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Mixed lanthanide–organic frameworks with borono groups for colorimetric detection of excess fluoride levels in rivers†

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Chronic fluoride (F[−]) toxicity has been endemic at least 25 countries around the world due to prolonged consumption of contaminated water, posing a great threat to human health. Rapid and convenient visual methods for F[−] ion detection are hence needed for public safety. In this work, we show a series of novel mixed lanthanide–organic frameworks, namely {[Eu_xTb_{2−x}(BIPA)₃(DMF)(H₂O)₃]·2DMF·3H₂O}_n (H₂BIPA = 5-boronoisophthalic acid; x = 0, 0.12, 0.28, 0.30, 0.68, 1.04 and 2 for **1–7**, respectively), with abundant recognition sites of borono groups for convenient and visual detection of excess F[−] ions in river water. Wide linear range for F[−] ion detection can be obtained through systematic optimization of sensing materials. A rare double dynamic sensing process between F[−] ions and lanthanide–organic frameworks was clearly revealed though single-crystal X-ray diffraction and transient fluorescence techniques.

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1. Introduction

As the fluoridation process of public drinking water and daily necessities accelerate, fluoride ions (F[−]) have been of easy access in daily life and are beneficial to human health at low concentrations.^{1,2} However, chronic overconsumption of F[−] ions will cause severe adverse effects such as dental and skeletal fluorosis, fracture-proneness, urolithiasis, and impaired thyroid.^{3–6} According to World Health Organization (WHO) guidelines for drinking-water quality in 2004, the concentration limit of F[−] ions for drinking water should be no more than 1.5 mg L^{−1} for preventing osteofluorosis.⁷ Convenient and accurate visual detection of excess F[−] ion levels in drinking water is hence needed for public safety. Up to now, different methods have been developed for F[−] ion level determination, including fluorescence, use of electrodes, and chromatography.^{8–10} Nevertheless, these methods either have

complex operations and take a long time or are poor in stability and not convenient for on-site detection.

As multifunctional porous crystalline materials, luminescent metal–organic frameworks (MOFs) have been paid wide attention in chemical sensing not only because of their devisable architectures and abundant luminescence sites but also due to the advantages in the designability of size and energy level matching.^{11–15} Lanthanide–organic frameworks (Ln–MOFs) stand out from these materials because they can also fully demonstrate the excellent luminescence properties of lanthanide metals, such as long lifetime and high spectral resolution.^{16–20} Mixed Ln–MOFs constructed with multi-lanthanide centers can reduce systematic error and improve sensitivity because of their special self-calibration function through ratiometric dual output modes.^{21–25} To realize accurate F[−] detection in drinking water, adding precise recognition sites to mixed Ln–MOFs can greatly improve the selectivity and anti-interference ability. To this end, 5-boronoisophthalic acid (H₂BIPA) was selected as a ligand for constructing mixed Ln–MOFs with europium (Eu³⁺) and terbium (Tb³⁺) ions for the following points: (i) in previous work, it has been found that H₂BIPA can effectively sensitize the luminescence of Eu³⁺ and Tb³⁺ via the “antenna effect”,^{26–28} (ii) H₂BIPA contains electron-deficient borono group, which may capture F[−] ions according to the well-known Lewis theory of acids and bases, (iii) the interaction between F[−] ions and H₂BIPA may change the energy levels of the ligand, thereby changing the energy transfer path inside of Ln–MOFs, and thus regulating the fluorescence of Ln–MOFs and finally realizing the detection of F[−]

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ions, and (iv) in previous work, it has been demonstrated that borono-functionalized Ln-MOFs can be used to detect F⁻ ions, but detailed crystal data and F⁻ capture process have not been clearly reported.²⁸

In this work, a series of novel Ln-MOFs, {[Eu_xTb_{2-x}(BIPA)₃(DMF)(H₂O)₃]₂DMF·3H₂O}_n (Eu_xTb_{2-x}-MOF; x = 0, 0.12, 0.28, 0.30, 0.68, 1.04 and 2 for 1–7, respectively; DMF: N,N-dimethylformamide), were synthesized and characterized in detail for highly efficient visual detection of F⁻ ions. Isomorphous Gd₂-MOF (8) was synthesized for energy level studies. After the stepwise optimization of sensing materials, 5 was screened out for F⁻ ion detection and displays high sensitivity, excellent selectivity, and a low limit of detection (LOD) of 0.165 ppm. The best sensing performance of 5 may be due to its highest intramolecular energy transfer efficiency (E) from Tb³⁺ to Eu³⁺ ions. The further detection of F⁻ ions in actual water samples from a river show that 5 can be used in practice.

2. Experimental

2.1. Materials and methods

All chemicals purchased were of reagent grade and used without further purification. The single-crystal data of 7 and F@7 were collected using a Rigaku XtaLAB Mini II single-crystal diffractometer equipped with graphite-monochromatic Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Structures were solved by SHELXS (direct methods) and refined by SHELXL (full matrix least-squares techniques) in the *Olex 2* package.^{29,30} Powder X-ray diffraction (PXRD) experiments were performed using a Bruker D2 PHASER diffractometer with Cu-K α radiation ($\lambda = 1.54186 \text{ \AA}$) through scanning over the range of 5–50° at a scan rate of 0.2° s⁻¹ at room temperature. Simulations of PXRD patterns were carried out with the single-crystal data and diffraction crystal module of the Mercury program available free of charge via <https://www.ccdc.cam.ac.uk/mercury/>. Thermogravimetric analysis (TGA) was carried out with a NETZSCH STA 449F5 (TG/DTA) thermal analyzer under nitrogen flow. Fourier transform infrared spectroscopy (FTIR) was conducted using a Bruker AXS TENSOR-27 FTIR spectrometer with pressed KBr pellets in the range of 4000–400 cm⁻¹. Elemental analysis (EA) for C, H and N was carried out using a Vario EL cube elemental analyzer. Inductively coupled plasma-atomic emission spectrometry (ICP-AES) analyses were conducted using an Agilent 7900 instrument. Ultraviolet-visible (UV-vis) absorption spectra were measured with a Hitachi U-3010 UV-vis spectrophotometer. X-ray photoelectron spectroscopy (XPS) data were acquired using a Thermo Scientific K-Alpha instrument. Luminescence spectra were recorded using an Edinburgh FS5 fluorescence spectrophotometer equipped with a xenon lamp and pulsed flash lamp at room temperature. Photos were taken with a HUAWEI Nova 8 pro under 278 nm excitation of a Hitachi RF6000 fluorescence spectrometer. The F⁻ ion selective electrode (PF-1Q9) was purchased from Shanghai Ruosull Technology Co. Ltd.

2.2. Synthesis

H₂BIPA (0.1 mmol, 0.021 g), pinacol (0.1 mmol, 0.012 g), 1 mL DMF and 4 mL H₂O were added to a 20 mL glass bottle to form a solution under ultrasound. Then, 1 mL of europium acetate tetrahydrate (Eu(AC)₃·4H₂O) aqueous solution (0.1 mol L⁻¹) was added. The glass bottle was sealed and heated at 90 °C for 24 h, and colorless crystals (7) were formed at the bottom of the glass bottle. 7 was collected by filtration and washed with distilled water three times and then dried in air. 1–6 were obtained using a similar method to that for 7 by replacing Eu(AC)₃ aqueous solution with terbium/europium/gadolinium acetate aqueous solution with different volumes (1 mL in total). Yield: 41%, 38%, 33%, 31%, 33%, 35%, 34% and 36% based on H₂BIPA for 1–8, respectively. The feed volume and chemical composition of 1–7 were further confirmed by ICP-AES and EA (Table S1†). F@7 was obtained after treating 7 with an aqueous solution with 33 ppm F⁻ ions at 80 °C for 12 h.

2.3. Luminescence measurements

Finely ground lanthanide MOFs (1–7) (10 mg) were dispersed into distilled water (50 mL) to form aqueous suspensions, which were then sonicated for 5 min. Luminescence spectra upon excitation at 278 nm were measured *in situ* after incremental addition of freshly prepared analyte solutions to a 3 mL suspension of 1–7. For selectivity and anti-interference experiments, aqueous suspensions were similarly prepared, with addition of 50 μ L of 1 mmol L⁻¹ aqueous solution of NaCl, NaBr, KBr, KOCN, KSCN, KSeCN, BaCl₂, CaCl₂, MnCl₂, Na₂SO₄, NiCl₂, SrCl₂, MgCl₂ and/or 31.2 ppm NaF into the aqueous suspensions of 5.

2.4. Experiments for actual water samples

As-obtained water samples from Yangtze River (1–3) were treated by centrifugation at 10 000 rpm for 5 min to obtain clear liquids at the top of centrifuge tubes for direct spike-and-recovery experiments using 5. The same batch of samples were also used for F⁻ ion detection by F⁻ ion selective electrode for comparison. Saturated calomel electrode was used as the reference electrode. Seven standard solutions including 10⁻¹, 10⁻², 10⁻³, 10⁻⁴, 10⁻⁵, and 10⁻⁶ M NaF standard solution was used for obtaining a standard curve for actual water sample detection.

3. Results and discussion

3.1. Structural description and characterizations

1–8 are crystallized in the *P* $\bar{1}$ space group through a fast self-assembly process of lanthanide ions and H₂BIPA under solvothermal conditions (Table S2†). Their crystal structure can be hence described in detail using 7 as a representative. The minimum asymmetric unit of 7 includes three BIPA²⁻, two Eu³⁺ ions, three coordination water molecules, a coordination DMF molecule and series of lattice species. Two crystallographically independent Eu³⁺ ions are in eight-coordination (Eu1)

and nine-coordination (Eu2) modes with oxygen atoms, forming biaugmented trigonal prism and muffin configuration, respectively (Fig. 1a, and Table S3†). Two congeneric Eu^{3+} ions are linked by four $\mu_2\text{-}\eta^1\text{:}\eta^1$ carboxyl groups of four BIPA $^{2-}$ to form a binuclear $\{\text{Eu}_2\}$ unit, and each BIPA $^{2-}$ is connected to two $\{\text{Eu}_2\}$ units to form a two-dimensional network in the *ac* plane (Fig. 1b), which is further connected into a three-dimensional framework through two $\mu_1\text{-}\eta^1\text{:}\eta^1$ carboxyl groups of BIPA $^{2-}$ (Fig. 1c). The topology of 7 can be simplified into *pcu* configuration by taking two kinds of six-connected $\{\text{Eu}_2\}$ units as nodes (Fig. 1d and Fig. S1†).

The PXRD patterns show that the diffraction peaks of as-synthesized compounds match well with simulated peaks from the single-crystal data of 7 (Fig. S2†). In addition, these isomorphous crystals displayed similar FTIR curves, confirming their phase purity (Fig. S3†). MOFs with great water stability should possess strong coordination bonds (thermodynamic stability) or significant steric hindrance (kinetic stability) to prevent the hydrolysis reaction that breaks metal-ligand bonds.^{31–33} For Ln-MOFs, Ln-O coordination bonds are relatively weak, and thus, it is desired to obtain the appropriate chelating model of ligands to form a rigid structure to prevent attack of water molecules.³⁴ As is shown in Fig. S4,† the diffraction peaks of 7 after immersion in water for 48 hours are in good agreement with those of the original compound, revealing its high water stability. The TGA of 7 was conducted in the temperature range of 40–800 °C (Fig. S5†). A clear weight loss of 4.75% was observed in the range of 40–102 °C, keeping up with the loss of three lattice water molecules (cal. 4.60%). Obvious weight loss of 11.92% was observed at 102–256 °C, agreeing with the loss of two lattice DMF molecules (cal. 11.47%). The loss of coordinated solvent molecules was observed before 427 °C, and further heating-induced sharp

weight losses were attributed to the decomposition of the frameworks.

3.2. Luminescent detection of F^- ions

The solid-state luminescence emission spectra of 1–7 were investigated with an excitation wavelength of 287 nm (Fig. 2a). Typically, 7 and 1 displayed characteristic emission peaks at 579, 592, 616, 652, 697 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_J, J = 0, 1, 2, 3, 4$) and 489, 545, 585, 621 nm ($^5\text{D}_4 \rightarrow ^7\text{F}_J, J = 6, 5, 4, 3$), respectively, while 2–6 show the characteristic emission peaks of the Eu^{3+} and Tb^{3+} ions, indicating the successful mixing of Eu^{3+} and Tb^{3+} . 1–7 display seven different gradient luminescence colors from green to red (Fig. 2a, inset), and 7 displays rare pure red color according to its *CIE-1931* chromaticity coordinates (Fig. 2b). The lifetimes of Tb^{3+} and/or Eu^{3+} in 1–7 were determined to investigate the energy transfer efficiency (*E*) between Tb^{3+} and Eu^{3+} according to the equation of $E = 1 - \tau_n/\tau_1$, where τ_n is the lifetime of Tb^{3+} in 1–6 (Fig. 2c). With an increase of Eu content, the *E* value first increases and further decreases, and 5 shows the highest *E* value of 29.8% (Fig. 2d).

The aqueous dispersions of 1–7 display similar luminescence emission spectra to those of their crystalline states (Fig. S6†), and their luminescence intensity remained constant for 15 minutes (Fig. S7†), indicating they are suitable for luminescent detection in water. Luminescent titrations of F^- ions were performed using aqueous dispersions of 1–7 (Fig. S8 and S9†). With the concentration of F^- ions increasing from 0 to 31.7 ppm, all intensities (*I*) at 544 and/or 616 nm for the seven compounds decreased (Fig. 3a), which obeyed the Stern-Volmer (S-V) equation: $I_0/I = K_{\text{SV}}[C] + 1$ in the low concentration ($[C]$) range of F^- ions, where K_{SV} is the quenching constant (Fig. S9 and S10†). K_{SV} values fitted by intensities at 544

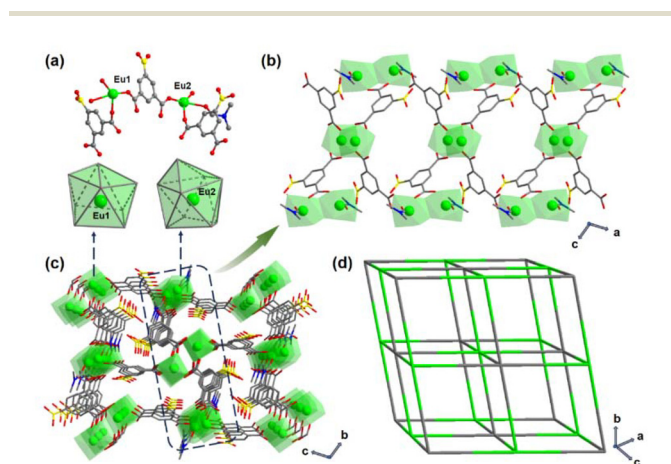


Fig. 1 (a) Minimum asymmetric unit of 7 and coordination configuration of the Eu^{3+} ions. (b) Connection of binuclear Eu_2 units and BIPA $^{2-}$ in the *ac* plane. (c) Three-dimensional framework of 7 in the *bc* plane. (d) Simplified *pcu* topological configuration of 7. Atoms: Eu (green), C (gray), O (red), N (blue), B (yellow); H atoms are omitted for simplification.

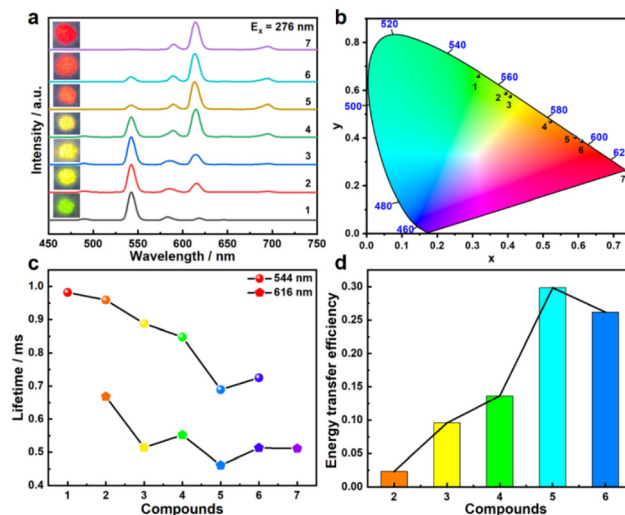


Fig. 2 Solid-state luminescence emission spectra (a) and *CIE-1931* chromaticity coordinates (b) of 1–7. Insets of (a) show solid luminescence pictures of 1–7 under 365 nm ultraviolet light. (c) Solid luminescence lifetimes of 1–7 at 544 and/or 616 nm. (d) Energy transfer efficiencies of 2–6.

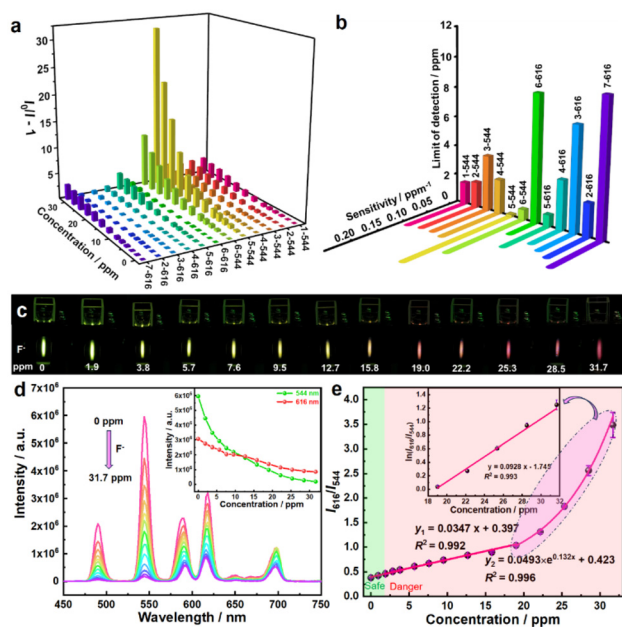


Fig. 3 (a) Stern–Volmer (S–V) plots of 1–7 at 544/616 nm vary with the concentration of F^- ions. (b) Sensing performance summary of 1–7 using intensities at 544 and/or 616 nm. (c) *In situ* color changes of 5 aqueous dispersion towards F^- ions with different concentrations. (d) Luminescence response of 5 aqueous dispersion towards F^- ions with different concentrations; inset shows the trend of change of luminescence intensity at 544 nm and 616 nm. (e) Intensity ratio (I_{616}/I_{544}) of 616 nm and 544 nm varies with the concentration of F^- ions; inset shows the logarithmic relationship between I_{616}/I_{544} and concentration at high concentration range. All data points of (d) and (e) are the average values of three measurements, and error bars show the 95% confidence interval.

and/or 616 nm of 1–7 were 0.0837, 0.0787/0.0546, 0.0793/0.0423, 0.0856/0.0289, 0.183/0.166, 0.125/0.739, and 0.0776 ppm $^{-1}$, respectively. With a further increase of concentration, all S–V points showed typical exponential function relationships: $I_0/I = a \times e^{b[C]} + c$, where a , b and c are constants. This phenomenon might be attributed to a self-absorption or energy transfer process.³⁵ The LODs of 1–7 are 1.5, 1.73/2.28, 3.74/7.03, 2.31/3.33, 0.166/0.83, 0.739/8.54 and 9.15 ppm, respectively, based on the 3σ IUPAC criteria.³⁶

The sensing performances including sensitivity and LOD of 1–7 are summarized and compared in Fig. 3b and Table S4.† 5 obviously behaved best and was screened out for further study. The reason for the best performance of 5 may be attributed to the highest E value from Tb^{3+} to Eu^{3+} ions discussed above. The higher the E value, the easier it is to influence through interacting with analyte (F^- ion), thus realizing higher sensitivity. Considering that there are two different emission centers (Eu^{3+} and Tb^{3+}) in 5, the ratiometric F^- ion detection behaviour was studied in detail. *In situ* titration experiment of 5 gives gradual changes of luminescence color from green to yellow and ultimately to red towards F^- ions from 0 to 31.7 ppm (Fig. 3c). As the concentration of F^- ions increases, the fluorescence intensity at 544 nm decreased rapidly, while

that at 616 nm decreased slowly (Fig. 3d). The difference in reduction in luminescence intensity at 544 and 616 nm may be attributed to the energy transfer process of Tb^{3+} to Eu^{3+} ions in 5.²⁶ The intensity ratio (I_{616}/I_{544}) of 616 nm and 544 nm showed two different response behaviours (Fig. 3e): (i) when the concentration of F^- ions is less than 19 ppm, I_{616}/I_{544} is linearly dependent on F^- ion concentration with the relationship of $y = 0.0347x + 0.397$; (ii) when the concentration of F^- ions is higher than 19 ppm, a clear exponential relationship of $y = 0.0493 \times e^{0.132x} + 0.423$ between I_{616}/I_{544} and F^- ion concentration was found. These results indicate that there are two distinct interactions between 5 and F^- ions. The LOD in this situation is 0.68 ppm, which is lower than the specified risk concentration (1.5 ppm) of F^- ions in water set by the WHO, indicating that 5 has potential applications for F^- ion detection in water.

Before practical application, the selectivity and anti-interference ability of 5 towards F^- ions were explored. After adding the major components of drinking water and some pseudo halogen ions, including NaCl, NaBr, KBr, KOCN, KSCN, KSeCN, BaCl₂, CaCl₂, MnCl₂, Na₂SO₄, NiCl₂, SrCl₂ and MgCl₂ (1 mmol L $^{-1}$, 50 μ L), the fluorescence of 5 dispersion remained green and I_{616}/I_{544} changed little, but it increased sharply, and the fluorescence turned to red when 31.2 ppm NaF was added (Fig. 4a and b). These results indicate that 5 shows excellent selectivity for F^- ions. Besides, when these metal salts coexist with NaF, I_{616}/I_{544} is roughly equal to that for NaF only (Fig. 4c), indicating that 5 displays satisfactory anti-interference ability for F^- ion detection. To verify the practical application ability, water samples from the Yangtze River were used for spike-and-recovery experiments, which show recoveries in the range of 97.0%–98.0%, confirming that 5 can be used for F^- ion detection in real samples (Table S5†). To verify the detection accuracy in this work, the same batch of samples were also used for detection of F^- ions using the well-known methods such as F^- ion selective electrodes (Fig. S11†). Detection results show that F^- ion concentrations in different river samples were all about 0.80 ppm, which were relatively

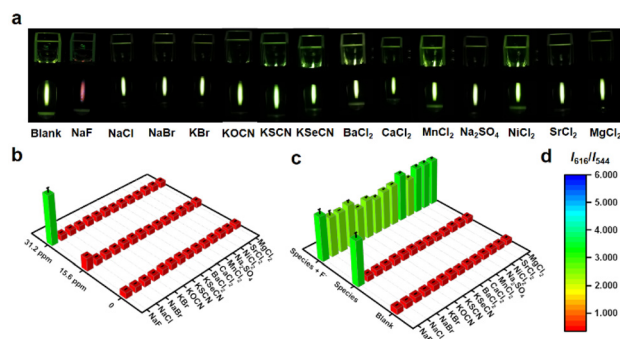


Fig. 4 (a) Pictures of 5 aqueous dispersion before and after adding different interfering species. Selectivity (b), anti-interference (c) and color map (d) of 5 toward F^- ions in common ions. All data points are the average values of three measurements, and error bars show the 95% confidence interval.

coincident with the detection results using **5**. In addition, the results of tests using **5** after adding standard F^- ion solution show lower standard deviation.

3.3. Sensing mechanism study

The detailed sensing mechanism was revealed by a series of spectroscopic studies and single-crystal structure analysis. The PXRD peaks of **5** before and after F^- ion treatment are consistent with the simulated peaks, indicating that F^- ions will not destroy the framework of **5** (Fig. S12†). The sensing of F^- ions is therefore caused by host-guest interactions. Compared with bonding energy of B 1s in **5** in view of XPS spectra, small changes (from 190.86 to 190.70 eV) can be found after treating **5** with F^- ions, indicating weak interactions exist between B atoms and F^- ions (Fig. S13†). These results are similar to those reported in the literature.^{8,26} Besides, new FTIR peaks at 706 and 750 cm^{-1} formed, which may be caused by the formation of B...F interaction (Fig. S14†).^{37,38} Considering that **7** and **5** are isomorphous, the interactions of **5** and F^- ions should be similar to those of **7** and F^- ions. Hence, the formed B...F interaction can be observed by comparing single-crystal X-ray diffraction results of **7** and F@**7** (Fig. 5a and Table S2†). The interaction distance of B...F is about 1.628 Å, which is longer than the traditional B-F bond length (about 1.38 Å). This result is consistent with the conclusion that weak interaction between borono group and F^- ions exists, which may be caused by the steric effect of water molecules interacting with borono group though hydrogen bond interactions. This interaction is different from electrostatic interaction between F^- ions and Ln-MOF or high affinity nature between F^- ions and Ln^{3+} ions.^{8,39} The singlet energy level and triplet energy level of the ligand are 41 152 and 22 936 cm^{-1} , respectively, which are suitable for sensitization of the Eu^{3+} and Tb^{3+} ions (Fig. S15†). With F^- ion concentration increasing, weak changes in UV-vis absorption spectra can be observed, indicating the singlet energy level of the ligand can be influenced by F^- ions (Fig. S16†). As a result, the energy transfer process

within **5** changes, eventually causing a change in luminescent color. This conclusion was further verified by transient fluorescence spectra of **5** before and after treating with F^- ions (Fig. S17 and S18†). As the concentration of F^- ions increases, the lifetime at 544 nm decreases first and later increases, while the lifetime at 616 nm increases all the way (Fig. 5b and c, S19 and Table S6†). The opposite changes in the fluorescence lifetimes of the Tb^{3+} and Eu^{3+} ions at the beginning not only indicate dynamic interactions between **5** and F^- ions but also indicate that F^- ions accelerate the energy transfer from the Tb^{3+} to Eu^{3+} ions under unacted saturated state. With the further increase of F^- ion concentration, the lifetimes of Eu^{3+} ion and Tb^{3+} ion increase simultaneously, indicating that the interactions between F^- ions and **5** can improve the energy transfer efficiency from ligand to Tb^{3+}/Eu^{3+} ions after saturation.

Hence, the sensing mechanism can be summarized as follows (Fig. 5d): under 278 nm excitation, luminescence of Eu^{3+} and Tb^{3+} ions can be emitted through the traditional “antenna effect” process. After a weak interaction between the ligand and F^- ions, the energy transfer from the Tb^{3+} to Eu^{3+} ions accelerates, and the linear change of I_{616}/I_{544} is induced with a slow color change. After saturation of this interaction, the energy transfer efficiency from ligand to Tb^{3+}/Eu^{3+} ions is promoted, causing the exponential growth of I_{616}/I_{544} with a fast color change.

4. Conclusions

In summary, we synthesized and characterized a family of lanthanide metal-organic frameworks with borono groups, which can be used for visual detection of F^- ions through the change of luminescence color from green to red. Through a series of spectral studies and crystal structure analysis, rare double dynamic interactions between F^- and lanthanide metal-organic frameworks have been revealed in detail, to give a deep understanding of double response relationships between fluorescence intensity ratio and concentration at low and high concentrations. The F^- ion response mechanism is thoroughly analyzed from the perspective of host-guest interaction, which provides new insights for the design, synthesis and application of MOF-based sensing materials for environmental pollutants.

Author contributions

H. M. designed the experiments, analyzed experimental data and completed the manuscript. Z. Z., M. H., and J. Z. did experiments. H. M., N. Z. and P. C. discussed the idea and polished the manuscript.

Conflicts of interest

There are no conflicts to declare.



Fig. 5 (a) Host-guest interaction between **5** and F^- ions. Transient fluorescence spectra of **5** at 544 nm (b) and 616 nm (c) before and after treating with F^- ions; insets show the lifetime-based S-V points and their change tendency or fitted result. (d) Energy transfer mechanism diagram.

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