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# A dual emission metal–organic framework for rapid ratiometric fluorescence detection of $\text{CO}_3^{2-}$ in seawater†

Yu Wei<sup>a</sup> and Yan Xia<sup>ab</sup>  \*abcd

A dual emission metal–organic framework (IRMOF-10-Eu) was prepared and used as a ratiometric fluorescent sensor for  $\text{CO}_3^{2-}$  detection. IRMOF-10-Eu had good stability and excellent luminescence in aqueous solution. IRMOF-10-Eu showed dual fluorescence emission from the ligand and  $\text{Eu}^{3+}$  with single excitation. Upon treatment with  $\text{CO}_3^{2-}$ , the fluorescence ratio ( $I_{624}/I_{358}$ ) of the probe displayed significant change. The relative fluorescence intensity ratio ( $I_{624}/I_{358}$ ) and  $\text{CO}_3^{2-}$  concentration had a linear relationship in 50–300  $\mu\text{M}$  range with a low detection limit of 9.58  $\mu\text{M}$ . And the luminescence probe of  $\text{CO}_3^{2-}$  showed a fast detection time. The possible mechanism was investigated.  $\text{CO}_3^{2-}$  changed the structure of IRMOF-10-Eu and interrupted the energy transfer process. Thus, the fluorescence emission intensity of the ligand was increased and  $\text{Eu}^{3+}$  was decreased with the addition of  $\text{CO}_3^{2-}$ . IRMOF-10-Eu was used to detect  $\text{CO}_3^{2-}$  in seawater, which showed good prospect in practical application. Subsequently, a highly selective and sensitive probe, IRMOF-10-Eu, may pave an efficient way for  $\text{CO}_3^{2-}$  detection in seawater.

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## 1. Introduction

With the development of modern industry and the combustion of fossil fuel, the content of  $\text{CO}_2$  in the atmosphere has increased year by year.<sup>1</sup> Ocean acidification is affected by the increase of the concentration of carbon dioxide in the atmosphere.<sup>2</sup> Carbonate ions are abundant and ubiquitous in the ocean.<sup>3</sup> Carbonates are important in maintaining pH in seawater and serve as essential components of skeletons, shells, and other marine structures.<sup>4</sup> It is vital to detect  $\text{CO}_3^{2-}$  in the cycle of carbon in ocean and environmental monitoring.<sup>5</sup> Therefore, it is urgent to develop an analytical method for the detection and quantification of  $\text{CO}_3^{2-}$ .

A variety of analytical methods have been reported for the identification of carbonate including ion selective electrodes,<sup>6</sup> Fourier transform infrared spectroscopy,<sup>7</sup> continuous-flow methods,<sup>8</sup> acoustic methods,<sup>9</sup> and coulometric methods.<sup>10</sup> However, these techniques were time-consuming, cumbersome and naked-eye-invisible. Because of high sensitivity, quick

response, low cost, and real-time monitoring, much more attention has been paid to develop fluorescent probes for sensing carbonate. The single emission may be interfered by probe and analyte concentration and the excitation intensity.<sup>11,12</sup> Ratiometric fluorescence which possesses dual fluorescence emission alleviates the problem. And ratiometric fluorescence was used to detect a variety of targets, such as  $\text{Al}^{3+}$ ,<sup>13</sup>  $\text{PO}_4^{3-}$ ,<sup>14</sup> and aromatic pollutants.<sup>15</sup> Until now, due to its relative strong alkaline and large hydration free energy, only a few sensors have been reported for the detection of  $\text{CO}_3^{2-}$ . Thus, there is an urgent need to design a fluorescent probe that can highly selective and sensitive detect  $\text{CO}_3^{2-}$ .

A class of multifunctional hybrid materials, metal–organic frameworks (MOFs), were formed by metal ions or clusters and organic ligands. MOFs have triggered enormous interest for their high permanent porosity coupled with structural tunability,<sup>16,17</sup> large surface areas,<sup>18,19</sup> and luminescence.<sup>20–25</sup> Several strategies have been developed to synthesize MOF-based ratiometric sensors.<sup>26</sup> The design strategies mainly includes introducing luminescence metal ions, dyes and carbon dots (CDs) into singular MOFs. MOF-based ratiometric sensors exhibit emission centers from one metal center with one organic center, bimetallic centers, or two organic emission centers. Lanthanide ions ( $\text{Ln}^{3+}$ ) is a commonly used metal emission center. However,  $\text{Ln}^{3+}$  luminescence is weak result from the forbidden f–f transition.<sup>27–29</sup> In order to solve it, intramolecular energy transfer from the organic ligands to the  $\text{Ln}^{3+}$  (antenna effect) was proposed, which can enhance the luminescence intensity and quantum yields of  $\text{Ln}^{3+}$  efficiently.<sup>30–33</sup> A dual emission MOF, IRMOF-10-Eu, was

<sup>a</sup>Research Center for Analytical Sciences, College of Chemistry, Nankai University, Tianjin 300071, China. E-mail: nkxiayan@nankai.edu.cn; Fax: +86-22-23503034; Tel: +86 13602063491

<sup>b</sup>Key Laboratory of Biosensing and Molecular Recognition, China

<sup>c</sup>State Key Laboratory of Medicinal Chemical Biology, China

<sup>d</sup>Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), China

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synthesized by two step. The advantages of IRMOF-10-Eu include the porosity of MOFs and the luminescence property of  $\text{Ln}^{3+}$  which can enhance sensitivity and the luminescence properties.

In this work, a fluorescence sensor, IRMOF-10-Eu, was developed for selective ratiometric fluorescence detection of  $\text{CO}_3^{2-}$ . The dual luminescence emission was derived from the ligand and  $\text{Eu}^{3+}$ , which decreased the environmental influence. Because  $\text{CO}_3^{2-}$  have an effect on the electronic structure of ligand, the selectivity of IRMOF-10-Eu was high in detecting  $\text{CO}_3^{2-}$ .  $\text{CO}_3^{2-}$  changed the relative fluorescence intensity ratio ( $I_{624}/I_{358}$ ). The possible mechanism was investigated.  $\text{CO}_3^{2-}$  changed the structure of IRMOF-10-Eu and interrupted the energy transfer process. Thus, IRMOF-10-Eu can be a potential sensor for efficient detection of  $\text{CO}_3^{2-}$ .

## 2. Materials and methods

### 2.1 Reagents and chemicals

Zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 99%) and europium(III) chloride hexahydrate ( $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ , 99.99%) were supplied by Aladdin Chemistry Co. (Shanghai, China). 4,4'-Biphenyldicarboxylic acid (BPDC, 98%) was supported by Energy Chemical (Shanghai, China). *N,N*-Dimethylformamide (DMF, AR grade) and ethanol (AR grade) were purchased from Tianjin Concord technology Co., Ltd. (Tianjin, China). Sodium carbonate anhydrous ( $\text{Na}_2\text{CO}_3$ , 99.9%) was supported by Macklin Biochemical Co., Ltd. (Shanghai, China). Sodium hydrogen carbonate ( $\text{NaHCO}_3$ , 99.5%) was purchased from Meryer Chemical Technology Co. Ltd. (Shanghai, China). Aqueous solution of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were prepared from corresponding chloride salts. Aqueous solution of  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$  were prepared from corresponding sodium salts. These chloride salts and sodium salts were analytical reagent grade and obtained from Guangfu Fine Chemical Research Institute (Tianjin, China). Ultrapure water (18.2 M $\Omega$  cm) used throughout all experiments was purchased from Tianjin Physical and Chemical Analysis Center.

### 2.2 Instruments

The fluorescence spectra were obtained on a Hitachi Model FL-4500 fluorescence spectrometer using a quartz cell with a 1 cm path length at room temperature. The UV-vis absorption spectrum was recorded by a UV-3600 visible spectrophotometer (Shimadzu, Japan) at room temperature. A Rigaku Smart Lab diffractometer (Rigaku, Japan) was utilized to record powder X-ray diffraction spectrometry (PXRD) patterns with a  $2\theta$  range from  $2-30^\circ$  and monochromated Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). A JSM-7500F scanning electron microscope (SEM) (JEOL, Japan) was used to obtain the morphology of the materials. Thermogravimetric analyses (TGA) were performed by a TG 8121 analyzer at heating rate of  $15^\circ\text{C min}^{-1}$  from room temperature to  $700^\circ\text{C}$  (Rigaku, Japan). A MAGNA-IR 560 spectrometer (Nicolet, USA) was used to record Fourier-transform infrared (FT-IR) spectrum in the range  $3000-400 \text{ cm}^{-1}$  with KBr tablet method. The mass spectral was recorded by 6520 Q-TOF LC/MS (Agilent, USA). An ICS-1100 ion chromatograph (IC) was used to

measure anions in seawater, which equipped with Dionex Ion-Pac<sup>TM</sup> AS14 column (Thermo, USA). The measurement of  $\text{Eu}^{3+}$  and metal ions in sea water was carried out on a Spectro Blue inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Spectro, Germany).

### 2.3 Synthesis of IRMOF-10 and IRMOF-10-Eu

IRMOF-10 was synthesized according to the reported procedure.<sup>34</sup> Typically, 1.38 mmol zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) and 4,4'-biphenyldicarboxylic acid (BPDC, 0.3 g, 1.2 mmol) were stirred for 15 min in 20 mL of *N,N*-dimethylformamide (DMF). Then, the homogenous solution was poured into a Teflon lined steel autoclave, which was placed in a pre-heated oven at  $100^\circ\text{C}$  for 8 h oven to yield rectangular prismatic crystals. Afterwards, it was separated by centrifugation and washed with DMF three times. And the product was immersed in chloroform for 3 days, during which the activation solvent was isolated, freshly replenished three times every day. The solvent was removed and the precipitate was dried in oven for 12 h under vacuum at 343 K.

IRMOF-10-Eu was facilely prepared by the mixture of 0.05 g IRMOF-10 and 0.3663 g  $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$  in 8 mL ethanol at  $60^\circ\text{C}$  for 24 h. The resulting white powder was centrifuged and washed with ethanol. The solid was dried at 353 K under a vacuum for 12 h.

### 2.4 UV-vis absorption, fluorescence excitation, and emission spectra of IRMOF-10-Eu

The concentration of the free ligand and IRMOF-10-Eu was  $0.05 \text{ mg mL}^{-1}$  for the absorption and luminescent property. For the UV-vis absorption, the scanning wavelength was set at the range from 800 nm to 200 nm and the split was 2.0. And the test solution was placed in cuvette (1 cm  $\times$  1 cm). To study the luminescent property, the slit of the free ligand and IRMOF-10-Eu was set at 5.0 nm  $\times$  5.0 nm and the PMT voltage was set at 700 V. And the excitation wavelength was set at 278 nm.

### 2.5 Day-to-day fluorescence stability and pH-dependence luminescent studies

The effects of time and pH were studied at  $25^\circ\text{C}$ . The day-to-day fluorescence stability of IRMOF-10-Eu was prepared by IRMOF-10-Eu introducing in aqueous solution. After soaking for a pre-determined time, the fluorescence data was collected. To study the pH-dependence luminescent, IRMOF-10-Eu was immersed in the aqueous solution, and the pH was adjusted with NaOH and HCl to the range of 2–10. The fluorescence data was collected after treatment for 5 min.

### 2.6 Ratiometric detection of carbonate ions

Luminescence responses of IRMOF-10-Eu toward  $\text{CO}_3^{2-}$  were investigated in their suspensions at room temperature. 1 mM aqueous solution of  $\text{Na}_2\text{CO}_3$  was diluted to the final concentration ranging from 0 to 500  $\mu\text{M}$ . Then 0.2 mg IRMOF-10-Eu was added in 4 mL aqueous solution of  $\text{CO}_3^{2-}$  and mixed well. After incubation for 5 min, their fluorescence spectra were recorded. For selectivity experiments, equal weight IRMOF-10-

Eu was soaked in 4 mL aqueous solution of metal ions ( $M = Na^+, Mg^{2+}, K^+$  or  $Ca^{2+}$ , 500  $\mu M$ ) or anions ( $A = F^-, Cl^-, Br^-, NO_3^-, PO_4^{3-}, SO_4^{2-}$ , or  $HCO_3^-$ , 500  $\mu M$ ). The emission spectra of the mixtures were recorded after treatment for 5 min. To study the anti-interference ability of IRMOF-10-Eu, equal weight IRMOF-10-Eu was soaked in 4 mL mixed aqueous solution of  $CO_3^{2-}$  and metal ions ( $M = Na^+, Mg^{2+}, K^+$ , or  $Ca^{2+}$ , 500  $\mu M$ ) or anions ( $A = F^-, Cl^-, Br^-, NO_3^-, PO_4^{3-}, SO_4^{2-}$ , or  $HCO_3^-$ , 500  $\mu M$ ). After treatment for 5 min, the emission spectra of the mixtures were recorded.

### 2.7 Determination of carbonate detection in seawater

The seawater was collected from Wenchanghai, Yellow Sea, Yinggehai, and Beibu Gulf (China). To remove impurities, the seawater was filtered with 0.45  $\mu m$  membranes. The 0.05 mg  $mL^{-1}$  sensor solution was prepared by introducing the IRMOF-10-Eu (0.5 mg) powder into 10 mL of the prepared seawater samples. After 5 min of incubation, the fluorescence emission data were collected.

## 3. Results and discussion

### 3.1 Characterization of IRMOF-10-Eu

As is shown in Fig. 1A, the PXRD pattern of IRMOF-10 was well matched with the simulated one, which indicated IRMOF-10 was prepared successfully.<sup>35</sup> The as-synthesized IRMOF-10 showed the typical peak at  $2\theta = 5.98^\circ$ , which can be ascribed to the presence of a nonporous phase as a result of structural degradation induced by water. IRMOF-10-Eu also showed the typical peak at  $2\theta = 5.98^\circ$ . Good agreement between IRMOF-10-Eu and IRMOF-10 PXRD pattern indicated that the framework of IRMOF-10-Eu still kept original type. Because  $Eu^{3+}$  was doped into the lattice, the peak at  $8.24^\circ$  had almost disappeared.<sup>36</sup> It can be observed in Fig. 1B, the SEM image of the IRMOF-10 showed rectangular prismatic crystals which had large dimension in the range of 30–40  $\mu m$ . After the doped of  $Eu^{3+}$ , IRMOF-10-Eu showed flower-like crystal (Fig. 1C). Elemental mapping of IRMOF-10-Eu showed that  $Eu^{3+}$  was distributed in framework, which demonstrated  $Eu^{3+}$  was successfully doped in IRMOF-10-Eu (Fig. S1†). As is shown in Fig. 1D, the TGA of IRMOF-10-Eu showed good thermal stability which was similar to IRMOF-10. Two events of weight losses were exhibited in the TGA curves. The first step gradual weight loss of 12.2% between  $57^\circ C$  and  $304^\circ C$  corresponded to the loss of coordinated  $H_2O$  and DMF molecules. In the second step, due to decomposition of the framework and the release of the ligand composite, the weight of IRMOF-10 and IRMOF-10-Eu decrease suddenly. Weight loss of 46.7% occurred in the range of  $304$ – $497^\circ C$  for IRMOF-10-Eu. The final residues are composed of  $Eu_2O_3$  and  $ZnO$ .<sup>37</sup> In the range of  $304$ – $601^\circ C$ , weight loss of 61.1% occurred for IRMOF-10. The final residues are composed of  $ZnO$ .

### 3.2 Optical properties

The optical properties of IRMOF-10-Eu in aqueous solution were recorded at room temperature. As can be seen from Fig. S2,† due to the  $\pi$ – $\pi^*$  transition of BPDC, the excitation

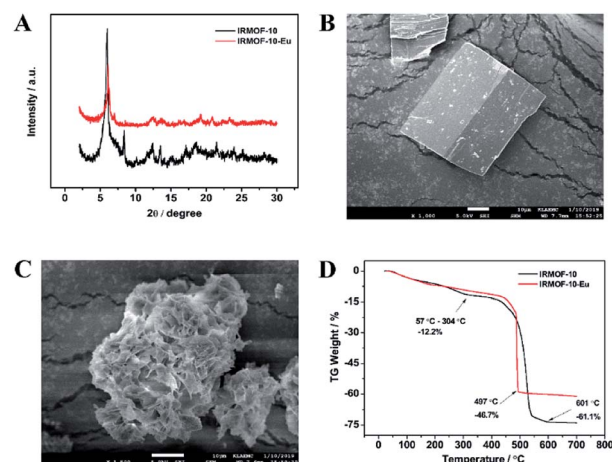


Fig. 1 (A) PXRD patterns of IRMOF-10 and IRMOF-10-Eu; SEM image of IRMOF-10 (B) and IRMOF-10-Eu (C); (D) TGA curve of IRMOF-10 and IRMOF-10-Eu.

spectrum of the ligand and IRMOF-10-Eu showed absorption band centred at 250 nm and 278 nm, respectively. Thus, the excitation peak of IRMOF-10-Eu originated from BPDC. The spectrum of IRMOF-10-Eu displayed a slight red shift, which was derived from the extensive  $\pi$ -conjugated system formed between  $Zn^{2+}$  and BPDC.<sup>38</sup> The emission spectra of IRMOF-10-Eu was displayed in Fig. 2. IRMOF-10-Eu showed dual fluorescence emission from ligand and  $Eu^{3+}$  under excited at 278 nm. The emission spectra consist of emission of BPDC and the characteristic emission of  $Eu^{3+}$ .  $Eu^{3+}$  ions have remarkable spectroscopic properties. However, the emission intensity of free  $Eu^{3+}$  ions was weak with the direct excitation, because the ultraviolet light absorption was weakened by the f–f forbidden transition of  $Eu^{3+}$  ions. It is clearly shown in Fig. S3†, the emission property of BPDC and  $EuCl_3$  was studied. A series of weak emission which appear at 599 nm ( $^5D_0 \rightarrow ^7F_1$ ), 624 nm ( $^5D_0 \rightarrow ^7F_2$ ) and 704 nm ( $^5D_0 \rightarrow ^7F_4$ ) were derived from  $Eu^{3+}$  upon excitation at 395 nm.<sup>39</sup> And BPDC showed strong luminescence intensity at 401 nm under excited at 250 nm. As

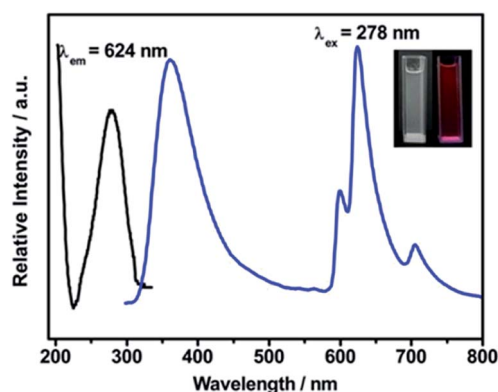


Fig. 2 The excitation and emission spectrum of IRMOF-10-Eu. Inset shows photograph of the mixture solution illustrate color under daylight (left) and ultraviolet light (right).





illustrated in Fig. S4†, under ultraviolet excitation, the electrons of ligand transit from  $S_0$  state to  $S_1$  state. Then intersystem crossing to  $T_1$  state was occurred. Finally, the ligand  $T_1$  state to  $Eu^{3+}$  ions was occurred in the process of energy transfer. Thus, emission from  $Eu^{3+}$  ions is observed. Above mentioned was antenna effect, which illustrate the strong emission of  $Eu^{3+}$  from IRMOF-10-Eu.<sup>40</sup> As illustrated in the inset photograph of Fig. 2, IRMOF-10-Eu dispersed in water was colorless under daylight. Under ultraviolet light, the mixture showed bright red luminescence. As is shown in Fig. S5†, the corresponding CIE chromaticity ( $x = 0.54, y = 0.31$ ) of IRMOF-10-Eu was consistent with the color under ultraviolet light. The excitation spectra showed that IRMOF-10-Eu can absorb the ultraviolet light efficiently (Fig. 2).

The effect of pH on the fluorescence stability of IRMOF-10-Eu was investigated. In the pH range of 6–8, IRMOF-10-Eu showed good fluorescence stability in aqueous solution (Fig. S6†). As illustrated in Fig. 3, IRMOF-10-Eu had good day-to-day fluorescence stability within 2 weeks, indicating the good solvent stability of IRMOF-10-Eu in aqueous solution.

### 3.3 Ratiometric detection of carbonate ions

Carbonate ions was detected to investigate the potential application of IRMOF-10-Eu. Fig. S7† was the fluorescence spectra of the IRMOF-10-Eu in 100  $\mu M$   $CO_3^{2-}$  solution with different reaction time and the plot of the intensity ratio of  $I_{624}/I_{358}$  versus time. In the first 3 min, the fluorescence spectra of the mixed solution had a big change. After 3 min, it became stable. Thus, after 5 min of IRMOF-10-Eu interaction with  $CO_3^{2-}$ , the fluorescence spectra were recorded. Fig. 4A showed the emission spectra of IRMOF-10-Eu added in  $CO_3^{2-}$  solution with different concentration. The emission intensity at 358 nm enhanced progressively with the concentration of  $CO_3^{2-}$  increased (0–500  $\mu M$ ), but the emission at 624 nm was decreased. Energy transfer and structure of IRMOF-10-Eu can be influenced by  $CO_3^{2-}$ . The detailed explanation was discussed in the part of mechanism of carbonate detection. And the corresponding CIE chromaticity of IRMOF-10-Eu in the presence and absence of  $CO_3^{2-}$  was displayed in Fig. S8†, which showed the color change with the concentration of  $CO_3^{2-}$ .

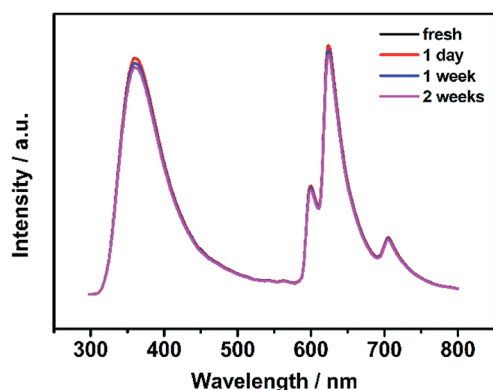


Fig. 3 Day-to-day fluorescence stability of IRMOF-10-Eu (0.05 mg  $mL^{-1}$ ) under excitation at 278 nm.

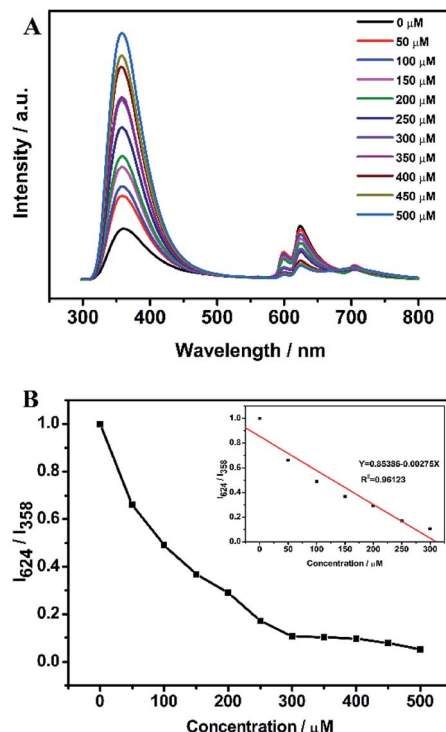


Fig. 4 (A) The emission spectra of IRMOF-10-Eu added in  $CO_3^{2-}$  solution with different concentration under excitation at 278 nm. (B) Plot of the relative luminescence intensity ( $I_{624}/I_{358}$ ) versus the concentration of  $CO_3^{2-}$ .

increased. Fig. 4B showed the relationship between the intensity ratio of the emission at 624 and 358 nm ( $I_{624}/I_{358}$ ) and  $CO_3^{2-}$  concentration in the range from 0  $\mu M$  to 500  $\mu M$ . In the range from 50  $\mu M$  to 300  $\mu M$ , a good linear correlation was obtained between  $I_{624}/I_{358}$  and  $CO_3^{2-}$  with a coefficient of  $R^2 = 0.9612$ . The calculation of detection limit was shown in Text S1.† The LOD was calculated to be 9.58  $\mu M$  at a signal-to noise ratio of 3. As is shown in Table S1,† LOD was lower than the other methods, which shown that IRMOF-10-Eu had a great advantage in detecting  $CO_3^{2-}$ . Therefore, the dual-emission of IRMOF-10-Eu can quantitatively detect  $CO_3^{2-}$  through ratiometric fluorescence method.

It is important that the selectivity of IRMOF-10-Eu was investigated to evaluate the performance of the sensor. In regard to this, IRMOF-10-Eu was soaked in aqueous solutions of various common ions in seawater and recorded the fluorescence intensity. As is shown in Fig. 5, different degrees of changes on the luminescence intensity were observed while  $CO_3^{2-}$  caused the most significant change. According to the theory of Hard-Soft Acid-Base (HSAB theory),<sup>41</sup> the hard base ( $F^-$ ) is prone to interact with the intermediate acid ( $Zn^{2+}$ ) by Coulomb force, which resulted in the fluorescence change. After introducing different ions, the corresponding CIE chromaticity diagram was displayed in Fig. S9.† We can see that  $CO_3^{2-}$  caused significant emission color change. In addition, the absorption of IRMOF-10-Eu is increased with the addition of  $CO_3^{2-}$ , indicating the conformation change of BPDC induced by  $CO_3^{2-}$  (Fig S10A†).  $CO_3^{2-}$  decreased the efficiency of energy

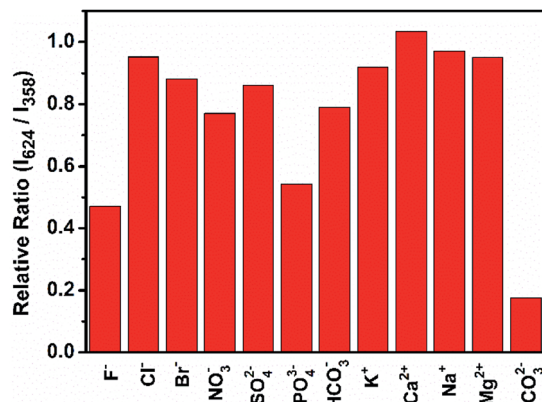


Fig. 5 Luminescence ratio of  $I_{624}/I_{358}$  from the responses of IRMOF-10-Eu in the presence of 300  $\mu\text{M}$  carbonate ions and 500  $\mu\text{M}$  interference ions.

transfer between BPDC and  $\text{Eu}^{3+}$ . Thus, the emission of BPDC increased and  $\text{Eu}^{3+}$  decreased. In addition of other ions, the absorbance of IRMOF-10-Eu not obvious (Fig. S10B†). Due to the steric effect,<sup>42</sup>  $\text{PO}_4^{3-}$  which is large size triggered slight enhancement in absorbance. In summary, the selectivity of IRMOF-10-Eu was high in detecting  $\text{CO}_3^{2-}$ . To validate the anti-interference of IRMOF-10-Eu toward  $\text{CO}_3^{2-}$ , IRMOF-10-Eu was immersed in aqueous solution of different metal ions or anions with  $\text{CO}_3^{2-}$  ions. Fig. S11† showed that the foreign ions caused a negligible change compared with the pure  $\text{CO}_3^{2-}$  aqueous solutions. IRMOF-10-Eu can detect  $\text{CO}_3^{2-}$  well in the presence of foreign ions. Thus, IRMOF-10-Eu had a great potential for detecting  $\text{CO}_3^{2-}$ .

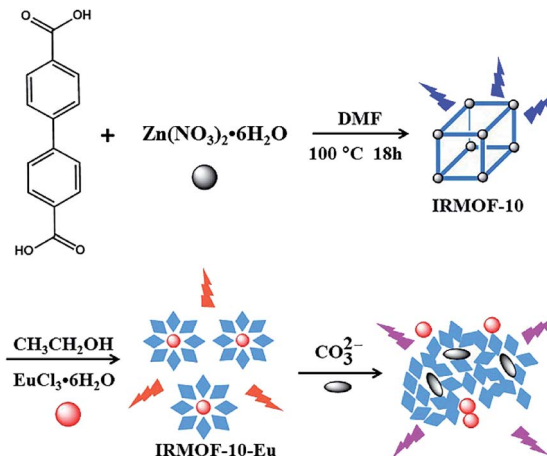
### 3.4 Mechanism of carbonate detection

To understand the carbonate detection mechanism of IRMOF-10-Eu, a series of experiments was explored. As can be seen in Table S2†, the concentration of  $\text{Eu}^{3+}$  in the aqueous solution was increased gradually as the concentration of  $\text{CO}_3^{2-}$  solution increased. It is assumed that  $\text{CO}_3^{2-}$  changed the structure of IRMOF-10-Eu, releasing free  $\text{Eu}^{3+}$ . Energy transfer process was disturbed and the transfer efficiency was decreased. The fluorescence intensity of  $\text{Eu}^{3+}$  was decreased (Scheme 1).

The phenomenon was proved by SEM. As shown in Fig. 1C, the morphology of IRMOF-10-Eu was flower-like crystal, which became slice after added  $\text{CO}_3^{2-}$  ions (Fig. S12†). The change suggested that  $\text{CO}_3^{2-}$  changed their structure.

XRD was explored to evidence the phenomenon also. Fig. S13† showed the XRD patterns of before and after immersed in  $\text{CO}_3^{2-}$  solution. After interacting with  $\text{CO}_3^{2-}$ , the typical peak  $5.98^\circ$  was shifted to  $5.82^\circ$ , which indicated the change of the crystal structure of IRMOF-10-Eu.  $\text{Eu}^{3+}$  released from IRMOF-10-Eu. Energy transfer process was disturbed. Thus, the emission of  $\text{Eu}^{3+}$  decreased.

Then, the UV-vis spectroscopic method was used to understand the fluorescence intensity at 358 nm which was increased as the concentration of  $\text{CO}_3^{2-}$  solution increased. As is shown in Fig. S14†, the absorption peak of BPDC at 241 nm. After the



Scheme 1 A plausible mechanism for detection of  $\text{CO}_3^{2-}$  using IRMOF-10-Eu.

addition of  $\text{CO}_3^{2-}$ , the major absorption peak is increased and shifted to 278 nm. The red-shift and increasing absorption indicated that the conformation change of BPDC induced by  $\text{CO}_3^{2-}$ .<sup>43</sup> FT-IR was explored to study the phenomenon also. As can be seen from Fig. S15†, the peak of BPDC at  $1508\text{ cm}^{-1}$  which was C=C stretching vibration in benzene ring<sup>44</sup> was disappear after the addition of  $\text{CO}_3^{2-}$ . It is evident that conjugation effect between BPDC and  $\text{CO}_3^{2-}$ . Then, we studied the absorption of IRMOF-10-Eu after the addition of  $\text{CO}_3^{2-}$ . As can be seen from Fig. S10A†, the absorption of IRMOF-10-Eu is increased with the addition of  $\text{CO}_3^{2-}$ . The phenomenon was proved by FT-IR. As is shown in Fig. S16†, the peak at  $1607\text{ cm}^{-1}$ ,  $1577\text{ cm}^{-1}$ ,  $1525\text{ cm}^{-1}$  and  $1405\text{ cm}^{-1}$  was C=C stretching vibration in benzene ring. After the addition of  $\text{CO}_3^{2-}$ , different degrees of changes on these peaks were observed.  $\text{CO}_3^{2-}$  had an effect on the C=C stretching vibration of the benzene ring. Because the metal-organic framework cannot be dissolved in organic solvents, we studied the mass spectrum of BPDC before and after the addition of  $\text{CO}_3^{2-}$  (Fig. S17†). The peak of BPDC does not change before and after interaction with  $\text{CO}_3^{2-}$ . It is evident that no host-guest complex form between  $\text{CO}_3^{2-}$  and BPDC. In summary,  $\text{CO}_3^{2-}$  influenced the conformation of aromatic ring in IRMOF-10-Eu and decreased the efficiency of energy transfer from ligand to Eu. And as the concentration of  $\text{Eu}^{3+}$  decreased, the energy transfer from BPDC to  $\text{Eu}^{3+}$  decreased.<sup>45</sup> Thus, the fluorescence intensity at 358 nm was increased gradually.

### 3.5 Detection of carbonate ions in real samples

The potential of IRMOF-10-Eu for  $\text{CO}_3^{2-}$  detection in sea water was evaluated. The sea water was chosen as real sample, which contained carbonate and other ions. ICP-OES and ion chromatography methods demonstrated that real sea water mainly contained  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ , which was listed in Table S3.† The most cation in seawater was sodium ions and the most anion was chloride ion. IRMOF-10-Eu was used to detect  $\text{CO}_3^{2-}$  in sea water. As can be



Table 1 Results of  $\text{CO}_3^{2-}$  detection in seawater ( $n = 3$ )

Sea area	Titrimetric analysis ( $\mu\text{M}$ )	This method ( $\mu\text{M}$ )
Yinggehai	294.5	286.7
Wenchanghai	233.2	258.4
Beibu Gulf	223.1	278.5
Yellow Sea	114.1	142.3

seen in Table 1, the results of ratiometric fluorescence method were corresponded with those from titrimetric analysis. Thus, IRMOF-10-Eu had a great potential to detect  $\text{CO}_3^{2-}$  in sea water.

To detect  $\text{CO}_3^{2-}$  conveniently and quickly, a test plate was prepared. IRMOF-10-Eu was dispersed in 0.5% aqueous carboxymethylcellulose sodium (CMC) and ultrasound for 5 min to form a uniform suspension, which was coated on the glass plate to form a film. Then the testing solvents were added to the test strip. After contact for 5 min, the content of  $\text{CO}_3^{2-}$  was judged rapidly by naked eyes with observable color change under the irradiation of UV light of 254 nm (Fig. S18†).

## 4. Conclusions

In summary, this work represents a ratiometric fluorescent sensor (IRMOF-10-Eu) for selective and quantitative detection of  $\text{CO}_3^{2-}$ . Characterization and optical properties of IRMOF-10-Eu was studied. IRMOF-10-Eu had good stability and excellent luminescence in aqueous solution. IRMOF-10-Eu displayed dual-emission under single excitation at 278 nm. After interacting with  $\text{CO}_3^{2-}$ , the emission of ligand was increased and  $\text{Eu}^{3+}$  was decreased. The relative fluorescence intensity ratio and  $\text{CO}_3^{2-}$  concentration have linear relationship with wide detection range and low detection limit. Because  $\text{CO}_3^{2-}$  have an effect on the electronic structure of BPDC, the selectivity of IRMOF-10-Eu was high in detecting  $\text{CO}_3^{2-}$ . The possible detection mechanism can be explained by energy transfer and structural change. IRMOF-10-Eu can be a promising sensor for the detection of  $\text{CO}_3^{2-}$  under real conditions in the future.

## Conflicts of interest

The authors have declared no conflict of interest.

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