



DOI: [10.29026/oea.2021.200063](https://doi.org/10.29026/oea.2021.200063)

# Water-sensitive multicolor luminescence in lanthanide-organic framework for anti-counterfeiting

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Supplementary information for this paper is available at <https://doi.org/10.29026/oea.2021.200063>



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## Section 1: Materials

All reagents were commercially available and used as received. All organic solvents were of analytical-reagent grade and dried to eliminate any water residue before the experiment. Extra dry tetrahydrofuran and ethanol were purchased from Energy Chemical.

*Synthesis of Tb(BDC-NH<sub>2</sub>):* H<sub>2</sub>BDC-NH<sub>2</sub> (131.3 mg, 0.725 mmol), Tb(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (328.4 mg, 0.725 mmol), 2-FBA (812.6 mg, 5.8 mmol), DMF (36.5 mL), H<sub>2</sub>O (3 mL), and HNO<sub>3</sub> (2 mL, 3.5 M in DMF) were sealed into a 100 mL Teflon cup. After the resulting solution was heated to 110 °C for 60 h and cooled to room temperature. The colorless polyhedral crystals were collected and washed with DMF.

*Synthesis of Gd(BDC-NH<sub>2</sub>):* H<sub>2</sub>BDC-NH<sub>2</sub> (131.3 mg, 0.725 mmol), Gd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (327.2 mg, 0.725 mmol), 2-FBA (812.6 mg, 5.8 mmol), DMF (36.5 mL), H<sub>2</sub>O (3 mL), and HNO<sub>3</sub> (2 mL, 3.5 M in DMF) were sealed into a 100 mL Teflon cup. After the resulting solution was heated to 110 °C for 60 h and cooled to room temperature. The colorless polyhedral crystals were collected and washed with DMF.

## Section 2: Measurements

Powder X-ray diffraction (PXRD) data were collected in the  $2\theta = 5^\circ\text{--}50^\circ$  range on a PANalytical X'Pert Pro X-ray diffractometer using Cu-K $\alpha$  ( $\lambda = 1.542 \text{ \AA}$ ) ( $1 \text{ \AA} = 10^{-10} \text{ m}$ ) beam at room temperature. Elemental analyses (EA) for C, H, and N were performed on an EA1112 microelemental analyzer. Infrared spectrum (IR) was recorded in the range of 4000–400 cm<sup>-1</sup> on Thermo Fisher Nicolet iS10 spectrometer using KBr pellets. Thermogravimetric analyses (TGA) were conducted on a Netzsch TGA 209 F3 thermogravimetric with a heating rate of 10 K min<sup>-1</sup> in N<sub>2</sub> atmosphere. The emission, excitation and phosphorescence spectra were recorded by an Edinburgh Instrument F920 spectrometer. Inductively coupled plasma spectroscopy (ICP) was performed on a Thermo IRIS Intrepid II XSP spectrometer. The ultraviolet-visible absorption spectra were measured by FL2000 spectrophotometer from Shimadzu Corporation of Japan.

## Section 3: X-ray collection and structure determination

Crystallographic measurements were taken on a Bruker APEX-II diffractometer with an CCD detector using graphite-monochromatic Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 296 K. The determination of the unit cell and data collection for both crystals of both materials was performed with CrysAlisPro. The data reduction was carried out with Bruker SAINT. The data sets were corrected by empirical absorption correction using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm. The structure of both materials were determined by direct methods and refined by the full-matrix least-squares method with the SHELX-2013 program package. All non-hydrogen atoms were located successfully from Fourier maps and were refined anisotropically. The H atoms on the ligands were placed in idealized positions and refined using a riding model. The amino units of ligands are disordered, which are split into four parts during structural refinement. The disordered lattice DMF could not be located successfully from Fourier maps in the refinement cycles. The scattering from the highly disordered lattice guest molecules were removed using the SQUEEZE procedure implemented in the PLATON package. Crystallographic data are summarized in Table S1.

## Section 4: Fluorescence titrations measurements

The fluorescence properties of MOFs were investigated in the solid state and in various solvent emulsions at room temperature. In typical experimental setup, 0.5, 1.0, or 1.5 mg of Eu(BDC-NH<sub>2</sub>) was weighed and added to cuvette containing 2 mL of organic solvents and then ultrasonically dispersed. The emission spectra of Eu(BDC-NH<sub>2</sub>) suspension were in-situ measured after incremental addition of water. After the addition of water, the cuvette was sealed to isolate the water in surrounding air and emission spectra were recorded instantly. The suspension was stirred at constant rate during experiment to maintain homogeneity. The luminescence signal stability of the suspension was confirmed using the luminescence spectra at different times.

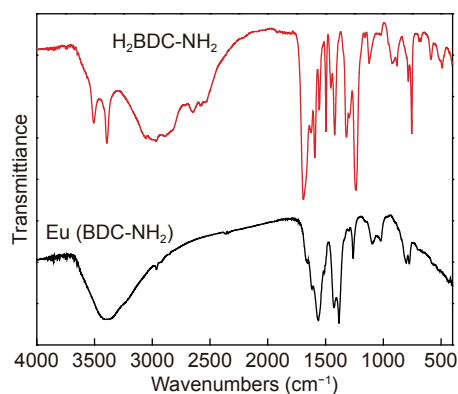
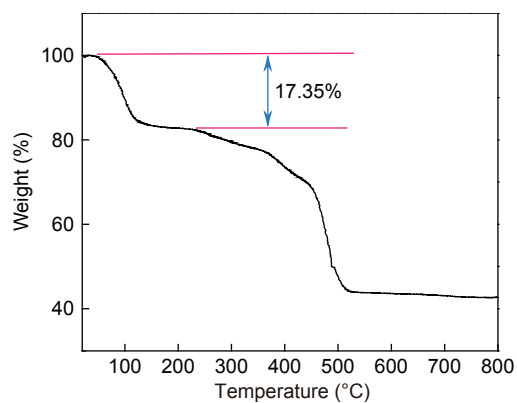
## Section 5: Table S1

Table S1 | Crystallographic data collection and refinement result for Eu(BDC-NH<sub>2</sub>).

Eu(BDC-NH <sub>2</sub> )	
Chemical formula	C <sub>67</sub> H <sub>101</sub> Eu <sub>6</sub> N <sub>13</sub> O <sub>43</sub>
Formula weight	2688.39
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system	Cubic
Space group	<i>Fm</i> $\bar{3}$ <i>m</i>
Unit cell dimensions (Å, deg.)	$a = b = c = 21.7579(3)$ $\alpha = \beta = \gamma = 90$
<i>V</i> (Å <sup>3</sup> )	10300.3(4)
<i>Z</i>	4
Density (calculated g·cm <sup>-3</sup> )	1.418
Absorbance coefficient (mm <sup>-1</sup> )	3.663
<i>F</i> (000)	4120
Crystal size (mm <sup>3</sup> )	0.2 × 0.2 × 0.2
<i>R</i> (int)	0.0444
Goodness of fit on <i>F</i> <sub>2</sub>	1.234
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )] <sup>a)</sup>	0.0328, 0.1034
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data) <sup>a)</sup>	0.0391, 0.1082
Largest difference peak and hole (e Å <sup>-3</sup> )	1.116, -0.745

<sup>a)</sup> $R_1 = \sum(|F_o| - |F_c|) / \sum|F_o|$ ;  $wR_2 = [\sum w(|F_o| - |F_c|)^2] / \sum wF_o^2^{1/2}$ .

## Section 6: Figures S1–S21

Fig. S1 | FT-IR spectra of H<sub>2</sub>BDC-NH<sub>2</sub> and Eu(BDC-NH<sub>2</sub>).Fig. S2 | The TGA curve of Eu(BDC-NH<sub>2</sub>).

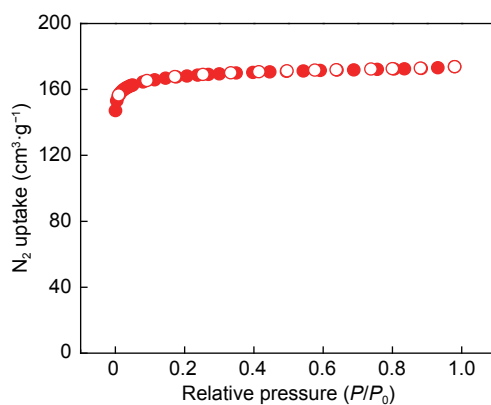


Fig. S3 |  $N_2$  sorption isotherms of methanol-exchanged  $\text{Eu}(\text{BDC-NH}_2)$  at 77 K. Solid symbols: adsorption, open symbols: desorption

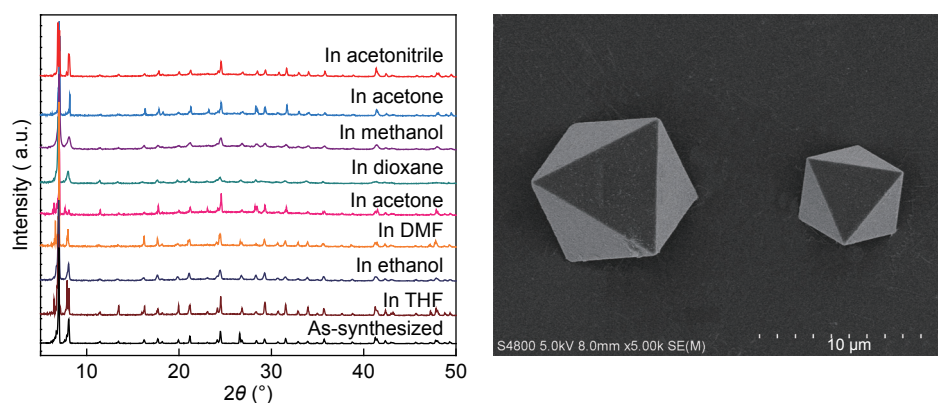


Fig. S4 | (a) Powder X-ray diffraction patterns of  $\text{Eu}(\text{BDC-NH}_2)$  samples treated with various organic solvents at room temperature for 48 h. (b) The SEM imaged of Ln-MOFs materials.

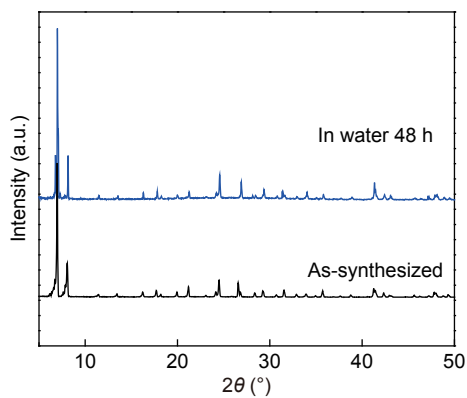


Fig. S5 | Powder X-ray diffraction patterns of  $\text{Eu}(\text{BDC-NH}_2)$  samples soaked in water at room temperature for 48 h.

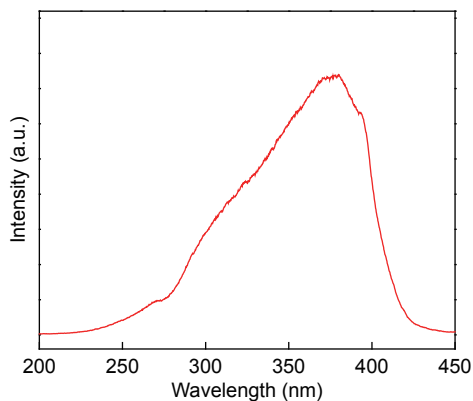


Fig. S6 | Excitation spectrum of solid-state Eu(BDC-NH<sub>2</sub>) monitored at 614 nm.

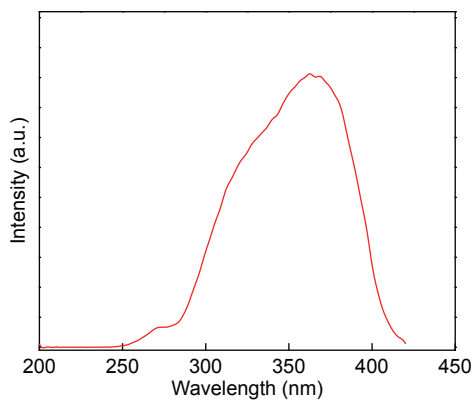


Fig. S7 | Excitation spectrum of Eu(BDC-NH<sub>2</sub>) suspended in THF monitored at 614 nm.

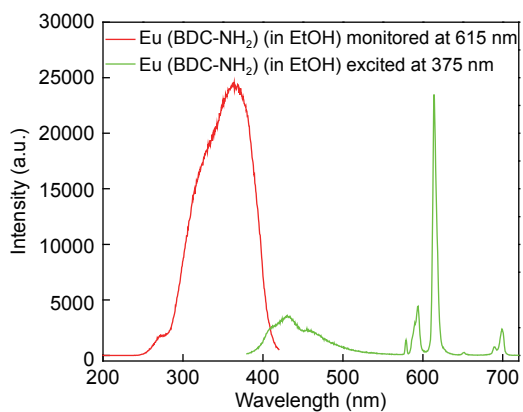


Fig. S8 | Excitation and emission spectra of Eu(BDC-NH<sub>2</sub>) suspended in EtOH.

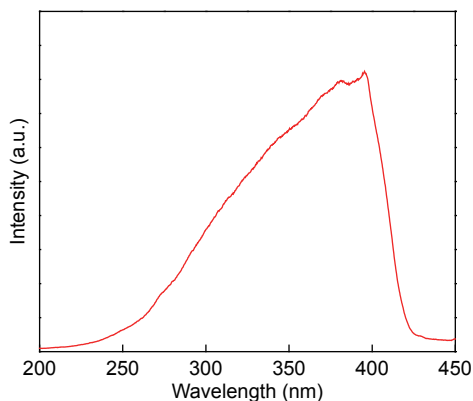


Fig. S9 | Excitation spectra of solid-state Tb(BDC-NH<sub>2</sub>) monitored at 544 nm.

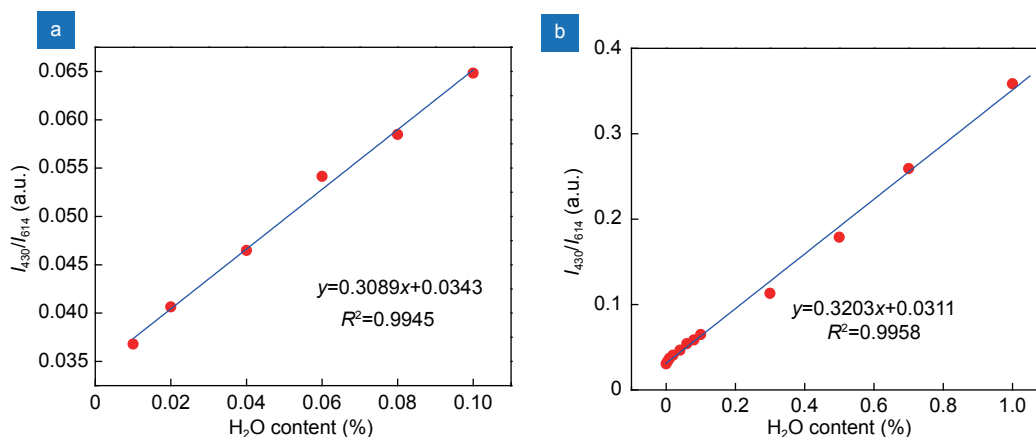


Fig. S10 | The relationship of luminescence intensity ratio ( $I_{430}/I_{614}$ ) and water content in the range of 0–0.1 vol% and 0–1 vol% in THF.

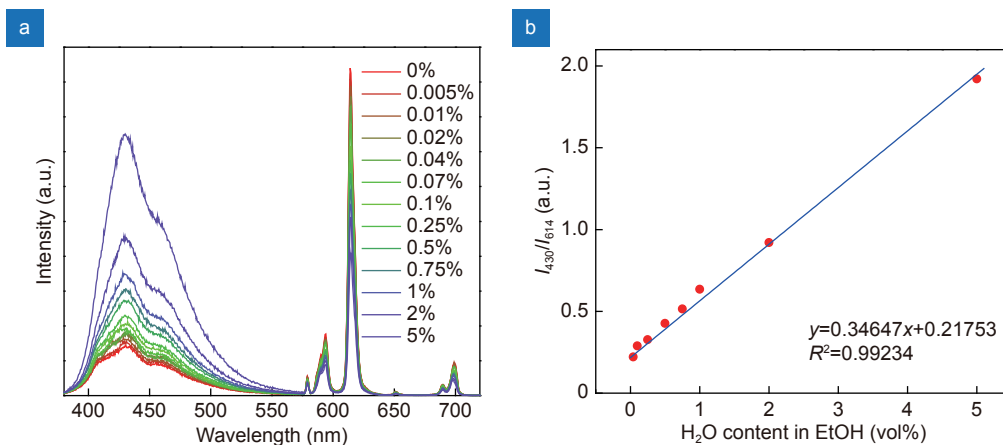
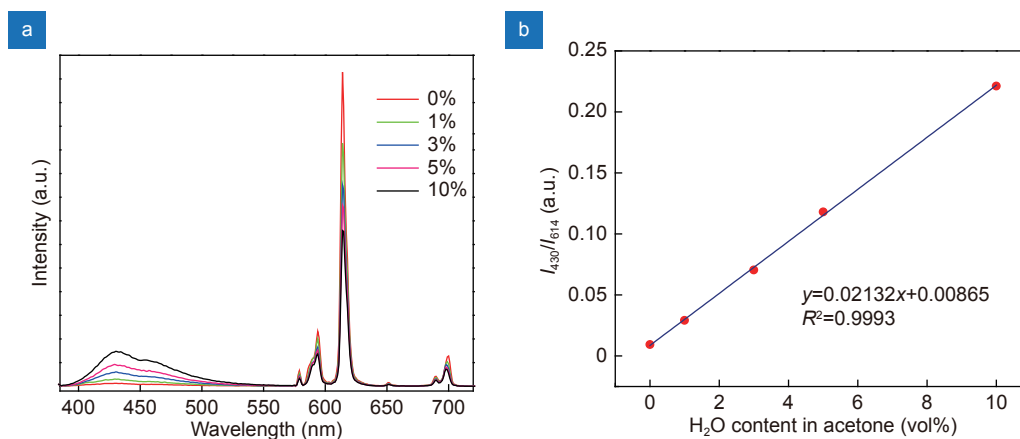
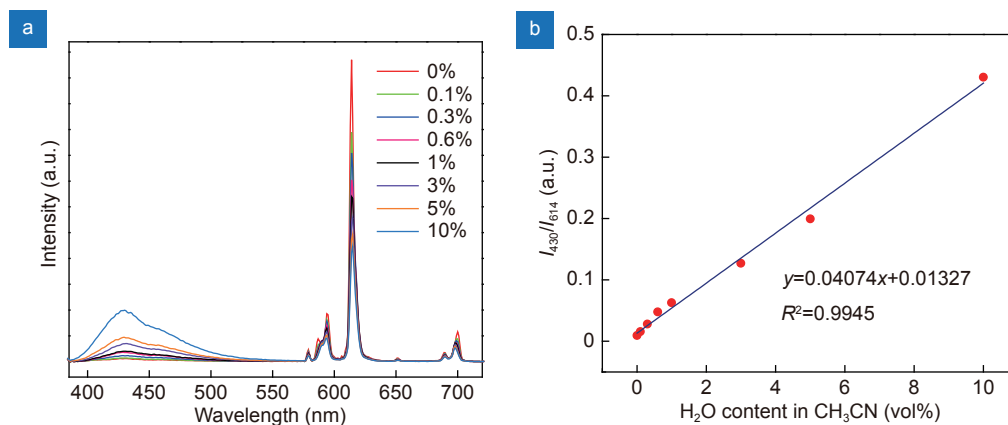


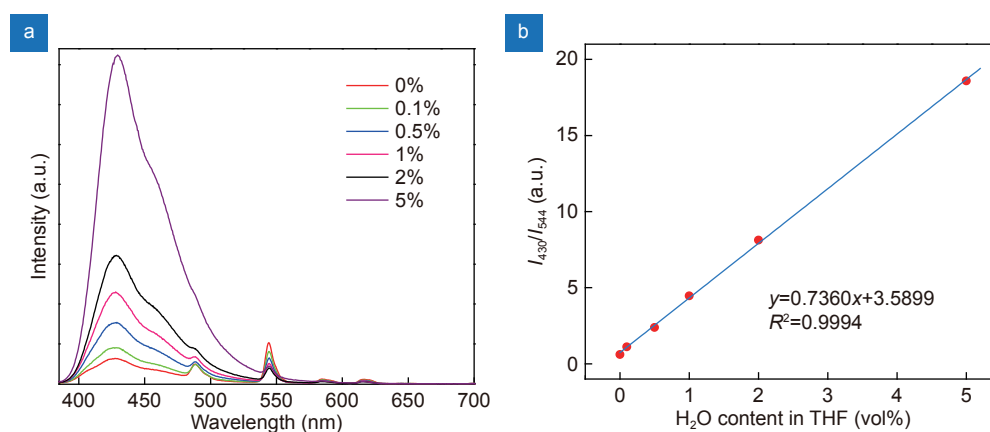
Fig. S11 | (a) Emission spectra of Eu(BDC-NH<sub>2</sub>) suspended in EtOH with different water content excited at 375 nm. (b) The relationship of luminescence intensity ratio ( $I_{430}/I_{614}$ ) and water content in EtOH.



**Fig. S12** | (a) Emission spectra of Eu(BDC-NH<sub>2</sub>) suspended in acetone with different water content excited at 375 nm. (b) The relationship of luminescence intensity ratio ( $I_{430}/I_{614}$ ) and water content in acetone.



**Fig. S13** | (a) Emission spectra of Eu(BDC-NH<sub>2</sub>) suspended in CH<sub>3</sub>CN with different water content excited at 375 nm. (b) The relationship of luminescence intensity ratio ( $I_{430}/I_{614}$ ) and water content in CH<sub>3</sub>CN.



**Fig. S14** | (a) Emission spectra of Tb(BDC-NH<sub>2</sub>) suspended in THF with different water content excited at 380 nm. (b) The relationship of luminescence intensity ratio ( $I_{430}/I_{544}$ ) and water content in THF.

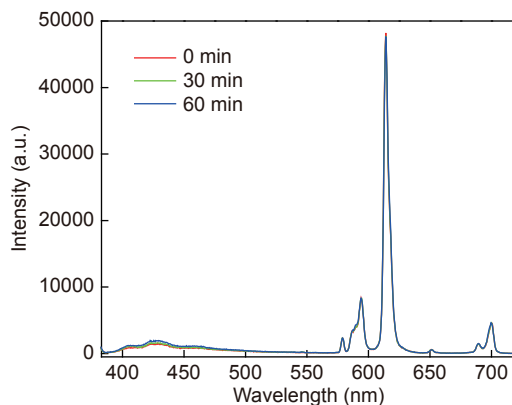


Fig. S15 | The emission spectra of Eu(BDC-NH<sub>2</sub>) suspended in THF recorded at different times.

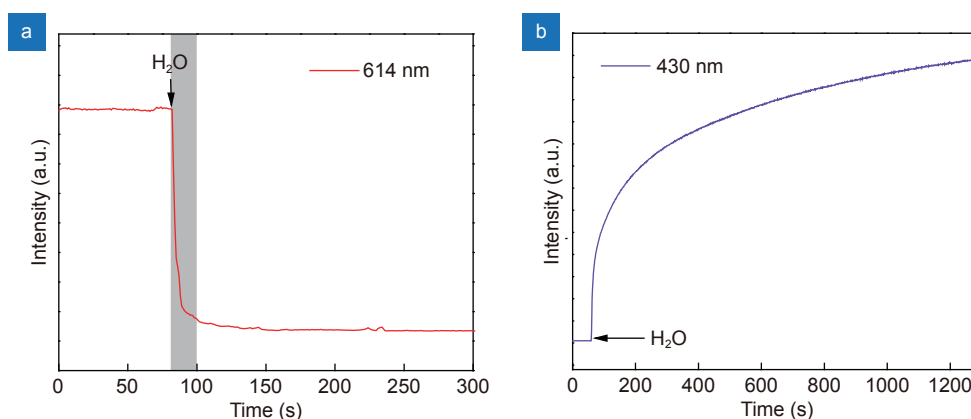


Fig. S16 | Response time of two emission peaks (614 nm and 430 nm) toward water in Eu(BDC-NH<sub>2</sub>) suspension.

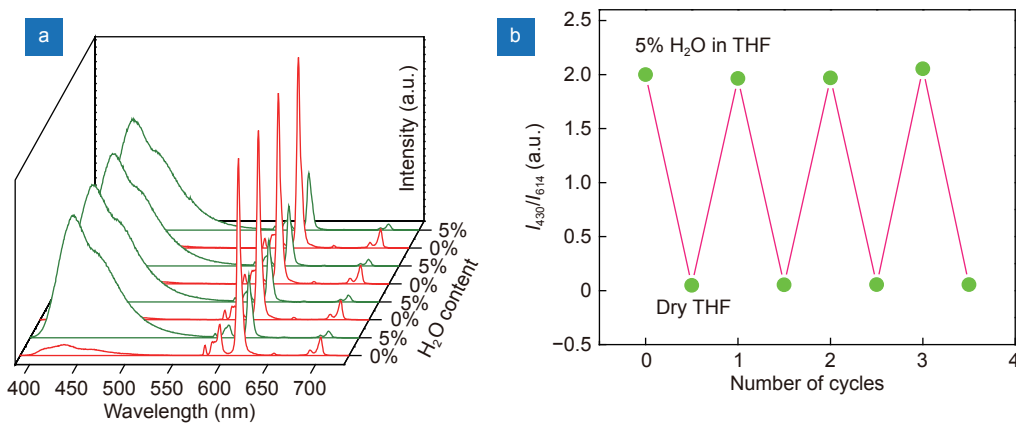


Fig. S17 | Reusability test of Eu(BDC-NH<sub>2</sub>) for the detection of trace water in THF. The lower symbols represent the initial luminescent intensity ratio in dry THF and the upper symbols represent the intensity ratio in THF/H<sub>2</sub>O mixture with 5 vol% water, respectively.



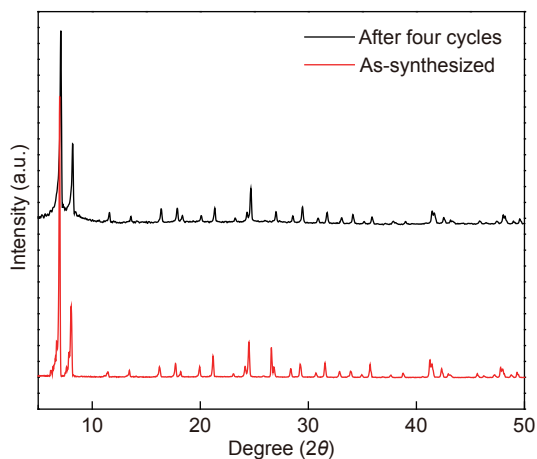


Fig. S18 | PXRD pattern of Eu(BDC-NH<sub>2</sub>) after four detection cycles.

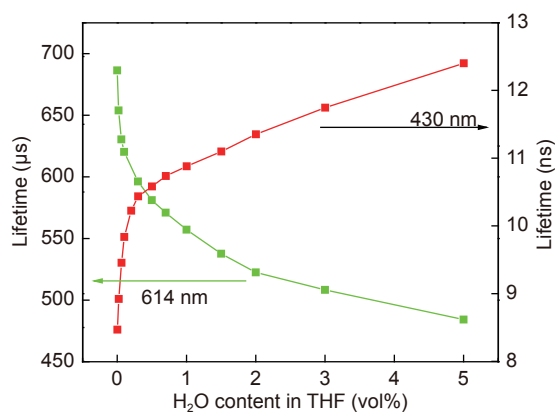


Fig. S19 | Fluorescence lifetime of <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>2</sub> transition (Eu<sup>3+</sup>, 614 nm) and ligand emission (430 nm) of Eu(BDC-NH<sub>2</sub>) at different water content in THF.

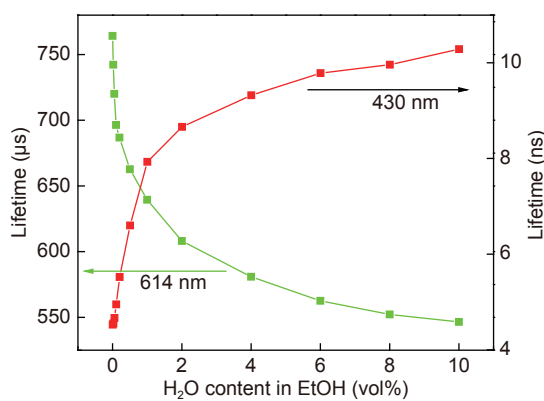
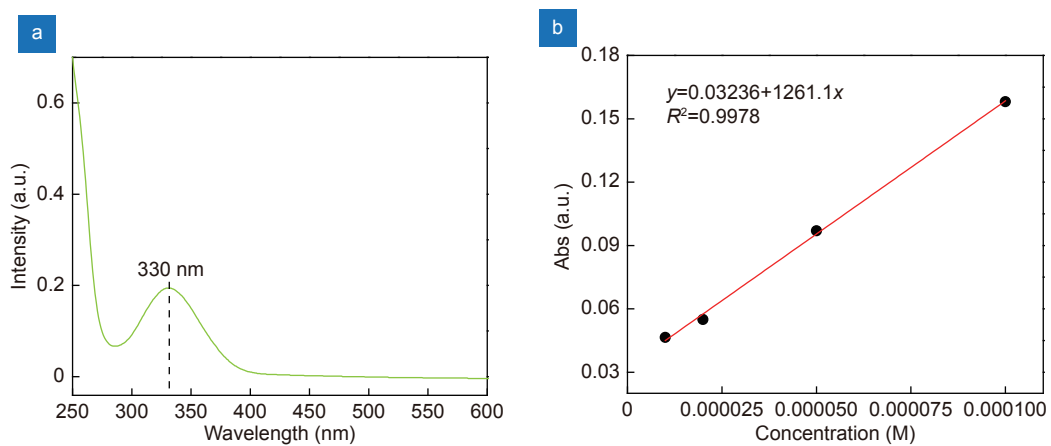


Fig. S20 | Fluorescence lifetime of <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>2</sub> transition (Eu<sup>3+</sup>, 614 nm) and ligand emission (430 nm) of Eu(BDC-NH<sub>2</sub>) at different water content in EtOH.



**Fig. S21** | (a) UV absorption spectrum ( $2 \times 10^{-4}$  mol·L<sup>-1</sup>) and (b) standard curve of H<sub>2</sub>BDC-NH<sub>2</sub> in water.