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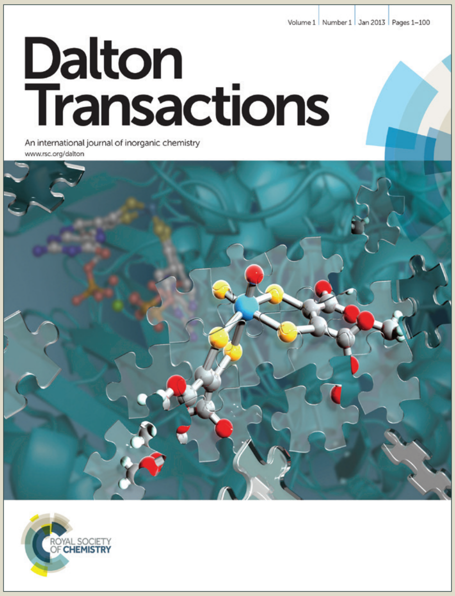

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COMMUNICATION

A flexible zwitterion ligand based lanthanide metal-organic framework for luminescence sensing of metal ions and small molecules

Rong-Mei Wen, Song-De Han, Guo-Jian Ren, Ze Chang, Yun-Wu Li* and Xian-He Bu*

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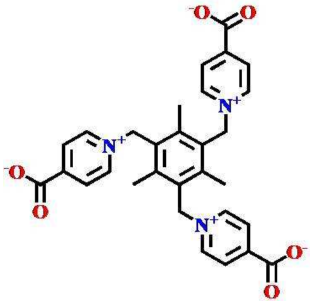
A new lanthanide metal−organic framework has been constructed by using a tripodal flexible zwitterion (H_3LBr_3) ligand which taking chair-shaped configuration. The luminescence of the compound displays highly selective sensing of Fe^{3+} ion and nitrobenzene.

As a new class of porous materials, metal-organic frameworks (MOFs) have achieved great progress for the construction of various novel topological architectures and their wide applications in a variety of scientific fields.[1-6] In particular, lanthanide metal−organic frameworks (LnMOFs) have been a rapidly developing area due to their potential applications in fluorescence probes and luminescence bioassays.[7] It is noted that their unique luminescence properties,[8] such as long excited-state luminescence lifetimes, sharp transitions, substantial Stokes shifts (>200 nm) and high colour purity, originate from f–f or f–d transitions tuned by suitable adjacent chromophores which called as "antenna effect".[7a,9] In the past decade, studies on luminescent LnMOFs for sensing metal ions and small organic solvents have flourished the development of this area, and some representative examples about the selective sensing of metal ions such as Cu^{2+} or Fe^{3+} have been successfully exploited.[10,11] Among the different lanthanide ions, Eu^{3+} is one of best candidates for sensing applications due to its strong visible luminescence in the red regions.[9b,12]

Despite recent exciting and compelling developments, the design and construction of LnMOFs are still a great challenge because of their high coordination numbers and flexible coordination environments.[13] Fortunately, Ln^{3+} ions usually have a high affinity for hard donor atoms, so ligands containing oxygen atoms are frequently employed in the construction of LnMOFs.[14] Compared with rigid carboxylates with monotonous conformations, flexible carboxylates can adopt various conformations according to the geometric requirements of diverse metal ions, which may generate some unexpected structural models with beautiful aesthetics and useful properties.[15] Among various multi-carboxylates ligands, there are rarely exploration for zwitterion ligands, which often function as ionic liquid precursors or ionic liquids for potential applications as an environmentally acceptable solvents solution in organic processes.[15a,16]

To date, a few d-block transition metal coordination frameworks with a tripodal flexible zwitterion ligand 1,1′,1″-(2,4,6-trimethylbenzene-1,3,5-triyl)tris(methylene)-tris(4-carboxypyridinium)tribromide ($H_3\mathbf{L}Br_3$) (Scheme 1) has been isolated.[15a] However, LnMOFs built by $H_3\mathbf{L}Br_3$ ligand remain unexplored, and the reported $H_3\mathbf{L}Br_3$ ligand only shows a single bowl-shaped configuration. Herein, we report a new 3D porous carboxylic LnMOF, $[Eu\mathbf{L}(OH)_2](NO_3)\cdot x(\text{solvent})$ (**1**), based on $H_3\mathbf{L}Br_3$ and its properties for sensing metal ions and small molecules. Different from the previously reported conformation, it is interesting to note that **L** presents a new chair-shaped configuration, in which carboxylate groups orientate to two sides of the basic phenyl group. More importantly, luminescent studies revealed that the emission intensity of **1** in DMAC (N,N′-dimethylacetamide) solvent can be essentially completely quenched by Fe^{3+} ion and fluorescent response showed high selectivity for Fe^{3+} ion compared with other metal ions. Meanwhile, its emission intensity is largely dependent on the small solvent molecules. The result implies that **1** could be served as luminescent probes for sensing of metal ions and small molecules.



Scheme 1. The **L** ligand.

Single-crystal analysis reveals that **1** crystallizes in the triclinic space group *P*-1 and exhibits a non-interpenetrated 3D porous structure. The asymmetric unit of **1** is composed of one crystallographically independent Eu^{3+} center, one **L** ligand, two terminal hydroxyl groups, a free nitrate anion, and some disorder solvent molecules. As shown in Fig. S5, each Eu^{3+} center exhibits an eight-coordinated environment with six oxygen atoms deriving from six individual **L** carboxylate groups and other two oxygen atoms originating from two individual hydroxyl groups to form distorted dodecahedron geometry. The Eu–O bond lengths are among 2.343-2.486 Å in **1** which are comparable to those reported Eu^{3+} complexes.[17] All the **L** ligands adopt unique chair-shaped configuration using each deprotonated carboxylate group to bridge two Eu^{3+} centers by a *syn–syn* bridge coordination mode. The adjacent Eu^{3+} centers are linked alternately through two or four bridging bidentate carboxylate groups to generate 1D infinite Eu-chains (Fig. S7). More importantly, adjacent six identical Eu-chains are linked together through **L** ligands to give a complicated 3D network with 1D column-like channels along *a* axis (Fig. 1). The size of the channel is *ca.* 8.1 Å × 12.8 Å, in which the NO_3^- anions locate on the surfaces of the channels (Fig. 1). The solvent-accessible volume of **1** is estimated by the PLATON program to be about 36.4 % of the total crystal volume.[18]

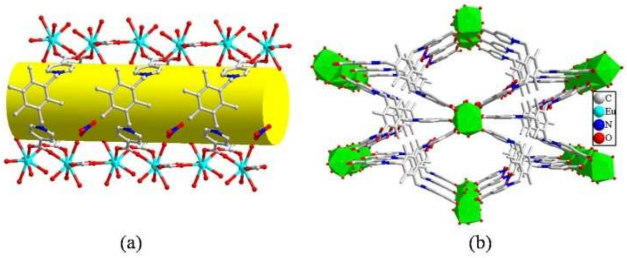


Fig. 1 (a) The 1D column-like channels; (b) Perspective view of the 3D framework with 1D channels.

Considering the excellent luminescent properties of lanthanide ions and their sensitive antenna effect, the luminescence spectra of the free **L** ligand and the as-synthesized sample of **1** in the solid state were investigated at room temperature under excitation at 305 and 375 nm, respectively. The emission spectrum of the free **L** ligand exhibits two broad emission bands at 425 and 473 nm upon excitation at 305 nm, which can be assigned to the ligand-centered electronic transition (Fig. S8a). The luminescence sharp peaks of **1** at 591, 616, 648, and 696 nm are attributed to $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ transitions of the Eu^{3+} ion, respectively (Fig. S8b). Among these transitions, $^5D_0 \rightarrow {}^7F_2$ red emission is the strongest. When compound **1** were excited with a UV lamp (365 nm), the Eu^{3+} emitted red light which was readily observed with the naked eye (Fig. S8b). These characteristic emission bands indicate that **L** ligand is an excellent chromophore for sensitization of lanthanide complexes.

In order to investigate the properties of compound **1** for sensing metal ions and small molecules, its suspension-state luminescences were obtained. Here, compound **1** was dispersed in 10^{-3} M DMAC solutions containing $M(NO_3)_x$ (M = Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Al^{3+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ag^+, Zn^{2+}, Cd^{2+}, Pb^{2+}) without changing its original structure (Fig. S9) for luminescence studies. The result indicated that the red luminescence of **1**, monitored at 618 nm for $^5D_0 \rightarrow {}^7F_2$ transition, was essentially completely quenched when Fe^{3+} ion is involved. However, the luminescent intensities do not change or only slightly change in the presence of other tested metal ions (Fig. 2). The remarkable quenching effect might be used to easily detect a small amount of Fe^{3+} ion by naked-eye observation, since the emissive visible red light from **1** suspension containing Fe^{3+} is obviously darker than that from **1** suspension without any metal ions under UV light (Fig. S10). To further examine the sensing sensitivity toward Fe^{3+} ion, **1** was dispersed in DMAC solutions with gradually increased Fe^{3+} concentration in the range of 10^{-7}–10^{-1} M. Interestingly, the luminescence intensity of Fe^{3+}-incorporated **1** is heavily dependent on the concentration of the metal ions. As seen in Fig. 3, nearly 70% of the emission intensity was decreased when Fe^{3+} ions concentration increase from 10^{-7} to 10^{-4} M and completely quenched to 10^{-3} M. It is very remarkable that this material features such highly sensitive and selective sensing for Fe^{3+} ions in DMAC solution.

It is well known that the luminescent intensity of lanthanide ions depends on the efficiency of the energy transfer from ligands to the lanthanide ions.[6c] As shown in Fig. S11, **L** ligand presents similar sensing phenomenon. So for the possible sensing mechanisms, we speculate that the luminescence change of **1** in DMAC solutions containing $M(NO_3)_x$ is attributed to a competition of absorption the light source energy and the electronic interaction between the metal ions and **L** moieties. The metal ions filter the light adsorbed by **L** moieties, then decrease subsequent energy transfer from **L** to the lanthanide ions, which conduces the observed dramatical changes in the luminescence intensity.

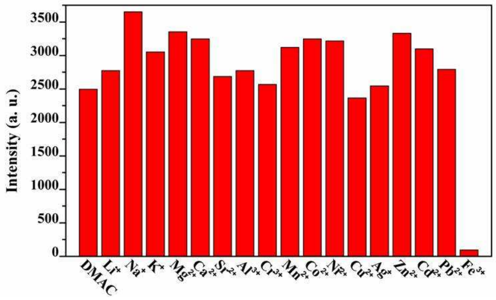


Fig. 2 The luminescent intensities of a $^5D_0$- $^7F_2$ transition for an emulsion of **1** in DMAC (10^{-3} M) at 618 nm upon the addition of various cations (excited at 375 nm).

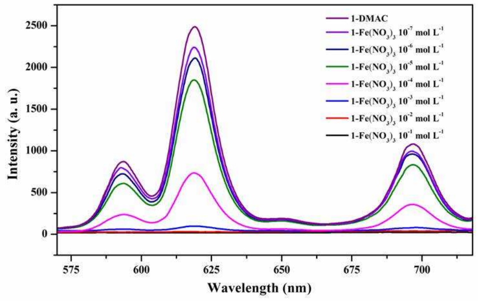


Fig. 3 Fluorescence titration of **1** dispersed in DMAC with the addition of different concentrations of Fe^{3+} (excited at 375 nm).

To confirm the possible reason for such luminescence quenching by metal ions, detailed studies on the UV-Vis absorption of DMAC solutions containing $M(NO_3)_x$ or **1** were carried out. As we all know, the luminescent intensity of **1** is expected to exhibit stronger quenching effects along with higher UV-Vis absorbance at excited 375 nm. As shown in Fig. S12, excited intensity and absorptive intensity of **1** gradually increase with the decreasing of wavelength. The UV-Vis absorption spectrum data show that the absorption spectrum of the DMAC solutions containing Fe^{3+} is significantly greater than the absorption spectrum from the other metal ions excited at 375 nm, which is possible response for the observed quenching of luminescence (Fig. S12a). Excellent agreement between absorptive intensity of the DMAC solutions containing different concentration of Fe^{3+} and luminescent intensity of **1** in the DMAC solutions containing the same concentration Fe^{3+} further provide support to the aforementioned mechanisms (Fig. S12b and Table S3).

Meanwhile, the sensing of small organic molecules by **1** was also examined in different organic solvents. As shown in Fig. S13, it can be found that the luminescent intensity is largely dependent on identity of the solvent molecules, especially in the case of nitrobenzene (NB), which shows a significant quenching effect. These results suggest that **1** might be a promising luminescent probe for detecting NB. The possible reason for such luminescence quenching might be ascribed to a competition of absorption of light source and the electronic interaction between the analytes and **L** moieties.[1d,19]

In summary, a new luminescence LnMOF was successfully synthesized based on a tripodal flexible zwitterion **L** ligand showing chair-shaped configuration. Most importantly, the luminescent property studies imply that **1** shows a high selectivity and sensing for Fe^{3+} ions and NB, suggesting that it may be used as a luminescent probe to detect some metal ion and small molecules. Further studies are under way in our lab.

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Notes and References

Department of Chemistry, TKL of Metal- and Moecule-Based Material Chemistry and Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin 300071, P. R. China.
E-mail: liyunwu@lcu.edu.cn; buxh@nankai.edu.cn.
Fax: +86-22-23502458; Tel: +86-22-23502809.

†Electronic Supplementary Information (ESI) available: Crystallographic details (CIF), Supplementary Table, Structural Figures and Scheme, Luminescence spectra, UV-Vis spectra, and additional Characterizations. This material is available free of charge via the Internet at http://pubs.acs.org. See DOI: 10.1039/b000000x/.

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Synopsis

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