

Short communication

A luminescent coordination polymer with potential active site for the sensing of metal cation, anion and nitrobenzene explosive

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ABSTRACT

A new 1D Zn-based coordination polymer (CP), $\{[\text{Zn}(\text{HBTB})(\text{pdp})]\cdot\text{H}_2\text{O}\}$ (**1**) (H_3BTB = 1,3,5-benzenetribenzoic acid and pdp = 2-(4,6-di(pyridine-2-yl)pyridine-2-yl)pyridine), has been synthesized under solvothermal condition and structurally characterized. The compound displays intense luminescence in solid state at room temperature with high thermal stability. Interestingly, Luminescent studies indicate that **1** could be an efficient multifunctional fluorescence material for high sensitivity metal ions, anions and organic small molecules, especially for Cu^{2+} , CrO_4^{2-} and nitrobenzene (NB) by luminescent quenching. The probable quenching mechanism of different analytes was also discussed.

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Chemical sensors for fast and highly selective detection of high explosives and related substances have attracted increasing attention concerning homeland security, environmental and humanitarian implications [1–5]. Until now, more and more nanoscale materials (such as oligomeric, polymeric materials) are used for fluorescence detection. These materials are capable of quick and efficient detection of various metal ions or small organic molecules. However, there are still some hindrances, such as stability and sensitivity, thus it is a significant and challenging task to synthesize novel materials for fluorescence detection of metal ions or small organic molecules [6–11].

Luminescent coordination polymers or metal-organic frameworks (LMOFs) can be used to detect heavy-metal ions and small organic molecules through photoluminescence. To date, scientists have developed all kinds of LMOFs' sensors in various application fields [12–16]. For example, Dinca's group has reported the Zn-based LMOFs which show high sensitivity to NH_3 [12]. Wang and his co-worker have reported a new Zn-MOF that can reversibly detect H_2O by color conversion caused by hydration [13]. Chen and Qian synthesized a LMOF that can even function as the thermometer in the range of 10–300 K [14]. The above studies are mainly concerned with the choice and design of synthesizing different LMOFs which could provide potential space within the channel/pore or coordination sites for molecular sensing. Many LMOFs have the uncoordinated carboxylate group of the ligands for molecular sensing. Nitrogen sites within pyridyl derivative also have the capability to selectively sense metal ions.

Taking these into consideration, we herein select π -conjugated ligand of 2-(4,6-di(pyridine-2-yl)pyridine-2-yl)pyridine (pdp) with Lewis basic pyridyl sites and the multi-carboxylate ligand of 1,3,5-benzenetribenzoic acid (H_3BTB) as potential organic linkers to build novel luminescent sensor systems. A new CP of $\{[\text{Zn}(\text{HBTB})(\text{pdp})]\cdot\text{H}_2\text{O}\}$ (**1**) with potential active site, has been synthesized and structurally characterized. Interestingly, **1** can work as highly sensitive sensors to Cu^{2+} , CrO_4^{2-} and nitrobenzene (NB) explosive by luminescent quenching. The probable quenching mechanism of different analytes was also discussed.

The compound **1** was generated by $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, pdp and H_3BTB in H_2O under solvothermal condition [17]. The asymmetric unit of **1** contains one Zn(II) atom, one pdp ligand, one HBTB^{2-} and one lattice water molecules. Each Zn(II) cation shows distorted trigonal bipyramid geometry defined by two carboxylate oxygen atoms from two different HBTB^{2-} and three nitrogen atoms from one pdp ligand (Fig. 1a). The Zn–O/N distance are in the normal ranges and are agreed with the reported Zn polymers [18]. In HBTB^{2-} ligand, the two carboxylic groups show monodentate mode, whereas the third carboxylic group is undeprotonated and is used to balance the full charge of network. The adjacent Zn(II) centers are linked by the HBTB^{2-} spacers to form a 1D zigzag array along the b-axis and the pdp ligands are decorated at the sides of the chain, as shown in Fig. 1b. The chains are further extended via the intermolecular $\pi\cdots\pi$ interactions, C—H $\cdots\pi$ hydrogen bonds and strong O—H \cdots O hydrogen bonds into a 3D supramolecular structure Fig. 1c and Fig. S1.

To confirm the phase purity of compound, the original sample was characterized by X-ray powder diffraction (XRPD) at room temperature. The pattern that was simulated from the single-crystal X-ray data of

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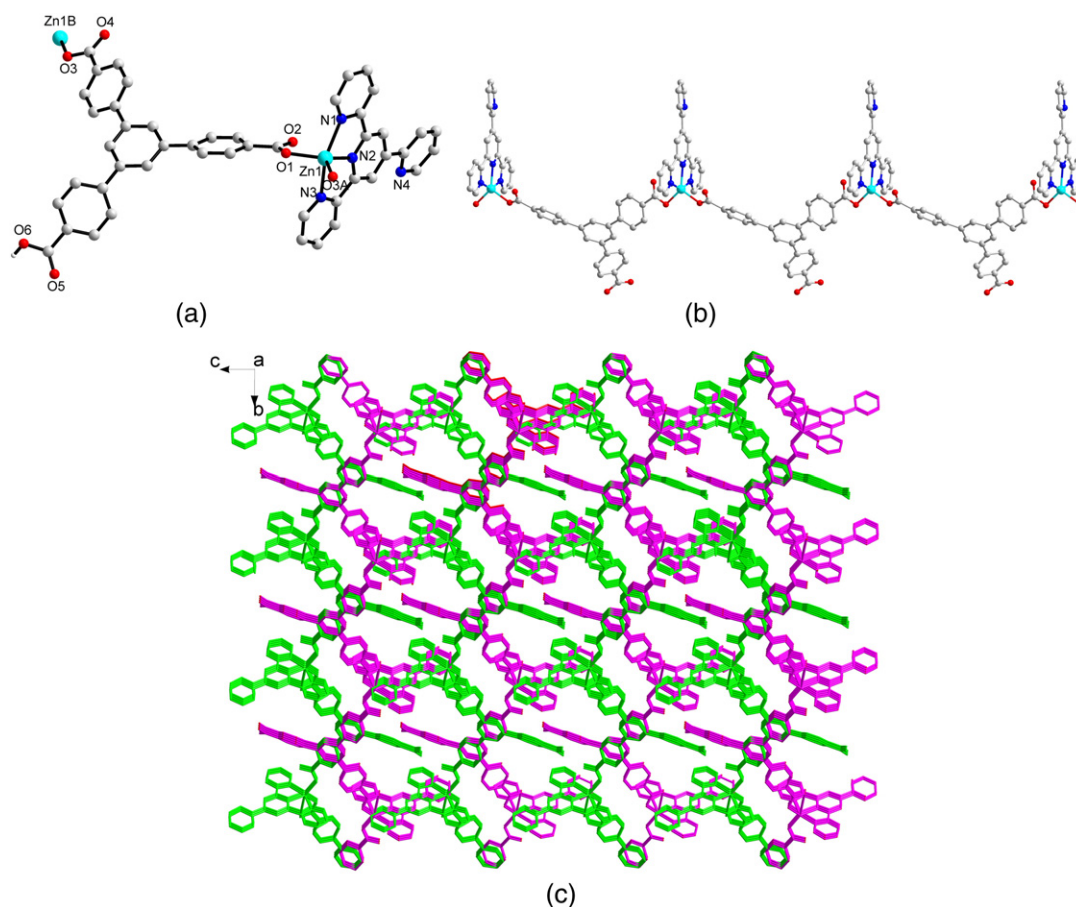


Fig. 1. (a) The coordination environment of Zn atom in **1** (symmetry code: A: $1 + x, 1 + y, z$; B: $-1 + x, -1 + y, z$); (b) The 1D zigzag chain along the b-axis; (c) The 3D supramolecular architecture of **1**. (all H atoms and uncoordinated water molecules are omitted for clarity).

compound was in agreement with those that was observed, as shown in Fig. S2. Additionally, to study the stability of the polymer, thermogravimetric analysis (TGA) of complex **1** was performed (Fig. S3). The first observed weight loss of 2.4% in the range of 25 to 90 °C is corresponding to the loss of the crystallization water molecule (calcd 2.2%). The TGA curve of compound **1** shows that no obvious weight loss is observed until the decomposition of the framework occurs at about 390 °C. This suggests that **1** has high thermal stability.

The photoluminescence (PL) spectra of **1** in the solid state were recorded at room temperature (Fig. S4). **1** exhibited an emission peak at 370 nm upon excitation at 291 nm. This emission band can be assigned

to ligand-centered emission, because the emission was observed at 368 nm ($\lambda_{\text{ex}} = 255$ nm) for the free pdp ligand [19] and 363 nm ($\lambda_{\text{ex}} = 325$ nm) for the free H₃BTB ligand (Fig. S4). In addition, the fluorescence properties of **1** in different solvent emulsions were investigated (Fig. 2a and Fig. S5). The predominant feature is that the PL intensities are largely dependent on the solvent molecules, particularly in the case of nitrobenzene (NB), which exhibits significant quenching behavior. To examine sensing sensitivity towards NB in more detail, a batch of suspensions of **1** with gradually increasing NB contents in DMF was prepared to monitor the emissive response (Fig. 2b and Fig. S6). The luminescence intensity decreased to 50% at 160 ppm, and

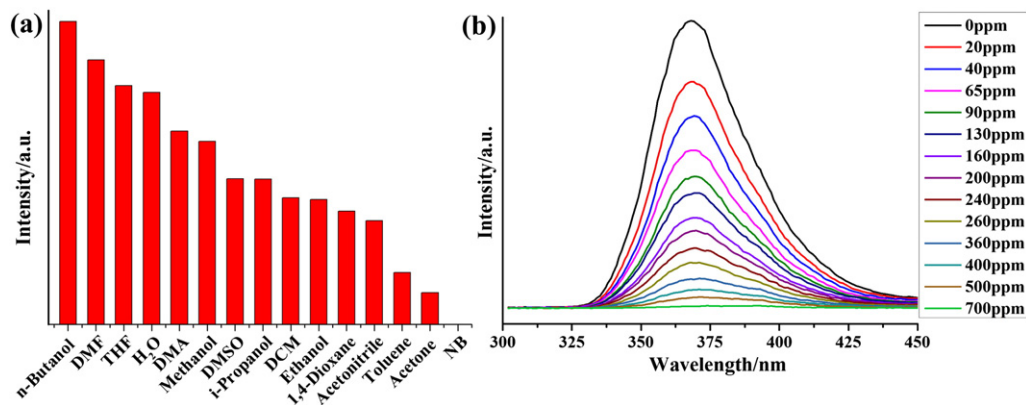


Fig. 2. (a) Comparison of the relative luminescence intensities of various **1**@solvents (left); (b) Emission spectra of **1** (right) dispersed in DMF with the titration of NB, and the quenching of the original emission band.

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