

# A New Zn(II) Coordination Polymer Constructed from 4-(1H-pyrazol-3-yl)pyridine as Fluorescent Sensor for Fe<sup>3+</sup><sup>①</sup>

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**ABSTRACT** A new Zn(II) coordination polymer, [Zn(4-PP)(1,4-BDC)·(H<sub>2</sub>O)]<sub>n</sub> (**1**, 4-PP = 4-(1H-pyrazol-3-yl)pyridine, 1,4-H<sub>2</sub>BDC = 1,4-benzenedicarboxylic acid), has been synthesized and structurally characterized by single-crystal X-ray diffraction as well as elemental analysis, IR spectra, XRPD and TG. Structural analysis reveals that Zn(II) ions are bridged by COO<sup>-</sup> from 1,4-BDC<sup>2-</sup> to form a binuclear structure as the second building units (SBUs). Zn<sub>2</sub> clusters can be clarified as 4-connected nodes, so the framework of **1** can be considered as a 2D (4<sup>4</sup>·6<sup>2</sup>)-*sql* sheet. Fluorescence measurements show that **1** has highly selective and sensitive detection of Fe<sup>3+</sup> in water medium.

**Keywords:** 4-(1H-pyrazol-3-yl)pyridine, crystal structure, luminescence, sensor, zinc complex;  
**DOI:** 10.14102/j.cnki.0254-5861.2011-2266

## 1 INTRODUCTION

Coordination polymers (CPs), as the new type of organic-inorganic hybrid materials, have received much attention in recent two decades due to their fascinating architectures and potential applications in gas storage and separation, magnetism, catalysis, fluorescence sensing, and so on<sup>[1]</sup>, because both the inorganic and organic moieties can provide the platforms to generate luminescence and some guest molecules within CPs can also emit and/or induce luminescence<sup>[2]</sup>. There is an increasing trend in the exploration and discovery of functional luminescent CPs, based on transition-metal ions in *d*<sup>10</sup> configuration in virtue of their excellent luminescent performance, as fluorescent probes for the detection of a variety of analytes like nitro-explosives, anions, cations, small molecules, biomolecules and volatile

organic compounds<sup>[3]</sup>. Metal ion sensing and detection are essential for environmental and biomedical applications<sup>[4]</sup>. Especially, Fe<sup>3+</sup> ion is crucial for biological and environmental systems because it can participate in oxygen uptake, oxygen metabolism and electron transfer, and either deficiency or overloading can lead to various biological ailments, such as anemia<sup>[5]</sup>. Thus, the development of fast response, highly selective/sensitive and water-stable CP-based sensors for the detection of Fe<sup>3+</sup> ions is a great deal in environmental and biomedical field<sup>[6]</sup>.

At the same time, it is a huge challenge for chemists to fully predict and control the structure of CPs since it is influenced by many factors including organic ligands, metal ions, solvent systems, temperature, pH and so on<sup>[7]</sup>. Among various factors, the choice of organic linker is critical for building

Received 5 December 2018; accepted 14 February 2019 (CCDC 1881212)

① The work was supported by the Science and Technology Program of Hengshui City (No. 2018011001Z)

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CPs<sup>[8]</sup>. N-containing ligands are widely popular for constructing novel architectures<sup>[9]</sup>. Among various N-containing linkers, 4-(1*H*-pyrazol-3-yl)pyridine (4-PP) is considered as an ideal linker choice to build novel networks<sup>[10]</sup>. Ongoing research in our laboratory has been directed toward the design and synthesis of novel coordination polymers with 4-PP<sup>[11]</sup>. To further extend coordination polymers based on 4-PP, herein we report the synthesis and structure of a new compound **1**, based on Zn<sup>2+</sup> ions for *d*<sup>10</sup> configuration, which can detect Fe<sup>3+</sup> with relative high sensitivity and selectivity in water medium.

## 2 EXPERIMENTAL

### 2.1 General procedures

4-(1*H*-pyrazol-3-yl)pyridine was prepared according to the published method<sup>[12]</sup>, and the other chemicals used for synthesis were of analytical grade and commercially available. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 240C analyzer. IR spectra were measured on a Tensor 27 OPUS (Bruker) FT-IR spectrometer with KBr pellets. The luminescence spectra were measured on an Edinburgh FS-5 luminescence spectrometer and all the measurements were carried out under the same experimental conditions. Thermogravimetric (TG) analyses were carried out on a Rigaku standard TG-DTA analyzer with a heating rate of 10 °C min<sup>-1</sup> from ambient temperature to 700 °C under air atmosphere, and an empty Al<sub>2</sub>O<sub>3</sub> crucible was used as reference. The X-ray powder diffraction spectra (XRPD) were recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA for a Cu-target tube and a graphite-monochromator. Simulation of the XRPD pattern was carried out by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program version 1.4.2 available free of charge via the Internet at <http://www.iucr.org>.

### 2.2 Synthesis

[Zn(4-PP)(1,4-BDC)·(H<sub>2</sub>O)]<sub>n</sub> (**1**) The mixture of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.029 g, 0.1 mmol), 4-(1*H*-pyrazol-3-yl)pyridine (0.016 g, 0.1 mmol) and 1,4-benzenedicarboxylic acid (0.016 g, 0.1 mmol) was dissolved in H<sub>2</sub>O (5 mL) and placed in a capped vial (10 mL). The vial was heated at 120 °C for 2 days and then cooled to room temperature, obtaining colorless block crystals (yield: 65% based on Zn). FT-IR (KBr pellets, cm<sup>-1</sup>): 3460 m, 3220 m, 1631 s, 1558 w, 1516 m, 1454 m, 1433 s, 1222 s, 1176 s, 1056 s, 841 s, 777 s, 713 m, 603 m and 526 m. The characteristic absorption bands of **1** at 1631 and 1433 cm<sup>-1</sup> were mainly attributed to the asymmetric and symmetric stretching vibrations of the carboxyl groups. Anal. Calcd. for C<sub>16</sub>H<sub>13</sub>N<sub>3</sub>O<sub>5</sub>Zn: C, 48.94; H, 3.34; N, 10.70%. Found: C, 48.87; H, 3.36; N, 10.68%.

### 2.3 Crystal structure determination and refinement

A colorless block single crystal of complex **1** (0.25mm × 0.25mm × 0.24mm) was mounted on glass fibers in a random orientation for single-crystal diffraction. The data were collected on a Rigaku SCX-mini diffractometer at 293(2) K with a Mo-*K*α radiation ( $\lambda = 0.71073 \text{ \AA}$ ) by using an  $\omega$  scan mode. The program SAINT was used for integration of the diffraction profiles<sup>[13]</sup>. The structure was solved by direct methods using the SHELXS program and refined by full-matrix least-squares methods with SHELXL (semi-empirical absorption corrections were applied using the SADABS program)<sup>[14]</sup>. Metal atoms were located from *E*-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on  $F^2$ . Hydrogen atoms of the ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. However, the hydrogen atoms of water were added by difference Fourier maps. Crystallographic data for **1**, triclinic system, space group  $P\bar{1}$  with *a*

$= 8.4055(17)$ ,  $b = 9.5590(19)$ ,  $c = 11.305(2)$  Å,  $\alpha = 68.11(3)$ ,  $\beta = 87.42(3)$ ,  $\gamma = 69.37(3)^\circ$ ;  $V = 784.9(3)$  Å<sup>3</sup>,  $Z = 2$ ,  $C_{16}H_{13}ZnN_3O_5$ ,  $M_r = 392.66$ ,  $D_c = 1.661$  g/cm<sup>3</sup>,  $F(000) = 400$ ,  $GOOF = 1.10$ , the final  $R = 0.055$ ,  $wR = 0.109$  ( $w = 1/[\sigma^2(F_o^2) + (0.1071P)^2]$ ),

where  $P = (F_o^2 + 2F_c^2)/3$ ,  $(\Delta\rho)_{\max} = 0.42$  and  $(\Delta\rho)_{\min} = -0.52$  e/Å<sup>3</sup>. The selected bond lengths, bond angles and hydrogen bond information for **1** are given in Tables 1 and 2, respectively.

**Table 1. Selected Bond Lengths (Å) and Bond Angles (°) for Complex 1**

Bond	Dist.	Bond	Dist.	Bond	Dist.
Zn(1)–O(3)	1.924(3)	Zn(1)–O(1)	1.978(5)	Zn(1)–O(2) <sup>i</sup>	1.988(3)
Zn(1)–N(1)	1.992(3)				
Angle	(°)	Angle	(°)	Angle	(°)
O(3)–Zn(1)–O(1)	109.25(13)	O(3)–Zn(1)–O(2) <sup>i</sup>	103.10(13)	O(1)–Zn(1)–O(2) <sup>i</sup>	115.62(13)
O(3)–Zn(1)–N(1)	129.73(14)	O(1)–Zn(1)–N(1)	101.31(13)	O(2) <sup>i</sup> –Zn(1)–N(1)	98.11(13)

Symmetry transformations used to generate the equivalent atoms: (i)  $-x+1, -y, -z+1$

**Table 2. Hydrogen Bond Information for 1**

D–H...A	d(D–H)	d(H...A)	d(D...A)	∠DHA
O(1w)–H(1wa)...O(1)	0.78	2.08	2.849	169
O(1w)–H(1wb)...N(2) <sup>i</sup>	0.75	2.12	2.817	156
N(3)–H(3)...O(1w) <sup>ii</sup>	0.83	1.92	2.720	164

Symmetry transformations used to generate the equivalent atoms: (i)  $x-1, y, z$ ; (ii)  $-x+2.5, -y, z+2.5$  for **1**

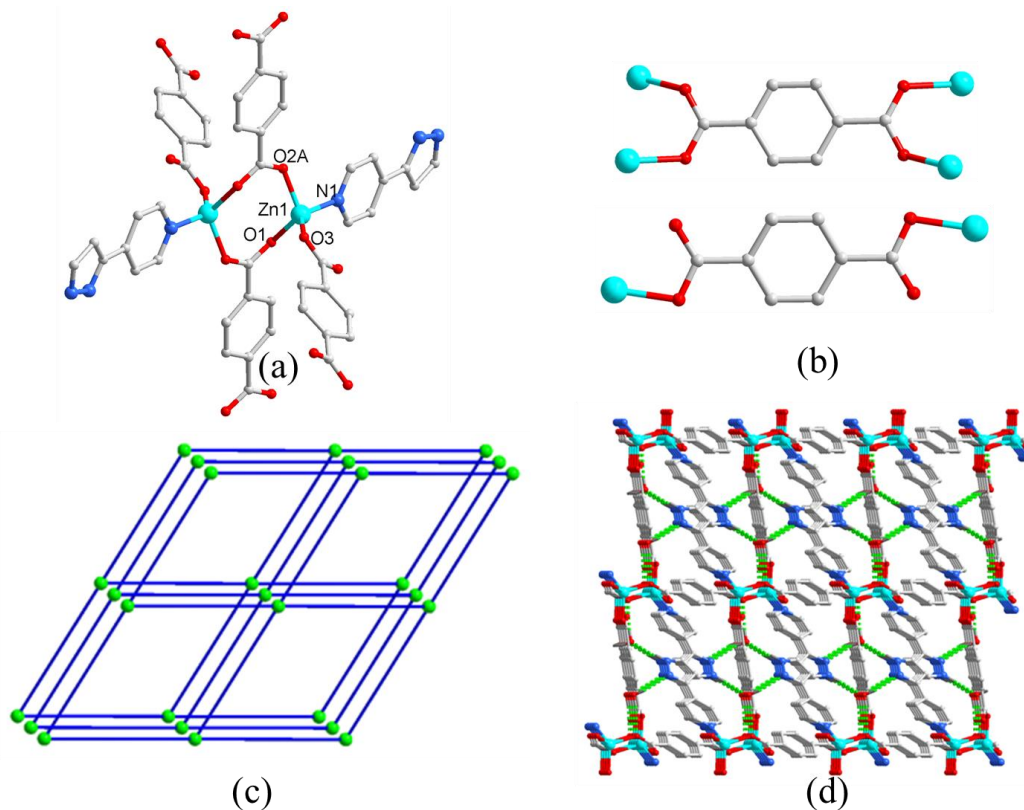
## 3 RESULTS AND DISCUSSION

### 3.1 Crystal structure of

#### [Zn(4-PP)(1,4-BDC)·(H<sub>2</sub>O)]<sub>n</sub> (**1**)

Single-crystal X-ray diffraction analysis reveals that complex **1** crystallizes in triclinic space group  $P\bar{1}$  with the asymmetry unit containing one Zn(II) ion, one 4-PP, two halves of 1,4-BDC<sup>2-</sup> and one free H<sub>2</sub>O molecule. The Zn(II) center is four-coordinated with three oxygen atoms (O(1), O(2A), O(3), symmetry code: A:  $1-x, -y, 1-z$ ) from three individual 1,4-BDC<sup>2-</sup> and one nitrogen atom (N1) from pyridine of 4-PP, forming a tetrahedral geometry (Fig. 1a). The Zn–O and Zn–N bond lengths (1.924(3) to 1.992(3) Å) and the coordination bond angles (98.11(13) to 129.73(14)°) are all within the ranges of those for other analogical Zn(II) complexes, respectively<sup>[15]</sup>. In

complex **1**, the 4-PP ligand serves as the terminal ligand, and 1,4-BDC<sup>2-</sup> adopts  $\mu_4-(\eta^1, \eta^1)-(\eta^1, \eta^1)$  and  $\mu_2-(\eta^1)-(\eta^1)$  coordination modes to connect Zn<sup>2+</sup> ions (Fig. 1b). Neighboring Zn(II) centers are bridged by two COO<sup>-</sup> from 1,4-BDC<sup>2-</sup> to form a binuclear structure as the second building units. The Zn<sub>2</sub> cluster is surrounded by four 1,4-BDC<sup>2-</sup> and two 4-PP, and the four 1,4-BDC<sup>2-</sup> connect four Zn<sub>2</sub> clusters (Fig. 1a). Thus, the Zn<sub>2</sub> cluster can be clarified as 4-connected nodes. The topological analysis approach is applied by using TOPOS 4.0 software<sup>[16]</sup>. In view of topology, the framework of **1** can be thought as a 2D (4<sup>4</sup>·6<sup>2</sup>)-sql sheet (Fig. 1c). Furthermore, the 2D sheets are extended into a three-dimensional (3D) supramolecular structure through O–H...O and N–H...O hydrogen bonding interactions (Fig. 1d).

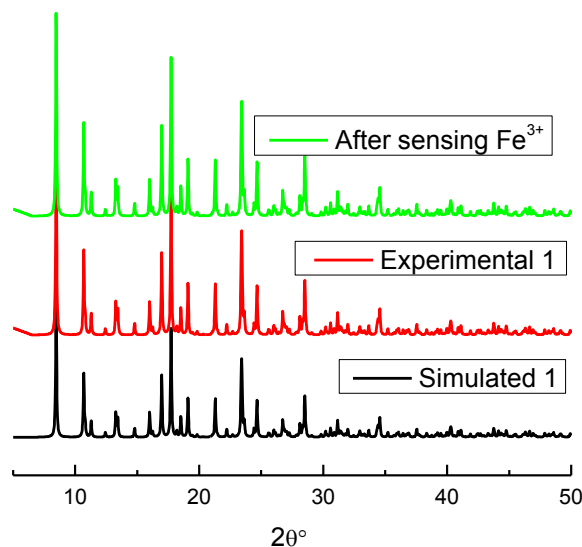


**Fig. 1.** (a) Coordination environment of Zn(II) ion in **1** with hydrogen atoms omitted for clarity. Symmetry code: A:  $1-x, -y, 1-z$ ; (b) Two kinds of coordination modes of 1,4-BDC<sup>2-</sup> in **1**. (c) *sql* topology (d) Three-dimensional supramolecular structure through hydrogen bonding interactions in **1**

### 3.2 X-ray powder diffraction of **1**

The experimental XPRD patterns of **1** correspond

well with the simulated XPRD pattern of **1**, demonstrating that the sample was a pure phase (Fig. 2).



**Fig. 2.** Simulated and experimental XPRD patterns of **1**

### 3.3 Thermal analysis

As shown in Fig. 3, the first weight loss of 4.56% (calcd.: 4.58%) in the range of 30 ~ 90 °C is

attributed to the removal of free water molecule per unit cell. Then, the weight of complex **1** is stable until 280 °C. Subsequently, the organic framework

of complex **1** dramatically collapses due to the decomposition of the organic ligands, and the final residues are ZnO (obs.: 20.80%, calcd.: 20.73%).

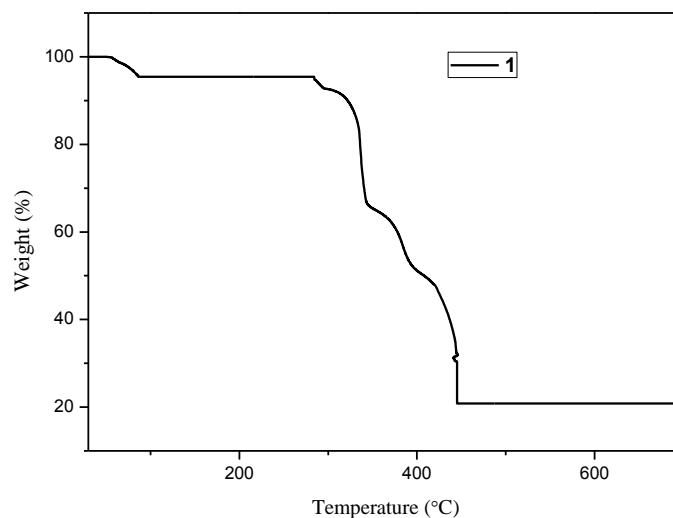


Fig. 3. TGA curve of the title complex **1**

### 3.4 Luminescent property

To examine the potential of complex **1** for sensing metal ions, the as-synthesized samples (3 mg) were ground and immersed in water medium (3 mL) of M(NO<sub>3</sub>)<sub>x</sub> (1 mmol/L, M = Zn<sup>2+</sup>, Cd<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Mg<sup>2+</sup>, Mn<sup>2+</sup>, Cu<sup>2+</sup>, and Fe<sup>3+</sup>). Each mixture was sonicated for 45 min to produce a uniform emulsion and then employed for luminescence test upon excitation at 370 nm. As shown in Fig. 4, the

luminescence intensities of complex **1** were different in various solution environments, indicating that various metal cations had different effects on this material, but it was found that the quenching effect of complex **1** was significant in Fe<sup>3+</sup> solution. The PXRD pattern after sensing Fe<sup>3+</sup> was similar to that of the as-synthesized one, which reveals quenching is not related to crystallographic alteration of the main framework (Fig. 2).

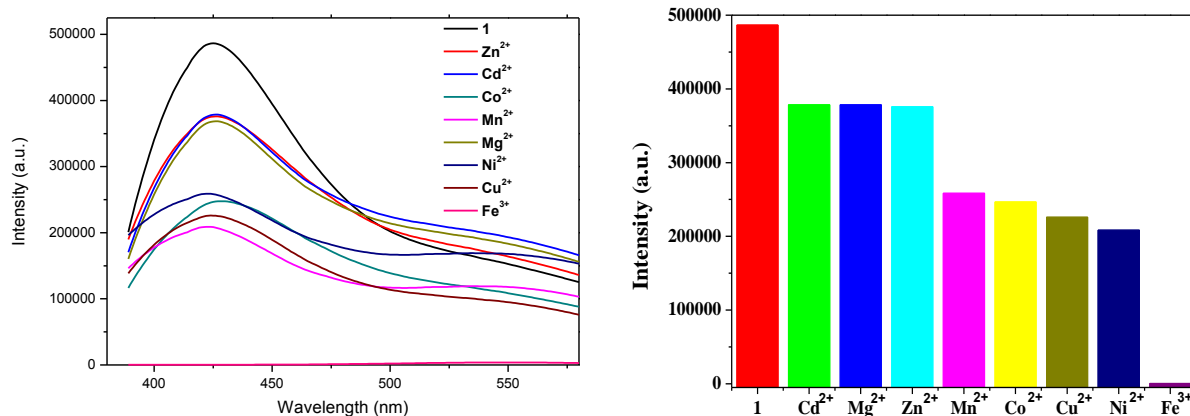


Fig. 4. (a) Emission spectra of **1** dispersed in water containing different metal ions. (b) The maximum emission intensities of **1** in water containing different metal ions (425 nm)

In order to further investigate the response of fluorescence of **1** to Fe<sup>3+</sup> ions, the luminescence titration upon the addition of Fe<sup>3+</sup> to **1** was performed. As shown in Fig. 5a, the luminescence

intensity of the emulsion gradually decreased with increasing the content of Fe<sup>3+</sup>. The quenching effect can be rationalized by the Stern-Volmer equation:  $I_0/I = K_{sv}[A] + 1$ , where  $I_0$  and  $I$  are the luminescent

intensity of complex **1** before and after adding  $\text{Fe}^{3+}$  respectively,  $[A]$  is the concentrations of the analytes and  $K_{\text{sv}}$  is the Stern-Volmer constant<sup>[17]</sup>. The Stern-Volmer plot for  $\text{Fe}^{3+}$  is typically linear at low concentrations (Fig. 5b). The equation  $I_0/I = K_{\text{sv}}[\text{Fe}^{3+}] + 0.990$  ( $R^2 = 0.9923$ ), which is similar to the ideal Stern-Volmer equation, shows that the interaction of  $\text{Fe}^{3+}$  with complex **1** is controlled by concentration diffusion<sup>[18]</sup>, that is, the luminescence

intensity of the material depends on the concentration of  $\text{Fe}^{3+}$  in the solution. The calculated Stern-Volmer constant for  $\text{Fe}^{3+}$  is  $K_{\text{sv}} = 3.29 \times 10^4 \text{ M}^{-1}$ . Such high  $K_{\text{sv}}$  value indicates that  $\text{Fe}^{3+}$  has strong effects of quenching for complex **1**. After the above calculations, it can be concluded that  $\text{Fe}^{3+}$  has a great impact on the fluorescence intensity of **1**, which thus can be used as a candidate material for detecting  $\text{Fe}^{3+}$  in water medium.

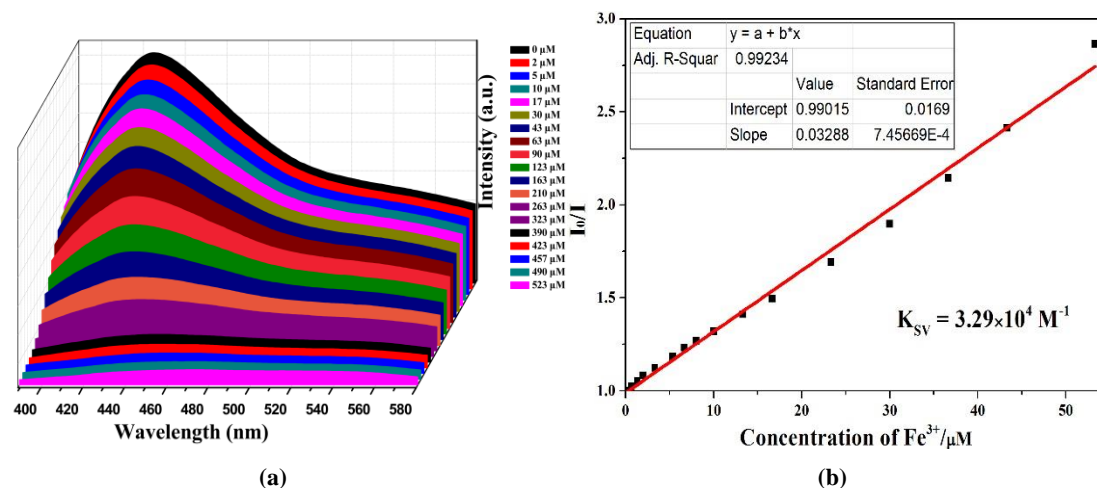


Fig. 5. (a) Emission spectra of **1** dispersed in  $\text{H}_2\text{O}$  upon increasing the addition of  $\text{Fe}^{3+}$ . (b) Stern-Volmer plot of  $I_0/I$  versus the concentration of  $\text{Fe}^{3+}$ .

## 4 CONCLUSION

In summary, under hydrothermal conditions, a new coordination polymer  $[\text{Zn}(4\text{-PP})(1,4\text{-BDC})\cdot(\text{H}_2\text{O})]_n$  (**1**) has been obtained. Complex **1**

exhibits a 2D  $(4^4\cdot 6^2)\text{-sql}$  sheet with  $\text{Zn}_2$  clusters as SBUs, and 4-PP ligand as the terminal ligand. **1** can be considered as highly selective probes for the detection of  $\text{Fe}^{3+}$  in aqueous solutions based on luminescence quenching.

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