



Short communication

A luminescent metal–organic framework for selective sensing of Fe³⁺ with excellent recyclability



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ABSTRACT

A new 3D luminescence metal–organic framework with open channels was constructed by the assembling of the zwitterionic H₃LCl ligand and Zn(II) ions under solvothermal conditions. The compound exhibits relatively high luminescence selective sensing for Fe³⁺ ions with surprisingly excellent recyclability, making it a promising candidate for sensing metal ions in practical.

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Porous metal–organic frameworks (MOFs) have attracted tremendous attention not only because of their fascinating architectures but also due to their potential applications in gas storage and separation, catalysis, magnetism, chemical sensors, drug delivery and so on [1–6]. Among these applications, fluorescence sensing based on luminescent MOFs is particularly interesting due to their quick-response, operability, high selectivity and excellent reversibility [7]. Over the past few years, studies on luminescents for sensing metal ions or organic molecules have been developed significantly and a large number of MOF-based fluorescence sensors have been reported [8,9]. For example, Chen and coworkers pioneered the luminescent Ln–MOF with Lewis basic pyridyl sites or open metal sites to sense metal ions or small molecules through partial fluorescence quenching [10].

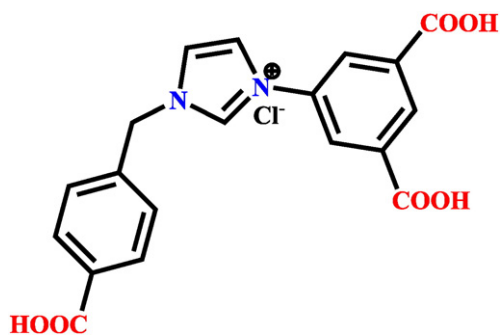
As is well known, Fe³⁺ ions play an essential part in human body as well as many living organisms due to their significance in a variety of vital cell functions such as hemoglobin formation, muscle and brain function, and electron transfer processes in DNA and RNA synthesis [11]. But excess and deficiency of Fe³⁺ may cause various physiological disorders and ultimately induce certain cancer [12]. Hence, selective detection or sensing of Fe³⁺ ions over other metal ions has always been an important issue in human health fields. Until now, several MOF-based fluorescence sensors have been developed for the detection of Fe³⁺ [13–15]. For example, Sun and coworkers reported an excellent work on a highly selective fluorescent probe for detection of Fe³⁺

through a cation-exchange approach [16]. Although numerous investigations focused on the MOF-based fluorescence sensors detecting Fe³⁺, very few examples were performed to practice due to the restrictions of its stability and reusability. Here, we successfully isolated a 3D porous luminescence MOF [ZnL]·xG (**1**, G = guest molecules, H₃LCl = N-(3,5-dicarboxylphenyl)-N'-(4-carboxylbenzyl) imidazolium chloride, Scheme 1), using the zwitterionic H₃LCl ligand and Zn(II) ions. It exhibits highly luminescence selective sensing for Fe³⁺ with surprisingly excellent recyclability.

Block-like pale yellow crystals of **1** were obtained via solvothermal reaction of H₃LCl and Zn(NO₃)₂·6H₂O in DMF solution at 90 °C. The single-crystal X-ray diffraction study reveals that compound **1** crystallizes in the monoclinic space group C2/c [17] and presents a 3D non-interpenetrating porous structure. As shown in Fig. 1a, each Zn(II) center is four-coordinated with the coordination spheres completed by four carboxylate oxygen atoms from four different L²⁻ ligands in a distorted tetrahedral geometry. Each L²⁻ ligand links four Zn(II) ions using its three carboxylate groups, two of which adopt monodentate coordination mode and the third one functions in a bridging mode. Thus, the central Zn(II) ions are connected by L²⁻ ligands through their bridging carboxylate groups to generate a dinuclear cluster {Zn₂} unit as sub-SBU, which was further connected to the monodentate-coordinated carboxylate groups to give rise to the 3D extended network with 1D column-like channels along the c axis (Fig. 1b). The size of the channel is ca. 8.0 × 8.0 Å². PLATON analysis showed that the effective free volume of **1** is 46.5% of the crystal volume (2670.2 Å³ out of the 5748.5 Å³ unit cell volumes) after squeezing guest molecules [18].

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Scheme 1. The structure of the zwitterionic ligand in the construction of **1**.

From the topological point of view, the $\{Zn_2\}$ units can be considered as a 6-connected node, while L^{2-} ligands can be regarded as a 3-connected node, respectively. Based on the simplification, the overall 3D network of **1** can be rationalized as a binodal (3,6)-connected **flu-3** topology with the Schläfli symbol of $(4^2.6)_2$ ($4^4.6^2.8^7.10^2$) (Fig. 1c).

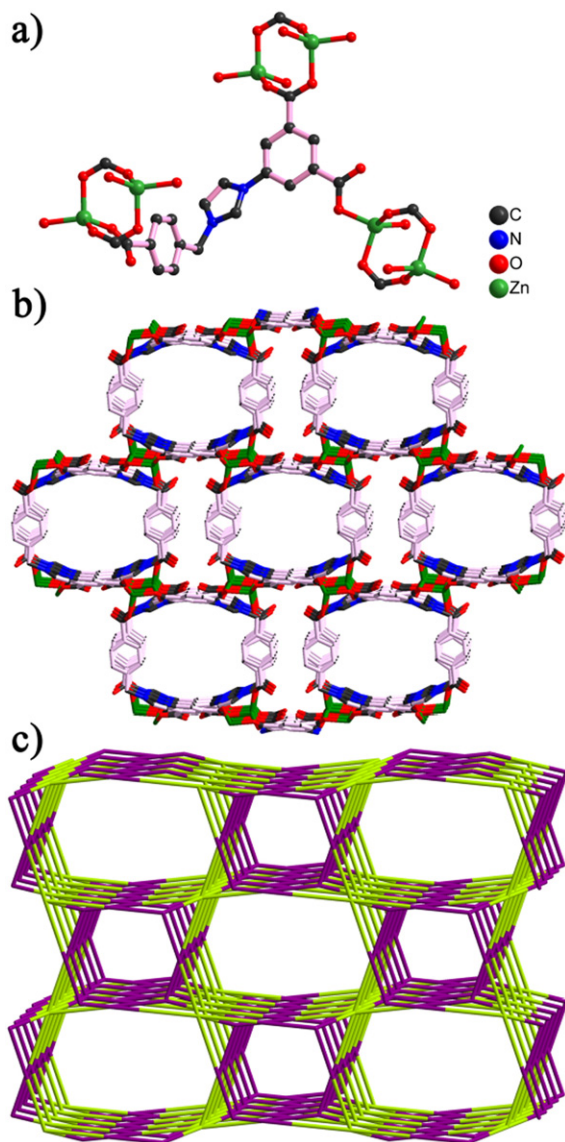


Fig. 1. (a) The coordination environment of L^{2-} and dinuclear Zn^{2+} cluster in **1** (hydrogen atoms were omitted for clarity); (b) Perspective view of the 3D framework with 1D column-like channels; (c) Schematic illustration of 3,6-connected **flu-3** topology of the 3D network of **1**.

Beside the structure investigation of the compound, it was also characterized by Powder X-ray diffraction (PXRD), thermal gravimetric analysis (TGA), IR spectroscopy (Fig. S3) and elemental analysis. The PXRD patterns of **1** correspond well with the results simulated from the single crystal data, indicating the high phase purity of the bulk samples (Fig. S1). In the case of TGA, the result curve for compound **1** shows it has one onset step from 107 °C to 235 °C to breathe out the structurally disordered solvent molecules, forming its guest-free phase $[ZnL]$, which is thermally stable up to 310 °C (Fig. S2).

Since compound **1** is constructed with a d^{10} electron configured Zn^{2+} and a fluorescent zwitterionic H_3LCl ligand, it has great potential for sensing functions and recognizing metal ions. The emission spectrum of compound **1** was investigated. As shown in Fig. S4, the luminescence spectra of the free H_3LCl ligand and the as-synthesized sample of **1** in the solid state gave a strong broad emission band at room temperature under the same excitation at 320 nm. In addition, the emission of **1** and H_3LCl in the suspension and solution state was tested (Fig. S5). The red shift for **1** at 474 nm may be attributed to the ligand-to-metal charge transfer [19].

To examine the potential of **1** for the sensing of metal ions, the as-synthesized samples were ground and suspended in 10^{-3} M DMAC solutions containing $M(NO_3)_x$ ($M = K^+, Li^+, Fe^{3+}, Al^{3+}, Mn^{2+}, Zn^{2+}, Cd^{2+}, Mg^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}, Ba^{2+}$, and Ca^{2+}) with the basic 3D framework remaining (Fig. S6). Interestingly, compound **1** shows significant quenching effect toward Fe^{3+} ions on the luminescence intensity of **1**. However, the luminescence intensities do not change or only slightly change in the presence of other tested metal ions (Figs. 2 and S7). These results indicate that **1** has a high selectivity for the detection and specific recognition of Fe^{3+} ions. To further investigate the sensing sensitivity toward the Fe^{3+} ions, **1** was dispersed in DMAC solutions with gradually increased Fe^{3+} concentration in the range of 10^{-7} – 10^{-1} M for luminescence studies. Interestingly, the luminescence intensity of Fe^{3+} -incorporated **1** is heavily dependent on the concentration of the metal ions. As seen in Fig. 3, with the increase of the Fe^{3+} concentration, the luminescence intensity decreases at different levels and almost completely quenched at a Fe^{3+} concentration of 10^{-3} M, which indicates the potential of **1** for the sensing of Fe^{3+} . In addition, the detection limit of the assay (Fig. S8) calculated with $3\sigma/k$ (k : slope, σ : standard) is about 6×10^{-5} M. On the other hand, the intensity quenching is not dependent on the anions (i.e. NO_3^- , Cl^- , ClO_4^-), because no signal change was observed with the corresponding $Fe(NO_3)_3$, $FeCl_3$ and $Fe(ClO_4)_3$ solutions adoption (Fig. S9). The influence of interrupting Fe^{3+} sensing by other metal ions was studied by conducting Fe^{3+} sensing in the presence of many other metal ions (Fig. S10). Emission spectra described no disturbance on selective Fe^{3+} sensing by any of the other metal ions.

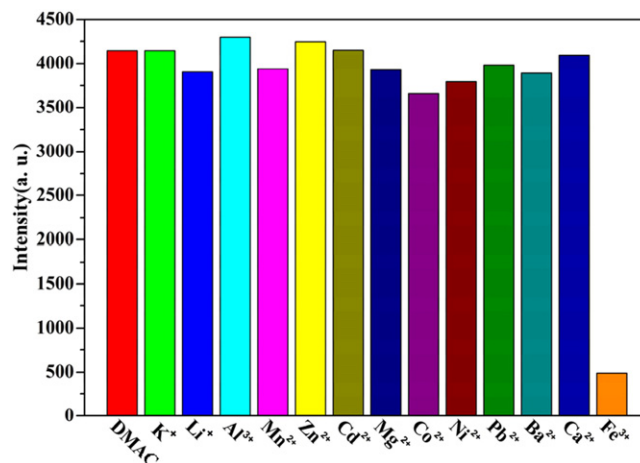


Fig. 2. The luminescent intensities for the emulsion of **1** in DMAC (10^{-3} M) at 473 nm upon the addition of various cations (excited at 314 nm).

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