

*Supporting Information for*  
**A multi-responsive luminescent Co(II) coordination polymer  
assembled from amide-functionalized organic units for  
effective pH and cation sensing**

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## Materials and characterization.

The ligand H<sub>4</sub>L was synthesized according to the reference [reference: H. Mehenni, H. Guillou, C. Tessier, J. Brisson, *Canadian Journal of Chemistry*, 2008, 86, 7-19.]. Other reagents were purchased and used without purity. The FT-IR spectra (4000–400 cm<sup>-1</sup> region) were recorded from KBr pellets with a NICOLET 6700F-IR spectrometer. Elemental analyses of C, H and N were carried out with a vario EL cube elemental analyzer. Powder X-ray diffraction (PXRD) data were collected over the 2θ range of 5–50° using a SmartLab diffractometer with Cu Kα radiation (λ=1.5418 Å) at room temperature. Thermal analyses were performed on STA 449 F5 Jupiter instrument from room temperature to 800°C with a heating rate of 10°C/min under flowing nitrogen. Emission and excitation spectra in solid state as well as time-resolved luminescence were carried out on a FLS1000 spectrophotometer analyzer of Edinburgh instruments. Luminescence sensing properties were recorded on the Hitachi F-7000 Luminescence spectrophotometer. X-ray photoelectron spectroscopy (XPS) characterization was carried out by using a Thermo Fisher Scientific ESCALAB Xi+ spectrometer with Al Kα X-rays (1486.6 eV) as the light source. UV-vis measurements were conducted with a UH 4150 spectrophotometer. The EDS mapping were recorded with FIB Helios G4.

## Synthesis of the Tb<sup>3+</sup>@LCU-112.

20 mg samples of LCU-112 were immersed in Tb<sup>3+</sup> aqueous solutions (10<sup>-3</sup> M, 10 mL) for three days. The post-synthesized sample of Tb<sup>3+</sup>@LCU-112 was obtained after filtration.

## X-ray crystallographic study.

Single-crystal X-ray data for LCU-112 were collected with an Agilent Xcalibur Eos Gemini CCD diffractometer at 293 K with Cu Kα radiation (λ = 1.54184 Å). The raw data frames were integrated into SHELX-format reflection files and corrected using SAINT program. Absorption corrections based on multi-scan were obtained by the SADABS program. The structure was solved with direct methods (SHELXS) and refined with full-matrix least-squares technique using the SHELXL-2018/3 programs. Displacement parameters were refined anisotropically, and the positions of the H-atoms were generated geometrically, assigned isotropic thermal parameters, and allowed to ride on their parent carbon atoms before the final cycle of refinement. Basic information pertaining to crystal parameters and structure refinement is summarized in Table S1. Selected bond lengths and angles are listed in Table S2.

**Table S1.** Crystal and refinement data for LCU-112.

LCU-112			
Empirical formula	C <sub>30</sub> H <sub>29</sub> CoN <sub>10</sub> O <sub>6</sub>	Formula weight	684.56
Temperature/ K	293	Crystal system	triclinic
Space group	$P\bar{1}$	Volume/Å <sup>3</sup>	1468.4(4)
a [Å]	10.7536(17)	$\alpha$ [°]	80.583(14)
b [Å]	11.7485(20)	$\beta$ [°]	79.812(13)
c [Å]	12.140(2)	$\gamma$ [°]	79.016(14)
Z	2	$D_{(\text{calc.})}$ [g/cm <sup>3</sup> ]	1.548
$\mu$ [mm <sup>-1</sup> ]	5.131	$\theta$ range	3.733-67.232
Index ranges	-12 ≤ $h$ ≤ 12	<sup>a</sup> R <sub>1</sub> ; <sup>b</sup> wR <sub>2</sub>	0.0520, 0.1287
	-14 ≤ $k$ ≤ 13	[ $I > 2\sigma(I)$ ]	
	-10 ≤ $l$ ≤ 14	GOF	1.036

$${}^aR_1 = \Sigma |F_o| - |F_c| / \Sigma |F_o|, {}^b wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$$

**Table S2.** Selected bond lengths [Å] and angles [°] for LCU-112.

LCU-112			
Co(1)-N(2)	2.122(3)	Co(1)-N(2) <sup>1</sup>	2.122(3)
Co(1)-N(5) <sup>2</sup>	2.191(3)	Co(1)-N(5) <sup>3</sup>	2.191(3)
Co(1)-O(3)	2.049(2)	Co(1)-O(3) <sup>1</sup>	2.049(2)
Co(2)-N(8) <sup>2</sup>	2.143(3)	Co(2)-N(8) <sup>4</sup>	2.143(3)
Co(2)-O(1)	2.102(2)	Co(2)-O(1) <sup>5</sup>	2.102(2)
Co(2)-O(6) <sup>5</sup>	2.130(2)	Co(2)-O(6)	2.130(2)
N(2)-Co(1)-N(2) <sup>1</sup>	180.00(12)	N(2) <sup>1</sup> -Co(1)-N(5) <sup>2</sup>	88.34(12)
N(2)-Co(1)-N(5) <sup>3</sup>	88.34(12)	N(2)-Co(1)-N(5) <sup>2</sup>	91.66(12)
N(2) <sup>1</sup> -Co(1)-N(5) <sup>3</sup>	91.66(12)	N(5) <sup>3</sup> -Co(1)-N(5) <sup>2</sup>	180.0
O(3)-Co(1)-N(2) <sup>1</sup>	85.98(10)	O(3) <sup>1</sup> -Co(1)-N(2)	85.98(10)
O(3) <sup>1</sup> -Co(1)-N(2) <sup>1</sup>	94.02(10)	O(3)-Co(1)-N(2)	94.02(10)
O(3)-Co(1)-N(5) <sup>3</sup>	95.30(11)	O(3) <sup>1</sup> -Co(1)-N(5) <sup>2</sup>	95.30(11)
O(3) <sup>1</sup> -Co(1)-N(5) <sup>3</sup>	84.70(11)	O(3)-Co(1)-N(5) <sup>2</sup>	84.70(11)
O(3) <sup>1</sup> -Co(1)-O(3)	180.0	N(8) <sup>2</sup> -Co(2)-N(8) <sup>4</sup>	180.0
O(1) <sup>5</sup> -Co(2)-N(8) <sup>2</sup>	91.95(10)	O(1)-Co(2)-O(8) <sup>2</sup>	88.05(10)
O(1) <sup>5</sup> -Co(2)-N(8) <sup>4</sup>	88.05(10)	O(1)-Co(2)-N(8) <sup>4</sup>	91.95(10)

O(1)-Co(2)-O(1) <sup>5</sup>	180.0	O(1) <sup>5</sup> -Co(2)-O(6)	90.95(9)
O(1)-Co(2)-O(6)	89.05(9)	O(1) <sup>5</sup> -Co(2)-O(6) <sup>5</sup>	89.05(9)
O(1)-Co(2)-O(6) <sup>5</sup>	90.95(9)	O(6)-Co(2)-N(8) <sup>4</sup>	89.32(11)
O(6) <sup>5</sup> -Co(2)-N(8) <sup>4</sup>	90.68(11)	O(6) <sup>5</sup> -Co(2)-N(8) <sup>2</sup>	89.32(11)
O(6)-Co(2)-N(8) <sup>2</sup>	90.68(11)	O(6)-Co(2)-O(6) <sup>5</sup>	180.0

Symmetry codes: <sup>1</sup>: -x, 1-y, 1-z. <sup>2</sup>: 1-x, 1-y, 1-z. <sup>3</sup>: -1+x, +y, +z. <sup>4</sup>: -1+x, -1+y, 1+z. <sup>5</sup>: -x, -y, 2-z.

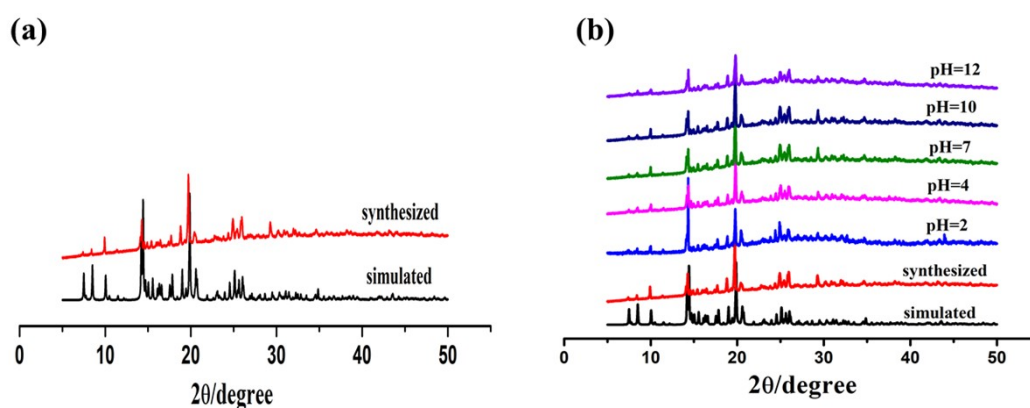
**Table S3.** Comparison of literature reports for CPs/MOFs as sensors for Pb<sup>2+</sup> and Al<sup>3+</sup> detection.

Luminescent material	Analyte	Detection mechanism	$K_{sv}/M^{-1}$	Detection limit	Reference
<b>ZIF-8</b>	Pb <sup>2+</sup>	Turn-off	$5.87 \times 10^4$	13.07 nM	S1
<b>CDs/QDs@ZIF-8</b>	Pb <sup>2+</sup>	Turn-off	$8.46 \times 10^4$	2.35 nM	S1
<b>ZnTCPP-MOF</b>	Pb <sup>2+</sup>	Turn-off	$1.6 \times 10^5$	$2.16 \times 10^{-5}$ M	S2
<b>[Ln<sub>2</sub>(FDC)<sub>3</sub>L(H<sub>2</sub>O)<sub>3</sub>]·4.5H<sub>2</sub>O</b>	Pb <sup>2+</sup>	Turn-on	$2.97 \times 10^3$	$8.22 \times 10^{-6}$ M	S3
<b>Zn (II)-MOF</b>	Pb <sup>2+</sup>	Turn-off	$1.18 \times 10^4$	$8.00 \times 10^{-7}$ M	S4
<b>[Zn(HL)(bipy)<sub>0.5</sub>(H<sub>2</sub>O)]·2H<sub>2</sub>O</b>	Pb <sup>2+</sup>	Turn-off	$1.18 \times 10^4$	0.8 μM	S4
<b>Tb-L</b>	Pb <sup>2+</sup>	Turn-on	----	$3.43 \times 10^{-7}$ M	S5
<b>MIL-101-NH<sub>2</sub></b>	Pb <sup>2+</sup>	Turn-off	2.2714	$5.20 \times 10^{-7}$ M	S6
<b>Tb-MOF</b>	Pb <sup>2+</sup>	Turn-off	$1.75 \times 10^4$	$3.40 \times 10^{-7}$ M	S7
<b>[Tb(L)(H<sub>2</sub>O)<sub>5</sub>]<sub>n</sub>·solvents</b>	Pb <sup>2+</sup>	Turn-off	$1.75 \times 10^4$	$3.4 \times 10^{-7}$ M	S7
<b>{[Tb(dppa)(H<sub>2</sub>O)<sub>2</sub>]·dima·H<sub>2</sub>O·0.5O}<sub>n</sub></b>	Pb <sup>2+</sup>	Turn-on	$8.691 \times 10^3$	0.45 μM	S8

<b>LMOF-263</b>	Pb <sup>2+</sup>	Turn-off	5.5017×10 <sup>4</sup>	19.7 ppb	S9
<b>[Tb(ppda)(npdc)<sub>0.5</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>n</sub></b>	Pb <sup>2+</sup>	Turn-on	1.05×10 <sup>5</sup>	9.44 × 10 <sup>-5</sup> M	S10
<b>[Eu(TTA)<sub>3</sub>(2-pyr)(H<sub>2</sub>O)]</b>	Pb <sup>2+</sup>	Turn-off	2.3×10 <sup>3</sup>	6.03 μM	S11
<b>MOF-5</b>	Pb <sup>2+</sup>	Turn-on	18.58	0.002 μM	S12
<b>Ru(II)@HPU-23</b>	Pb <sup>2+</sup>	Turn-on	----	52.4 nM	S13
<b>{[Zn<sub>2</sub>(1,4-ndc)<sub>2</sub>(3-abpt)]·2DMF}<sub>n</sub></b>	Al <sup>3+</sup>	Turn-on	6.98 × 10 <sup>4</sup>	----	S14
<b>{[Cd(1,4-ndc)(3-abit)]·H<sub>2</sub>O}<sub>n</sub></b>	Al <sup>3+</sup>	Turn-on	3.84 × 10 <sup>4</sup>	----	S14
<b>[Zn<sub>2</sub>(oba)<sub>2</sub>(bpta)]·(DMF)<sub>3</sub><sub>n</sub></b>	Al <sup>3+</sup>	Turn-on	1.40 × 10 <sup>3</sup>	0.0012 mM	S15
<b>Zn(DMA)(TBA)</b>	Al <sup>3+</sup>	Turn-on	1.33 × 10 <sup>4</sup>	1.97 μM	S16
<b>[Co(OBA)(DATZ)<sub>0.5</sub>(H<sub>2</sub>O)]</b>	Al <sup>3+</sup>	Turn-on	----	2.5 μM	S17
<b>{[Zn<sub>2</sub>(OH)(Br-1,4-bdc)<sub>1.5</sub>(Cz-3,6-bpy)]·0.5H<sub>2</sub>O}<sub>n</sub></b>	Al <sup>3+</sup>	Ratiometric Turn-off	5.71 × 10 <sup>3</sup>	0.59 μM	S18
<b>{[Zn<sub>2</sub>(OH)(Br-1,4-bdc)<sub>1.5</sub>(Cz-Pr-3,6-bpy)]·0.5H<sub>2</sub>O}<sub>n</sub></b>	Al <sup>3+</sup>	Ratiometric Turn-off	5.88 × 10 <sup>3</sup>	1.89 μM	S18
<b>[Zn(H<sub>2</sub>dhbdc)(Cz-3,6-bpy)]<sub>n</sub></b>	Al <sup>3+</sup>	Turn-on	4.3 × 10 <sup>3</sup>	0.62 μM	S19
<b>LCU-112</b>	Pb <sup>2+</sup>	Ratiometric Turn-on	3.57×10 <sup>5</sup>	0.1688 μM	this work
<b>LCU-112</b>	Al <sup>3+</sup>	Ratiometric Turn-on	4.11×10 <sup>4</sup>	1.7385 μM	this work

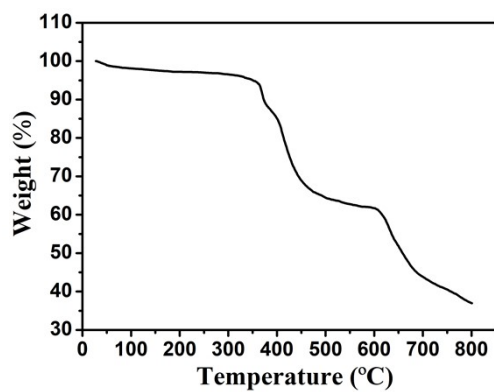
**Table S4.** Comparison of literature reports for CPs/MOFs as sensors for Tb<sup>3+</sup> detection.

Luminescent material	Analyte	Detection mechanism	$K_{sv}/M^{-1}$	Detection limit	Reference
<b>BTC-1</b>	Tb <sup>3+</sup>	Turn-on	----	8 ± 1 ppb	S20
<b>BTC-2</b>	Tb <sup>3+</sup>	Turn-on	----	13 ± 2 ppb	S20
<b>BTC-3</b>	Tb <sup>3+</sup>	Turn-on	----	10 ± 1 ppb	S20
<b>BPDC-1</b>	Tb <sup>3+</sup>	Turn-on	----	8.3 ± 0.8 ppb	S20
<b>BPDC-2</b>	Tb <sup>3+</sup>	Turn-on	----	5.7 ± 0.6 ppb	S20
<b>BPDC-3</b>	Tb <sup>3+</sup>	Turn-on	----	10 ± 2 ppb	S20
<b>BioMOF-100</b>	Tb <sup>3+</sup>	Turn-on	33.09	90 ± 3 ppb	S21
<b>HNU-25</b>	Tb <sup>3+</sup>	Turn-on	----	3 × 10 <sup>-11</sup> M	S22
<b>HNU-26</b>	Tb <sup>3+</sup>	Turn-on	----	2 × 10 <sup>-9</sup> M	S22
<b>CP1</b>	Tb <sup>3+</sup>	Turn-on	----	1.20 nM	S23
<b>LCU-112</b>	Tb <sup>3+</sup>	Turn-on	4.80 × 10 <sup>5</sup>	0.046 μM	this work

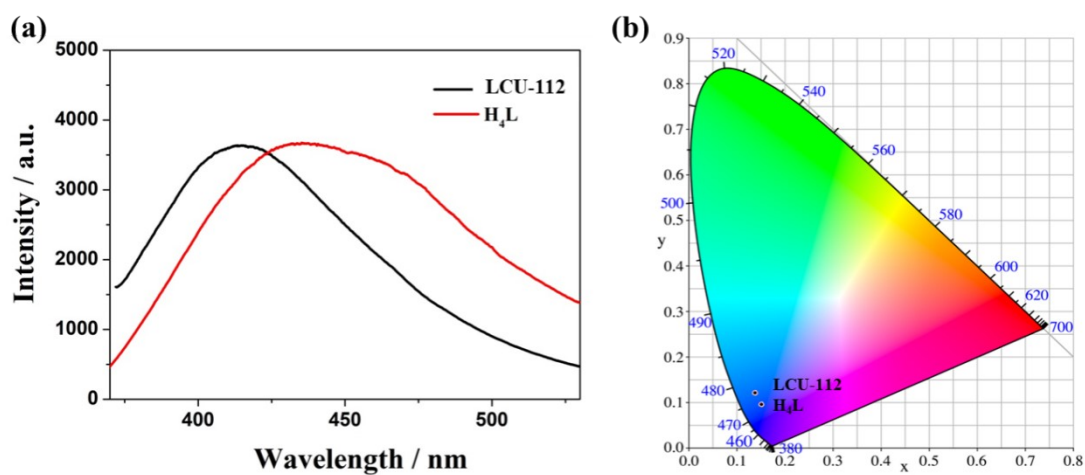


**Fig. S1** (a) PXRD of LCU-112. (b) PXRD of LCU-112 soaked in aqueous solution of different pH for three days.

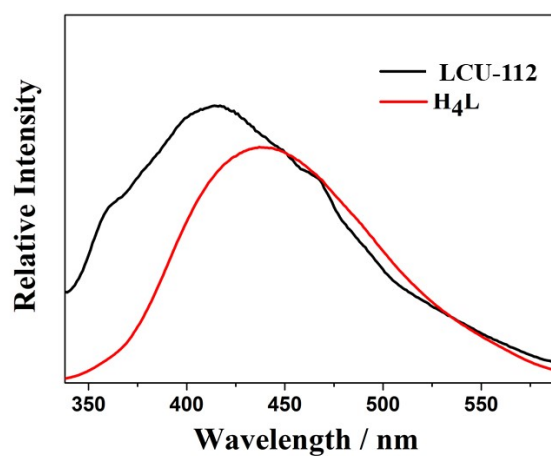




**Fig. S2** TG of LCU-112.



**Fig. S3** (a) The solid-state luminescence spectra of LCU-112. (b) The CIE coordinates of LCU-112 and H<sub>4</sub>L.



**Fig. S4** The emission spectra of LCU-112 and H<sub>4</sub>L in aqueous solution.

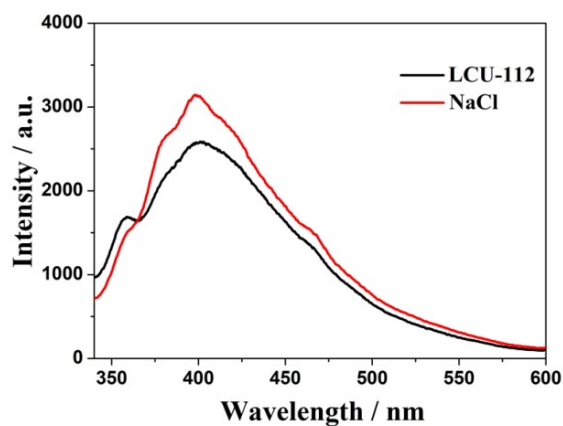


Fig. S5 Luminescence spectra of LCU-112 dispersed in NaCl.

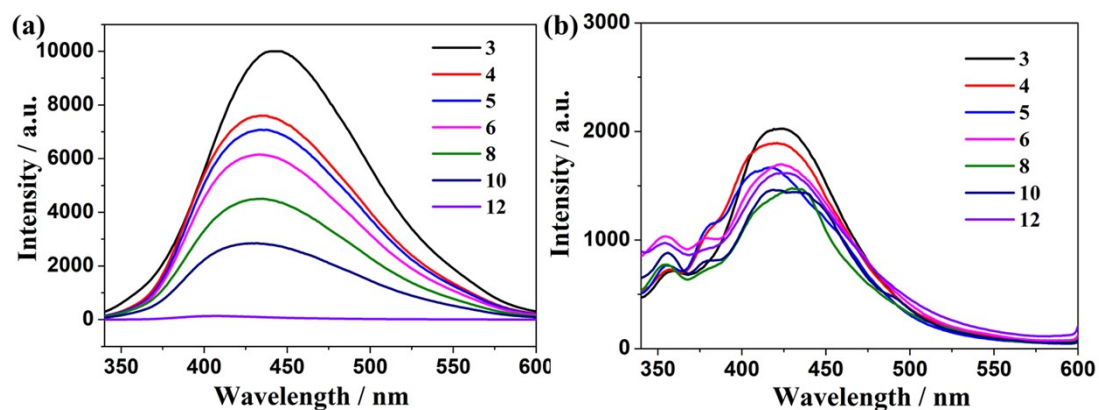


Fig. S6 Luminescence spectra of  $H_4L$  and ttmb at different pH values.

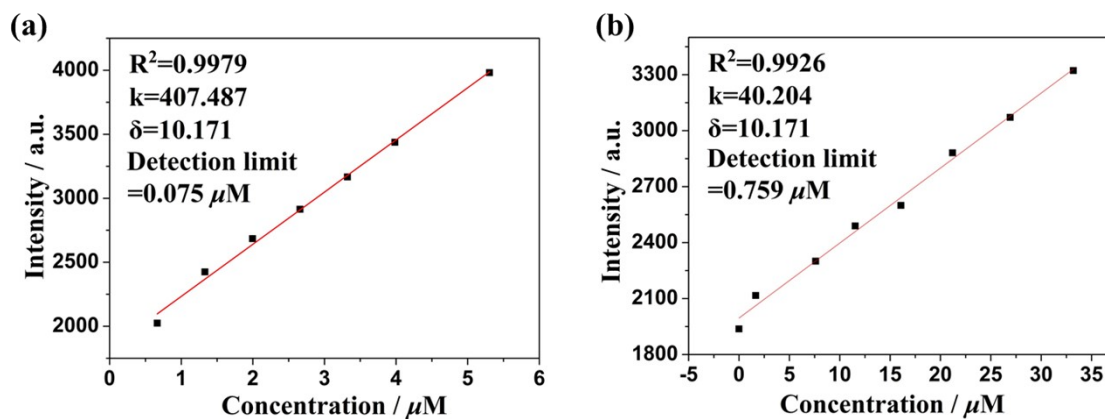
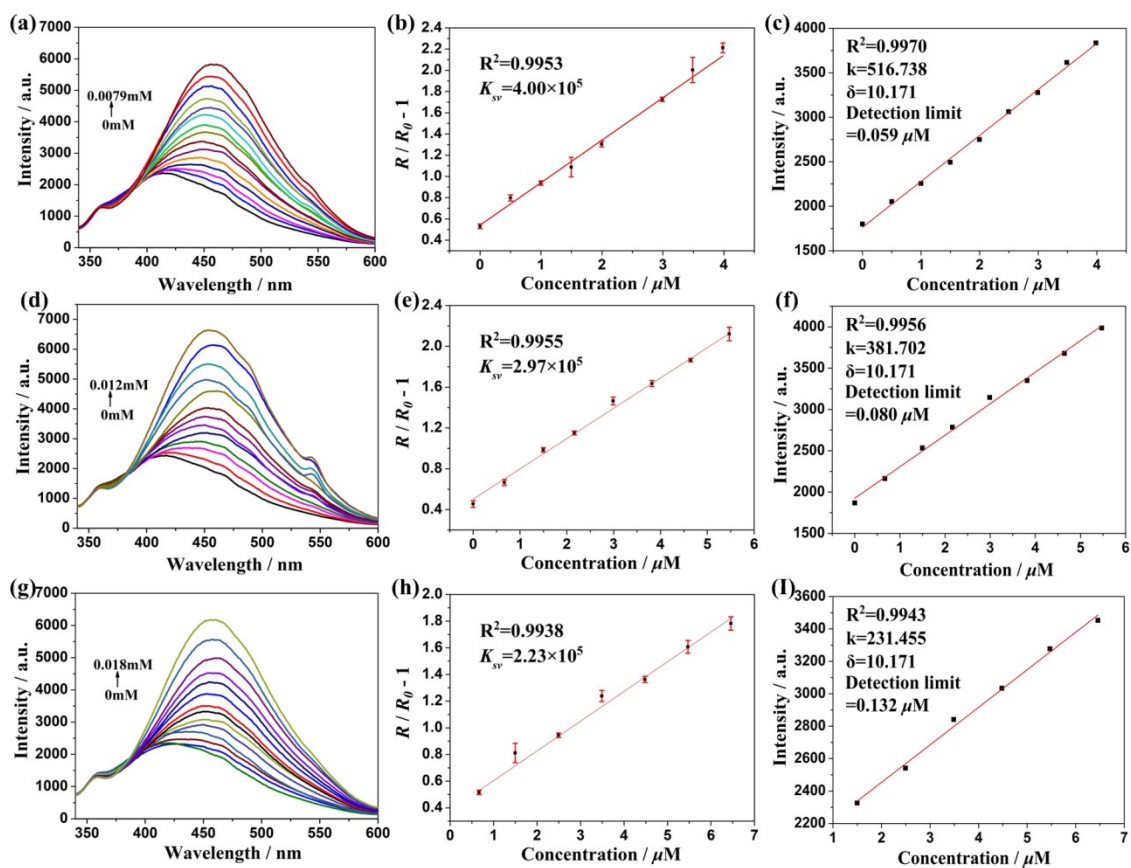
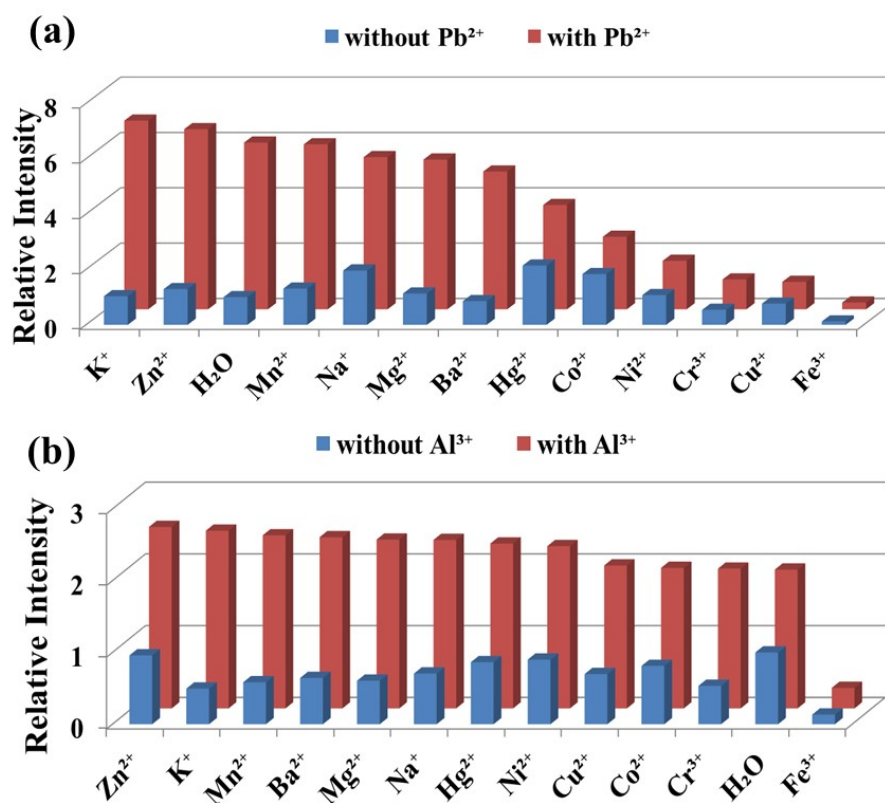


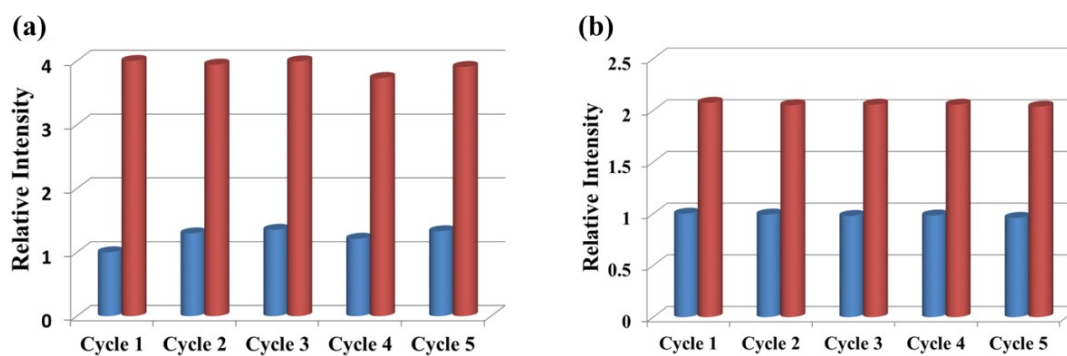
Fig. S7 (a) and (b) The detection limit of LCU-112 toward  $Pb^{2+}$  and  $Al^{3+}$  in aqueous suspensions of LCU-112.



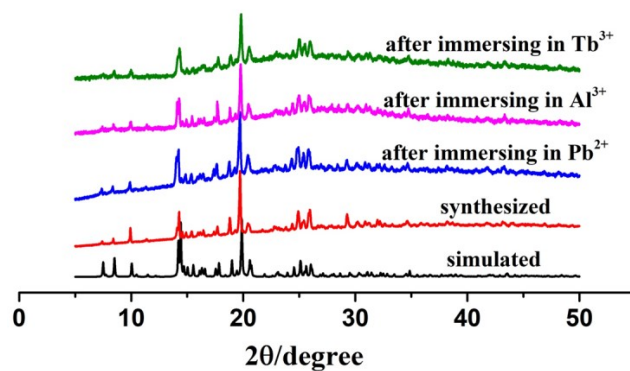
**Fig. S8** (a) (d) (g) Luminescence titration result of LCU-112 toward  $\text{Pb}^{2+}$  at pH = 5, 6, 7. (b) (e) (h) The  $K_{\text{sv}}$  of LCU-112 toward  $\text{Pb}^{2+}$  at pH = 5, 6, 7. (c) (f) (i) The detection limit of LCU-112 toward  $\text{Pb}^{2+}$  at pH = 5, 6, 7.



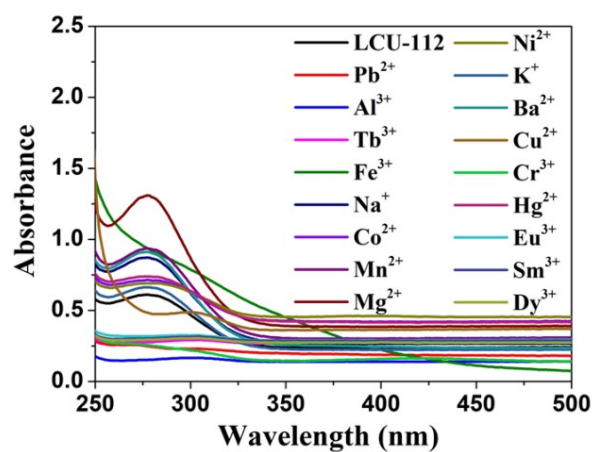
**Fig. S9** (a) and (b) Comparison of luminescence intensity of the chemicals with and without presence of  $Pb^{2+}$  and  $Al^{3+}$  at 415 and 460 nm, respectively.



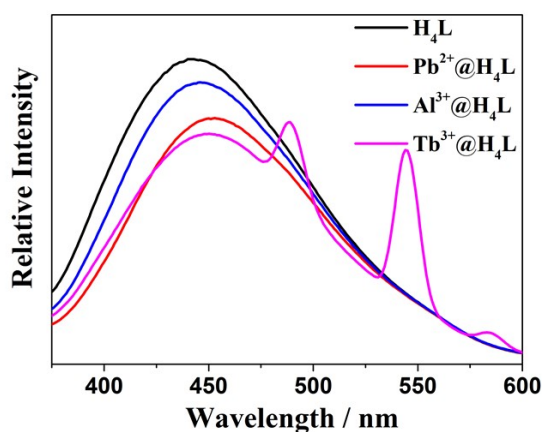
**Fig. S10** (a) and (b) The recycling experimental of  $Pb^{2+}$ ,  $Al^{3+}$  within five runs.



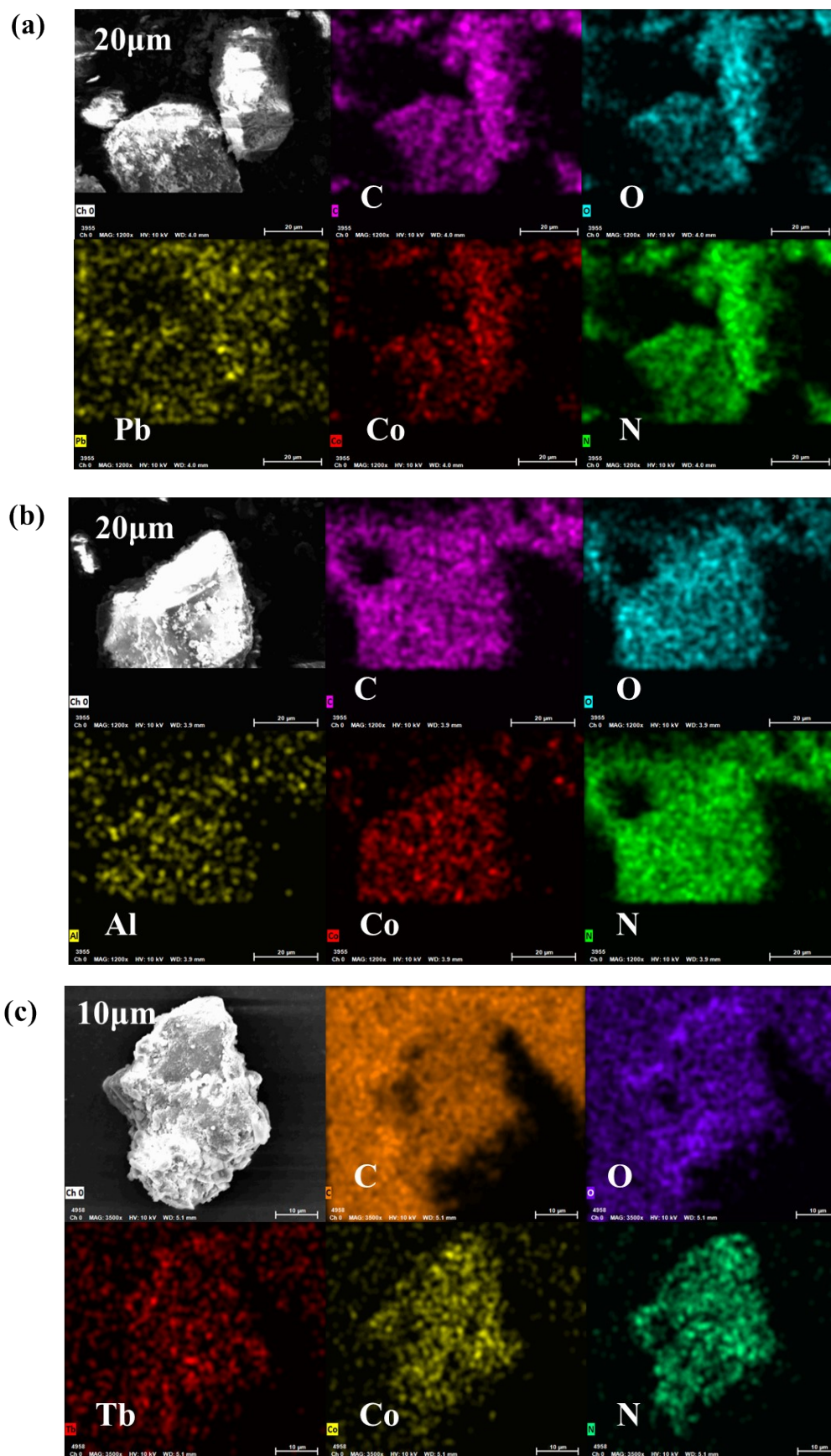
**Fig. S11** PXR D of LCU-112 soaked in aqueous solutions containing Pb<sup>2+</sup>, Al<sup>3+</sup> and Tb<sup>3+</sup> for three days.



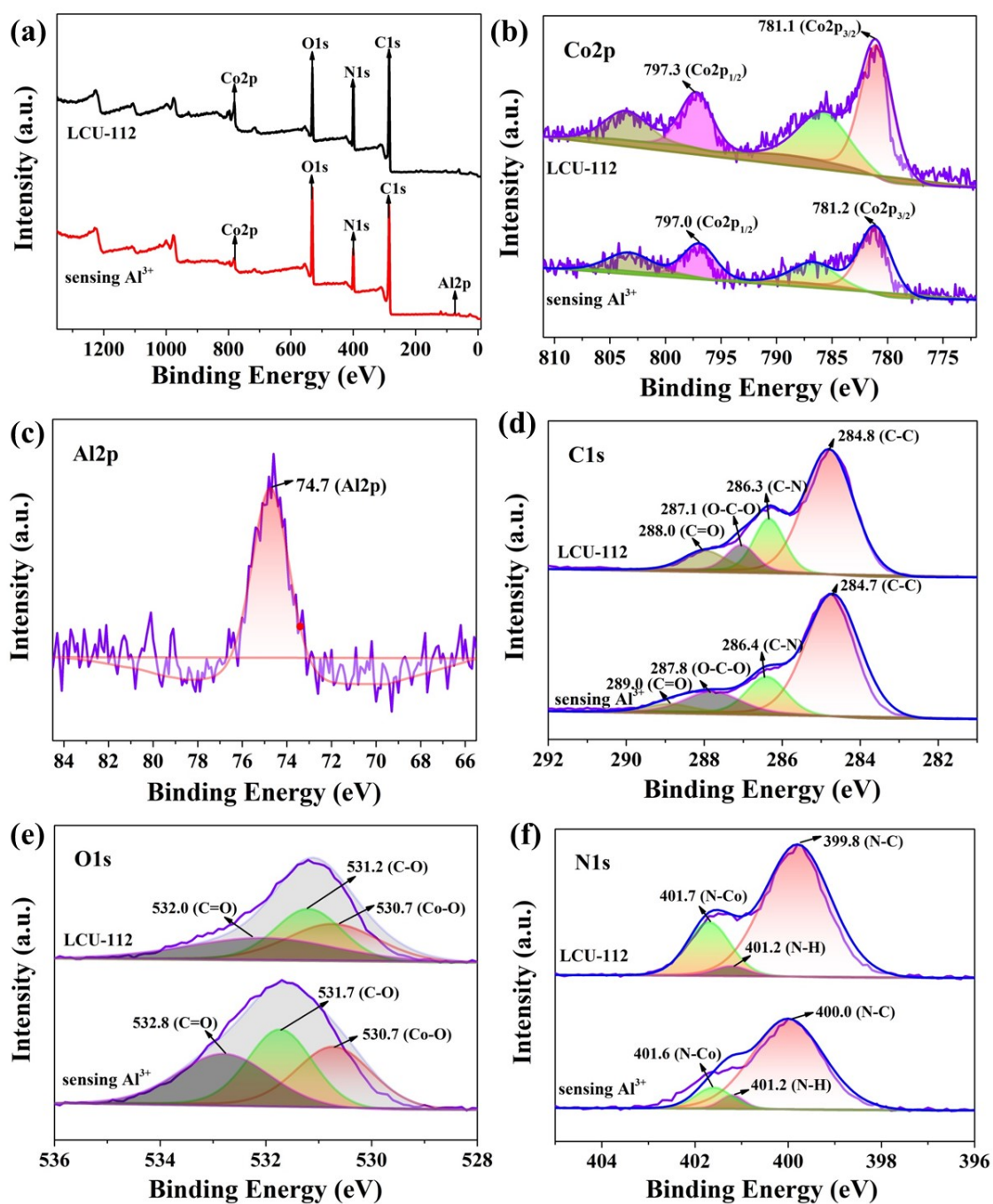
**Fig. S12** UV-vis absorption spectra of LCU-112 upon the addition of various cations.



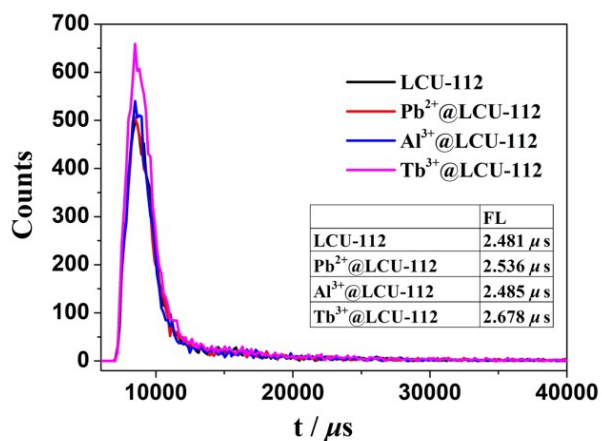
**Fig. S13** Luminescence spectra of H<sub>4</sub>L ligand in aqueous solutions with Pb<sup>2+</sup>, Al<sup>3+</sup> and Tb<sup>3+</sup>.



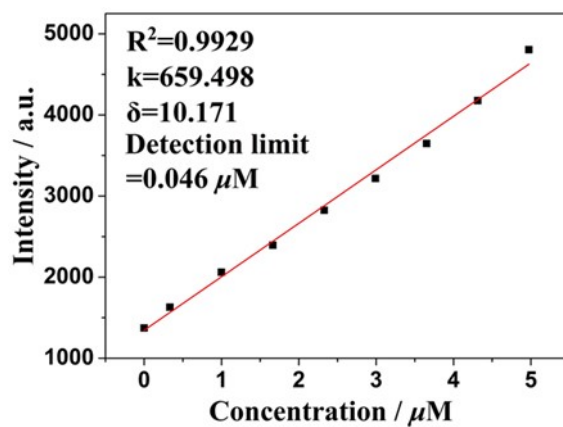
**Fig. S14** (a)-(c) The EDS mapping results of LCU-112 after immersing in  $Pb^{2+}$ ,  $Al^{3+}$  and  $Tb^{3+}$ , showing the uniform distribution of all elements.



**Fig. S15** (a) XPS spectra of LCU-112 before and after immersion in Al<sup>3+</sup>. (b)-(f) High resolution regions of Co2p, Al2p, C1s, O1s and N1s.

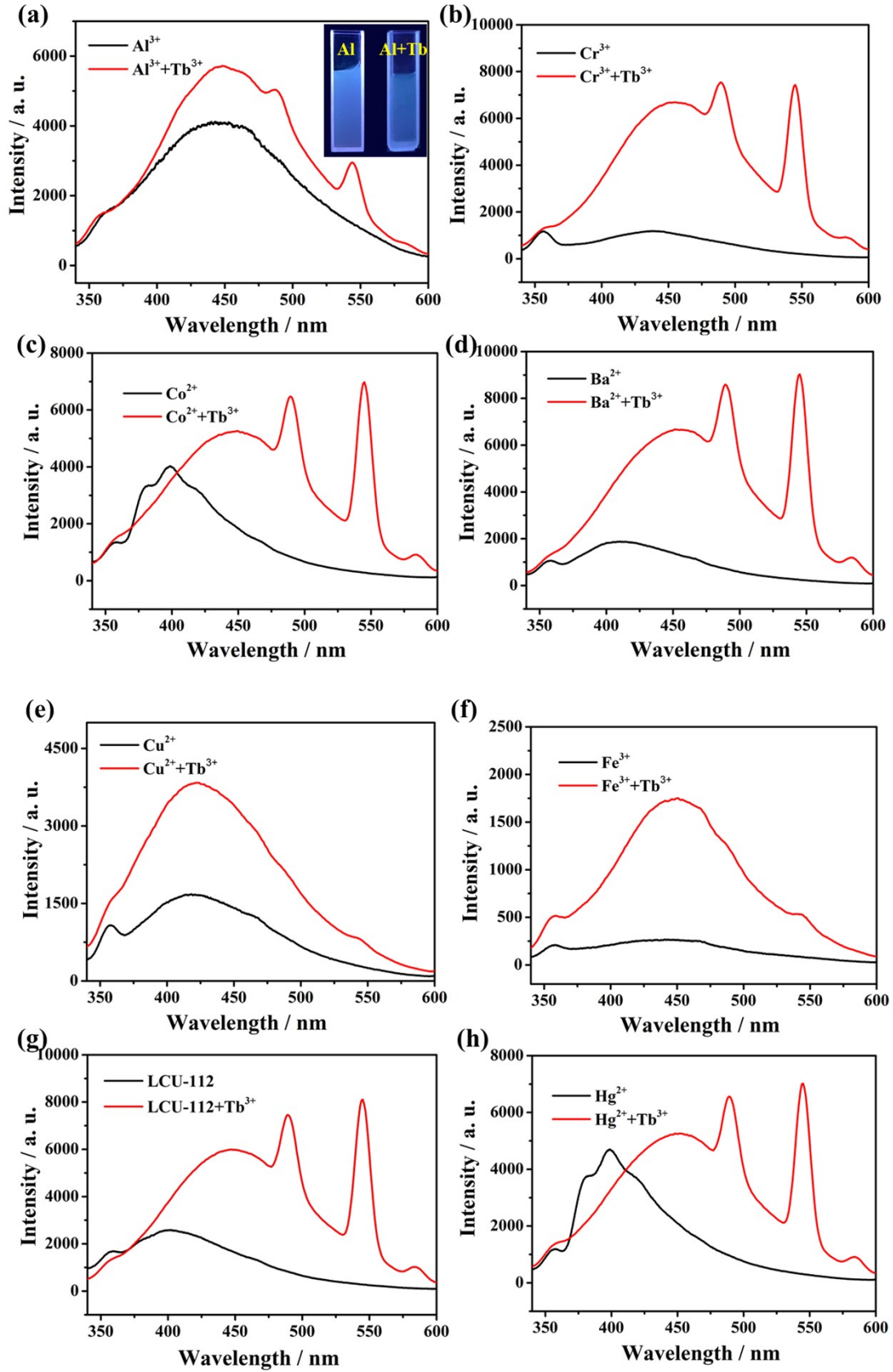


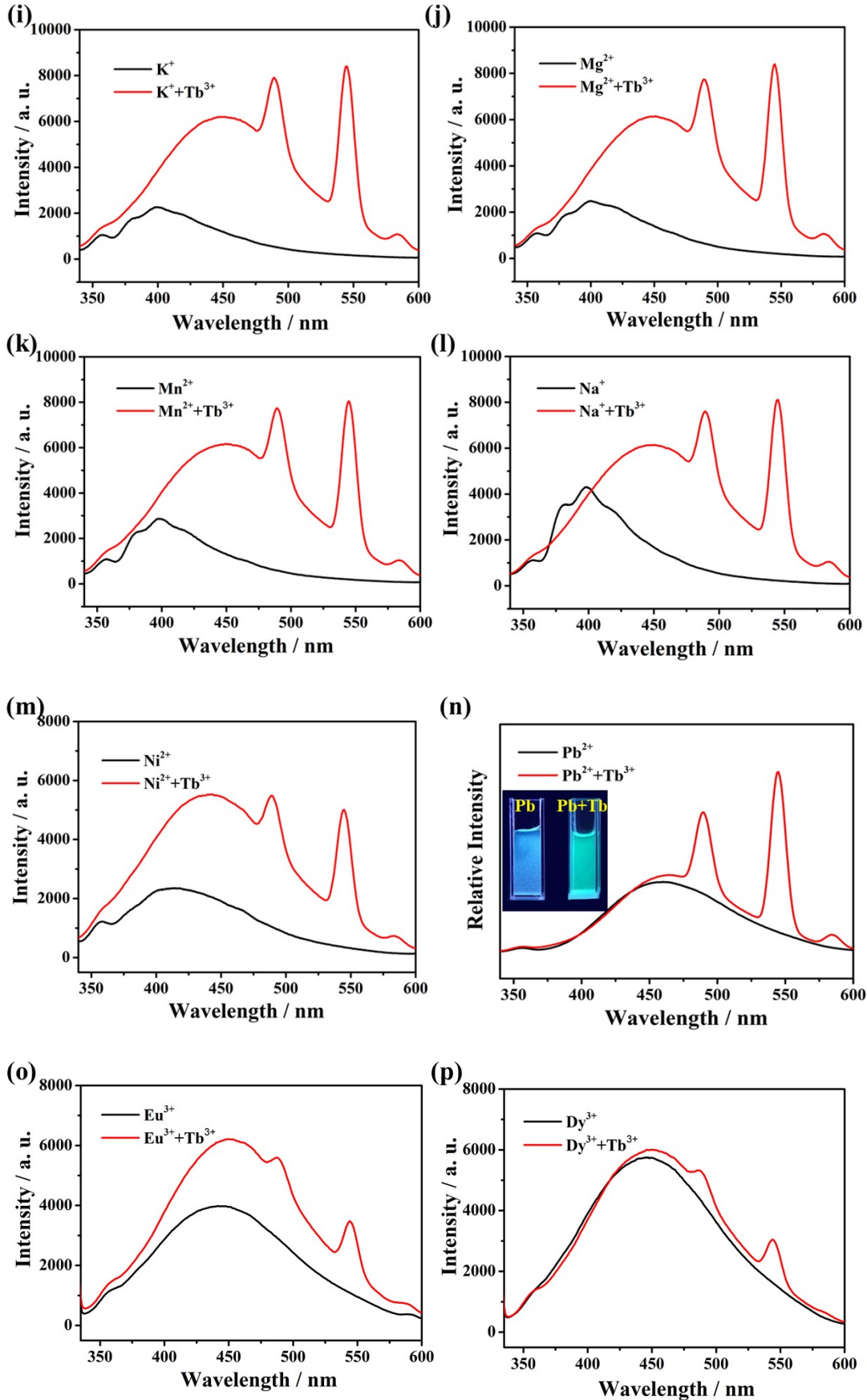
**Fig. S16** The luminescence decay lifetimes of the original LCU-112 and after soaked in aqueous solutions of Pb<sup>2+</sup>, Al<sup>3+</sup> and Tb<sup>3+</sup>.

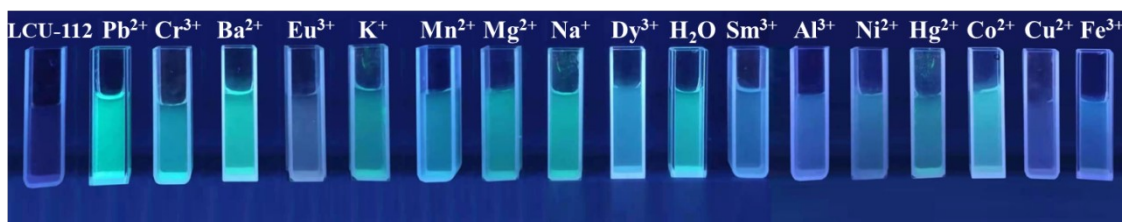
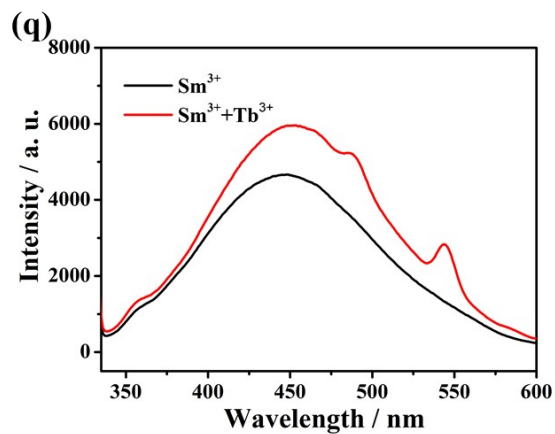


**Fig. S17** The detection limit of LCU-112 toward Tb<sup>3+</sup>.

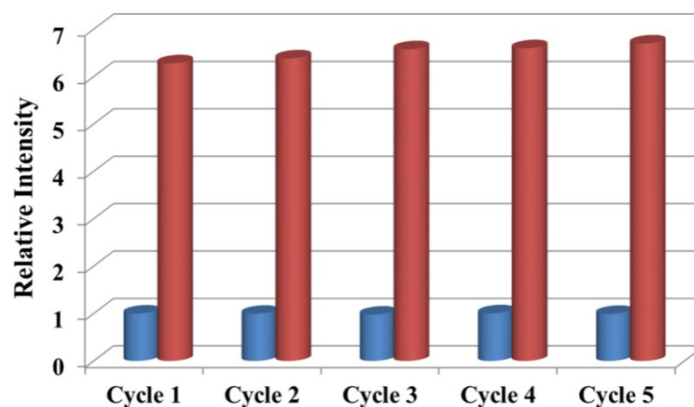




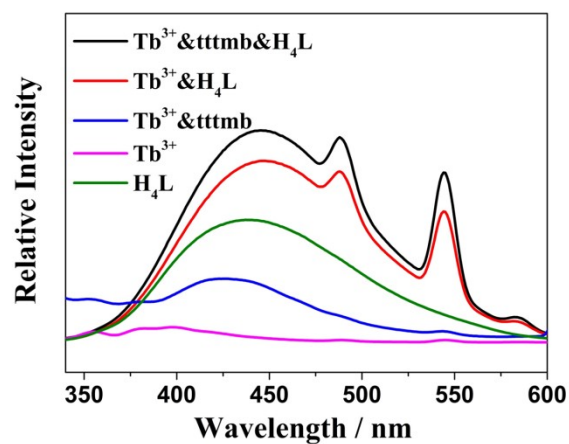




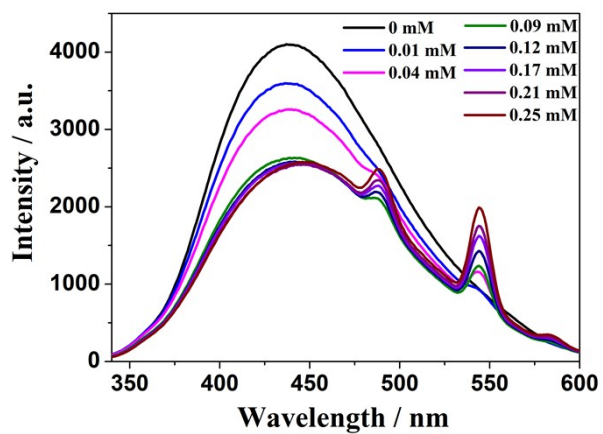
**Fig. S18** The luminescence emission of LCU-112 in aqueous solutions containing different cations with the absence and presence of  $Tb^{3+}$  and Photo by 254 nm UV lamp.



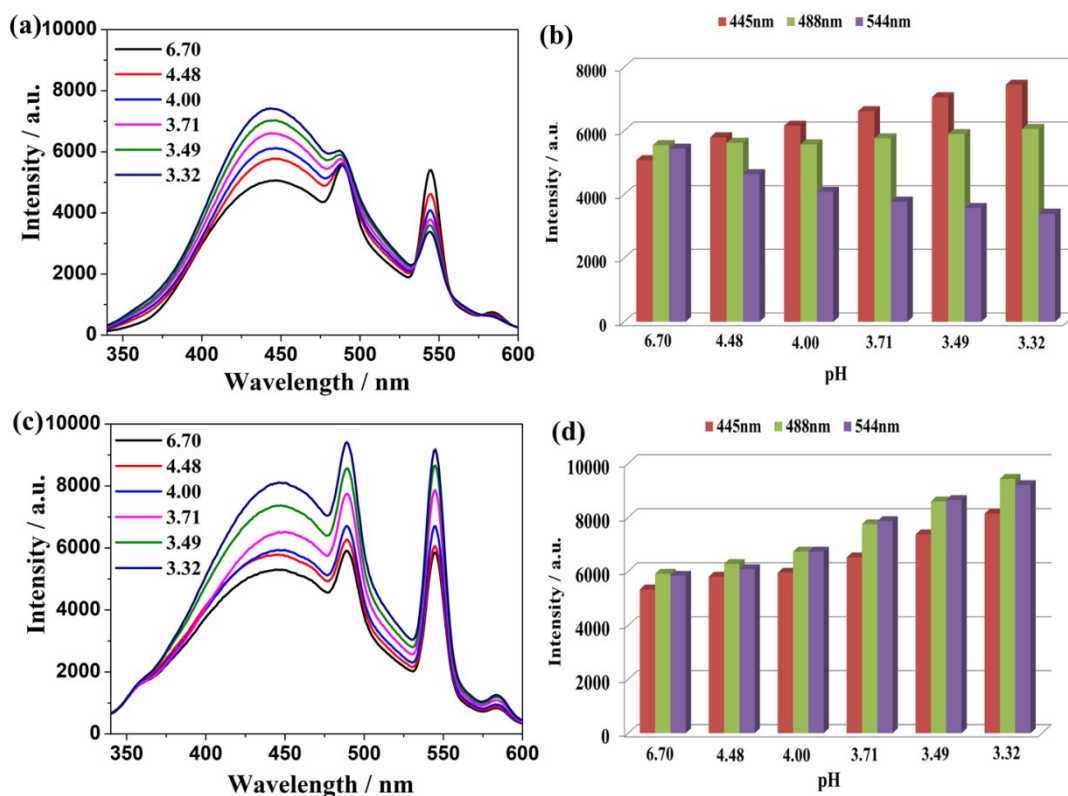
**Fig. S19** The recycling experimental of  $Tb^{3+}$  within five runs.



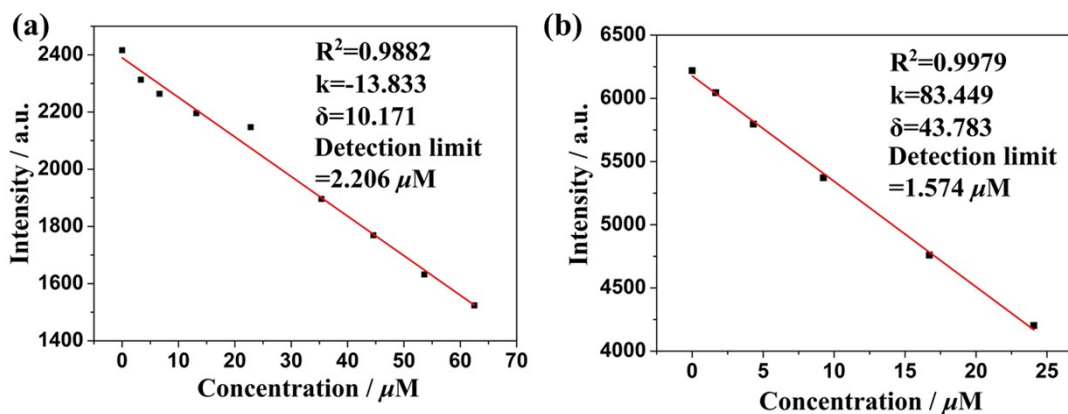
**Fig. S20** Luminescence spectra of  $H_4L$  ligand and  $ttmb$  in aqueous solutions with  $Tb^{3+}$ .



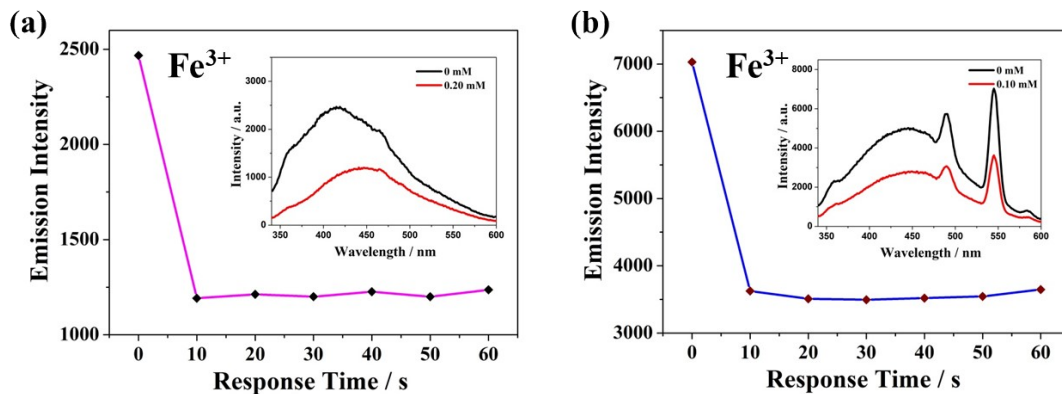
**Fig. S21** The titration experiment of  $Tb^{3+}$  solution into  $H_4L$ .



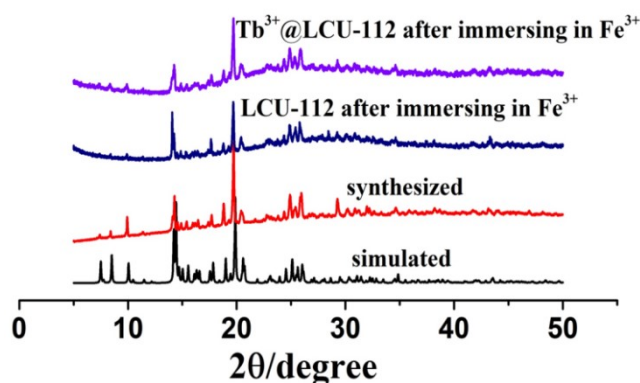
**Fig. S22** (a) and (b) Fluorescence diagram and histogram of  $Tb^{3+}$  fluorescence sensing by  $H_4L$  under different pH conditions. (c) and (d) Fluorescence diagram and histogram of  $Tb^{3+}$  fluorescence sensing by LCU-112 under different pH conditions.



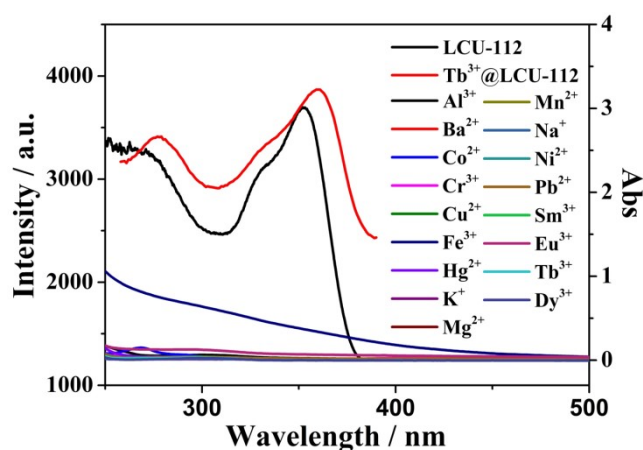
**Fig. S23** (a) and (b) The detection limit of LCU-112 and  $Tb^{3+}@LCU-112$  toward  $Fe^{3+}$ .



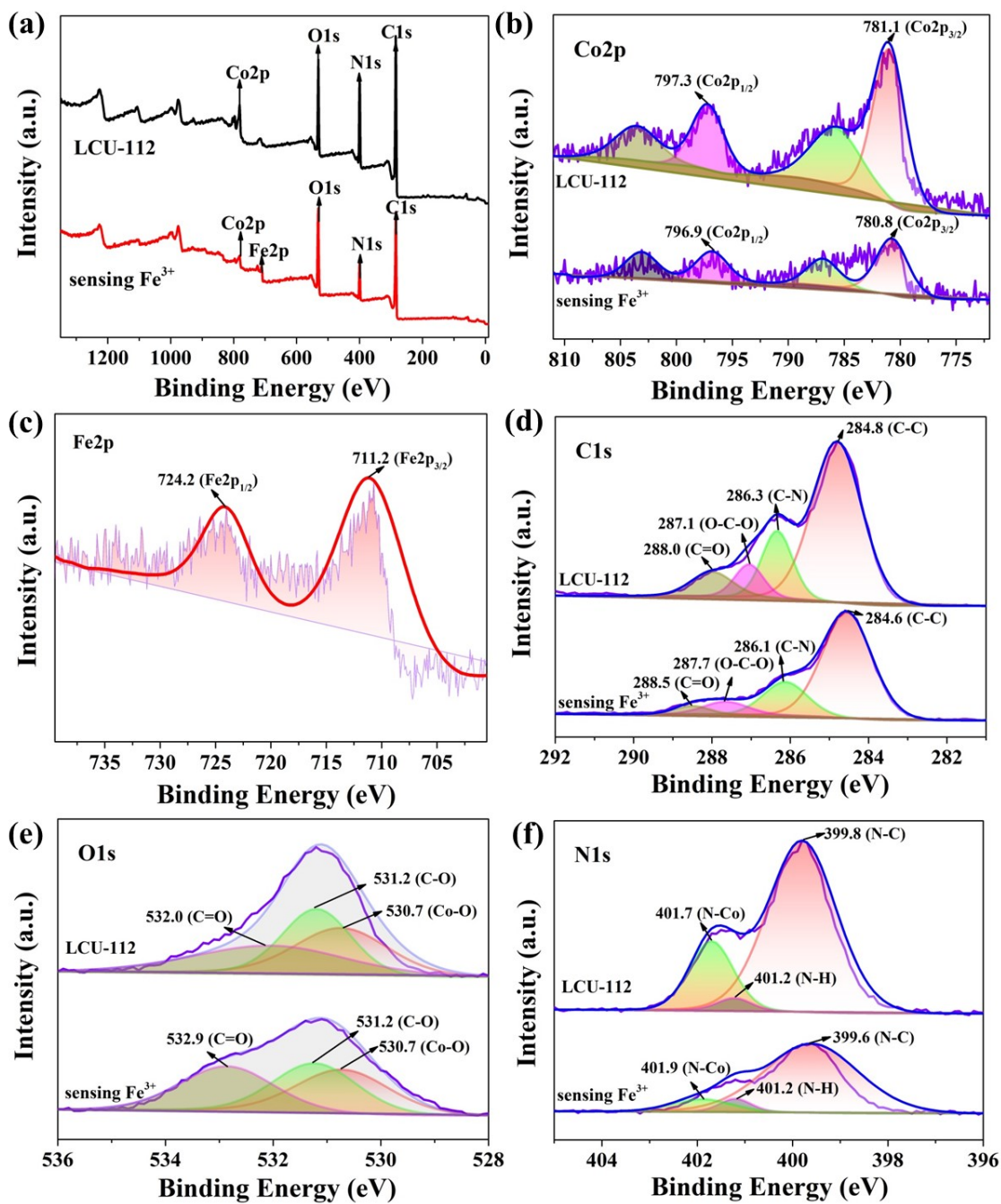
**Fig. S24** The time-dependent response of LCU-112 and  $\text{Tb}^{3+}$ @LCU-112 after adding  $\text{Fe}^{3+}$ .



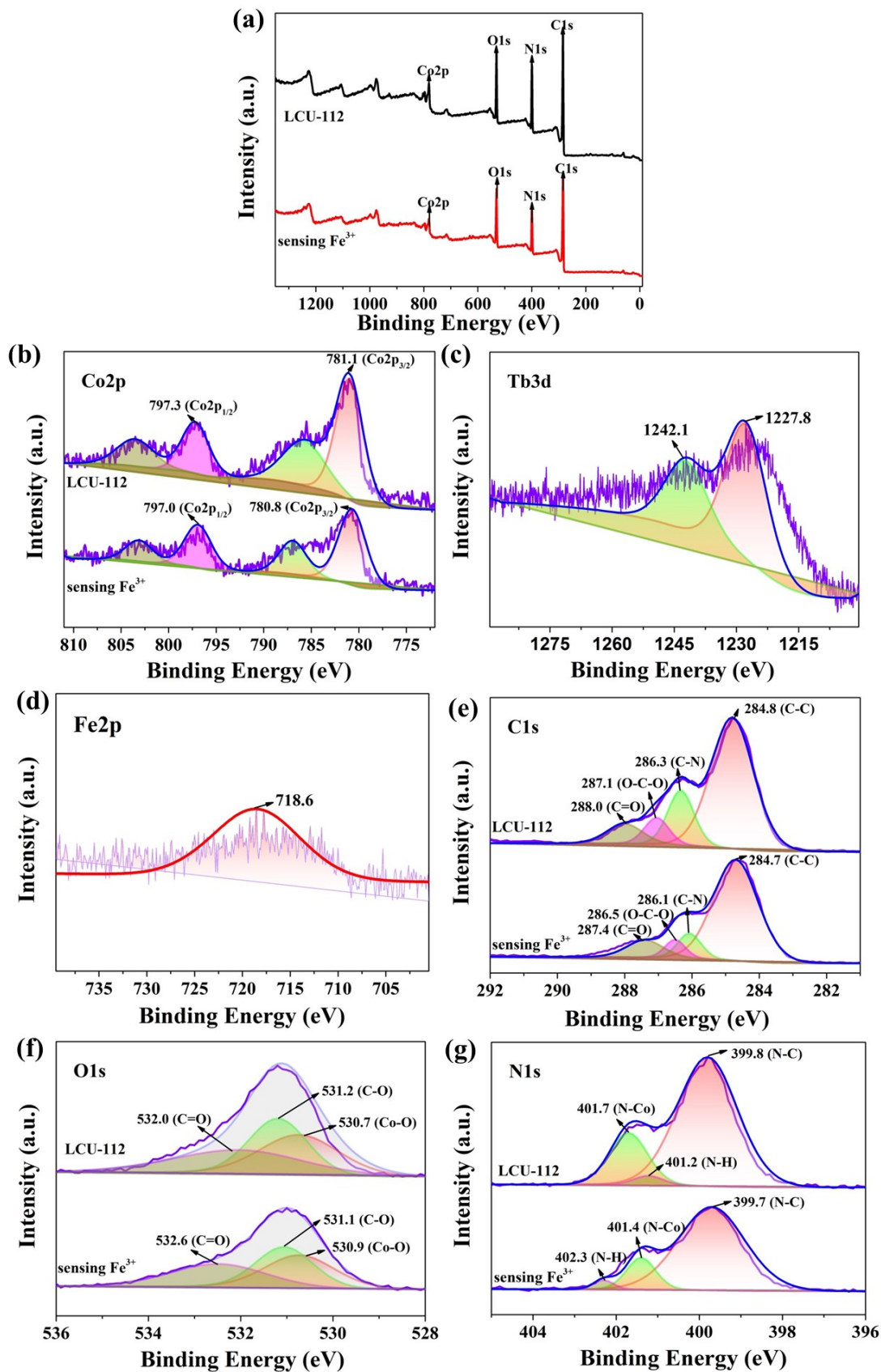
**Fig. S25** PXRD of LCU-112 and  $\text{Tb}^{3+}$ @LCU-112 soaked in aqueous solutions containing  $\text{Fe}^{3+}$  for three days.



**Fig. S26** The excitation of LCU-112 and  $\text{Tb}^{3+}$ @LCU-112 and UV-Vis spectra of cations.

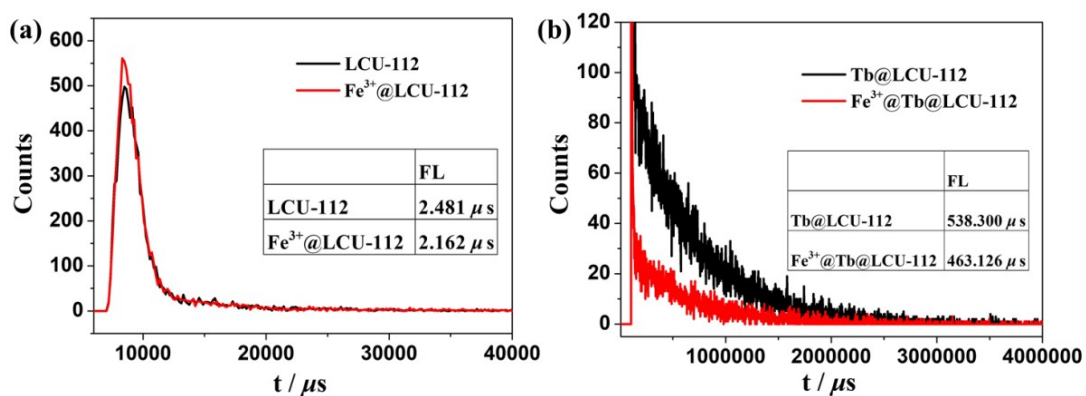


**Fig. S27** (a) XPS spectra of LCU-112 before and after immersion in  $\text{Fe}^{3+}$ . (b)-(f) High resolution regions of Co2p, Fe2p, C1s, O1s and N1s.



**Fig. S28** (a) XPS spectra of  $\text{Tb}^{3+}@$ LCU-112 before and after immersion in  $\text{Fe}^{3+}$ . (b)-(g) High resolution regions of Co2p, Tb3d, Fe2p, C1s, O1s and N1s.





**Fig. S29** (a) The luminescence decay lifetimes of the original LCU-112 and after soaked in aqueous solutions of Fe<sup>3+</sup>, (b) The luminescence decay lifetimes of Tb<sup>3+</sup>@LCU-112 and after soaked in aqueous solutions of Fe<sup>3+</sup>.

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