Electronic Supplementary Information (ESI) for:

Dual-Functional Ratiometric Fluorescent Sensor Based onMixed-LanthanideMetal-OrganicFrameworksfor

Detection of Trace Water and Temperature

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- Figure S29. (a) Temperature dependence of the energy transition efficiency (*E*) from Tb³⁺ to Eu³⁺ ions of Eu_{2.2}Tb_{97.8}-TCA. (b) The temperature dependence of the ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ (monitored at 544 nm) and ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ (monitored at 616 nm) transition lifetimes for the different materials with the increase of temperature from 300 to 380 K (excited at 350 nm).
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3. Supporting References

1. Experimental Methods and Instruments

1.1 Chemicals and Reagents.

All materials and reagents are of commercial sources and used without further treatment. Dried ethanol was obtained by distillation using magnesium powder and iodine.

1.2 Instrumentation and Characterization.

Inductively coupled plasma atomic emission spectroscopy (ICPs) measurement was conducted on the machine with (IRIS Adantage ER/S spectrophotometer). The powder X-ray diffraction (PXRD) patterns were measured with Cu-K α radiation (5 < $2\theta < 50^{\circ}$) under Rigaku MiniFlex 600. The TEM image and EDS elemental mapping images were collected by the field-emission high-resolution transmission electron microscopy (TEM) (FEI Talos F200S) working under a voltage of 200 kV. The scanning electron microscopy (SEM) images were obtained on S-3400N. Infrared spectra were obtained by a Nicolet 360 Fourier transform infrared (FTIR) spectrometry. The ¹H NMR spectra were measured with a Varian 300 MHz spectrometer. The thermogravimetric analysis (TGA) was performed on Netzsch STA-4449 F3 Jupiter raising temperature up to 800 °C at a heating rate of 10 °C ·min⁻¹ under nitrogen atmosphere. The UV-vis absorption spectra were recorded on Cary 5000 UV-Vis-NIR of Agilent Company. The photoluminescence (PL) spectra were collected on a Horiba Instruments FL-3 Fluorescence spectrometer (Side Entrance Slit: 1 nm, Side Exit Slit: 1 nm), and quantum yields were collected on Edinburgh fluorescence spectrometer.



Scheme S1. The synthetic routes to 4, 4', 4"-nitrilotribenzoic acid (H₃TCA).

1.3 Synthesis of ligand

(a) Synthesis of 4, 4', 4"-triacetyl triphenylamine¹

The solution of triphenylamine (1.0 g, 4.1 mmol) and AlCl₃ (1.8 g, 13.5 mmol) in dried CH₂Cl₂ (150 mL) was added acetyl chloride (2 mL, 28.28 mmol) dissolved in dried CH₂Cl₂ (50 mL). Then the reaction was carried out for 24 h at 60 °C. After reaction, deionized water (100 mL) was gradually added at 0 °C, and the aqueous layer was further extracted by CH₂Cl₂ (3×150 mL). Then the combined organic layers were dried by anhydrous Na₂SO₄ and was concentrated under reduced pressure to give crude product, which was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1, v/v) to afford yellow solid (0.86 g, 56.8%). ¹H NMR (300 MHz, CDCl₃, 298 K): δ = 7.90 (d, 6H, *J* = 9.0 Hz), 7.16 (d, 6H, *J* = 9.0 Hz), 2.59 (s, 9H).

(b) Synthesis of 4, 4', 4"-nitrilotribenzoic acid¹

The Br₂ (3 mL) were added dropwise to the solution of NaOH (7.0 g, 0.18 mol) in deionized water (30 mL) in ice bath, and further stirred for 20 min at room temperature. The solution was transferred into an isobarically funnel and was added dropwise to the solution of 4, 4, 4-triacetyl triphenylamine (2.0 g, 5.4 mmol) in 1,4-dioxane (50 mL), reacting for 12 h at 50 °C. Then the entirety was put into ice-bath, and saturated hydroxylamine HCl was added to deoxidize excessive sub-bromosodium. The solution was acidified by hydrochloric acid and the solid product was filtered and dried under vacuum. The crude was recrystallized from acetic acid to afford pure product as white solid. (1.76 g, 86%). ¹H NMR (300 MHz, DMSO-*d*₆, 298 K): $\delta = 12.79$ (s, 3H), 7.90 (d, 6H, J = 9.0 Hz), 7.15 (d, 6H, J = 9 Hz).

2. Supporting Figures and Tables



Figure S1. The ¹HNMR spectrum of 4, 4', 4"-nitrilotribenzoic acid.



Figure S2. (a) The fluorescent spectra of Eu_{1.1}Tb_{98.9}-TCA were recorded at different water contents in ethanol. (b) Normalized fluorescent intensity ratio (I_{545}/I_{614}) versus water content curve. (c) and (d) Normalized fluorescent intensity ratio (I_{545}/I_{614}) versus water content calibration curve in different ranges. LOD= 0.031% (V/V).



Figure S3. (a) The fluorescent spectra of $Eu_{2.9}Tb_{97.1}$ -TCA were recorded at different water contents in ethanol. (b) Normalized fluorescent intensity ratio (I_{545}/I_{614}) versus water content curve. (c) and (d) Normalized fluorescent intensity ratio (I_{545}/I_{614}) versus water content calibration curve in different ranges. LOD= 0.029% (V/V).



Figure S4. (a) The luminescent spectra of $Eu_{1.1}Tb_{98.9}$ -TCA were recorded from 300 to 380 K (excited at 350 nm). (b) Luminescent intensity ratio of Tb³⁺ (543 nm) to Eu^{3+} (613 nm) and the fitted curve for $Eu_{1.1}Tb_{98.9}$ -TCA at different temperature. (c) Relative sensitivity of $Eu_{1.1}Tb_{98.9}$ -TCA in the range of 300 to 380 K. $S_r = 1.16 \% \cdot K^{-1}$ (at 300 K).



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Figure S6. FTIR spectra of H₃TCA, Eu-TCA, Tb-TCA and Eu_{2.2}Tb_{97.8}-TCA.



Figure S7. EDX spectrum of Eu_{2.2}Tb_{97.8}-TCA.



Figure S8. SEM images of Eu_{2.2}Tb_{97.8}-TCA.



Figure S9. STEM image and EDS elemental mapping images of Eu_{2.2}Tb_{97.8}-TCA.



Figure S10. TGA curve of freshly prepared Eu_{2.2}Tb_{97.8}-TCA at the range of 20-800 °C.



Figure S11. (a) The simulated PXRD pattern of Tb-TCA, and PXRD patterns of $Eu_{2.2}Tb_{97.8}$ -TCA (b) before, (c) after the experiment of water detection, (d) in dried ethanol, (e) in water for 2 h, it indicated that $Eu_{2.2}Tb_{97.8}$ -TCA could keep stable for 2 h in water system, (f) in water for 3 h, (g) in water for 12 h.



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Figure S14. The solid emission spectra of (a) H_3TCA , (b) Tb-TCA, (c) Eu-TCA, and (d) $Eu_{2.2}Tb_{97.8}$ -TCA (excited at 350 nm).



Figure S15. The CIE chromaticity diagrams of 1 (H₃TCA), 2 (Tb-TCA), 3 (Eu-TCA), and 4 (Eu_{2.2}Tb_{97.8}-TCA) at 300 K ($\lambda_{ex} = 350$ nm).



Figure S16. Water content dependent intensity of the ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ transition for Tb-TCA and ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition for Eu-TCA.



Figure S17. The PL decay curves of (a) Tb-TCA, (b) $Eu_{2.2}Tb_{97.8}$ -TCA-Tb with the emission monitored by ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ transition at 544 nm. (c) Eu-TCA (d) $Eu_{2.2}Tb_{97.8}$ -TCA-Eu with the emission monitored by ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition at 614 nm ($\lambda_{ex} = 365$ nm, 10 W Phos lamp equipped in FL-3) at different amounts of water.



Figure S18. The ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ (monitored at 544 nm) and ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ (monitored at 614 nm) transition lifetimes for the different materials at various amounts of water (excited at 365 nm).



Figure S19. The PL decay curves of (a) Tb-TCA, (b) $Eu_{2.2}Tb_{97.8}$ -TCA-Tb with the emission monitored by ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ transition at 544 nm. (c) Eu-TCA (d) $Eu_{2.2}Tb_{97.8}$ -TCA-Eu with the emission monitored by ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition at 614 nm ($\lambda_{ex} = 365$ nm, 10 W Phos lamp equipped in FL-3) at different amounts of D₂O.



Figure S20. The ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ (monitored at 544 nm) and ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ (monitored at 614 nm) transition lifetimes for the different materials at various amounts of D₂O (excited at 365 nm).



Figure S21. The number of coordination water in the first coordination sphere of Tb^{3+} ions in (a) Tb-TCA, (b) $Eu_{2.2}Tb_{97.8}$ -TCA-Tb and Eu^{3+} ions in (c) Eu-TCA (d) $Eu_{2.2}Tb_{97.8}$ -TCA-Eu at various amounts of water in ethanol.



Figure S22. The phosphorescence spectra of (a) Gd-TCA dispersed in dried ethanol, (b) Gd-TCA dispersions in ethanol containing 0.63% v/v water.



Figure S23. UV-vis absorption spectra of H_3TCA , Gd-TCA (dispersed into dried ethanol), and Gd-TCA+ H_2O (dispersed into ethanol containing 0.63% v/v water).



Figure S24. The quantum yields of (a) Tb-TCA and (b) Eu-TCA dispersed into dried ethanol, (c) Tb-TCA and (d) Eu-TCA dispersed into ethanol containing 0.63% v/v water.



Figure S25. The LUMO, HOMO images and LUMO-HOMO gaps of H₃TCA bonded or not bonded with water obtained by using Materials Studio 2019 program package (Dmol 3 program).



Figure S26. Temperature dependent intensity of the ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ transition for Tb-TCA and ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition for Eu-TCA.



Figure S27. The CIE chromaticity diagram shows the fluorescent color coordinates of $Eu_{2,2}Tb_{97,8}$ -TCA with the increase of temperature from 300 to 380 K.



Figure S28. The PL decay curves of (a) Tb-TCA, (b) $Eu_{2.2}Tb_{97.8}$ -TCA-Tb with the emission monitored by ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ transition at 544 nm. (c) Eu-TCA (d) $Eu_{2.2}Tb_{97.8}$ -TCA-Eu with the emission monitored by ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition at 616 nm ($\lambda_{ex} = 350$ nm, 10 W Phos lamp equipped in FL-3) with the increase of temperature from 300 to 380 K.



Figure S29. (a) Temperature dependence of the energy transition efficiency (*E*) from Tb^{3+} to Eu^{3+} ions of $Eu_{2.2}Tb_{97.8}$ -TCA. (b) The temperature dependence of the ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ (monitored at 544 nm) and ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ (monitored at 616 nm) transition lifetimes for the different materials with the increase of temperature from 300 to 380 K (excited at 350 nm).



Figure S30. Phosphorescence spectrum of solid Gd-TCA at 77 K.

Ζ	Element	Family	Atomic	Atomic	Mass	Mass
			Fraction (%)	Error (%)	Fraction (%)	Error (%)
6	С	Κ	56.54	7.05	19.79	1.57
8	Ο	Κ	26.83	6.30	12.73	2.73
63	Eu	L	0.28	0.05	1.08	0.14
65	Tb	L	16.36	2.69	66.40	8.84

 $\label{eq:table_transform} \textbf{Table S1.} \ \text{EDX} \ \text{analysis of } Eu_{2.2} Tb_{97.8} \mbox{-} TCA.$

Table S2. The CIE color coordinates (x, y) associated with various water contents (v/v) / % in Eu_{2.2}Tb_{97.8}-TCA.

Water content	CIE coordinates	Water content	CIE coordinates
0	(0.3542, 0.3650)	0.504	(0.3284, 0.4600)
0.05	(0.3527, 0.3646)	0.543	(0.3246, 0.4729)
0.1	(0.3520, 0.3641)	0.584	(0.3235, 0.4795)
0.153	(0.3510, 0.3633)	0.625	(0.3225, 0.4831)
0.205	(0.3505, 0.3641)	0.667	(0.3219, 0.4824)
0.2586	(0.3499, 0.3701)	0.709	(0.3224, 0.4841)
0.315	(0.3447, 0.3767)	0.752	(0.3232, 0.4852)
0.35	(0.3426, 0.3782)	0.795	(0.3237, 0.4882)
0.387	(0.3402, 0.3988)	0.84	(0.3224, 0.5058)
0.426	(0.3369, 0.4205)	0.89	(0.3226, 0.5174)
0.451	(0.3318, 0.4373)		

Method/Materials	LOD (v/v	Sensing strategy	Linear range	References
	%)		(%, v/v)	
Karl-Fisher titration	0.04	Chemical reaction		2
Anthracene-boronic acid ester	0.1	PET ^a	0-1.3	3
Mg-MOFs	0.05	ESIPT ^b	0.05-5	4
Eu-MOFs/N, S-CDs	0.03	Energy transfer ^c	0.05-4	5
Ru@MIL-101-NH ₂	0.02	Protonation effect	0-100	6
$[Tb_{0.5}Eu_{0.5}Na(HL^2)_2(H_3L^2)_{0.5}]$	0.01	Energy transfer ^c	0.01-3.2	7
Eu-MOFs	0.02	ICT ^e	0.05-10	8
Eu _{0.02} Dy _{0.18} -MOFs	0.10	Energy transfer ^c	0-10	9
Tb _{97.11} Eu _{2.89} -L1	0.04	Energy transfer ^c	0-2.5	10
Eu-DPA/PTA-NH ₂	0.01	ICT ^d	0-100	11
Eu _{0.05} Tb _{0.95} (OBA)(H ₂ O)Cl	0.10	Energy transfer ^c	0-0.8	12
Eu _{2.2} Tb _{97.8} -TCA	0.016	Hydrogen-bond ^e	0-0.63	This work

Table S3. Comparison of the LOD of the Karl-Fisher titration method and other

 reported luminescence water sensors with ours.

^aphoto-induced electron transfer; ^bexcited-state intramolecular proton transfer; ^csuppressing energy transfer efficiency from the ligand to the lanthanide ions; ^dintramolecular charge transfer; ^eintermolecular hydrogen-bond.

Water content Coordinated water number (q) (v/v) / %d b а с 0 2.30 -0.30 -0.36 -0.28 0.067 -0.33 -0.66 -0.26 -0.28 -0.3 0.135 -0.34 -0.12 -0.28 0.2 -0.33 -0.34 -0.32 -0.28 0.274 -0.35 -0.97 -0.29 -0.31 0.345 -0.33 3.70 -0.3 -0.28 0.416 -0.36 5.28 -0.25 -0.30 0.49 4.00 -0.37 -0.18 -0.31 0.564 -0.76 2.82 -0.21 -0.63 0.638 -0.69 1.67 -0.3 -0.58 0.714 -0.40 1.32 -0.29 -0.33

Table S4. The calculated values of coordinated water number (q) in the first coordination sphere of Tb^{3+} in (a) Tb-TCA, (b) $Eu_{2.2}Tb_{97.8}$ -TCA-Tb and Eu^{3+} ions in (c) Eu-TCA (d) $Eu_{2.2}Tb_{97.8}$ -TCA-Eu at various amounts of water in ethanol.

Table S5. The CIE color coordinates (x, y) associated with different temperature in Eu_{2.2}Tb_{97.8}-TCA.

Temperature (K)	CIE coordinates	Temperature (K)	CIE coordinates
300	(0.4406, 0.3565)	345	(0.3521, 0.3378)
305	(0.4298, 0.3540)	350	(0.3459, 0.3347)
310	(0.4178, 0.3517)	355	(0.3408, 0.3332)
315	(0.4061, 0.3500)	360	(0.3367, 0.3310)
320	(0.3949, 0.3477)	365	(0.3326, 0.3278)
325	(0.3838, 0.3456)	370	(0.3320, 0.3283)
330	(0.3743, 0.3428)	375	(0.3300, 0.3262)
335	(0.3664, 0.3419)	380	(0.3291, 0.3262)
340	(0.3587, 0.3407)		

3. Supporting References

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