(1)–O(5)	2.358 (3)
O(2)–Zn(1)–N(5) ^b	113.00 (9)	O(2)–Zn(1)–O(4)	90.64 (11)
N(5) ^b –Zn(1)–O(4)	156.27 (12)	O(2)–Zn(1)–O(1)	86.24 (8)
N(5) ^b –Zn(1)–O(1)	92.33 (9)	O(4)–Zn(1)–O(1)	91.19 (9)
O(2)–Zn(1)–O(2) ^a	77.80 (9)	N(5) ^b –Zn(1)–O(2) ^a	94.61 (9)
O(4)–Zn(1)–O(2) ^a	88.24 (9)	O(1)–Zn(1)–O(2) ^a	164.02 (8)
O(2)–Zn(1)–O(5)	146.68 (10)	N(5) ^b –Zn(1)–O(5)	99.70 (10)
O(4)–Zn(1)–O(5)	57.14 (10)	O(1)–Zn(1)–O(5)	86.19 (10)
O(2) ^a –Zn(1)–O(5)	106.74 (10)		

Symmetry code for compounds: (**1**): (a) $-0.5 + x, -0.5 + y, z$. (**2**): (a) $-x, 1 - y, -z$; (b) $0.5 - x, -0.5 + y, 0.5 - z$.

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