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

Lin Wang,^a Zhao-Quan Yao,^a Guo-Jian Ren,^b Song-De Han,^b Tong-Liang Hu,^{*,a} and
Xian-He Bu^{a,b}

^a*School of Materials Science and Engineering, National Institute for Advanced Materials, Collaborative Innovation Center of Chemical Science and Engineering(Tianjin), Nankai University, Tianjin 300071, P. R. China.*

^b*College of Chemistry, Nankai University, Tianjin 300071, P. R. China*

Abstract A new 3D luminescence metal–organic framework with open channels was constructed by the assembling of the zwitterionic H₃LCI 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.

Keywords: Metal-organic framework; Luminescence; Detection; Fe³⁺; Recyclability

Corresponding author. Fax: +86-22-23502458. *E-mail address:* tlhu@nankai.edu.cn (T.-L. Hu).

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 fluorescent 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, Fe^{3+} 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 Fe^{3+} may cause various physiological disorders and ultimately induce certain cancer [12]. Hence, selective detection or sensing of Fe^{3+} ions over other metal ions has always been an important issues in human health fields. Until now, several MOF-based fluorescence sensors have been developed for the detection of Fe^{3+} [13-15]. For example, Sun and coworkers reported an excellent work on a highly selective fluorescent probe for detection of Fe^{3+} through a cation-exchange approach [16]. Although numerous investigations focused on the MOF-based fluorescence sensors detecting Fe^{3+} , 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 $[\text{ZnL}] \cdot x\text{G}$ (**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.

Scheme 1 (Insert here)

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].

From the topological point of view, the {Zn₂} units can be considered as a 6-connected node, while L²⁻ 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 (4².6)₂ (4⁴.6².8⁷.10²) (Fig. 1c).

Fig. 1 (Insert here)

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 complex **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 474nm 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 (Fig. 2 and Fig. 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 $\text{Fe}(\text{NO}_3)_3$, FeCl_3 and $\text{Fe}(\text{ClO}_4)_3$ 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 and Fig. 3 (Insert here)

Considering the importance of regeneration ability of luminescent probes in practical applications, the reversibility of **1** was also tested. For **1**, the samples were centrifuged, rinsed with DMAC several times, and dried in air after being submerged in 10^{-3} M Fe^{3+} solution for minutes. Such immersing and washing process was performed for twenty continuous cycles. The first ten quenching cycles are presented here (Fig. 4) and the full twenty cycles are performed as shown in Fig. S11. The result shows that the luminescence intensities and quenching efficiency of the recycled **1** are still well consistent with the initial sample. The PXRD were performed to conform that the framework is retained after twenty recycles (Fig. S12). This result indicates that compound **1** displays excellent regeneration without losing its crystalline and luminescence intensity when sensing Fe^{3+} . It is worth mentioning that MOF-based sensor with such high recycle performance to

detecting Fe^{3+} have not yet been reported [20].

Fig. 4 (Insert here)

To examine the possible mechanism for the selective luminescence quenching effect by Fe^{3+} ions, the UV-Vis absorption of DMAC solution containing $\text{M}(\text{NO}_3)_x$ or **1** as well as X-ray photoelectron spectroscopy (XPS) of $\text{Fe}@\mathbf{1}$ were tested. The XPS experiment on $\text{Fe}@\mathbf{1}$ showed that typical energy of Fe (710.4 and 715.8), demonstrating the interaction between Fe^{3+} and **1** (Fig. S13) [21]. To further understand the process of sensing, we introduced the solid samples of **1** into the 10^{-3}M Fe^{3+} solution for 2d to obtain the $\text{Fe}^{3+}@\mathbf{1}$ samples, and then filtered and washed with DMAC several times until the filtrate was completely colorless, then collected the filtrate. We analyzed the ICP of solid samples of $\text{Fe}^{3+}@\mathbf{1}$ and the filtrate (Table S4). The results indicated that there was no Fe^{3+} ions entering the channels of **1** or replacing $\text{Zn}(\text{II})$ ions in **1** during the sensing process. This may contribute to the solvent molecules in the pore and charge imbalance created by the interchange between the metal ions.

As is known, when the fluorophore and analyte are close to each other and the absorption band of the analyte has effective overlap with the emission band of the fluorophore, the resonance energy transfer can occur from fluorophore to non-emissive analyte. Resonance energy transfer can dramatically enhance fluorescence-quenching efficiency and also improves sensitivity [22]. The probability of resonance energy transfer depends upon the extent of spectral overlap between the absorption band of analyte and the emission band of the fluorophore [23]. Fig. S14 shows the strong absorption of Fe^{3+} from 310nm to 400nm, which has a large overlap emission spectrum of **1**, whereas almost no overlap was observed for other metal ions, indicating the efficient quenching occurs by an

energy transfer mechanism, which leads to a higher quenching response. In addition, the absorption spectrums of the DMAC solutions containing different concentrations of Fe^{3+} are performed, and the extent of spectral overlap between the analytes and **1** is in good agreement with the order of the quenching efficient, which is further providing support to the aforementioned mechanism (Fig. S14b and Table S5).

On the other hand, under excitation at 314nm, Fe^{3+} has a higher absorbance in comparison to other metal ions (Fig. S14 and Table S5), which can lead to lower absorption of the linker L^{2-} moieties. This implies that the stronger quenching effect of Fe^{3+} on the fluorescence intensity of **1** originates from the energy-transfer process between the ligands and metal centers [24]. Based on the above results, we concluded that there is a strong competition of absorption of the light source energy and the electronic interaction between the Fe^{3+} and L^{2-} moieties. The Fe^{3+} ions filter the excitation energy absorbed by L^{2-} moieties, so that decrease subsequent energy transfer from L^{2-} to the metal ions, therefore leading to the observed luminescence quenching. Besides, the absorptive intensity of the DMAC solutions containing different concentrations of Fe^{3+} are in good agreement with the luminescence intensity of **1** in the DMAC solutions containing the same concentration of Fe^{3+} , which further provide support to the aforementioned mechanism (Fig. S15b and Table S4).

In conclusion, a new 3D luminescence MOF consisting of open channels has been successfully prepared through the assembly of Zn(II) ions and the zwitterionic H_3LCl ligand. The compound can selectively sense Fe^{3+} ions through fluorescence quenching. The selectivity is ascribed to the energy transfer mechanism. What's more impressive is that the compound shows excellent reusability without losing its crystalline and luminescence intensity, which makes it a promising candidate as a fluorescent probe for Fe^{3+} ions in the field of detection application.

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- [17] Single crystal X-ray diffraction analyses of compound **1** was collected on a Rigaku 007 Saturn 70 diffractometer at 113.15(2) K with Mo-K α radiation ($\lambda = 0.71073$ Å). The crystal data were solved by direct methods and refined by a full-matrix least-square method on F2 using the SHELXL-97 crystallographic software package. Crystal data of **1**: C₁₉H₁₁O₆N₂Zn, $M_r = 428.69$,

monoclinic, space group $C2/c$, $a = 22.228(4) \text{ \AA}$, $b = 16.527(3) \text{ \AA}$, $c = 15.800(3) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 97.95(3)^\circ$, $\gamma = 90^\circ$, $V = 5749(2) \text{ \AA}^3$, $Z = 8$, $D_c = 0.991 \text{ g cm}^{-3}$, $F(000) = 3744$, $[R_{\text{int}} = 0]$, Reflns collected: 7673, unique: 6793, Final $R_1 = 0.0552$, $wR_2 = 0.1717$ for data with $I > 2\sigma(I)$. CCDC-1412401 for compound **1** contain the supplementary crystallographic data for this paper. The crystal data and refinement details for complexes **1** is summarized in Table S1. The selected bond lengths, and angles for **1** is listed in Tables S2.

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Figure Captions:

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

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**.

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).

Fig. 3. Fluorescence titration of **1** dispersed in DMAC with the addition of different concentrations of Fe^{3+} (excited at 314 nm).

Fig. 4. The luminescence intensity (474 nm) of ten recycles.

Scheme 1

Fig.1.

Fig.2.

Fig.3.

Fig.4