

Supporting Information

A hetero-MOF-based bifunctional ratiometric fluorescence sensor for pH and water detection

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Experimental

Materials and methods

The reagent and organic solvents were purchased from commercial sources. The organic solvents were distilled to remove water. Ionic liquid 1-butyl-3-methylimidazole iodide liquid ([BMI]I) was synthesized from reactions of 1-butyl iodine with 1-methylimidazole according to literature processes.^{1,2} Degassed 1-butyl iodine was refluxed with distilled 1-methylimidazole to give the [BMI]I. [BMI]I was washed with ethyl acetate and then dried under a vacuum for at least 10 h to give [BMI]I as a brown oil. The test paper Whatman 1# for paper-based sensors was used directly without further treatment.

PXRD data for the samples were collected at ambient temperature with a Rigaku MiniFlex 600 (Japan) diffractometer (Cu-K $\alpha_{1,2}$ X-radiation, $\lambda_1 = 1.540598 \text{ \AA}$ and $\lambda_2 = 1.544426 \text{ \AA}$), equipped with an X'Celerator detector and a flat plate sample holder in a Bragg-Brentano para-focusing optics configuration (40 kV, 15 mA). Intensity data were collected by the step counting method (step being 0.02°) in the continuous mode in the 2θ range of $5\text{-}60^\circ$. Fluorescence spectra were acquired on a Hitachi F-4600 fluorescence spectrophotometer with the excitation and emission slits set to 2.5 nm. The fluorescent decay curves of Eu³⁺ and Tb³⁺ in **3** were analyzed by an Edinburgh FLS 920 fluorescence spectrophotometer with a 150 W microsecond pulsed lamp as the excitation source. The quantum efficiencies of **1-3** were measured on the same a fluorescence spectrophotometer. Energy-dispersive X-ray spectroscopy (EDS) was carried on SEM (Philips-FEI Quanta 200, America). Elemental analyses of C and H were carried out on a Vario EL III elemental analyzer. FT-IR spectra

were collected from KBr pellets (Aldrich, >99%, FT-IR grade) with a Bruker Tensor 27 FT-IR spectrometer in the range of 4000-400 cm^{-1} .

Synthesis

[Eu(OBA)(H₂O)Cl] (1). 1.5 mmol $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (0.5496 g) and 0.25 mmol H_2OBA (0.0646 g) were placed in a crystallisation vial placed in a 25 mL teflon-lined stainless-steel autoclave mixed with 0.8 mL [BMI]I. The mixture was kept in a furnace at 160 °C for 1 day, and then cooled to ambient temperature. Colorless crystals suitable for X-ray diffraction were collected after clearing with ethanol. Yield based on H_2OBA : 0.0776 g, 67.58%. Elemental analysis (%), Found (calcd): C, 36.37 (36.42); H, 2.423 (2.183). FT-IR data (in KBr, cm^{-1}) for **1**: 3352(s), 1927(w), 1597(m), 1535(m), 1392(m), 1303(w), 1261(m), 1163(m), 1097(w), 1010(w), 883(w), 854(w), 783(m), 692(w), 555(w), 501(w).

[Tb(OBA)(H₂O)Cl] (2). Colorless crystals of **2** were obtained in a similar process to **1** with the same amount of substances of $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$, H_2OBA and [BMI]I as **1**. Yield based on H_2OBA : 0.0713 g, 61.12%. Elemental analysis (%), Found (calcd): C, 35.07 (35.88); H, 2.356 (2.151). FT-IR data (in KBr, cm^{-1}) for **2**: 3369(s), 3213(w), 3078(m), 2358(m), 2337(w), 1936(w), 1631(m), 1598(s), 1529(s), 1409(s), 1309(m), 1259(s), 1166(m), 1097(w), 1012(w), 885(m), 858(m), 781(s), 690(m), 651(s), 624(m), 559(m), 501(m), 414(m).

[Eu_{0.05}Tb_{0.95}(OBA)(H₂O)Cl] (3). The preparation process of **3** is as same as **1** with mixed $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (0.075 mmol, 0.0275 g), $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ (1.425 mmol, 0.5321 g) and 0.25 mmol H_2OBA (0.0646 g) in 0.8 mL [BMI]I. Yellow powder was collected after washing with ethanol. Yield based on H_2OBA : 0.0745 g, 63.92%. Elemental analysis (%), Found (calcd): C, 35.76 (35.91); H, 2.354 (2.153). FT-IR data (in KBr, cm^{-1}) for **3**: 3373(s), 3213(w), 3078(w), 1936(w), 1633(w), 1599(m), 1527(s), 1406(s), 1311(w), 1257(s), 1166(m), 1097(w), 1012(w), 970(w), 885(w), 858(w), 779(s), 692(m), 650(w), 625(w), 559(w), 499(m).

Crystal Structure Determination

Single crystal of **1** was manually harvested from crystallisation vials and mounted on Hampton Research CryoLoops using FOMBLIN Y perfluoropolyether vacuum oil with the help of a Stemi 2000 stereomicroscope equipped with Carl Zeiss lenses. Data was collected on a XtaLAB Synergy R, HyPix diffractometer (Rigaku Oxford diffraction) equipped with a PhotonJet R (Cu) X-ray radiation source ($\lambda = 1.54184 \text{ \AA}$) at 179.99(10) K by the ω scan measurement method and reduced by

CrysAlisPro 1.171.40.19a (Rigaku OD, 2018) program. The crystal structure of **1** was refined by ShelXL-2014/7 and solved by direct method using ShelXS-2014/7 of crystallographic software and refined by full-matrix least-squares technique on F^2 .³ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located at geometrically calculated positions to their carrier atoms and refined with isotropic thermal parameters included in the final stage of the refinement.

Crystallographic data (excluding structure factors) for **1** reported in this paper has been deposited with the Cambridge Crystallographic Data Centre (the deposition CCDC number: 2027427). The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Fluorescence measurement of **3** in different solvents.

2 mg **3** was dispersed into 2 mL eleven kinds of solvents respectively, including tetrahydrofuran (THF), carbon tetrachloride (CCl₄), cyclohexane, dimethylformamide (DMF), 1,4-dioxane, chloroform, N,N-dimethylacetamide (DMAC), isopropanol, ethanol, methanol and water. After 1 min vibration, the above suspensions were immediately transferred to 4 mL cuvettes for fluorescence measurement.

pH detection

2 mg **3** was dispersed into 2 mL HCl or NaOH aqueous solutions with pH ranging 1-13, vibrating for 1 min, then immediately transferred to a 4 mL cuvette for fluorescence measurement.

Detection of water content in DMF.

2 mg **3** was dispersed in DMF solutions with different water contents (v/v %, V_{H₂O}%). After vibrating for 1 min, the suspension was immediately transferred to a 4 mL cuvette for fluorescence measurement.

Preparation of paper-based sensors.

Test paper Whatman 1# was cut into small discs with a diameter of 0.5 cm. 5 mg **3** was dispersed in a 5 mL absolute ethanol, then vibrated for 1 minute, next the test paper was immersed in the solution for 10 min, finally the test paper was dried in an oven at 60 °C to obtain paper-based sensors.

Table S1. EDS analysis of **3**.

Compound	Element	At%1	At%2	At%3	Average At%	Average
3	EuL	00.21	00.05	00.21	0.47	1:18.55

Table S2. The structural determination and refinement data for **1**.

Empirical formula	$C_{14}H_{10}ClEuO_6$
Color and Habit	Colorless platelet
Crystal Size (mm^3)	$0.22 \times 0.20 \times 0.06$
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	15.35720(10)
b (Å)	11.16410(10)
c (Å)	8.40850(10)
β (°)	97.7260(10)
V (Å ³)	1428.54(2)
Z	4
F_w	461.63
D_{calcd} (Mg·m ⁻³)	2.146
μ (mm ⁻¹)	33.413
$F(000)$	888
θ (°)	2.904 to 75.990
Reflections measured	11560
Independent reflections	2864 [$R_{int} = 0.0258$]
Final R_1 , wR_2 indices (obs.)	$R_1 = 0.0185$, $wR_2 = 0.0465$
R_1 , wR_2 indices (all)	$R_1 = 0.0210$, $wR_2 = 0.0476$
S	1.010
$(\Delta\rho)_{max/min}$ (e·Å ⁻³)	0.949/-0.464

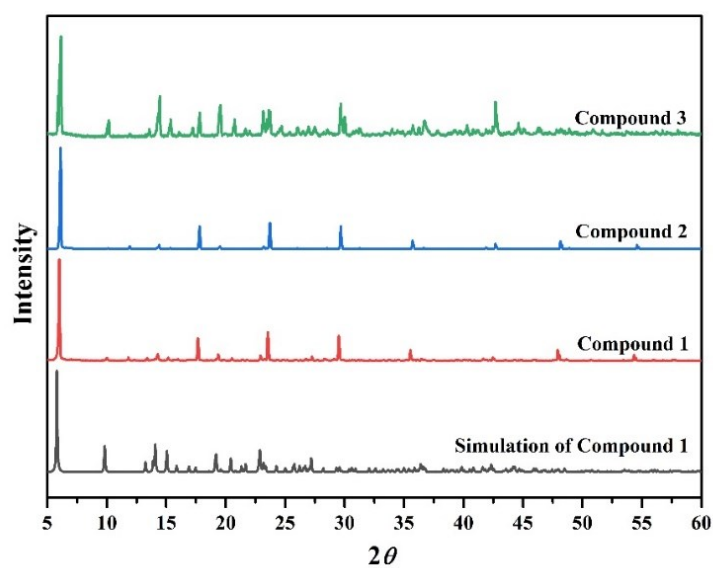


Fig. S1. Simulated and experimental PXRD patterns of **1-3**.

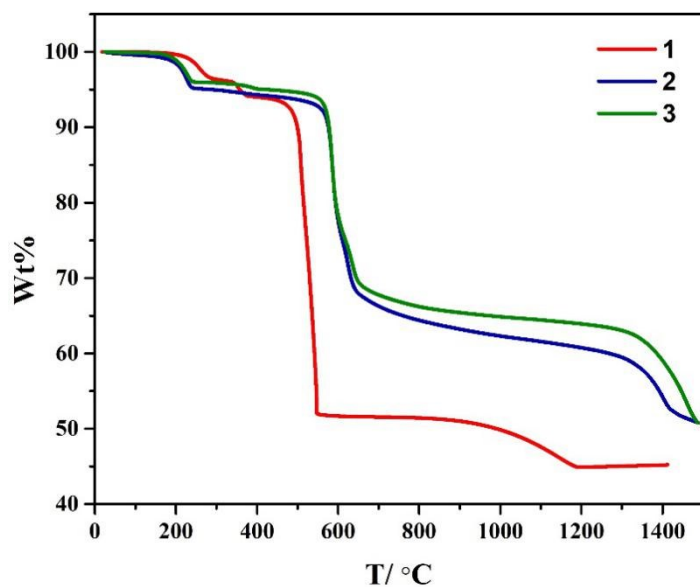


Fig. S2. TG curves of 1-3.

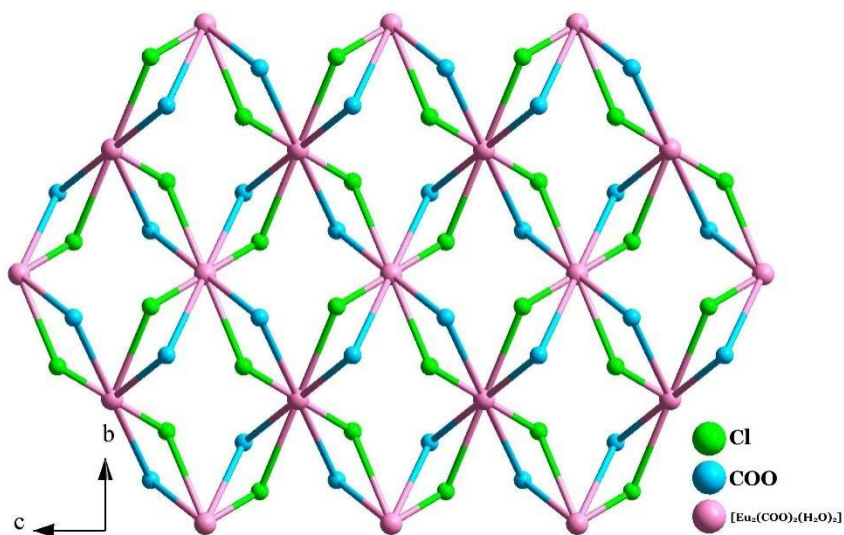


Fig. S3. The topological $\{4^4.8^{16}.12^8\} \{4\}_4$ 2D layer in 1.

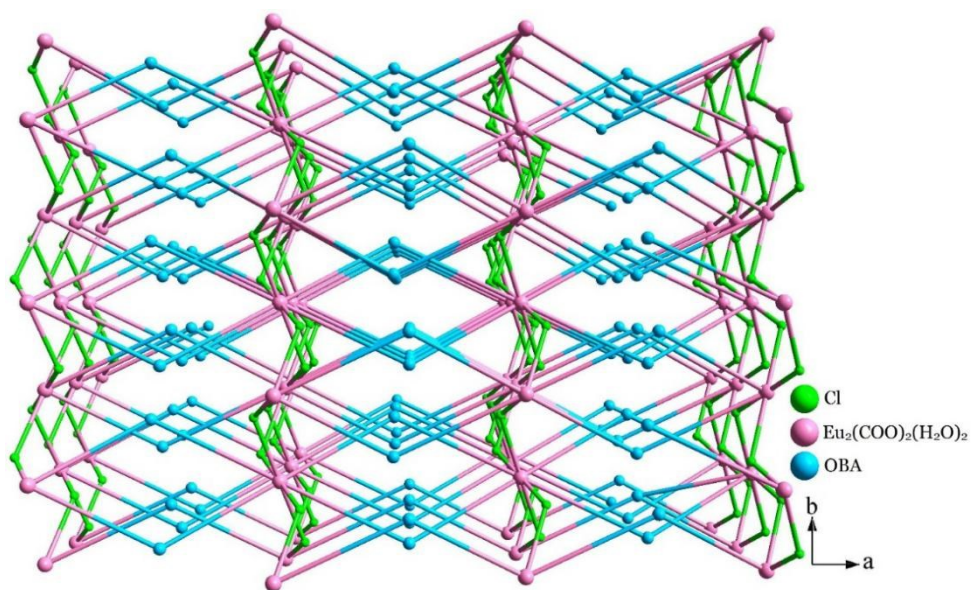


Fig. S4. The topological 2,2,8-connected 3-nodal $\{4^2.8^{20}.12^6\} \{4\}_2 \{8\}_2$ network in 1.

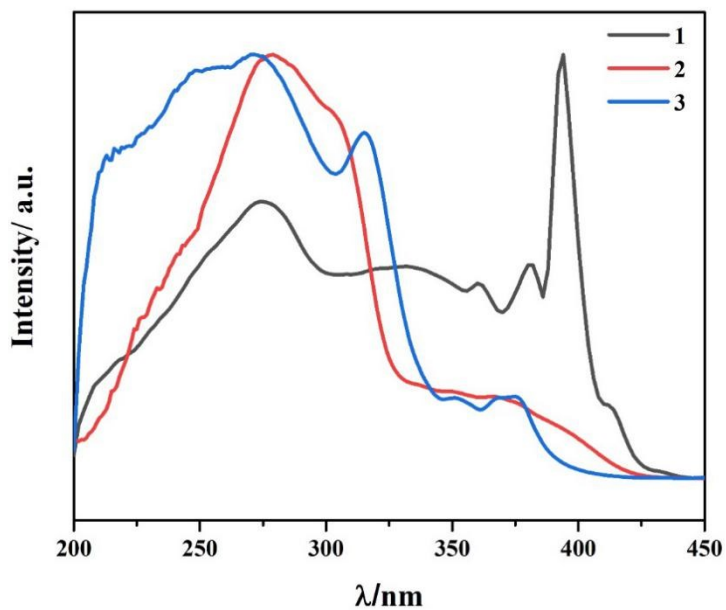


Fig. S5. The excitation spectra of 1-3.

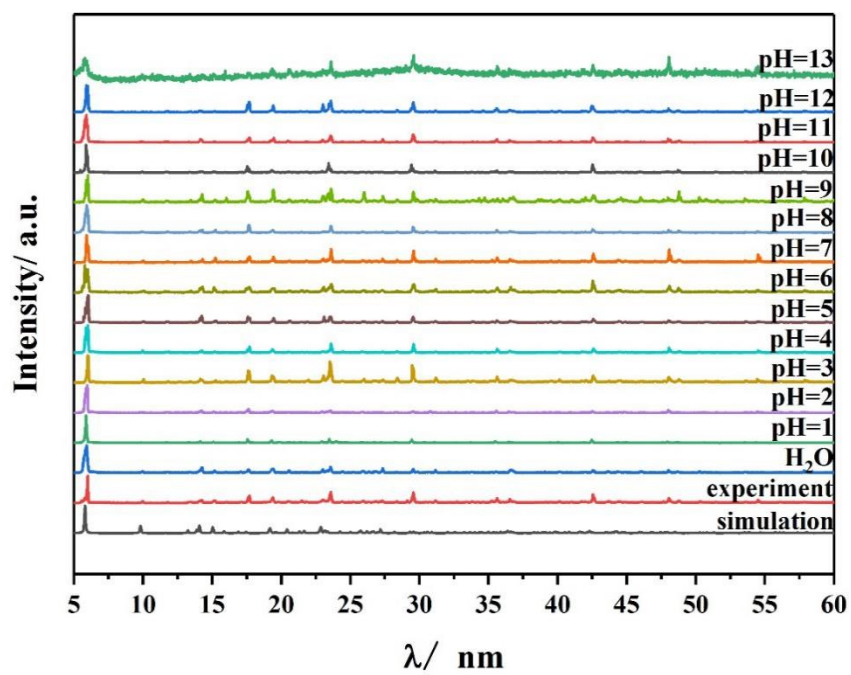


Fig. S6. PXRD patterns of 3 immersed in HCl or NaOH solutions with pH = 1-13 for 2 h.

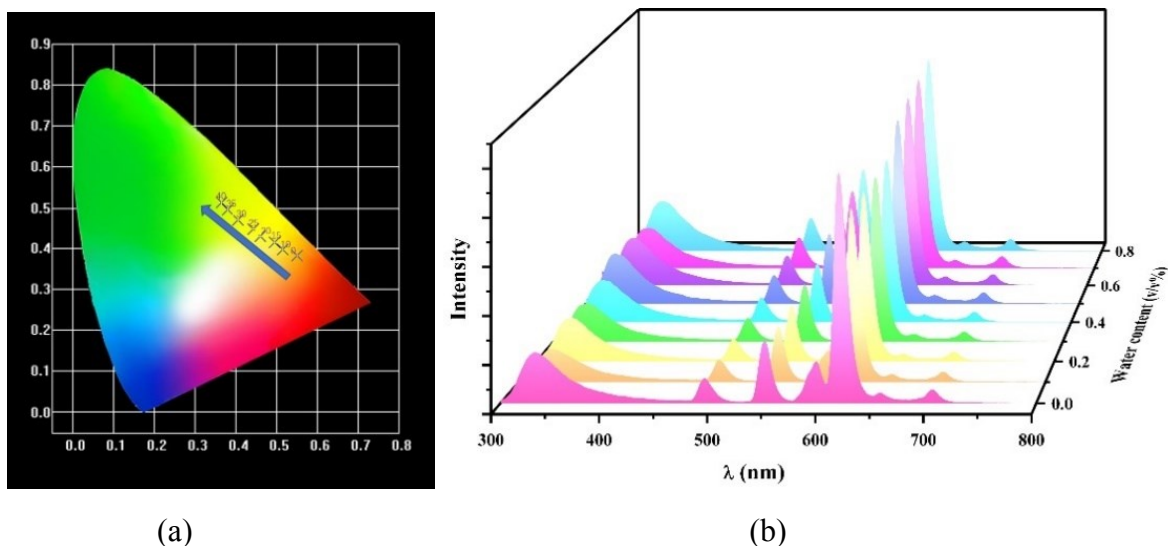


Fig. S7. (a) The CIE 1931 chromaticity diagram of **3** with water content ranging 0-40%; (b) the emission spectra of **3** in DMF solution with 0-0.8% water.

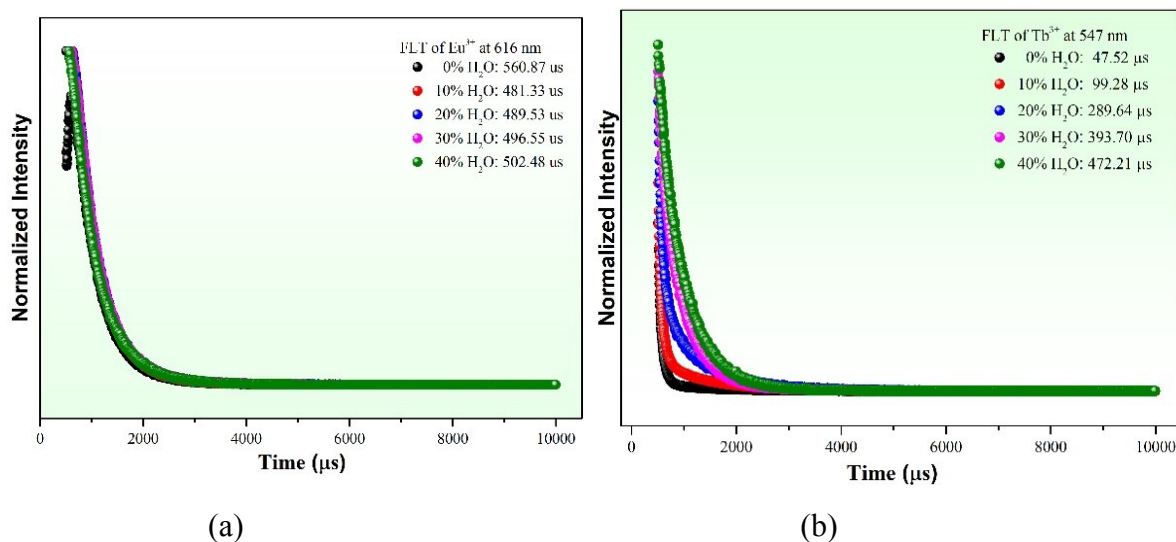


Fig. S8. Fluorescence lifetimes of the emissions at 616 nm (a) and 547 nm (b) in **3** with water content ranging 0-40%.

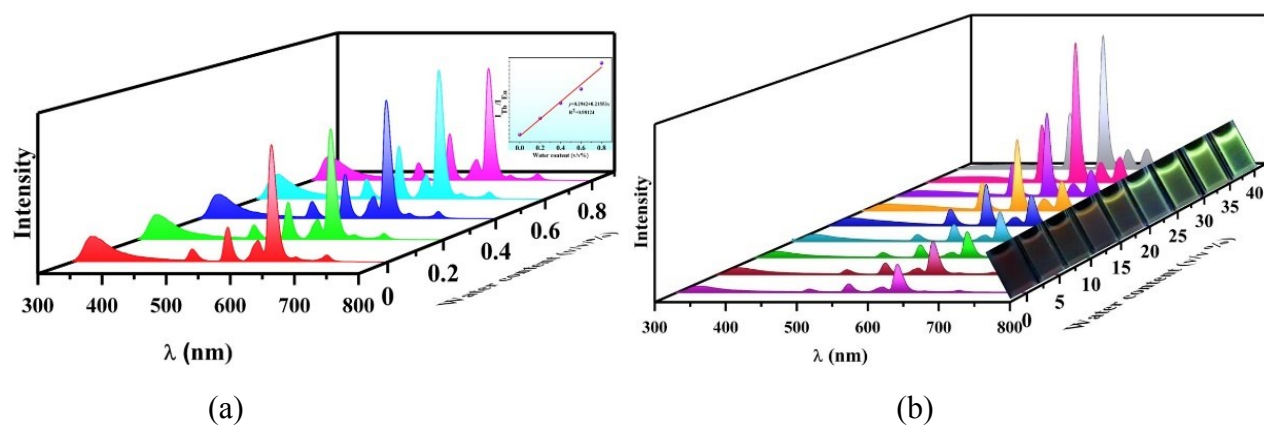


Fig. S9. (a) The emission spectra of **3** in DMAC solution with 0-0.8% and (b) 1-40% water content (inset: photos of emission colors taken under 254 nm UV lamp).

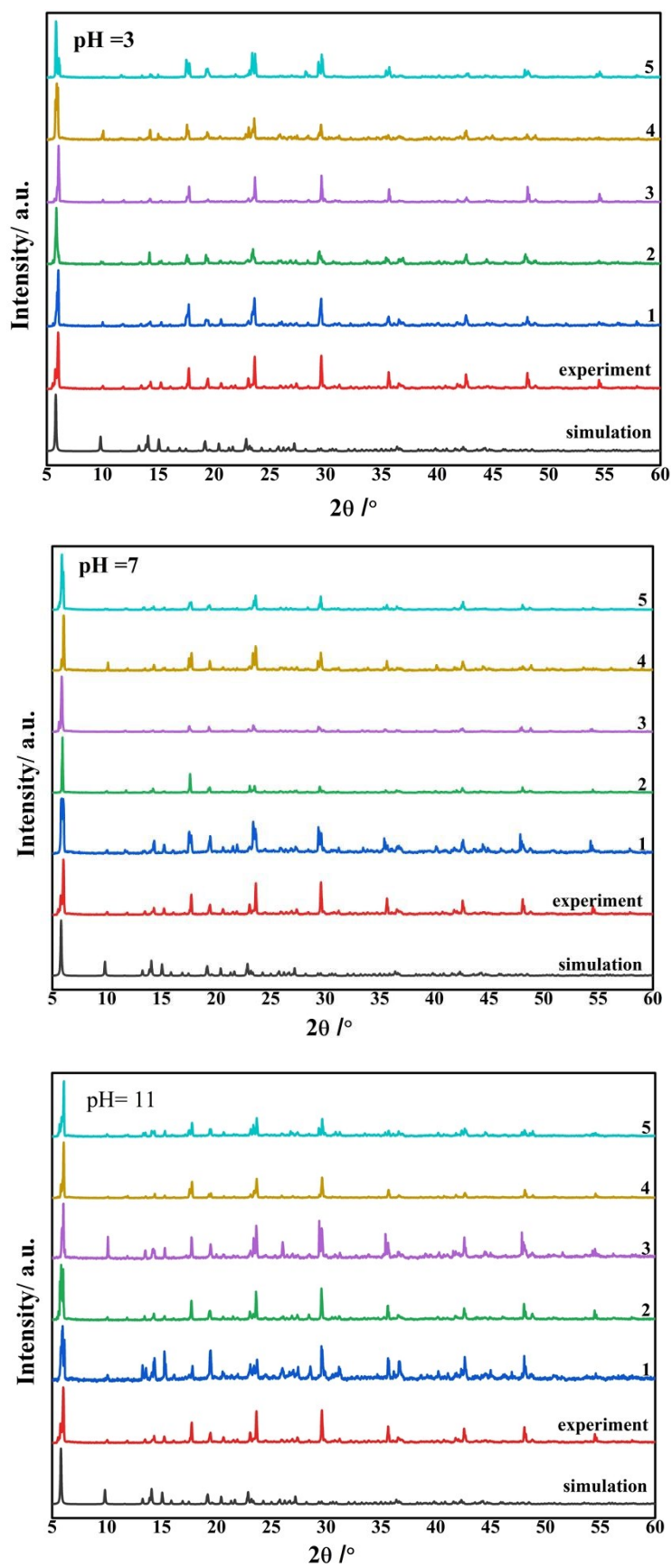


Fig. S10. The PXRD patterns of **3** after five detection cycles at pH = 3, 7, and 11.

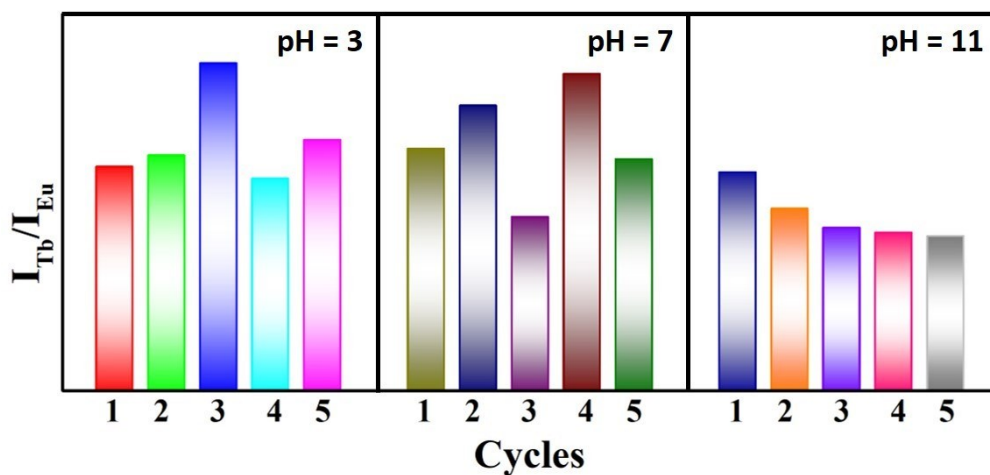


Fig. S11. The relative emission intensities I_{Tb}/I_{Eu} of **3** for five detection cycles.

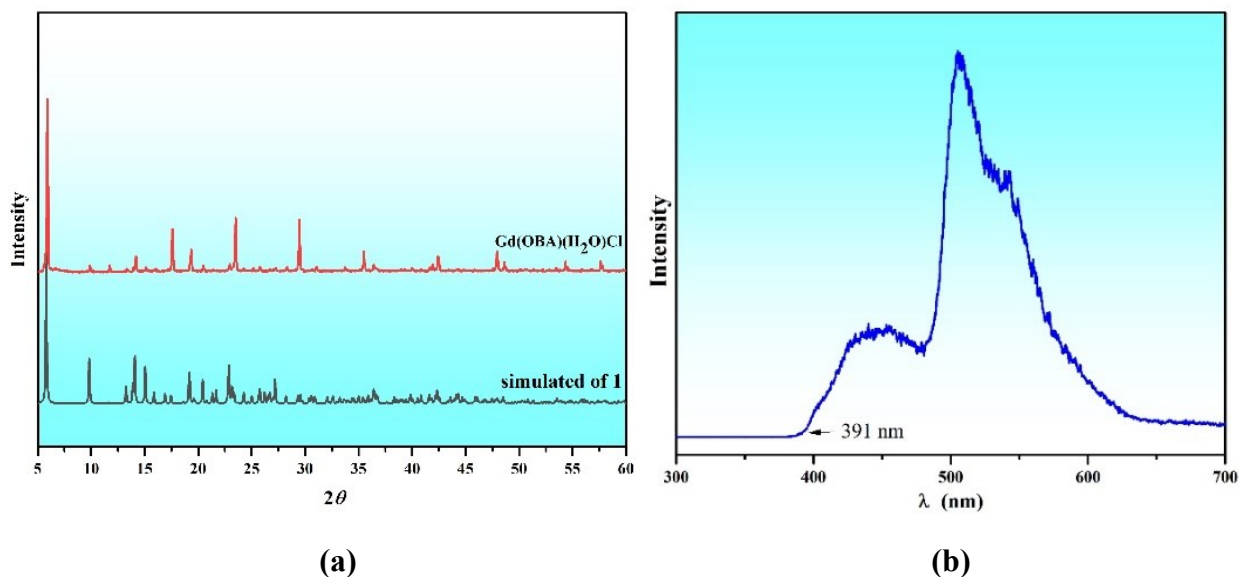


Fig. S12. (a) The PXRD pattern of $[Gd(OBA)(H_2O)Cl]$ compared to **1**; (b) the low-temperature phosphorescence spectrum of $[Gd(OBA)(H_2O)Cl]$ excited at 270 nm at 77 K.

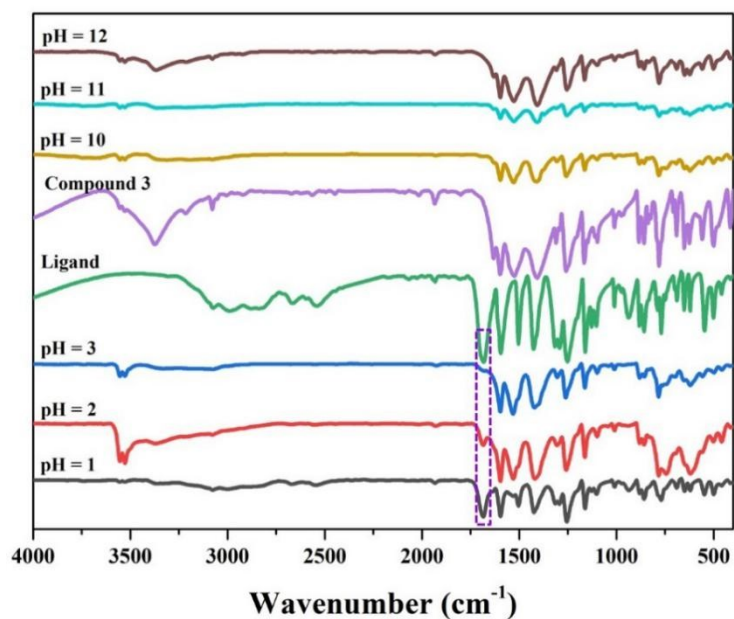


Fig. S13. FT- IR spectra of free H₂OBA, **3** and **3** immersed in HCl and NaOH solutions with pH = 1-3 and 10-12.

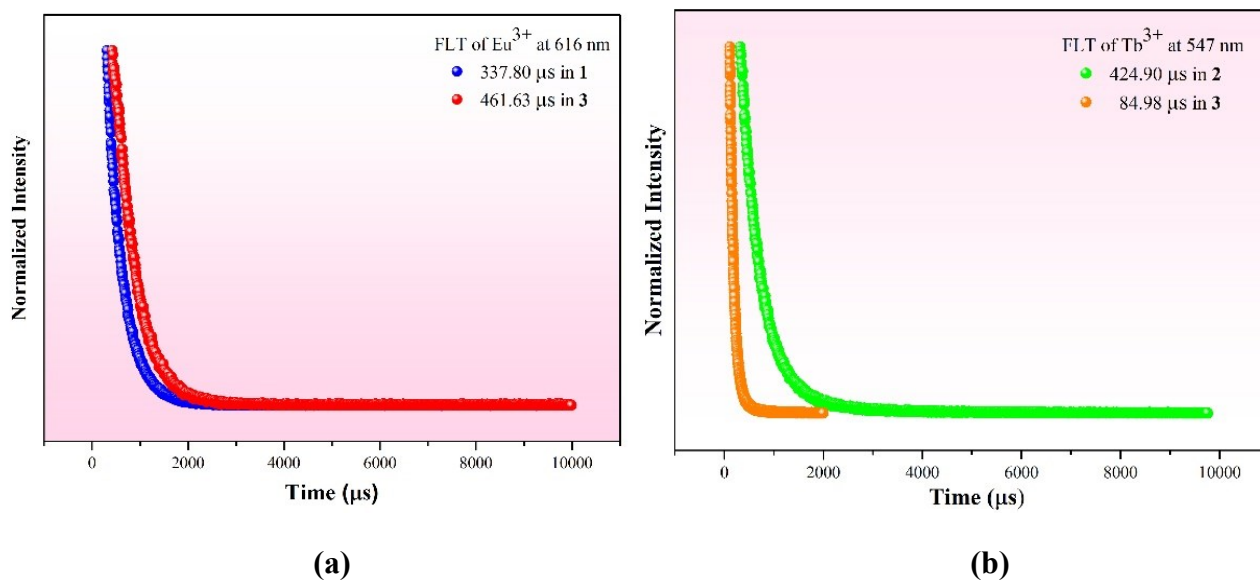


Fig. S14. Fluorescence lifetimes of the emissions ${}^5D_0 \rightarrow {}^7F_2$ of Eu^{3+} at 616 nm in **1** and **3** (a) and ${}^5D_4 \rightarrow {}^7F_5$ of Tb^{3+} at 547 nm in **2** and **3** (b).

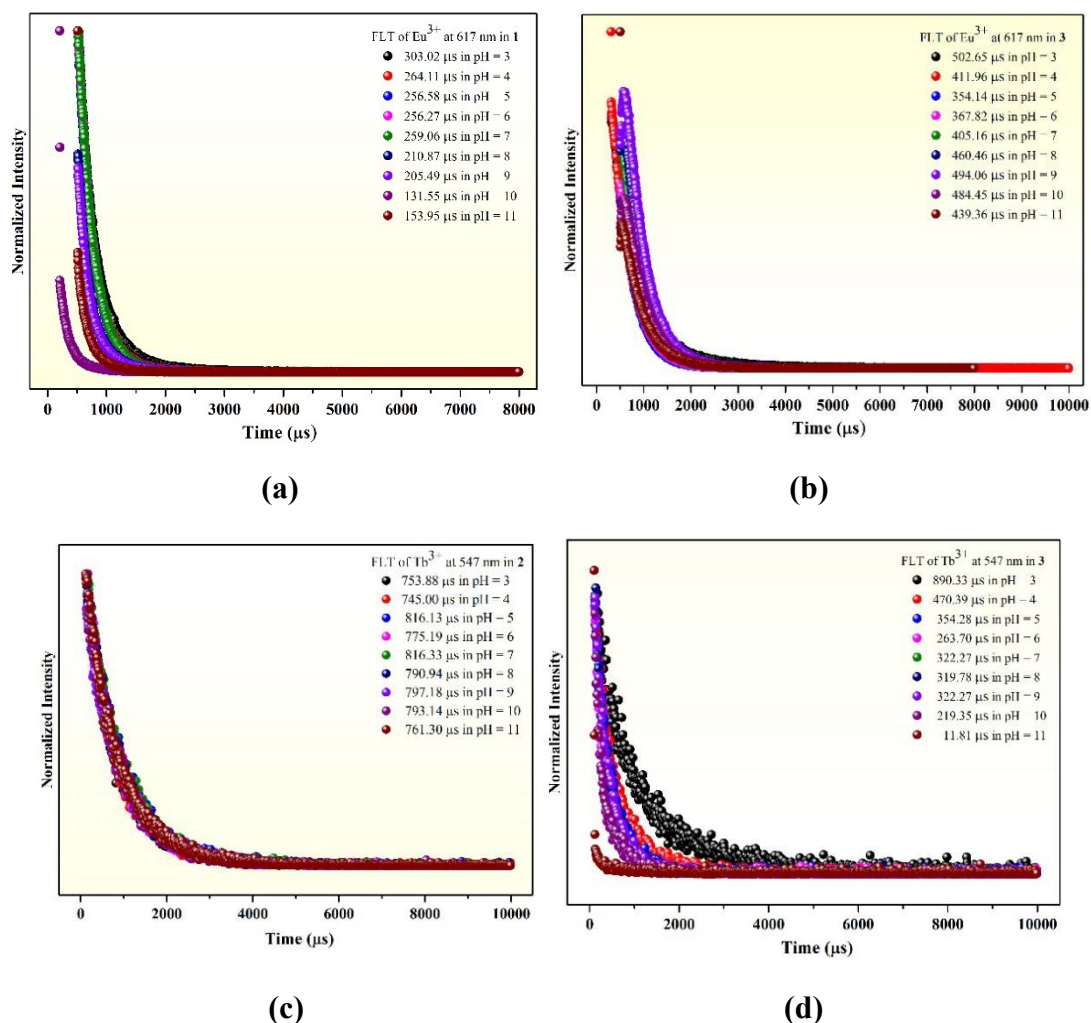


Fig. S15. Fluorescence lifetimes of the emissions ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ of Eu^{3+} at 616 nm in **1** and **3** (a and b) and ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$ of Tb^{3+} at 547 nm in **2** and **3** (c and d) as pH = 3-11.

References

1. E. R. Parnham and R. E. Morris, 1-alkyl-3-methyl imidazolium bromide ionic liquids in the ionothermal synthesis of aluminium phosphate molecular sieves, *Chem. Mater.*, 2006, **18**, 4882-4887.
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