Fast Response and High Sensitivity Europium Metal Organic Framework Fluorescent Probe with Chelating Terpyridine Sites for Fe$^{3+}$

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ABSTRACT: Iron is one of the most important elements in the metabolic process for all living systems. However, both its deficiency and excess from normal permissible limits can induce serious disorders. We synthesized a europium-based metal–organic framework (Eu-MOF), EuL$_3$ ($L = 4'-(4$-carboxyphenyl)$)-2,2':6',2"-terpyridine$, under hydrothermal conditions, and used it as a solid luminescence sensor for Fe$^{3+}$ ions. The robust EuL$_3$ shows fast response ($\sim 1$ min) and high sensitivity (Stern–Volmer constant $K_{sv} = 4.1 \times 10^4$ L/mol) for Fe$^{3+}$ ions in aqueous solution or biological systems due to the existence of chelating terpyridine and open channels. The simple and portable test paper based on the EuL$_3$ fluorescent sensor system provides a convenient and reliable detection of Fe$^{3+}$ in every day applications. This pioneering work contributes to extend the potential application of Ln-MOFs to the biological and environmental areas.

KEYWORDS: terpyridine, europium metal organic framework, fluorescent probe, Fe$^{3+}$ ion, Fe$^{3+}$ test paper, open channel

INTRODUCTION

Iron is a ubiquitous metal in cells and plays a crucial role in a variety of vital cell functions such as oxygen metabolism and electron transfer processes in DNA and RNA synthesis.‡ However, both excess and deficiency from the normal permissible limit can induce serious disorders. A deficiency of iron limits oxygen delivery to cells, resulting in fatigue, poor work performance, and decreased immunity.‡ Conversely, excess amounts of iron ions in a living cell can catalyze the production of reactive oxygen species (ROS) via the Fenton reaction, which can damage lipids, nucleic acids, and proteins.³ The cellular toxicity of iron ions has been connected with several other metal ions were shown to interfere, necessitating complicated pretreatment procedures and sophisticated instrumentation. Recently, fluorescent sensors have been widely investigated for selective detection of iron because of their ability to provide a simple, sensitive, selective, precise, and economical method for online monitoring without any pretreatment of the sample together with the advantages of spatial and temporal resolution.§

Lanthanides (Lns) are fascinating due to their versatile coordination geometry, unique luminescent and magnetic properties, and high framework stability.⁵–⁷ Particularly, the brilliant optical properties of Ln-MOFs make them attractive for potential applications such as fluorescent probes and luminescent bioassays.⁸–¹⁰ In fact, some Ln-MOFs have been successfully employed for the sensing of small molecules (for instance TNT¹¹ and acetone¹²) and ions (such as Zn$^{2+}$, Cu$^{2+}$, Mg$^{2+}$, Ag$^+$, F$^-$, etc.).¹³–¹⁵ However, little work has been devoted to the development of fluorescent probes that are sensitive to Fe$^{3+}$ ions.¹⁶–¹⁸ Very recently, Dang et al. showed the first example of Eu-MOF fluorescent sensor for Fe$^{3+}$.¹⁹ However, the detective sensitivity was limited by its fluorescent quenching caused by cation exchange.

In designing highly sensitive and selective fluorosensors, the chelating agent (receptor unit) should have the potential to interact with the target metal ion (analyte) selectively and efficiently, and also the chelating unit must be connected to a suitable fluorophore unit that produces a distinct fluorescence

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upon chelation. Once the analyte is recognized by the receptor, the fluorescence signals can be observed in the form of quenching or enhancement in the fluorescence maxima due to either electron transfer (ET), charge transfer (CT), or energy transfer (ET) processes.\textsuperscript{25,26} Herein, we present a luminescent MOF material \textit{EuL}_3 (HL = 4′-(4-carboxyphenyl)-2,2′: 6′,2″-terpyridine, see Figure 1a), as a fast response and high sensitivity solid fluorescent probe targeted for Fe\textsuperscript{3+} ions due to its dual functional ligand group. Owing to the preferential binding of lanthanide ions to carboxylic oxygen atoms over the pyridyl nitrogen atom in Ln\textsuperscript{3+}-pyridinecarboxylate complexes,\textsuperscript{19,27} free terpyridine groups are left as a high efficient receptor unit ready for detecting cations. At the same time, Eu\textsuperscript{3+} ion, as a luminescence center, is linked with the receptor unit through a phenylcarboxylic acid. Once Fe\textsuperscript{3+} ions bind with the terpyridine group, the luminescence of the fluorophore unit (Eu\textsuperscript{3+}) is quenched rapidly. That results in very short response time (∼1 min) of ground EuL\textsubscript{3} microcrystals on paper. The Stern–Volmer constant of EuL\textsubscript{3} in Fe\textsuperscript{3+} aqueous solution reaches 4.1 × 10\textsuperscript{3} L/mol, which is the best value for the solid Ln-MOF fluorescent probe to our knowledge.

\section*{EXPERIMENTAL SECTION}

\subsection*{Typical Synthesis of HL and EuL\textsubscript{3}}
All reagents were purchased commercially and used without further purification. HL was synthesized according to the literature method with some modification.\textsuperscript{28} EuL\textsubscript{3} was prepared by hydrothermal reaction of Eu(NO\textsubscript{3})\textsubscript{3}·6H\textsubscript{2}O (0.10 mmol), L (0.10 mmol), and NaOH (0.10 mmol) in 10 mL of deionized water at 160 °C for 24 h.\textsuperscript{25} The reaction products were single crystals of microscale with a chemical composition of C\textsubscript{66}H\textsubscript{42}EuN\textsubscript{9}O\textsubscript{6} as determined by single-crystal X-ray diffraction. (See Table S1 in Supporting Information). Thermodgravimetric analysis (Supporting Information Figure S1a) results indicate that there is no solvent molecule (water) in the MOF structure, because L is bulky and multidentate, and thus can prevent the lanthanide ions from coordinating with solvent molecules and anions. The phase purity of the bulk material was independently confirmed by powder X-ray diffraction (XRD, red line in Figure 6). The X-ray structure analysis reveals a 1D framework of EuL\textsubscript{3} (Figure 1a), in agreement with the Hu group’s report.\textsuperscript{25} Each Eu\textsuperscript{3+} ion is nine-coordinated by six oxygen atoms from three L-anions and three nitrogen atoms from one L-anion with distorted triçapped trigonal prism geometry. In this compound, L-anions coordinate to Eu\textsuperscript{3+} ions in two different coordination fashions and play different roles in the formation of the frameworks (Figure 1a): (1) on the backbone, L-anions adopt pentadentate coordination fashion in which the carboxylate group adopts the bidentate chelating coordination mode and the terpyridyl moiety acts as the tridentate-chelating coordination mode with two terminal pyridyl rings in a cis arrangement, forming a 1D infinite chain running along the a axis; (2) on the arms, the carboxylate group adopts a bidentate chelating coordination mode and the terpyridyl moiety is free with two terminal pyridyl rings in a trans arrangement. These free Lewis basic terpyridyl sites are expected to accept small Lewis acidic molecules or metal ions. Moreover, the neighboring chains pack together through the π–π stacking interactions and C–H–π interactions to form a 3D supramolecular structure. It is

\textbf{Paper Based Fluorescent Sensor.} The filter paper was cut into strips of 1 cm × 2.5 cm. The strips were dipped in the dispersion of EuL\textsubscript{3} in ethanol for 1 min, and then taken out and left to dry at room temperature. The EuL\textsubscript{3} strips were immersed into aqueous Fe(NO\textsubscript{3})\textsubscript{3} solution of different concentrations for 1 min.

\section*{RESULTS AND DISCUSSION}

EuL\textsubscript{3} was prepared by hydrothermal reaction of Eu(NO\textsubscript{3})\textsubscript{3}·6H\textsubscript{2}O (0.01 mol), HL (0.01 mol) and NaOH (0.0001 mol) in 10 mL of deionized water at 160 °C for 24 h.\textsuperscript{25} The reaction products were single crystals of microscale with a chemical composition of C\textsubscript{66}H\textsubscript{42}EuN\textsubscript{9}O\textsubscript{6} as determined by single-crystal X-ray diffraction (See Table S1 in Supporting Information). Thermodgravimetric analysis (Supporting Information Figure S1a) results indicate that there is no solvent molecule (water) in the MOF structure, because L is bulky and multidentate, and thus can prevent the lanthanide ions from coordinating with solvent molecules and anions. The phase purity of the bulk material was independently confirmed by powder X-ray diffraction (XRD, red line in Figure 6). The X-ray structure analysis reveals a 1D framework of EuL\textsubscript{3} (Figure 1a), in agreement with the Hu group’s report.\textsuperscript{25} Each Eu\textsuperscript{3+} ion is nine-coordinated by six oxygen atoms from three L-anions and three nitrogen atoms from one L-anion with distorted triçapped trigonal prism geometry. In this compound, L-anions coordinate to Eu\textsuperscript{3+} ions in two different coordination fashions and play different roles in the formation of the frameworks (Figure 1a): (1) on the backbone, L-anions adopt pentadentate coordination fashion in which the carboxylate group adopts the bidentate chelating coordination mode and the terpyridyl moiety acts as the tridentate-chelating coordination mode with two terminal pyridyl rings in a cis arrangement, forming a 1D infinite chain running along the a axis; (2) on the arms, the carboxylate group adopts a bidentate chelating coordination mode and the terpyridyl moiety is free with two terminal pyridyl rings in a trans arrangement. These free Lewis basic terpyridyl sites are expected to accept small Lewis acidic molecules or metal ions. Moreover, the neighboring chains pack together through the π–π stacking interactions and C–H–π interactions to form a 3D supramolecular structure. It is
worth noting that the channels formed between the layers (Figure 1b) are very helpful to cation transportation.

The luminescence spectra of EuL₃ are shown in Figure 2. The excitation peak around 250 nm is ascribed to the absorption of L ligands, and those at 313 and 342 nm are from the absorption of the Eu³⁺ ion. The emission spectra of EuL₃ excited at 350 nm reveals well-resolved magnified luminescence of the f–f transitions, attributed to the energy transfer from L ligands to Eu³⁺ ions. Characteristic transitions of the Eu³⁺ ion are also evident with peaks at 592, 612, 649, and 696 nm, which could be attributed to ⁵D₀ → ⁷F₂, ⁵D₀ → ⁷F₃, ⁵D₀ → ⁷F₄, and ⁵D₀ → ⁷F₅ transitions, respectively.

EuL₃ was simply immersed in an aqueous solution of 0.01 mol/L M(NO₃)₂ (M = Na⁺, K⁺, Mg²⁺, Ca²⁺, Ba²⁺, Fe³⁺, Ni²⁺, Al³⁺, Cr³⁺, Pb²⁺, Cd²⁺, Cu²⁺, Zn²⁺, Ag⁺, Co²⁺, Fe³⁺, respectively) for 20 h to form metal-ion-incorporated M⁺⁺-EuL₃ as solids for luminescence studies. The photoluminescence properties of M⁺⁺-EuL₃ are recorded and compared in Figure 3. Characteristic emissions of the Eu³⁺ ion are evident for most of M⁺⁺-EuL₃ except in the case of the Fe³⁺ ion. Most interestingly, the luminescence intensity of M⁺⁺-EuL₃ heavily depends on the type of metal ion: alkaline metal ion such as K⁺ and alkaline-earth metal ions have basically no effect on the Eu-luminescence, while transition metal cations have varying degrees of quenching effects on the luminescence intensity. The luminescence intensity at 612 nm is about half of the original one after immersing into 0.01 mol/L Zn²⁺, Ag⁺, and Co²⁺ aqueous solution for 20 h. Impressively, there is almost no characteristic emission of Eu³⁺ ions for Fe³⁺-EuL₃ within a very short period. The main reason is that binding of Fe³⁺ to the free terpyridyl nitrogen atoms results in fluorescence quenching of EuL₃ crystals. Probably, the paramagnetic effect caused by the unpaired d-electrons present in Fe³⁺ promotes dissipation of the excited state energy in a nonradiative process. Compared with other metal cations, EuL₃ shows a high selectivity to Fe³⁺ ion. The quenching effect of EuL₃ was examined as a function of Fe(NO₃)₃ concentration in solution of 0–0.05 mol/L. The EuL₃ solid samples were immersed in different concentrations of Fe(NO₃)₃ for 24 h, and then their luminescence intensity at 612 nm was recorded. As shown in Figure 4, the fluorescence intensity vs [Fe³⁺] plot can be curve-fitted into \( I_0/I = 1 = K_{SV}[Fe^{3+}] \) close to the Stern–Volmer equation:

\[
I_0/I = 1 = K_{SV}[M]
\]

where \( I_0 \) and \( I \) are the luminescence intensity before and after metal ion incorporation, respectively; [M] is the metal ion molar concentration; and \( K_{SV} \) is the Stern–Volmer constant. On the basis of the experimental data in Figure 4, the \( K_{SV} \) value is calculated to be \( 4.1 \times 10^3 \) L/mol. This \( K_{SV} \) value is comparable to those in well-designed solution base organic compounds for sensing of Fe³⁺ (typical \( K_{SV} \) of about \( 10^4 \) L/mol).

The existence of channels and chelating terpyridine groups in the EuL₃ MOF provides an opportunity for fast response to the analyte Fe³⁺. To confirm this hypothesis, the fluorescence intensity of EuL₃ at 612 nm (\( \lambda_{ex} = 350 \text{ nm} \)) was measured as a function of immersion time in aqueous solution of 0.01 mol/L. As shown in Figure 5, more than half of the PL intensity of pure EuL₃ was decreased when EuL₃ was treated with Fe(NO₃)₃ solution for 10 min. This response is much faster than that in the previous report (about 24 h). The main reason is that Fe³⁺ ions can rapidly diffuse into the channels of EuL₃ crystals and bind to the free terpyridine groups, and the interaction between Fe³⁺ and L reduces the energy transfer efficiency from L to the Eu³⁺ ion, resulting in immediate photoluminescence quenching. With more and more Fe³⁺ ions binding to free
terpyridine groups, when the immersing time is 2 h, the PL intensity of the sample decreases to 6.3%. In case that all free terpyridine groups are coordinated, the Eu cations of EuL3 will be gradually exchanged by Fe3+ so that the PL is totally quenched when the sample is treated in Fe3+ solution for 24 h. This speculation is further confirmed by the TGA analyses of EuL3 and the Fe3+-EuL3 (Supporting Information Figure S1). It is observed that EuL3 has good thermal stability, it is stable up to 490 °C, and the final residue is composed of Eu2O3 (8.8%). The TGA result of Fe3+-EuL3 (Fe3+-24h) shows that the 11.1% weight loss before 320 °C corresponds to the removal of solvent molecules; 57.4% weight loss between 320 and 435 °C results from the loss of the organic component in the framework built of Fe3+ and terpyridine, while the weight loss of 16.2% between 435 and 535 °C is due to the loss of the organic component in the framework built of Eu3+ and terpyridine. The final residues are composed of Fe2O3 and Eu2O3 (15.4%).

In order to elucidate the possible mechanism for such photoluminescence quenching by the metal ions, powder XRD was employed to monitor the structure changes during Fe3+ solution treatment. The powder XRD patterns of the samples of EuL3 immersed in Fe3+ solution for 10 min and 2 h are similar to that of pristine EuL3 (Figure 6), suggesting that the main framework of EuL3 crystals does not change although the photoluminescence is mostly quenched. It can be concluded that the PL quenching within a short period mainly results from complex formation between the receptor unit (terpyridine) and analyte (Fe3+). Twenty-four hours later, a few new peaks (marked with asterisks) come out in the XRD pattern besides the pattern of EuL3. That indicates that a new kind of structure may form after a long time of immersing. However, the main framework of EuL3 does not change.

It is well-known that a typical fluorescence probe contains a receptor unit, a luminescence center, and a linker. In the framework of EuL3, Eu is the luminescence center, while the ligand L functions as both a linker and a receptor. On the one hand, one-third of the L ligands are located on the main chain, and they act as chemical linkers of adjacent Eu ions, with the carboxylate group connected to one Eu ion and the terpyridine moieties chelated to the other Eu ion to form a 1D infinite chain; on the other hand, two-thirds of the L ligands are perpendicular to the main chain, and they not only provide receptors for Fe3+ but also act as an optical linker between the central Eu ions and the Fe3+ ions. Once the Fe3+ ions in the solution are captured by the free terpyridine groups to form Fe-terpyridine complexes, the energy transfer process from L to the central Eu3+ ions will be forbidden, resulting in fluorescence quenching of EuL3 (Scheme 1, Step 1). Furthermore, the channels in EuL3 enable Fe3+ ions to pass through crystals smoothly, and therefore, the photoluminescence of EuL3 crystals can be quenched in a very short period. Finally, the Eu3+ ions in the EuL3 are replaced by Fe3+ ions for long time immersion, and some original frameworks rearrange to form new frameworks. However, the main framework of EuL3 still keeps its original structure (Scheme 1, Step 2).

To explore the potential of such a highly selective and sensitive MOF sensor in a biological system, EuL3 was immersed in the simulated physiological conditions (0.02 mol/L HEPES aqueous buffer solution, pH = 7) with different concentrations of Fe3+ ions. The luminescence tests (Figure 7a) and XRD (Figure 7b) were then carried out on EuL3 crystals. With increasing concentration of Fe3+ ions, the luminescence intensity of Eu decreased dramatically. The Eu luminescence was almost completely quenched when the Fe3+-concentration was increased to 0.01 mol/L. The PXRD results suggest that

Figure 5. Variation of fluorescence intensity of Fe3+-EuL3 solid sample at 612 nm with immersion time in Fe(NO3)3 solution of 0.01 mol/L, λex = 350 nm.

Figure 6. Powder XRD patterns of pristine EuL3 and EuL3 treated in 0.01 mol/L of Fe3+ solution for different times; the new peaks are marked with asterisks.

Scheme 1. Possible Mechanism of Fluorescence Quenching of EuL3 by Fe3+
the original frameworks of EuL₃ transformed after immersion in HEPES/(0.01 mol/L Fe³⁺ ions) solution for 24 h. In conclusion, compound EuL₃ displays fluorescence behavior under biological condition similar to that in aqueous solution, and therefore, it can be used as a promising luminescence sensor for Fe³⁺ ions in a biological system.

In order to make the detection simple and portable, we developed a fluorescence test paper for rapid detection of Fe³⁺ in aqueous solution. The test paper was prepared by immersing a filter paper (1 × 2.5 cm²) in the dispersion of ground EuL₃ in ethanol and drying it at room temperature. For the detection of Fe³⁺ in water, the test paper was immersed Fe(NO₃)₃ aqueous solutions for 1 min and then exposed to air for drying. As shown in Figure 8, under the irradiation of UV light of 365 nm, the test paper showed a bright red color. The fluorescent colors of the test paper changed to red, dark red, faint dark red, and finally black as soaked in 0.0001, 0.0005, 0.001, and 0.005 mol/L of Fe(NO₃)₃ aqueous solution. To the naked eye, one can distinguish the colors of different intensities.

**CONCLUSIONS**

We have demonstrated a highly selective and sensitive method to detect Fe³⁺ ions in aqueous solution or in biological systems based on the specific affinity between Fe³⁺ ions and chelating terpyridyl sites in EuL₃. On the basis of the fluorescence quenching of EuL₃ caused by Fe³⁺ ions, the Fe³⁺ ions of as low as 0.0005 mol/L can be detected without interference from other metallic ions. By using this compound, a test paper was prepared easily and its response to Fe³⁺ ions in one minute was visible to the naked eye. Therefore, EuL₃ and its test paper may find practical applications in the laboratory and in daily life in the near future.

**REFERENCES**

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**ASSOCIATED CONTENT**

© Supporting Information
Crystal data and TGA curve of EuL₃. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**
The authors declare no competing financial interest.