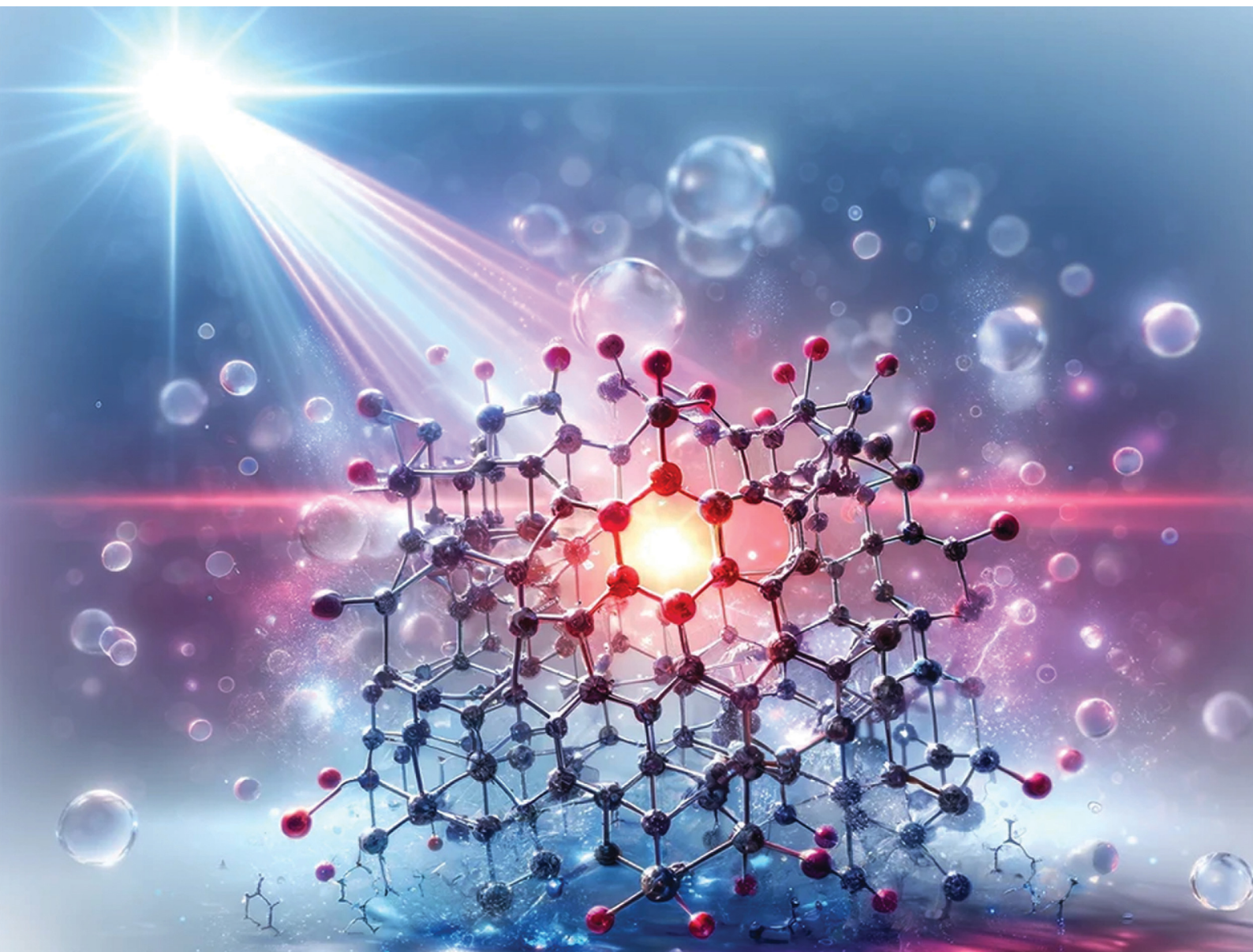


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Solvent-induced luminescence behavior of Ce/ Eu@Gd-MOF for ratiometric detection of D₂O in H₂O†

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The solvent environment has a significant impact on the luminescence performance of Ln-MOFs, but the related research studies are still limited. In this work, a Ln-MOF using 1,3,5-benzenetricarboxylic acid as ligands and Ce³⁺/Eu³⁺ as luminescence centers was prepared. The photoluminescence behaviors of Ce/Eu@Gd-MOFs were studied in H₂O and D₂O. The emission intensity of the Ce/Eu@Gd-MOFs dispersed in D₂O is improved by 711.19% compared to that dispersed in H₂O. After excluding the effects of solvent reabsorption and pH, the difference in vibrational frequencies of the functional groups in H₂O and D₂O is considered to be the main reason for the enhanced luminescence. Deuterated hydroxyl groups have lower vibrational frequencies than hydroxyl groups, resulting in effective weakening of nonradiative transitions. Vibrational coupling occurs between the deuterated hydroxyl groups, H₃BTC ligands and Ce³⁺, because of the proximity of the vibrational frequency of the deuterated hydroxyl groups and the energy level gaps between H₃BTC ligands and Ce³⁺. This facilitates the energy transfer through vibration–vibration interaction in non-radiative processes. The enhancement in luminescence and energy transfer efficiency of Ce/Eu@Gd-MOFs in D₂O is attributed to the synergistic effect of the above mechanisms. This solvent-induced luminescence behavior of Ce/Eu@Gd-MOFs holds potential as an approach for detecting D₂O in H₂O. The detection sensitivity reaches 0.001%. This study contributes to the understanding of the Ln-MOF luminescence and offers insights into its practical applications.

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1. Introduction

Lanthanide metal–organic frameworks (Ln-MOFs) have emerged as a fascinating class of framework materials in recent years, attracting considerable attention.^{1–5} The integration of lanthanide ions and organic ligands confers outstanding optical properties to Ln-MOFs, rendering them with extensive applications in biochemical sensing, nonlinear optics, and white light-emitting diodes.^{6–8} The solvent environment is one of the most crucial factors affecting the luminescence performance of Ln-MOFs in applications. Ln-MOFs are dispersed in solution accompanied by a framework breathing effect.⁹ The porous structure of Ln-MOFs leads to direct interactions between solvent molecules and the lanthanide ions. This results in alterations of intermolecular interactions in Ln-MOFs, causing Ln-MOFs to exhibit distinct properties in the

solvent environment compared to their solid-state counterparts.^{10–12} However, there is still a lack of comprehensive knowledge regarding the influence of solvents on the luminescence of Ln-MOFs. The intricate differences including chemical reactivity, dispersibility, hydrogen bonding, pH, and reabsorption among different solvent molecules pose challenges.¹³ The systematic study for the influence of solvents on the Ln-MOFs luminescence performance is of great significance for customizing luminescence functionalities and advancing their practical applications.

D₂O is an important isotope of H₂O, exhibiting a similar modular structure.^{14–16} It possesses irreplaceable application value in chemical analysis, nuclear energy production, spectroscopic characterization and bioanalysis.^{17–19} The similarity in the physical and chemical properties renders D₂O and H₂O highly suitable candidates for exploring solvent-induced luminescence behavior, minimizing the influence of factors such as solvent viscosity, chemical reactivity, and dispersibility.^{20–22} From another perspective, the investigation of the luminescence behavior of Ln-MOFs in H₂O and D₂O also presents an opportunity to provide a rapid and convenient approach for detecting D₂O content in H₂O.

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Herein, we prepared a Ln-MOF using a one-pot solvothermal method, with 1,3,5-benzenetricarboxylic acid (H_3BTC) as ligands and $\text{Ce}^{3+}/\text{Eu}^{3+}$ as luminescence centers. The doping concentrations of Ce^{3+} and Eu^{3+} in MOFs help in optimizing the photoluminescence (PL) performance. The PL properties of $\text{Ce}/\text{Eu}@\text{Gd}$ -MOFs in H_2O and D_2O were investigated systematically. The impacts of solvent reabsorption, pH value, vibration frequency of solvent molecules and energy gap on luminescence processes, particularly on the energy transfer process, were discussed in detail. The energy transfer efficiencies of Ce^{3+} and Eu^{3+} in H_2O and D_2O were calculated based on the time-resolved spectra. The detection of D_2O content in H_2O was achieved based on the $\text{Ce}/\text{Eu}@\text{Gd}$ -MOFs showing application potential.

2. Experimental section

2.1 Materials and chemicals

CH_3COONa , $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$, 1,3,5-benzenetricarboxylic acid (H_3BTC) and N,N -dimethylformamide (DMF) were purchased from Macklin Reagent Co., Ltd. D_2O was purchased from Aladdin Reagent Co., Ltd. Deionized water was used in all aqueous solutions. All chemicals were analytical grade reagents and used directly without further purification.

2.2 Preparation of MOFs

A series of $\text{Ce}@\text{Gd}$ -MOFs, $\text{Eu}@\text{Gd}$ -MOFs, and $\text{Ce}/\text{Eu}@\text{Gd}$ -MOFs were synthesized by a solvothermal method. An example of preparing $\text{Ce}_{0.01}/\text{Eu}_{0.002}@\text{Gd}_{0.987}$ -MOFs: the starting materials $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.0043 g), $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ (0.3608 g), $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (0.0008 g) and H_3BTC (0.1050 g) were weighed according to the stoichiometric ratio. Then, the ingredients were dissolved in DMF (100 mL). The solution was sonicated for 10 min at room temperature. The component CH_3COONa (0.1360 g) was added to the solution and sonication continued for 30 min. The mixed solution was transferred to an autoclave and kept at 120°C for 24 h. Finally, a white product was obtained, washed by DMF, ethanol and deionized water and dried at 60°C for 24 h.

2.3 Characterization

The morphology of the MOFs was characterized by scanning electron microscopy (SEM, JEOL, JSM-7800F Prime) energy dispersive X-ray (EDX) spectroscopy. The crystal phase of all the phosphor samples was identified by using X-ray powder diffraction (XRD) analysis with a Rigaku D/MAX-RB diffractometer (Tongda TD-3500 automatic X-ray diffractometer system). Fourier transform infrared (FTIR) transmittance spectra of the MOFs were characterized by using a Nicolet IS10 spectrometer under a liquid nitrogen environment. The emission and excitation spectra were measured by using a fluorescence spectrometer (Hitachi, F-7000). Time-resolved fluorescence spectra of the MOFs were recorded by using a transient optical testing system (Quanta Master 400, Photon Technology International).

3. Results and discussion

3.1 Phase identification

The MOF is composed of lanthanide ions (Gd^{3+} , Ce^{3+} and Eu^{3+}) and H_3BTC ligands by coordination. The unit of the MOF consists of a seven-coordinate Gd^{3+} cation, a coordinated water molecule, and a H_3BTC ligand (Fig. 1a). The metal sites of Gd^{3+} can be occupied by Ce^{3+} and Eu^{3+} due to similar ionic radii and valence states. The coordination environment of the metal ions and H_3BTC is shown in Fig. 1b. Fig. 1c reveals that the metal ions are connected through carboxylic bridges to form a one-dimensional helical chain. These chains are further linked with H_3BTC ligands to construct a three-dimensional framework structure (Fig. 1d). Fig. 1e displays the XRD patterns of $\text{Ce}@\text{Gd}$ -MOFs, $\text{Eu}@\text{Gd}$ -MOFs and $\text{Ce}/\text{Eu}@\text{Gd}$ -MOFs. The XRD patterns are matched well with the diffraction peaks reported in the literature.^{23–25} This indicates that the doping of rare earth ions has no impact on the formation of the crystal structure of the MOFs. Fig. 1f is the FTIR spectrum of $\text{Ce}/\text{Eu}@\text{Gd}$ -MOFs and H_3BTC . The spectrum of precursor H_3BTC is provided for comparison. The broad band centered at 3397 cm^{-1} is owing to the stretching vibration of hydroxyl groups. In the $\text{Ce}/\text{Eu}@\text{Gd}$ -MOFs spectrum, the peaks at 1617 cm^{-1} , 1550 cm^{-1} , 1440 cm^{-1} and 1375 cm^{-1} are assigned to the antisymmetric and symmetric stretching mode vibrations of carboxyl groups. They exhibit a shift compared to those in the spectrum of H_3BTC . This originated from the coordination between H_3BTC ligands and metal ions. The SEM image of $\text{Ce}/\text{Eu}@\text{Gd}$ -MOFs is shown in Fig. 1g. The MOFs exhibit a rod-like morphology. Fig. 1h presents the element distribution of $\text{Ce}/\text{Eu}@\text{Gd}$ -MOFs. The elements of O, C, Ce, Eu and Gd are observed in the EDX analysis. This indicates that Ce^{3+} , Eu^{3+} and Gd^{3+} are successfully formed MOFs with H_3BTC ligands.

3.2 Luminescence properties

Fig. 2a presents the emission spectra of $\text{Ce}@\text{Gd}$ -MOFs, $\text{Eu}@\text{Gd}$ -MOFs and $\text{Ce}/\text{Eu}@\text{Gd}$ -MOFs. The MOFs all have a broad

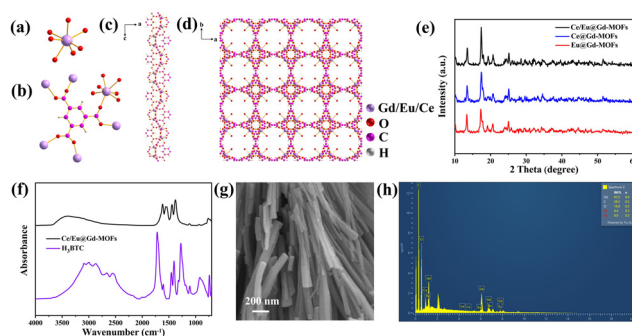


Fig. 1 (a) The coordination environments of Gd^{3+} , Eu^{3+} and Ce^{3+} in Ln-MOF. (b) Coordination mode of the BTC^{3-} ligand and the coordination environments of Gd^{3+} , Eu^{3+} and Ce^{3+} . (c) 1D metal-organic framework along the b axis. (d) 3D metal-organic framework along the c axis. (e) XRD patterns of $\text{Ce}@\text{Gd}$ -MOFs, $\text{Eu}@\text{Gd}$ -MOFs, and $\text{Ce}/\text{Eu}@\text{Gd}$ -MOFs. (f) FTIR spectra of benzene-1,3,5-tricarboxylic acid and $\text{Ce}/\text{Eu}@\text{Gd}$ -MOFs samples. (g) SEM image of $\text{Ce}/\text{Eu}@\text{Gd}$ -MOFs. (h) Energy dispersive X-ray (EDX) spectrum of $\text{Ce}/\text{Eu}@\text{Gd}$ -MOFs.

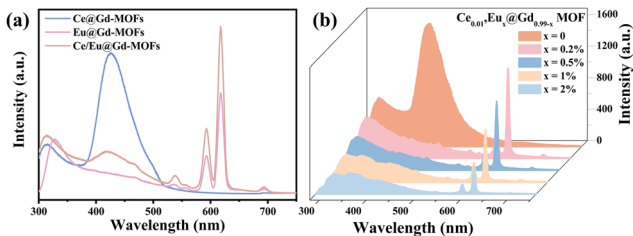


Fig. 2 (a) Emission spectra of Ce@Gd-MOFs, Eu@Gd-MOFs and Ce/Eu@Gd-MOFs, and (b) emission spectra of Ce/Eu@Gd-MOFs ($\lambda_{\text{ex}} = 260$ nm).

emission band in the range of 315–345 nm, assigned to the $\pi-\pi^*$ transition of the ligands.²⁶ The Ce@Gd-MOFs show blue emission under 260 nm excitation. The broad emission band centered at 425 nm is ascribed to parity-allowed $5d \rightarrow 4f$ transitions of Ce^{3+} .²⁷ The emission spectrum of Eu@Gd-MOFs shows peaks at 595 nm, 613 nm, and 690 nm. They arise from $^5\text{D}_0 \rightarrow ^7\text{F}_j$ ($j = 1, 2, \text{ and } 4$) transitions of Eu^{3+} .^{28,29} The co-doped Ce/Eu@Gd-MOFs exhibit both characteristic emissions of Ce^{3+} and Eu^{3+} . In order to optimize the PL performance, the doping concentration of Eu^{3+} was regulated.^{30,31} The emission spectra of $\text{Eu}_x\text{@Gd}_{1-x}$ -MOFs ($x = 0, 0.002, 0.005, 0.01, \text{ and } 0.02$) and $\text{Ce}_{0.01}/\text{Eu}_x\text{@Gd}_{0.99-x}$ -MOFs ($x = 0.002, 0.005, 0.01, \text{ and } 0.02$) are recorded in Fig. S1 (ESI[†]). The emission intensity of Ce/Eu@Gd-MOFs increases by 763.33% compared to the MOFs with only Eu^{3+} doping. The emission spectra of $\text{Ce}_{0.01}/\text{Eu}_x\text{@Gd}_{0.99-x}$ -MOFs ($x = 0, 0.002, 0.005, 0.01, \text{ and } 0.02$) under 260 nm excitation are shown in Fig. 2b. It was clearly found that the emission intensity of Ce^{3+} decreased with Eu^{3+} concentration increasing. The Eu^{3+} optimum doping concentration is $x = 0.002$. This implies that energy transfer occurs between Eu^{3+} and Ce^{3+} in the MOFs. Ce^{3+} is excited from the ground state $4f$ to the excited state $5d$. One part of the energy of the excited Ce^{3+} returns to the ground state, while the rest of the excited Ce^{3+} returns to the excited state ($^5\text{D}_0$) of Eu^{3+} .

The solvent environment plays a crucial role in the luminescence behavior and energy transfer processes of rare earth ions.^{13,21,32} The PL properties of Ce/Eu@Gd-MOFs dispersed in H_2O and D_2O are shown in Fig. 3a. The Eu^{3+} emission intensity at 617 nm improves by 711.19% when the MOFs are dispersed in D_2O compared to that in H_2O (Fig. S2, ESI[†]). The reasons for the solvent-induced luminescence behavior require further investigation. The UV-Vis-NIR absorption spectra of H_2O and D_2O were characterized to study the effect of solvent molecules on the emission and excitation of Ce/Eu@Gd-MOFs. As shown in Fig. 3b, H_2O has two absorption bands centered at 977 nm and 1181 nm, respectively. D_2O presents a weak absorption band at 1322 nm. This indicates that H_2O and D_2O have no effect on the emission (425 nm and 617 nm) and excitation (260 nm) of Ce/Eu@Gd-MOFs. The differences on the pH values of the solvent may cause protonation or deprotonation. The emission spectra of Ce/Eu@Gd-MOFs dispersed in H_2O (pH value from 2 to 12) are recorded in Fig. 3c. The emission intensity of Ce/Eu@Gd-MOFs exhibits a trend of initially increasing and then decreasing with pH value from 2 to 12. When the pH value is between 6 and 8, the emission intensity reaches its maximum and remains nearly constant. This indicates that the difference of pH value between H_2O (pH = 6.4–7.0) and D_2O (pH = 7.5) is not the main factor for the luminescence variation. FTIR spectra of H_2O and D_2O are shown in Fig. 3d. H_2O has characteristic absorption bands positioned at 3325 cm^{-1} , 1637 cm^{-1} , and 736 cm^{-1} . These absorption bands correspond to the stretching vibration, variable angle vibration, and oscillation vibration of hydroxyl groups. The absorption bands of deuterated hydroxyl groups in D_2O show a blue shift, demonstrating that the deuterated hydroxyl groups have lower vibrational frequencies. The luminescence behavior and energy transfer processes of Eu^{3+} and Ce^{3+} can be affected by the vibrational frequencies of solvent molecules. According to Hook's Law:

$$v = \frac{1}{2\pi} \sqrt{\frac{k}{u}}$$

$$u = m_1 \cdot m_2 / (m_1 + m_2)$$

where v is the chemical bond vibrational frequency, k is the telescopic force constant, and m is the relative atomic mass. The $k_{\text{O-H}} \approx k_{\text{O-D}} \approx 7.8$, $u_{\text{O-H}} < u_{\text{O-D}}$. The vibrational frequencies of hydroxyl groups are greater than those of the deuterated hydroxyl groups. Low vibrational frequencies of the deuterated hydroxyl groups can help in avoiding vibrational relaxation and reduce the probability of non-radiative transitions.^{33,34} The impact of solvent molecule vibration frequency on the energy transfer process in MOFs needs further exploration.

3.3 Effect of solvent on energy transfer in MOFs

Fig. 4 illustrates the energy transfer between H_3BTC ligands, Ce^{3+} and Eu^{3+} in the PL process of Ce/Eu@Gd-MOFs. The H_3BTC ligands absorb photons *via* the antenna effect and are excited from the singlet state (S_1 , 36978 cm^{-1}) to the triplet

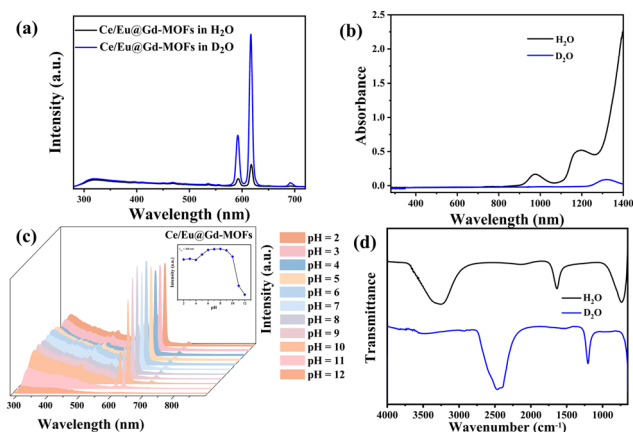


Fig. 3 (a) Emission spectra of Ce/Eu@Gd-MOFs dispersed in H_2O and D_2O . (b) UV-Vis-NIR absorption spectra of H_2O and D_2O . (c) Emission spectra of Ce/Eu@Gd-MOFs in H_2O (pH = 2–12). The inset expresses luminescence intensity at 260 nm. (d) FTIR spectra of H_2O and D_2O .

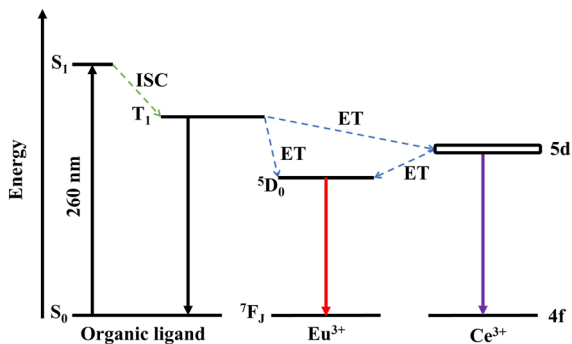


Fig. 4 The energy level diagram and possible energy transfer schemes among H₃BTC ligands, Ce³⁺ and Eu³⁺.

state (T₁, 26491 cm⁻¹) through intersystem crossing (ISC) according to the Reinhold empirical rule.^{1,35–37} The triplet state of H₃BTC ligand transfers energy to the 5d excited state of Ce³⁺ and ⁵D₀ of Eu³⁺ via a non-radiative process.^{38–42} The energy gap between the T₁ of H₃BTC ligands, Ce³⁺ and Eu³⁺ is 2453 cm⁻¹ and 9685 cm⁻¹, respectively. This means that the sensitization effect of H₃BTC ligands on Ce³⁺ is significantly higher than that on Eu³⁺. The excited state of Ce³⁺ further transfers energy to Eu³⁺, leading to the emission of Eu³⁺ from ⁵D₀ to ⁷F_J.

Time-resolved PL decay curves were tested to further study the excited-state radiative relaxation and energy transfer processes of Ce/Eu@Gd-MOFs in H₂O and D₂O (Fig. 5). All of the decay traces of the Ce/Eu@Gd-MOFs are well fitted with a biexponential function. As the concentration of Eu³⁺ increases, the decay times for both Ce³⁺ and Eu³⁺ ions decrease. This stems from the effective energy transfer from the sensitizer (Ce³⁺) to the activator (Eu³⁺), leading to a decrease in the decay times as the concentration of the activator increases (Table 1).²⁶ Both the lifetimes of Ce³⁺ and Eu³⁺ are extended when the dispersing solvent of Ce/Eu@Gd-MOFs is changed from H₂O to

D₂O. This arises from the low vibrational frequency of deuterated hydroxyl groups in D₂O weakening vibrational relaxation.⁴³ Moreover, the stretching vibration frequency of deuterated hydroxyl groups (2469 cm⁻¹) is close to the energy gap between Ce³⁺ and the H₃BTC ligands (T₁-5d, 2453 cm⁻¹). This implies the vibrational coupling occurring between the excited state of the ligands and Ce³⁺, resulting in increased probability of vibrational relaxation. This vibrational relaxation tends to hinder radiative transition processes, but it is beneficial for vibration–vibration interaction of energy transfers between the H₃BTC ligands and Ce³⁺. The luminescence of Ce/Eu@Gd-MOFs is consequently enhanced.

The energy transfer efficiencies of Ce³⁺ and Eu³⁺ in H₂O and D₂O were calculated by the following formula:^{44,45}

$$\eta = 1 - \frac{\tau}{\tau_0}$$

η represents the energy transfer efficiency between Ce³⁺ and Eu³⁺ in H₂O or D₂O, τ and τ_0 stand for the luminescence lifetimes of Ce³⁺ with doped and undoped Eu³⁺ in MOFs dispersed in H₂O or D₂O. As the concentration of impurity Eu³⁺ increases, the energy transfer efficiencies in H₂O and D₂O both gradually improve (Fig. S3, ESI[†]). The energy transfer efficiency in H₂O is 28.97%, and in D₂O is 29.32% (Table 1). This indicates that the decreased vibration frequency of deuterated hydroxyl groups reduces non-radiative transitions during the luminescence process. The decreased electron migration rate among Eu³⁺ and Ce³⁺ consequently leads to an increase in energy transfer efficiency.

3.4 D₂O detection

The distinctive PL behaviors in H₂O and D₂O of Ce/Eu@Gd-MOFs can be utilized for detecting D₂O in H₂O. The emission intensity of the ligands at 316 nm has no significant changes in both H₂O and D₂O. It can serve as a reference for achieving self-calibration in ratio detection. The emission intensity of Eu³⁺ at 617 nm rises significantly with the increase in the content of D₂O in H₂O from 0% to 100% (Fig. 6a). The ratio of the emission intensities at 617 nm ($F_{617 \text{ nm}}$) and 316 nm ($F_{316 \text{ nm}}$) shows the expected linear relationship with the proportion of D₂O in H₂O. (Fig. 6b). The limit of detection (LOD) is calculated as 0.001%. This result suggests that the Ce/Eu@Gd-MOFs are capable of serving as a ratiometric luminescence probe for the sensitive detection of D₂O in H₂O. The selectivity of D₂O detection has been evaluated by comparing the emission intensities at 316 nm and 617 nm of the Ce/Eu@Gd-MOFs dispersed in the presence of common species. The interfering species include methanol, ethanol, acetone, Na⁺, K⁺, Ca²⁺, Mg²⁺ and Zn²⁺. The results are presented in Fig. S4 (ESI[†]). They demonstrate that the Ce/Eu@Gd-MOFs have an acceptable selectivity in D₂O detection.

4. Conclusions

In summary, Ce/Eu@Gd-MOFs were synthesized using H₃BTC as a ligand and Ce³⁺/Eu³⁺ as luminescence centers. The

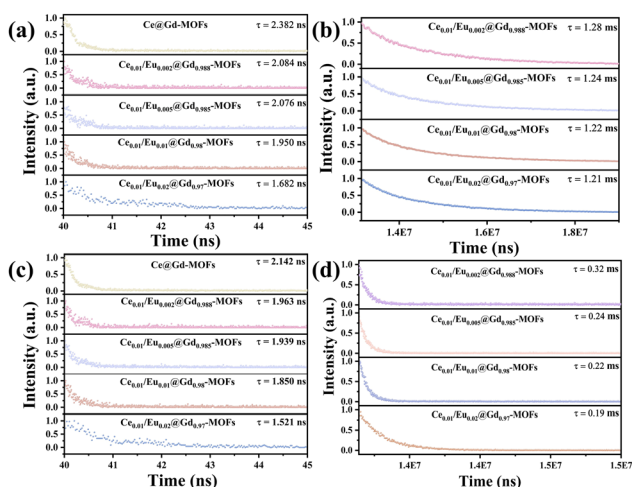


Fig. 5 Time-resolved PL decay curves of Ce/Eu@Gd-MOFs (a) Ce³⁺ in D₂O, (b) Eu³⁺ in D₂O, (c) Ce³⁺ in H₂O, and (d) Eu³⁺ in H₂O. The excitation wavelength is 280 nm. The monitored wavelength is 394 nm for Ce³⁺ and 617 nm for the decay curve of Eu³⁺.

Table 1 Ce³⁺ and Eu³⁺ lifetimes in D₂O and H₂O depending on Eu³⁺ concentration

Eu ³⁺ concentration (mol)	Ce ³⁺ lifetime (ns) in D ₂ O	Eu ³⁺ lifetime (ms) in D ₂ O	Ce ³⁺ lifetime (ns) in H ₂ O	Eu ³⁺ lifetime (ms) in H ₂ O
0	2.382		2.142	
0.002	2.084	1.28	1.962	0.32
0.005	2.076	1.24	1.939	0.24
0.01	1.950	1.22	1.850	0.22
0.02	1.682	1.21	1.521	0.19
Max energy transfer efficiency (η)	29.32%		28.97%	

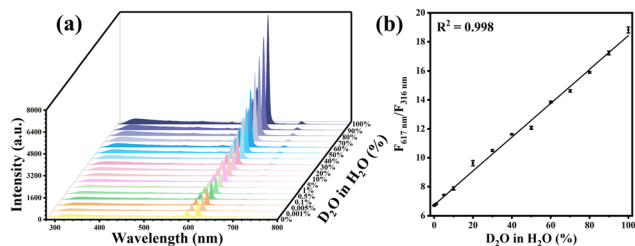


Fig. 6 (a) Luminescence spectra of Ce/Eu@Gd-MOFs with D₂O content ranging from 0% to 100%. (b) Correlation between D₂O content and $F_{617\text{ nm}}/F_{316\text{ nm}}$.

differentiated luminescence behaviors of Ce/Eu@Gd-MOFs in H₂O and D₂O are attributed to the differences in vibrational frequencies between hydroxyl groups and deuterated hydroxyl groups. The PL enhancement of Ce/Eu@Gd-MOFs dispersed in D₂O is attributed to the combination of low vibrational frequency and matching with the energy level gaps of deuterated hydroxyl groups. The energy transfer efficiency of Ce³⁺ and Eu³⁺ in the MOF increases from 28.97% to 29.32% as the solvent changes from H₂O to D₂O. The Ce/Eu@Gd-MOFs were used as ratiometric luminescence probes for detecting D₂O in H₂O. The LOD is calculated as 0.001%. This work is expected to provide guidance for the solvent-involved applications of MOFs in bioimaging, therapies, sensing, solar cells, etc.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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