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Short communication

A fluorescent sensor for selective, sensitive, and recyclable detection of mercury(II) in aqueous solution based on a zinc(II) coordination polymer

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ABSTRACT

A fluorescent coordination polymer $[Zn(H_3TTA)(H_2O)_2]\cdot 2H_2O$ (**JLNU-3**, JLNU = Jilin Normal University; H_3TTA = [2,2′:6′,2″-terpyridine]-4,4′,4″-tricarboxylic acid) has been hydrothermally synthesized and carefully characterized. Particularly, stable suspension of **JLNU-3** in aqueous solution showed significant quenching towards Hg^{2+}. The quenching efficiency is up to 98% in the existence of 10^{-2} M Hg^{2+}. **JLNU-3** can be regenerative for 5 cycles by centrifugation of the solution after use and washing several times with H_2O. In addition, **JLNU-3** displays preeminent anti-interference ability and could be used for sensing in the systems with complicated components. Therefore, **JLNU-3** can be used as a fluorescent probe for selective, sensitive and recyclable sensing of heavy-metal cation Hg^{2+} in aqueous solution.

Environmental pollution and public health is of growing worldwide concern, regarding the condition of clean water all around the world [1,2]. There are numerous pollutants in waste water contaminations, especially heavy-metal ions, leading to a wide range of severe diseases and environmental issues as reported in the list of hazardous substances compiled by the United States Environmental Protection Agency (U.S. EPA) [3,4]. Ionic mercury (Hg^{2+}), as one of the extremely toxic and dangerous contaminant heavy-metal ion, has bring grave threat to human health and environment resulting from its high toxicity and non-biodegradable properties [5–7]. In addition, the bioaccumulation of Hg^{2+} in the human body not only gives rise to a variety of diseases like digestive, kidney, and neurological diseases [8–10], but also causes disorders and damages to immune and nervous system, the endocrine system and other organs [11,12]. The maximum allowable level of Hg^{2+} in drinking water is only 10 nM (2 ppb) by U.S. EPA standard [13]. Consequently, it could be a big challenge that detecting low concentrations of Hg^{2+} in laboratory model systems and even in waste water.

Currently, considerable efforts have been devoted to establish reliable and rapid methodologies for effective detection and removal of Hg^{2+}, including atomic absorption spectroscopy [14], atomic fluorescence spectrometry [15], liquid chromatography [16], mass spectroscopy [17], gas chromatography, capillary electrophoresis [18] and inductively coupled plasma-mass spectrometry [19–21], and so on. Nevertheless, there are some defects that limit the application of these methods in practice, for instance, sophisticated instrumentation, complicated pre-treatment procedures and time-consuming. Among these techniques, fluorescence-based probe, as a high sensitive, rapid responsive, and visual method, has been widely used through the changes of the fluorescence intensity or wavenumber. Nowadays, a variety of covalent organic frameworks (COFs) [22,23], organic dyes [24,25], metal nanoparticles [26–28], carbon nanomaterials [29,30] and semiconductor quantum dots [31,32] have been utilized as fluorescence probes for sensing Hg^{2+}. In the past decades, luminescent coordination polymers (CPs) have been emerging as promising candidates for detecting trace amounts of Hg^{2+} [33–44]. On one hand, the designable/modifiable architectures, robust functionalized recognized sites, and tunable chemical and physical properties of CPs are beneficial to molecular-ion recognition [45–48]. On the other hand, the metal cations or clusters and organic ligands in CPs can provide the platform to generate luminescence, which can add another dimension to luminescent functionalities [49,50]. However, it remains a labor-intensive endeavor to synthesize stable, sensitive and anti-interferential materials for fluorescence detection of Hg^{2+}.

Given Hg^{2+} has a higher affinity to nitrogen atoms and a larger ionic radius than other metal cations, the sensory property can be enhanced by introducing pyridine group into framework. Herein, we chose the organic ligand [2,2′:6′,2″-terpyridine]-4,4′,4″-tricarboxylic acid (H_3TTA, Fig. S2) to construct a luminescent CP for Hg^{2+} sensing in aqueous solution through fluorescence quenching.

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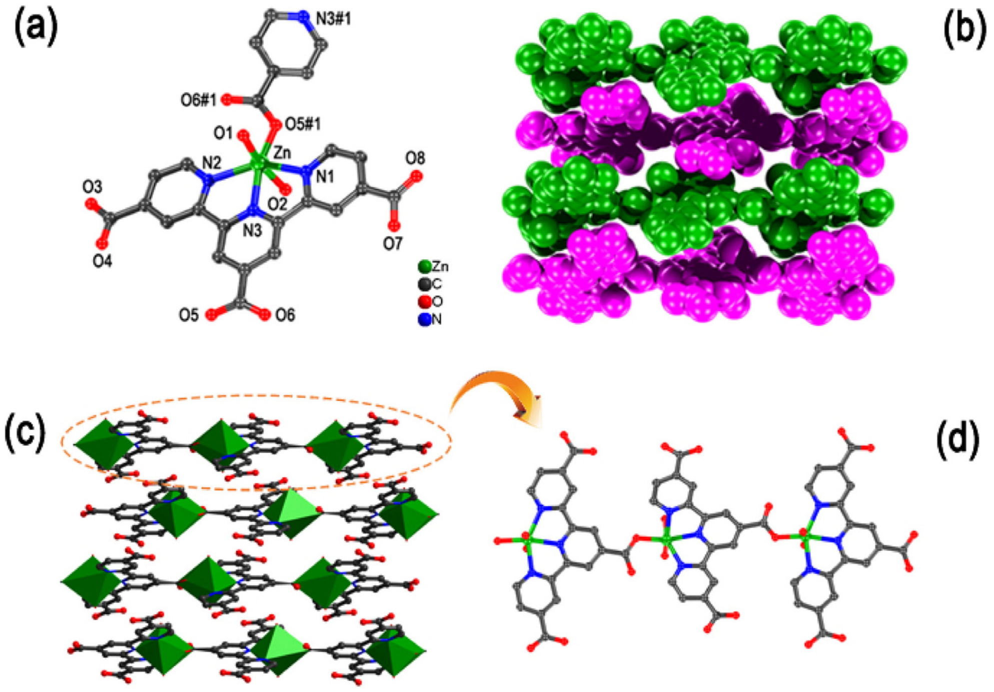

Fig. 1. (a) Coordination environments of Zn^{2+} ion in **JLNU-3**. Symmetry code: #1 $x, -y + 0.5, z - 0.5$. (b) and (c) The interlaced arrangement of the chains in **JLNU-3**. (d) The 1D chain in **JLNU-3**.

A hydrothermal reaction of $Zn(SO_4)_2 \cdot 7H_2O$ and H_3TTA in H_2O gave the colorless block crystal **JLNU-3**. Single-crystal X-ray diffraction (SXRD) study revealed that **JLNU-3** crystallizes in monoclinic space group $P2_1/c$ (Table S1). The fundamental building unit of **JLNU-3** consists of one independent Zn^{2+}, one H_3TTA and two isolated H_2O molecules (Fig. 1a). Zn^{2+} is coordinated by three oxygen atoms and three nitrogen atoms in octahedronal coordination geometry (Fig. 1c): one oxygen atom from one bridging carboxylate groups of H_3TTA, two oxygen atoms from coordinated H_2O molecules and three nitrogen atoms from the coordinated H_3TTA. The crystallographically independent unit connects each other by the ligand and form 1D chain (Fig. 1b and d). In the meantime, the arrangement of the chain is interlaced (Fig. 1b and c). The Zn—N and Zn—O bond lengths vary from 2.097 (4) to 2.221(4) Å and 1.980(3) to 2.323(4) Å, respectively (Table S2). The phase purity of this bulk **JLNU-3** was confirmed by powder X-ray diffraction (PXRD), in which the simulated and the as-synthesized patterns match well in key positions, indicating **JLNU-3** samples possess excellent phase purity (Fig. S3). It is worthwhile to note that the PXRD pattern of **JLNU-3** bulk sample immersed in water for 72 h evidenced the maintenance of the framework, illustrating the feasibility of **JLNU-3** as a fluorescent probe in aqueous solution (Fig. S3). The thermal stability of **JLNU-3** was studied by thermogravimetric analysis (TGA, Fig. S4). There is a weight loss between 30 and 180 °C, which corresponds to the loss of coordinated and isolated H_2O molecules, and the structure was maintained until 233 °C. The second weight loss between 233 °C and 310 °C is attributed to the loss of ligand composite. The final residual for **JLNU-3** is expected mainly to be zinc (II) oxide.

The photoluminescence (PL) spectra of **JLNU-3** and H_3TTA in the solid state were investigated under ambient conditions (Fig. S5). It was found that free H_3TTA ligands display an intense emission band at 523 nm upon excitation at 381 nm, which may be caused by the intraligand π–π^* transition. **JLNU-3** exhibits the maximum emission at 500 nm when excited at 325 nm. Compared to the free H_3TTA ligand, **JLNU-3** has a blue shift of 23 nm for maximum emission, which may originate from a charge transition between the ligand and metal ions [51]. In order to examine the potential of **JLNU-3** for sensing cations, a well ground sample of **JLNU-3** was dispersed in 3 mL of aqueous solution individually containing 10^{-2} M different metal cations (Zn^{2+}, Cd^{2+}, Ba^{2+}, K^+, Mg^{2+}, La^{3+}, Ca^{2+}, Cu^{2+}, Mn^{2+}, Cr^{3+}, Ni^{2+}, Co^{2+}, and Hg^{2+}) for 3 h to form uniform dispersion suspensions for fluorescence

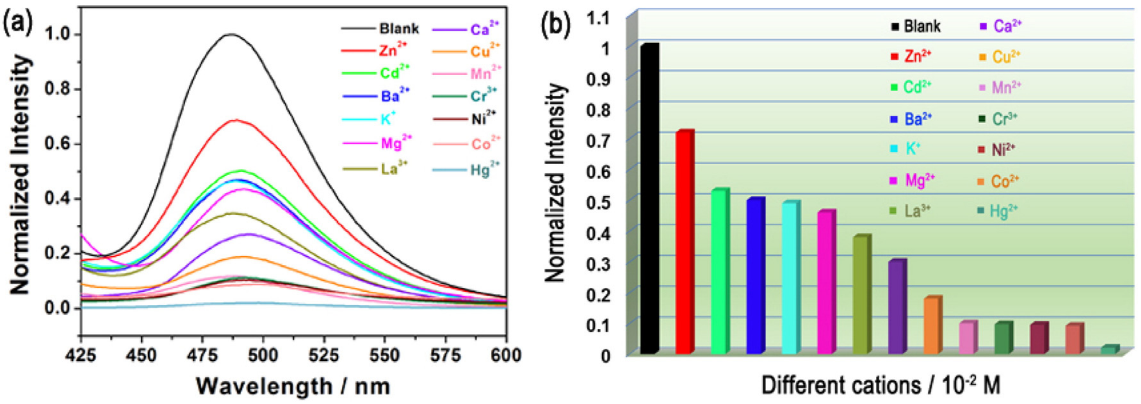

Fig. 2. (a) Emission spectra and (b) corresponding normalized intensities of **JLNU-3** treated with different metal cations (10^{-2} M) in aqueous solution.