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ARTICLE TYPE

Heterometal-organic frameworks as highly sensitive and highly selective luminescent probes to detect I⁻ ions in aqueous solutions

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Two cationic heterometal-organic frameworks (Eu-Zn (1·NO₃⁻) and Tb-Zn (2·NO₃⁻)) with counter-anions NO₃⁻ in the channels are structurally and luminously characterized. Both of them can serve as highly sensitive and highly selective luminescent probes to detect I⁻ ions in aqueous solutions. In particular, 2·NO₃⁻ can selectively and reversibly detect I⁻ with a fast response time of just 10 s and an extremely low detection limit of 0.001 ppm. Mechanism studies reveal that I⁻ is quickly oxidized to form I₃⁻ under the help of 1·NO₃⁻ or 2·NO₃⁻, leading to the luminescence quenching. This represents the first report of MOF-based luminescent probes for the detection of I⁻ in aqueous solutions.

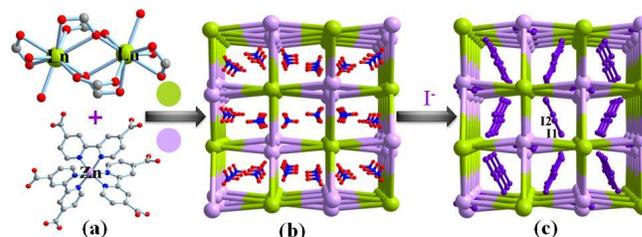
In recent decade, there is an escalating interest in developing metal-organic frameworks (MOFs) as luminescent probes due to not only their desirable advantages in detection field, but also their promising applications in biological and environmental systems.¹⁻⁶ As luminescent probes, MOFs can selectively detect various size molecules or ions for their adjustable porosity.⁷ In addition, the detected objects can be enriched in the pores of MOFs by adsorption/exchange and/or various interactions with frameworks, resulting in fast response and low detection limits.⁶ Moreover, the luminescence signals can be visualized with different targets, making the measurement simple and accurate. Furthermore, MOFs generally possess good thermal and solvent stabilities, providing a foundation for practical applications. Indeed, considerable advancements can be witnessed in exploring MOFs as luminescent probes to detect molecules, cations, anions, temperature and so on.⁶⁻²⁴ Albeit the employment of MOF-based luminescent probes to recognize molecules and cations has been extensively studied,⁴ the utilization of them to detect anions has been much less explored.¹⁰⁻¹⁴ In particular, it remains a challenge to use MOFs as probes to detect anions in aqueous solutions especially for some pollutant anions (e.g. F⁻, Br⁻, I⁻, PO₄³⁻, SO₃²⁻, etc) in waste water, which have become an important issue due to their harmfulness to human health and environments.²⁵

It is well known that iodine is widely utilized as nucleophilic reagent in organic reactions, sensitizer in photoplate, dye in industry, and disinfectant in medicine. However, improper discharge of them will cause serious health and environmental problems.²⁶ In particular, the nuclear leaking of Fukushima nuclear plant in Japan three years ago urges the development of alternative technologies for fast monitoring the concentration of

iodine in nuclear waste from nuclear plant²⁷ when the radiation detectors in nuclear plant accidentally lost their functions. This could turn to the employment of MOFs as luminescent probes to detect I⁻ ions in aqueous solutions, which however has not yet been reported.

In this contribution, we demonstrate for the first time two heterometallic cationic MOFs [Ln₂Zn(L)₃(H₂O)₄](NO₃)₂·12H₂O_n (Ln = Eu, 1·NO₃⁻; Ln = Tb, 2·NO₃⁻; L = 4,4'-dicarboxylate-2,2'-dipyridine anion, Electronic Supplementary Information, Scheme S1) which can serve as highly sensitive and highly selective luminescent probes for reversible detection of I⁻ ions in aqueous solutions with a fast response time of 10 s and a very low detection limit 0.001 ppm.

Fig. 1 (a) [Ln₂] unit and [Zn(L)₃] unit; (b) 3D framework of 1·NO₃⁻ and



2·NO₃⁻, and the position of NO₃⁻ in the channels; (c) I-I bonds in the channels (C, gray; N, blue; O, red; H atoms and free water molecules are omitted for clarity).

1·NO₃⁻ and 2·NO₃⁻ are isostructural, crystallizing in the monoclinic system with space group C2/c. They contain the 3D cationic framework [Ln₂Zn(L)₃(H₂O)₄]²⁺, which is composed of [Ln₂(COO)₆(H₂O)₄] (abbr. as [Ln₂]) and [Zn(L)₃] units, and the counter anions are NO₃⁻ (Fig. 1a, 1b). In each asymmetric unit, Ln³⁺ is nine-coordinated with distorted tricapped trigonal prism geometry, consisted of seven carboxylic oxygen atoms and two water molecules. Two adjacent Ln³⁺ ions are connected by six carboxyl groups from L²⁻ into [Ln₂] unit. Six nitrogen atoms of three L²⁻ complete the octahedral coordinated environment of Zn²⁺. L²⁻ connects the [Ln₂] units and Zn²⁺ into the 3D framework. The framework shows a 1D channel along the c direction, filled with free water molecules and counter anions NO₃⁻. Interestingly, in the later studies on luminescence mechanisms, the single crystals of 2·I⁻ can be obtained from single-crystal to single-crystal transformation and anion exchange with 2·NO₃⁻, and the two compounds are isostructural (Fig. 1c

and Supporting Information, Fig. S1). Typical I-I bonds are observed for I_3^- residing in the channels of $2 \cdot \Gamma^-$.

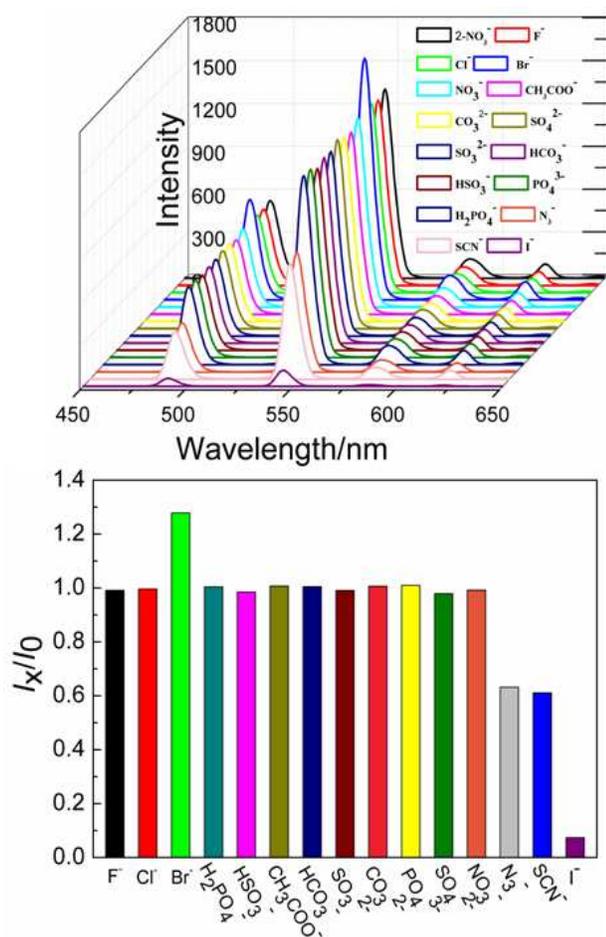


Fig. 2 PL spectra of $2 \cdot \text{NO}_3^-$ after immersed in various 5×10^{-5} mmol K_mX and NaN_3 aqueous solutions (excited at 343 nm, top); The ratio of $^5D_4 \rightarrow ^7F_5$ transition intensities of $2 \cdot \text{NO}_3^-$ immersed in various K_mX and NaN_3 aqueous solutions (I_x) to the $2 \cdot \text{NO}_3^-$ immersed in distilled water (I_0) (monitored at 545 nm, bottom).

In principle, the counter anions NO_3^- in the 1D channel can be readily exchanged with other anions, and as a result, $1 \cdot \text{NO}_3^-$ or $2 \cdot \text{NO}_3^-$ may recognize some anions based on different luminescence responses. At the excitation of 343 nm, the aqueous suspension of $2 \cdot \text{NO}_3^-$ emits the characteristic peaks of Tb^{3+} at 490, 545, 585 and 621 nm, attributed to the $^5D_4 \rightarrow ^7F_J$ ($J = 6, 5, 4, 3$) transitions (Fig. 2). Subsequently, the common inorganic salt aqueous solution was added to 950 μL aqueous suspensions of $2 \cdot \text{NO}_3^-$ to investigate the effect of various guest anions on the luminescence of $2 \cdot \text{NO}_3^-$. It was observed that Br^- causes the luminescence enhancement by 30 %, whereas both SCN^- and N_3^- make the luminescence intensity at 545 nm decrease by 40%, and Γ^- almost quenches the luminescence. Especially for the peaks at 585 and 621 nm, they still are clearly observed under the introduction of SCN^- and N_3^- , but disappear after the addition of Γ^- . In comparison, other anions hardly exhibit significant luminescence response. These results imply $2 \cdot \text{NO}_3^-$ can serve as luminescence probes to recognize Br^- and Γ^- in aqueous solutions with the luminescence response to Γ^- more sensitive than that of

Br^- . Negligible change on the luminescence was observed when all of the K_mX mentioned in the experimental section except Br^- and Γ^- were added to the aqueous suspensions of $2 \cdot \text{NO}_3^-$ to form $2 \cdot X$. Interestingly, after equimolar KI aqueous solution was added to $2 \cdot X$, the corresponding luminescence of $2 \cdot X$ exhibits obvious decrease (Figs. S2, S3). The results suggest that $2 \cdot \text{NO}_3^-$ can highly selectively detect Γ^- in aqueous solution with background anions of F^- , Cl^- , CH_3COO^- , NO_3^- , H_2PO_4^- , HSO_3^- , HCO_3^- , CO_3^{2-} , SO_4^{2-} , SO_3^{2-} and PO_4^{3-} .

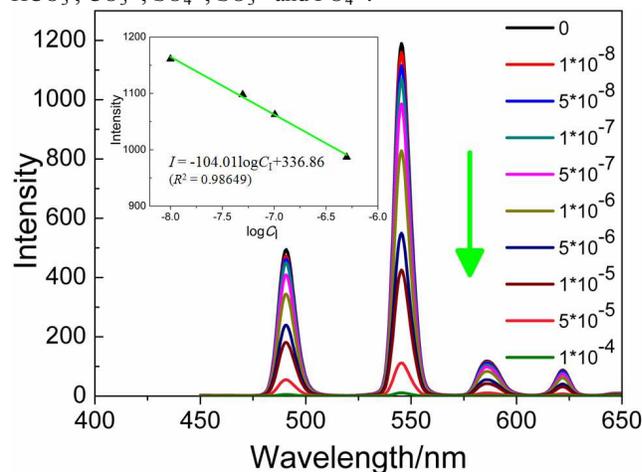


Fig. 3 The liquid PL spectra of $2 \cdot \text{NO}_3^-$ under different concentrations of KI aqueous solution (mol/L) upon excited at 343 nm and the corresponding plots of intensity vs $\log C_I$ in the concentration range of $1 \times 10^{-8} \sim 1 \times 10^{-6}$ mol·L $^{-1}$ (inset).

The luminescence response of $2 \cdot \text{NO}_3^-$ was further investigated with different concentrations of Γ^- . As shown in Fig. 3, the luminescence of $2 \cdot \text{NO}_3^-$ quickly decreases with increasing the concentration of Γ^- . The lowest detection limit of Γ^- can reach 1×10^{-8} mol·L $^{-1}$ (0.001 ppm). Interestingly, 1×10^{-4} mol·L $^{-1}$ Γ^- can completely quench the luminescence of $2 \cdot \text{NO}_3^-$. It's noteworthy that all of the luminescence measurements were performed within only 10 s, among which is the fastest response time for MOF-based luminescent probes reported thus far (Table S1). These results therefore highlight $2 \cdot \text{NO}_3^-$ as highly sensitive luminescent probe to detect Γ^- with very short response time and extremely low detection limit (Fig. S4). For $2 \cdot \text{NO}_3^-$, the plots of luminescence intensity vs $\log C_I$ (C_I : the concentration of Γ^-) well follow a linear relationship (inset in Fig. 3, S5) within the concentration range of $1 \times 10^{-8} \sim 1 \times 10^{-4}$ mol·L $^{-1}$. It should be noted that two intervals are observed in the plots of luminescence response for Γ^- , corresponding to the concentration range of $1 \times 10^{-8} \sim 1 \times 10^{-6}$ and $1 \times 10^{-6} \sim 1 \times 10^{-4}$ mol·L $^{-1}$. The results suggest $2 \cdot \text{NO}_3^-$ can qualitatively determine the concentration of Γ^- in the concentration range mentioned above. In addition, the quenching effect of Γ^- was estimated by Stern-Volmer constant 28 (K_{SV}), which is obtained based on the experimental data and Stern-Volmer equation ($I_0/I - 1 = K_{SV}C_I$) (where I_0 and I are the luminescence intensity before and after the addition of Γ^- respectively, Fig. S6). The K_{SV} value in $2 \cdot \text{NO}_3^-$ is 1.8×10^5 L·mol $^{-1}$, which is comparable with the reported Pt^{\square} -compound as phosphorescent sensors for Γ^- . 29

Luminescence studies indicate $1 \cdot \text{NO}_3^-$ can also sensitively and selectively detect Γ^- ions in aqueous solutions with fast response

time of 10 s (Figs. S7-S11). As shown in Fig. S12, with increasing the concentration of Γ , the luminescence of $1 \cdot \text{NO}_3^-$ decreases, and the low detection limit is $5 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1}$ (0.06 ppm). The K_{SV} value in $1 \cdot \text{NO}_3^-$ is $2.3 \times 10^4 \text{ L} \cdot \text{mol}^{-1}$, which is smaller than that in $2 \cdot \text{NO}_3^-$, indicative of that $2 \cdot \text{NO}_3^-$ has higher sensitivity in detection of Γ than $1 \cdot \text{NO}_3^-$ (Fig. S13).

The reversibility of a probe is an important consideration to ensure its repeatable use. Regenerated experiments were carried out for $2 \cdot \Gamma$, which was immersed in KNO_3 aqueous solution for 3 h. The following experimental phenomena were observed: (1) the yellow of the $2 \cdot \Gamma$ faded gradually, indicating that yellow species can fast exchange with NO_3^- (Fig. 4); (2) when $0.1 \text{ mol} \cdot \text{L}^{-1}$ AgNO_3 was dropped into the solution, yellow precipitate (AgI) generated immediately. X-ray photoelectron spectroscopy (XPS) measurements were conducted (Fig. S14, S15), and the typical peaks of iodine can be observed in the AgI precipitate but disappeared in the regenerated $2 \cdot \text{NO}_3^-$, which further confirms the release of iodine and the thorough regeneration of $2 \cdot \text{NO}_3^-$. Notably, the regeneration cycle from $2 \cdot \text{NO}_3^-$ to $2 \cdot \Gamma$ and to regenerated $2 \cdot \text{NO}_3^-$ can be at least repeated for ten times, and the sample can still sensitively recognize Γ (Fig. S16). Actually, the reversibility is one of the important parameters for ideal luminescent probes,^[31] although a reliable process to quickly restore the activity of the probe remains to be addressed. Additionally, the 3D frameworks of $1 \cdot \text{NO}_3^-$ and/or $2 \cdot \text{NO}_3^-$, as well as those after anion exchange or immersing in aqueous for two weeks remain intact as suggested by PXRD studies, indicating the high chemical stability of the luminescent probes (Fig. S17).



Fig. 4. The color of the solid samples of $2 \cdot \Gamma$ (left) and $2 \cdot \text{NO}_3^-$ (right).

We explored the luminescence response mechanisms. One remarkable phenomenon is that the colour of the samples changes from colourless ($2 \cdot \text{NO}_3^-$) to yellow ($2 \cdot \Gamma$) after $2 \cdot \text{NO}_3^-$ was immersed in KI solution (Fig. 4). Then the solid sample $2 \cdot \Gamma$ was separated from the solution by centrifugation, and the UV-Vis spectra of the filtrate show the characteristic absorption peak of NO_3^- around 300 nm (Fig. S18), indicating that the NO_3^- in the channels can enter the solution by anion exchange. Additionally, no absorption peaks of MOFs were observed above 330 nm, indicative of that the 3D framework of $2 \cdot \text{NO}_3^-$ is rather stable in KI aqueous solutions and insoluble in aqueous solution. Energy Dispersive Spectrometer (EDS) and XPS analyses also confirm the existence of iodine in $2 \cdot \Gamma$ (Fig. S19). The yellow and regeneration of $2 \cdot \Gamma$ mean that I_3^- instead of I_2 exists in channels because I_2 molecules would not exchange with NO_3^- , as is clearly confirmed by the characteristic peak of I_3^- at 109 cm^{-1} in Raman spectra (Fig. S20)^[32]. In 10s, the luminescence can be quenched, which may imply that Γ was fast oxidized into I_2 in under the help of $2 \cdot \text{NO}_3^-$ and further combines with Γ to form I_3^- . The I_3^-

anions in the channels result in the yellow colour of $2 \cdot \Gamma$. The single crystal structure determination of $2 \cdot \Gamma$ confirms the existence of I-I bonds (3.04 Å) in I_3^- located in the channels (Fig. S1).

It is rather rare that Γ under the existence of MOFs was fast oxidized into I_2 , although it is well known that O_2 in air can slowly finish the task. Accordingly, the following controlled experiments were performed in air for 1 h: (a) KI aqueous solution; (b) H_2L and KI aqueous solution; (c) H_2L , $\text{Tb}(\text{NO}_3)_3$, $\text{Zn}(\text{NO}_3)_2$ and KI aqueous solution. UV-Vis analyses reveal that no I_2 molecules are detected in the three types of solutions mentioned above (Fig. S21), suggesting none of ligand H_2L , Tb^{3+} , Zn^{2+} and NO_3^- can oxidize Γ into I_2 , and O_2 in air does not complete the oxidization within 1 h. Therefore, it can be deduced that the extremely fast oxidation of Γ finishes under the help of cationic framework of $1 \cdot \text{NO}_3^-$ or $2 \cdot \text{NO}_3^-$, although the framework itself can not serve as the oxidant. Additionally, the oxidation from Γ to I_2 depends on the amount of O_2 , confirmed by the experiment under mionectic environments (Fig. S22).

The above results thereby facilitate the explanation of luminescent quenching by Γ . At the excitation of 343 nm, the energy can be effectively transferred from L^{2-} to Tb^{3+} , leading to strong luminescence. However, I_3^- can effectively absorb the energy of excitation light and/or the excited state of ligand because the absorption peaks of I_3^- in UV-Vis spectra appear at 285 and 350 nm, and the energy transfer from L^{2-} to Tb^{3+} (Fig. S23) would be significantly weakened. Therefore, with increasing the concentration of Γ , the luminescence intensity declines gradually until quenching completely. Additionally, Thermogravimetric analysis (TGA) of $1 \cdot \text{NO}_3^-$ and $2 \cdot \text{NO}_3^-$ and the possible luminescence response mechanism for Br^- , SCN^- and N_3^- were studied. Detailed information is presented in ESI (Fig. S24-S28).

In summary, two heterometallic MOFs were synthesized and structurally characterized. The luminescent studies reveal that $2 \cdot \text{NO}_3^-$ can serve as highly sensitive, highly selective, reversible and qualitative luminescent probe to detect Γ in aqueous solutions with fast response time (10 s) and low detection limit of Γ (0.001 ppm). Mechanistic studies revealed that I_3^- existed in the channels via the fast oxidation of Γ into I_2 under the help of $2 \cdot \text{NO}_3^-$ framework, and it should be accountable for the luminescence quenching. To the best of our knowledge, our work herein represents the first report of MOF-based luminescent probes to detect Γ in aqueous solutions. Our studies thereby pave a way to develop MOFs as a new type of luminescent probes for applications in environmental protection and/or monitoring fields, especially in detecting the leaking of radioactive species into water from nuclear plants.

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Notes and references

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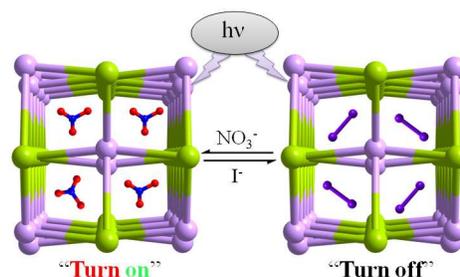
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[†] Electronic Supplementary Information (ESI) available: Experimental details, X-ray crystallographic files, CCDC number, PXRD, UV-vis, XPS, EDS, TGA, Raman and Luminescent measurements. For ESI and crystallographic data in CIF or other electronic format see DOI:10.1039/b000000x/

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TOC



Cationic heterometal-organic frameworks serve as highly sensitive and highly selective luminescent probes to detect I⁻ ions in aqueous solutions.