Supplementary Information

Ratiometric fluorescent detecting trace water in organic solvent based on bimetallic lanthanide metal-organic frameworks

General procedures

All the commercial reagents were used as received without further purification. Elemental analyses (EA) for C, H, N were performed with a German Elementary Vario EL III instrument. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) data were carried out on an Ultima-2 ICP emission spectrometer. The semiquantitative energy-dispersive X-ray spectroscopy (EDX, JEOL-SEM, JSM-6700F) analysis of the mixed crystals showed the presence of elements Eu and Tb. Infrared (IR) spectra were used KBr pellets in the range of 4000-400 cm^{-1}, and carried out on a Nicolet Magna 750 FT-IR. The powder X-ray diffraction (PXRD) patterns were collected by Cu-Kα radiation (λ = 1.5406 Å) at a Rigaku Mini 600 X-ray diffractometer. ^{1}H-NMR and ^{13}C-NMR spectra were obtained on a Bruker Avance 400 and 100 using the deuterated solvents, respectively. The UV absorption spectra of solid sample were recorded on lambda 950. The photoluminescence (PL) spectroscopy were collected on a FLSP920 Edinburgh fluorescence spectrometer at room temperature, and quantum yields were collected on FLS1000 luminescence equipment.
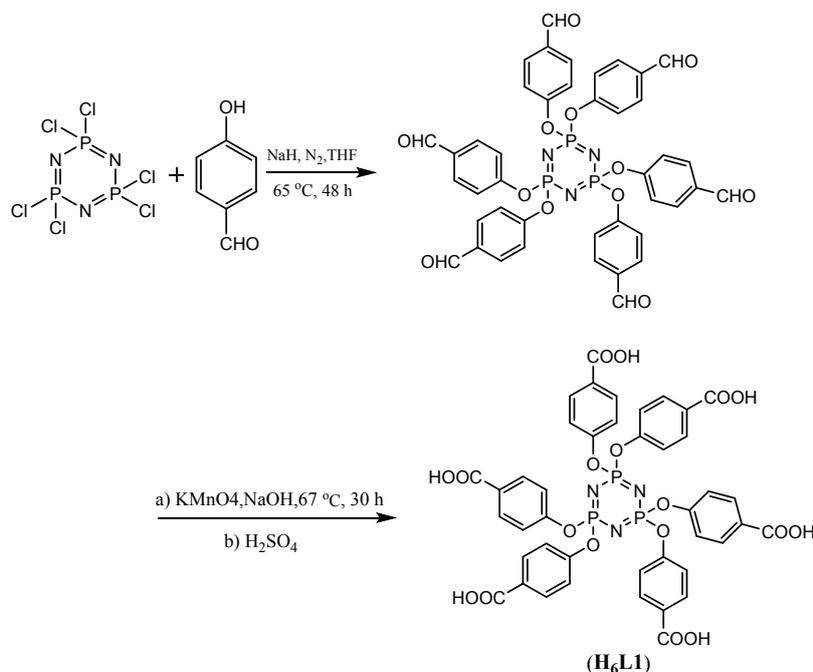
Scheme 1 The synthetic route of ligand **H$_6$L1**

Synthesis of H$_6$L1 ligand

The **H₆L1** ligand was prepared as the reported methods (scheme 1).[1] ^{1}H NMR (400 MHz, DMSO-d6): δ 7.86-7.83 (m, 12 H), 7.05-7.03 (m, 12 H). ^{13}C NMR (100 MHz, DMSO-d6): δ 120.99, 128.74, 131.72, 153.19, 166.73.

Prepare of Tb-L1

To a mixture of $Tb(NO_3)_3 \cdot 6H_2O$ (0.20 mmol, 90 mg) and **H₆L1** (0.010 mmol, 10 mg), 2 mL of DMA was added in the present of 400 μL of acetic acid. The vial was capped and heat at 120 °C for five days. Colorless bulk crystals of **Tb-L1** were obtained in a yield of 65 % based on **H₆L1**. Anal. calcd. for $C_{84}H_{51}N_6O_{45}P_6Tb_5 \cdot 6H_2O$ (%): N, 2.83; C, 34.01; H, 2.53; found: N, 2.73; C, 34.64; H, 2.62.

Prepare of Eu-L1

To a mixture of $Eu(NO_3)_3 \cdot 6H_2O$ (0.20 mmol, 90 mg) and **H₆L1** (0.010 mmol, 10 mg), 4 mL of DMA was added in the present of 600 μL of acetic acid. The vial was capped and heat at 120 °C for fifteen days. Colorless bulk crystals of **Eu-L1** were obtained in a yield of 50 % based on **H₆L1**. Anal. calcd. for $C_{84}H_{51}N_6O_{45}P_6Eu_5 \cdot 6H_2O$ (%): N, 2.87; C, 34.40; H, 2.56; found: N, 2.88; C, 34.17; H, 2.94.

Prepare of Tb₉₇.₁₁Eu₂.₈₉-L1

To a mixture of $Eu(NO_3)_3 \cdot 6H_2O$ (0.0044 mmol, 2 mg), $Tb(NO_3)_3 \cdot 6H_2O$ (0.20 mmol, 88 mg) and **H₆L1** (0.010 mmol, 10 mg), 4 mL of DMA was added in the present of 600 μL of acetic acid. The vial was capped and heat at 120 °C for five days. Colorless bulk crystals of **Tb₉₇.₁₁Eu₂.₈₉-L1** were obtained in a yield of 50 % based on **H₆L1**.

Detection of traces of water in organic solvent

Before collecting the PL spectroscopy, crystals were respectively soaked in fresh DMA and acetonitrile for four days, wiped off the solvents under vacuum condition and protected by argon. Then 2.5 mL dry acetonitrile was added under argon atmosphere, and the suspension was transferred to a sealed cuvette immediately. The original PL spectroscopy was collected prior to the addition of mixed solution (dry acetonitrile : deionized water = 2 : 1).

X-ray crystallographic data

The crystal of **Eu-L1** was kept at 100 K during data collection on a Bruker diffractometer equipped with Cu-Kα radiation (λ = 1.5418 Å). The crystal of **Tb-L1** was kept at 150 K during data collection on a SuperNova diffractometer equipped with Cu-Kα radiation (λ = 1.5418 Å). The crystal structures were solved by direct method and refined by full-matrix least squares on F^2 using SHELXTL package.[2] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms on the aromatic rings were located at geometrically calculated positions and refined by riding. In the refined model for **Eu-L1** or **Tb-L1**, one of benzoate group and

water (O19) was modelled as two disordered parts with the same occupancy of 50 %. Because O22 and O23 are only 2.026 Å apart, O22 is refined as half occupied. The free solvent molecules are highly disordered in **Eu-L1** and **Tb-L1**, and attempts to locate and refine the solvent peaks were unsuccessful. The diffused electron densities resulting from these solvent molecules were removed using the SQUEEZE routine of PLATON[3]; structures were then refined again using the data generated. In the structure of **Eu-L1**, the electrons found in S.A.V. are about 2134 and the mass loss of solvents in TGA is 25.4%, which corresponds to 8 DMA and 176 water molecules in S.A.V. Hence, the moiety formula of **Eu-L1** is $C_{84}H_{57}Eu_5N_6O_{42}P_6 \cdot 2DMA \cdot 44H_2O$ ($C_{92}H_{163}Eu_5N_8O_{88}P_6$), and the theoretic mass fraction of solvents is 25.8%. Similarly, the electrons found in S.A.V. are about 1897 and the mass loss of solvents in TGA is 22.7% for **Tb-L1**, which corresponds to 4 DMA and 172 water molecules in S.A.V. The moiety formula of **Tb-L1** is $C_{84}H_{57}N_6O_{42}P_6Tb_5 \cdot DMA \cdot 43H_2O$ ($C_{88}H_{152}N_7O_{86}P_6Tb_5$), and the theoretic mass fraction of solvents is 23.5%. And then, the moiety formula of **Eu-L1** and **Tb-L1** were used to calculate the Mr, Density, F000 etc. in subsequent refinement processes.

Table S1. Crystal data and structure refinement for **Eu-L1** and **Tb-L1**

CCDC No.	1902862	1902863
Empirical formula	$C_{92}H_{163}Eu_5N_8O_{88}P_6$	$C_{88}H_{152}N_7O_{86}P_6Tb_5$
Formula weight	3734.91	3664.58
Temperature (K)	100	150
Wavelength (Å)	1.54178	1.54184
Crystal system	monoclinic	monoclinic
Space group	$C2/c$	$C2/c$
	$a = 33.9147(12)$ $\alpha = 90$	$a = 34.1382(10)$ $\alpha = 90$
Unit cell dimensions (Å, °)	$b = 18.5857(8)$ $\beta = 106.765(2)$	$b = 18.2040(11)$ $\beta = 107.899(4)$
	$c = 29.5768(10)$ $\gamma = 90$	$c = 29.7178(13)$ $\gamma = 90$
Volume (Å)	17850.7(12)	17574.3(15)
Z	4	4
Calculated density (g cm^{-3})	1.390	1.385
Absorption coefficient (mm^{-1})	13.664	10.974
F_{000}	7520	7328
Crystal size (mm^3)	$0.30 \times 0.25 \times 0.10$	$0.30 \times 0.28 \times 0.25$
θ range for data collection (°)	3.847 to 68.625	3.456 to 73.690
Miller index ranges	$-33 \leq h \leq 40, -22 \leq k \leq 22, -35 \leq l \leq 32$	$-42 \leq h \leq 39, -21 \leq k \leq 22, -33 \leq l \leq 36$
Reflections collected	56195	34242
Independent reflections	16361 [$R_{int} = 0.0491$]	17064 [$R_{int} = 0.0693$]
Completeness to θ_{max} (%)	0.992	0.961
Max. and min. transmission	0.82 and 1.00	0.11312 and 1.00000
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	16361 / 759 / 711	17064 / 789 / 713
Goodness-of-fit on F^2	1.097	0.966
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0688$, $wR2 = 0.2121$	$R1 = 0.0797$, $wR2 = 0.2130$

| R indices (all data) | $R1 = 0.0844$, $wR2 = 0.2283$ | $R1 = 0.1504$, $wR2 = 0.2558$ |
| Largest diff. peak and hole (e Å^{-3}) | 1.305 and -1.119 | 1.173 and -0.846 |
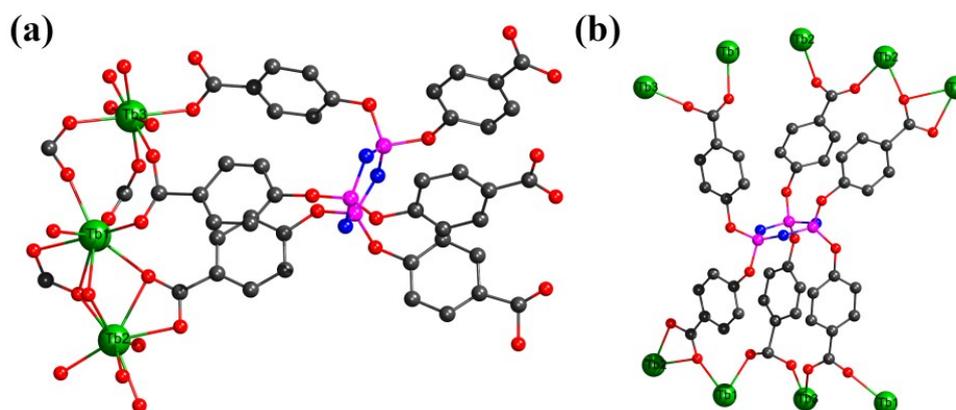
Figure S1. (a) Coordinated model of metal ions. (b) Coordinated model of ligand. (Tb, green; C, black; O, red; N, blue; P, pink; H atoms are omitted for clarity).
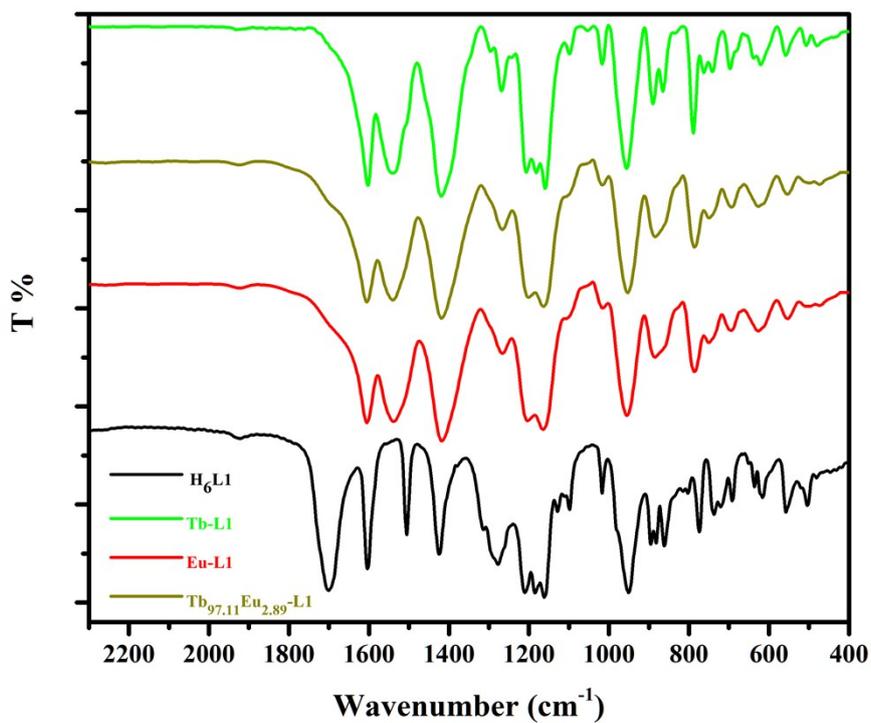
Figure S2. IR spectra of **H$_6$L1, Eu-L1**, **Tb-L1** and **Tb$_{97.11}$Eu$_{2.89}$-L1**
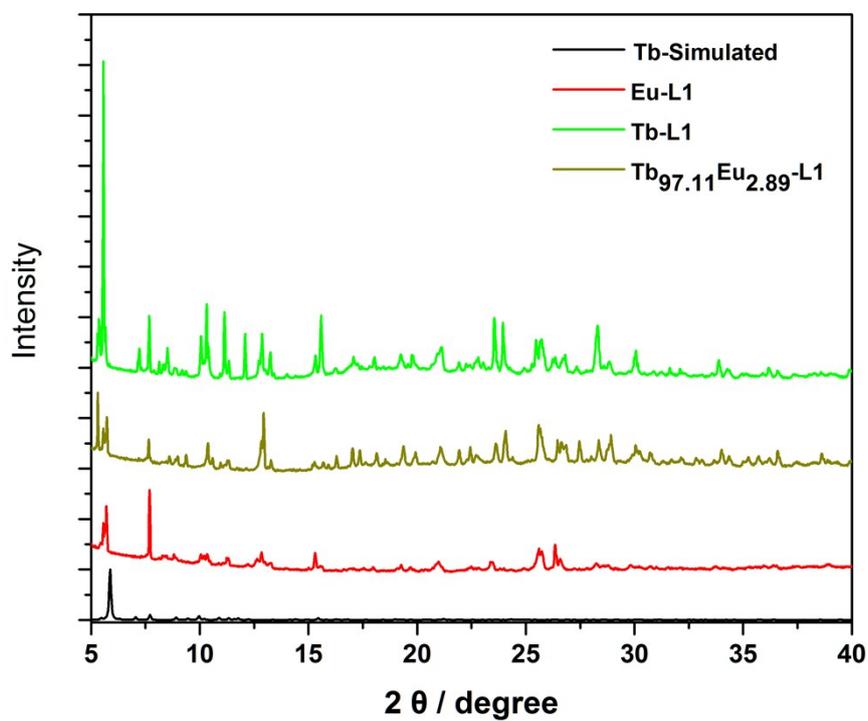
Figure S3. PXRD of **Tb-simulated**, **Eu-L1**, **Tb-L1** and **Tb$_{97.11}$Eu$_{2.89}$-L1**
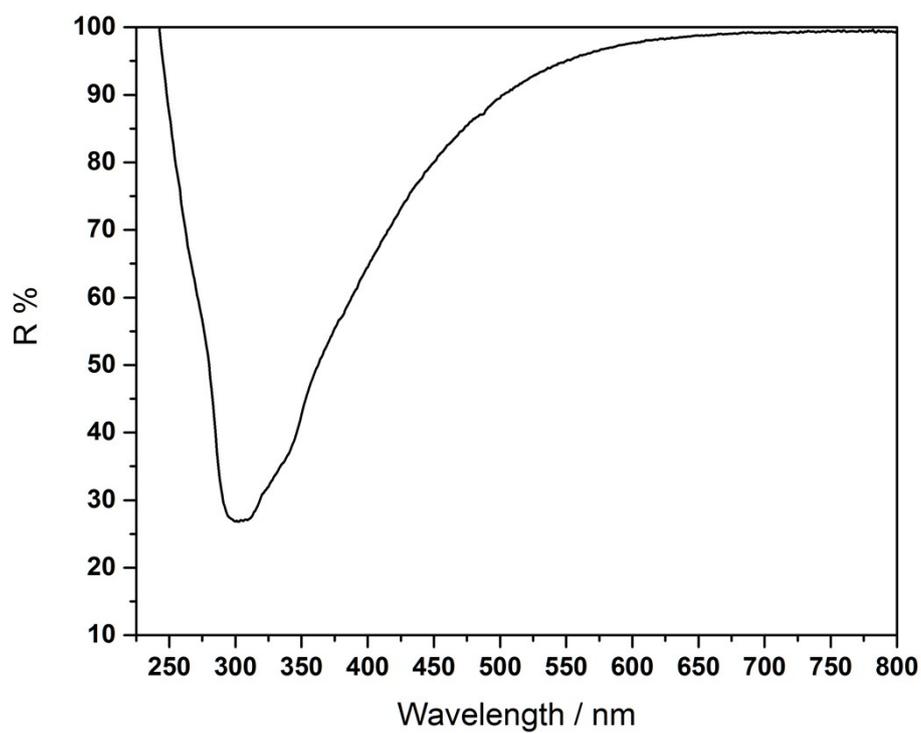
Figure S4. Absorption spectrum of solid **Tb-L1**
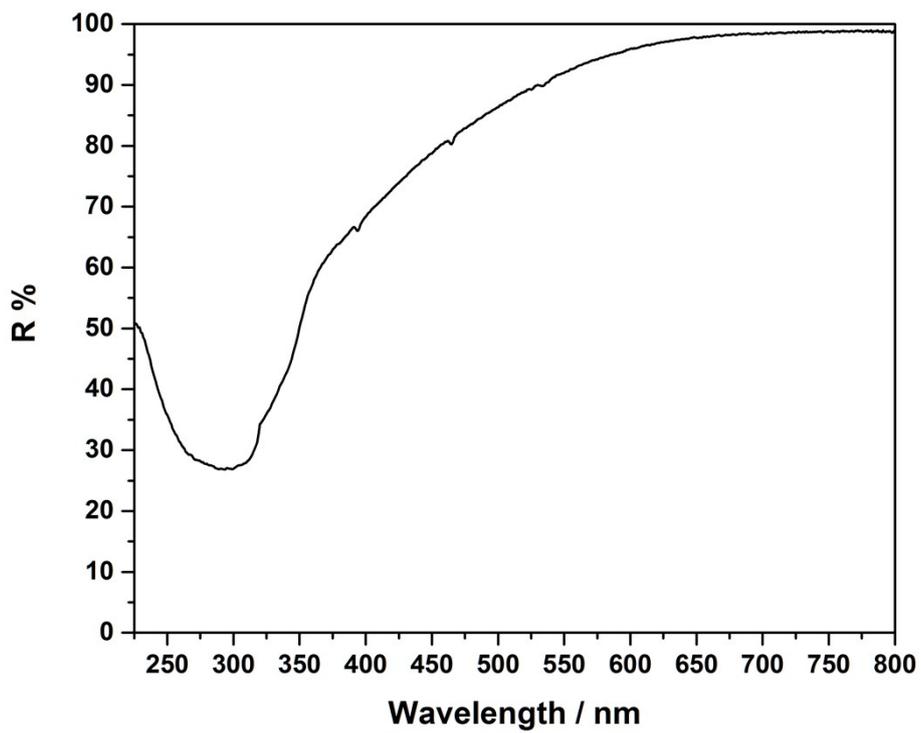
Figure S5. Absorption spectrum of solid **Eu-L1**
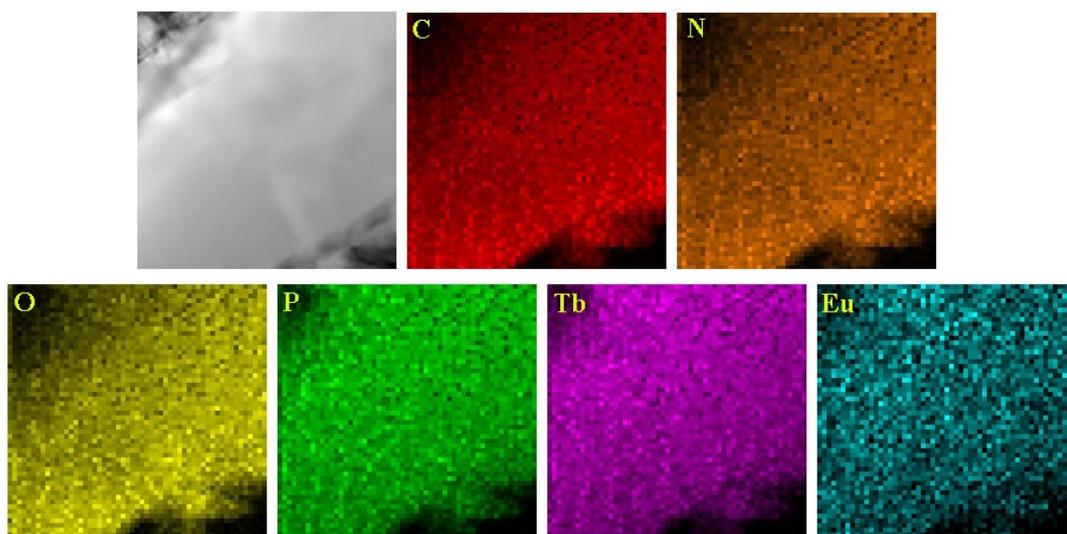
Figure S6. TEM images of **Tb$_{97.11}$Eu$_{2.89}$-L1** and EDS elemental mapping.
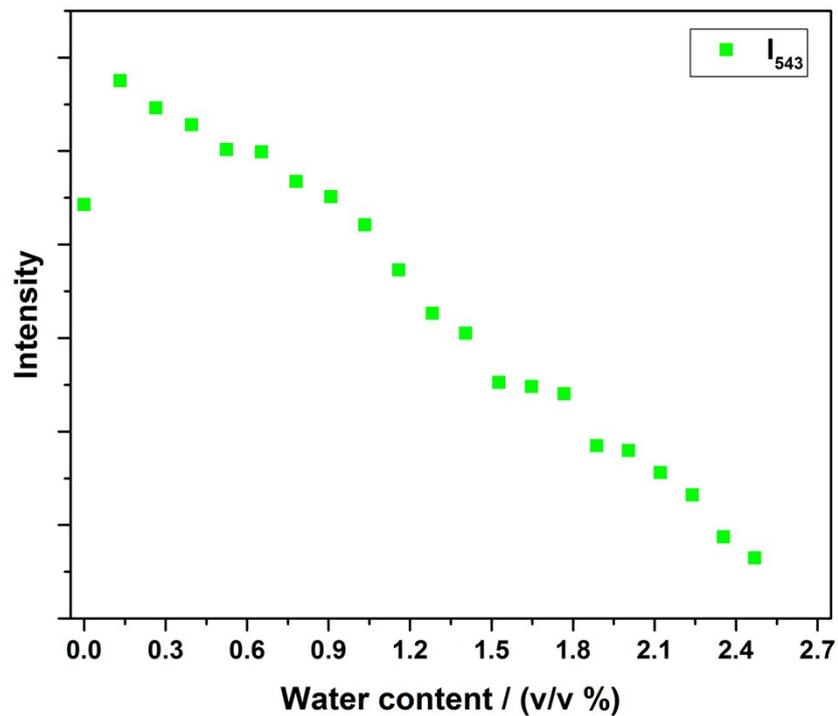
Figure S7. The relationship between water content and intensity of **Tb-L1** located at 543 nm
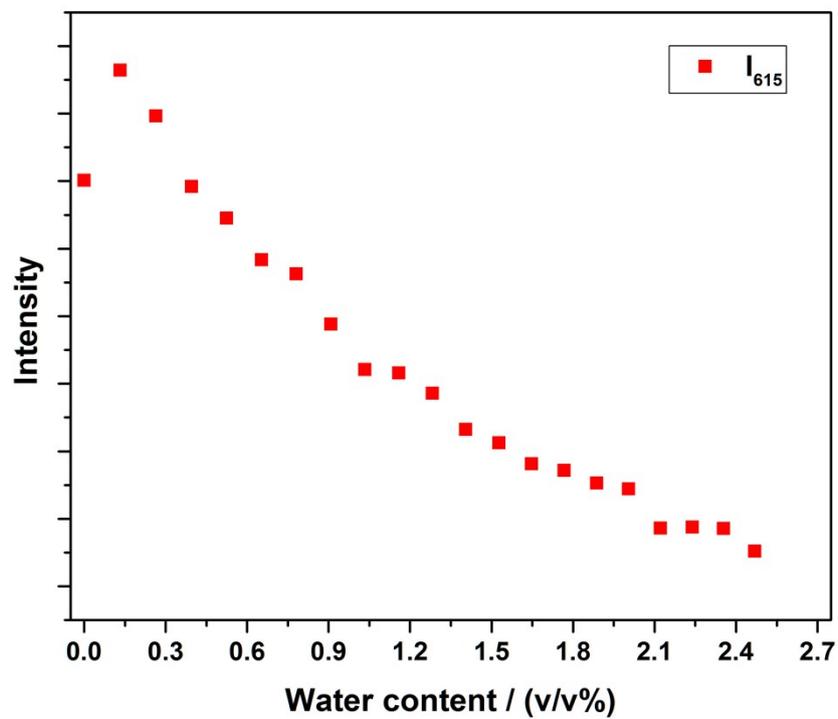
Figure S8. The relationship between water content and intensity of **Eu-L1** located at 615 nm
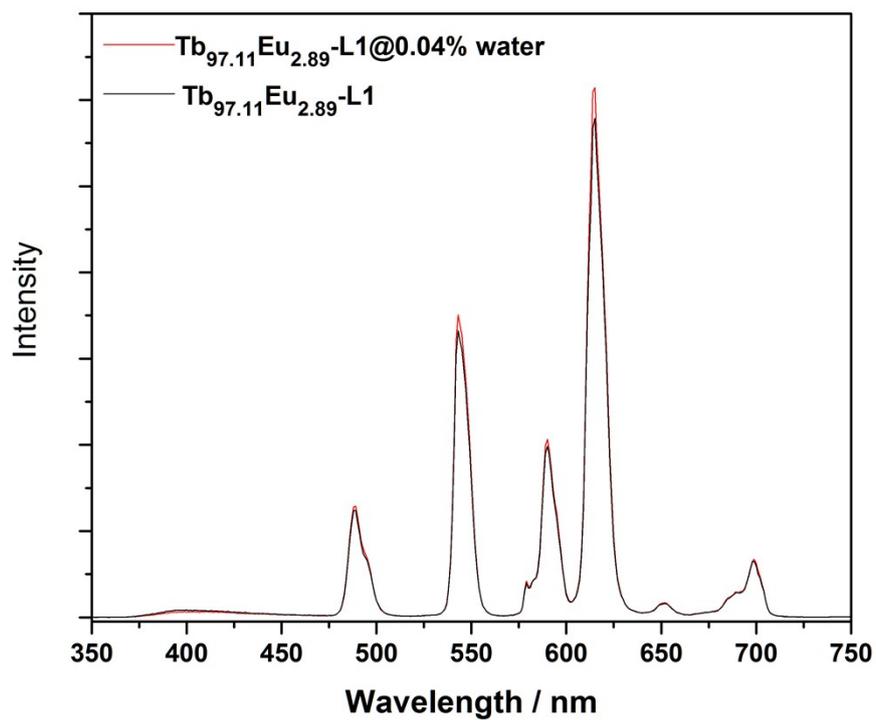
Figure S9. The fluorescent intensity of **Tb$_{97.11}$Eu$_{2.89}$-L1** changes after adding 0.04% water content
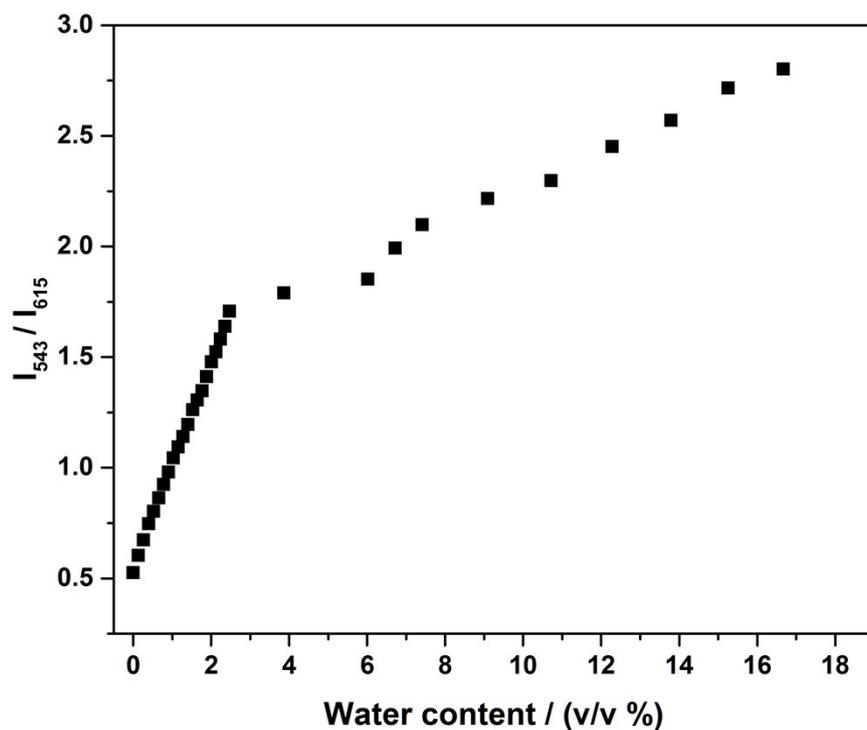
Figure S10. The relationship between water content and intensity of **I$_{543}$/I$_{615}$**
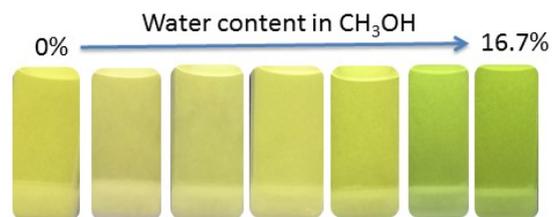
Figure S11. Optical images of **Tb$_{97.11}$Eu$_{2.89}$-L1** under a 254 nm UV lamp after treatment with various amounts of water in CH$_3$OH
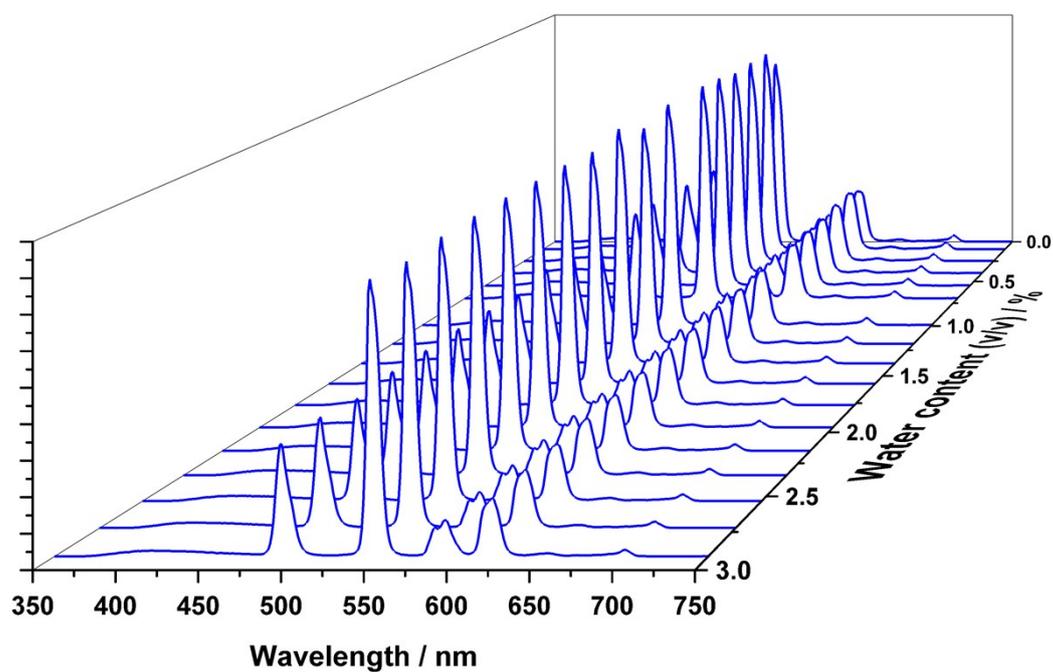
Figure S12. The fluorescence spectra of **Tb$_{97.11}$Eu$_{2.89}$-L1** for different amounts of water in CH$_3$OH

Figure S13. The linear relationship between the fluorescence intensity I_{543}/I_{615} and the water content in CH_3OH

Figure S14. Optical images of **Tb$_{97.11}$Eu$_{2.89}$-L1** under a 254 nm UV lamp after treatment with various amounts of water in DMF
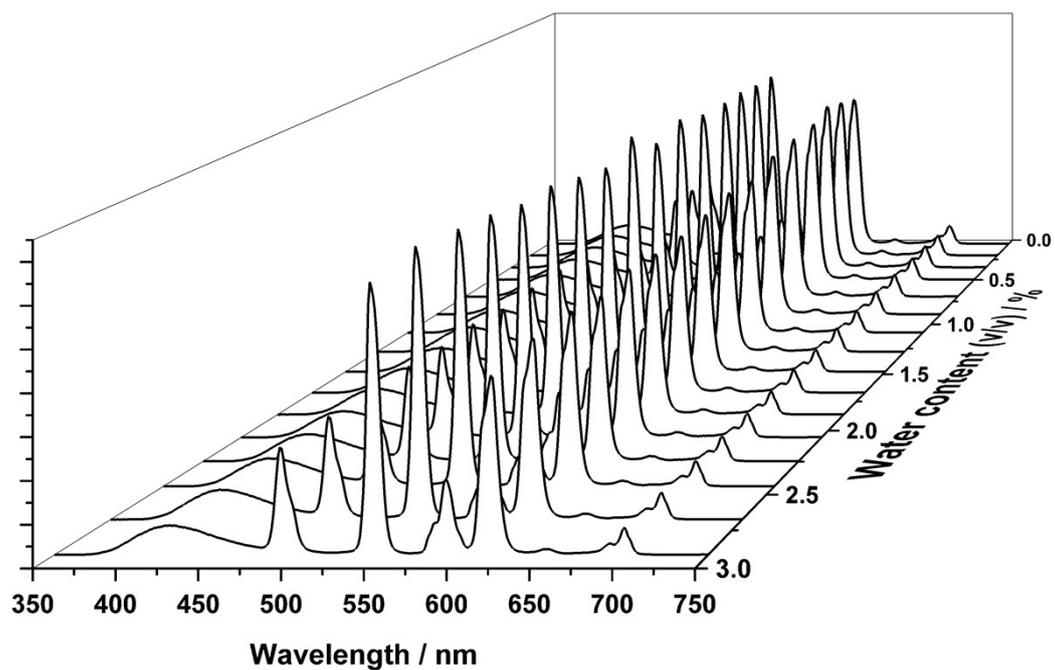
Figure S15. The fluorescence spectra of **Tb$_{97.11}$Eu$_{2.89}$-L1** for different amounts of water in DMF
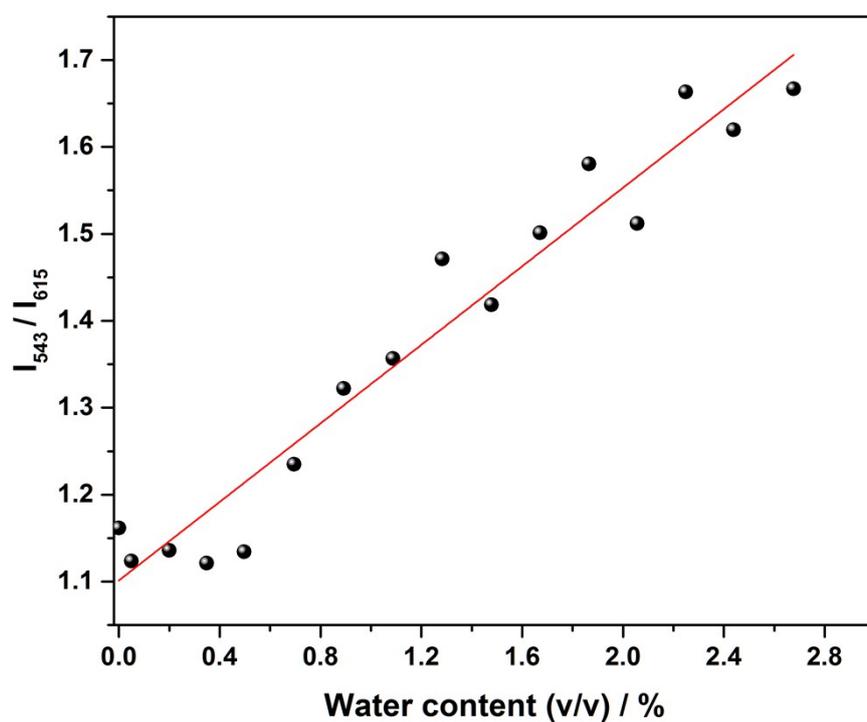
Figure S16. The fluorescence spectra of **Tb$_{97.11}$Eu$_{2.89}$-L1** for different amounts of water in DMF
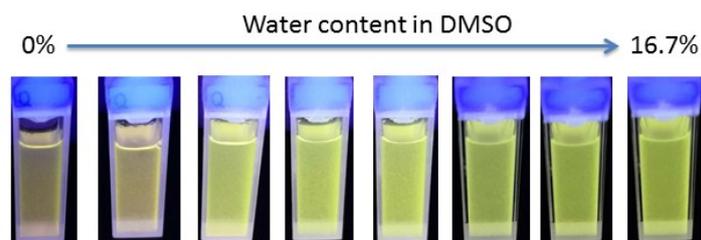
Figure S17. Optical images of **Tb₉₇.₁₁Eu₂.₈₉-L1** under a 254 nm UV lamp after treatment with various amounts of water in DMSO
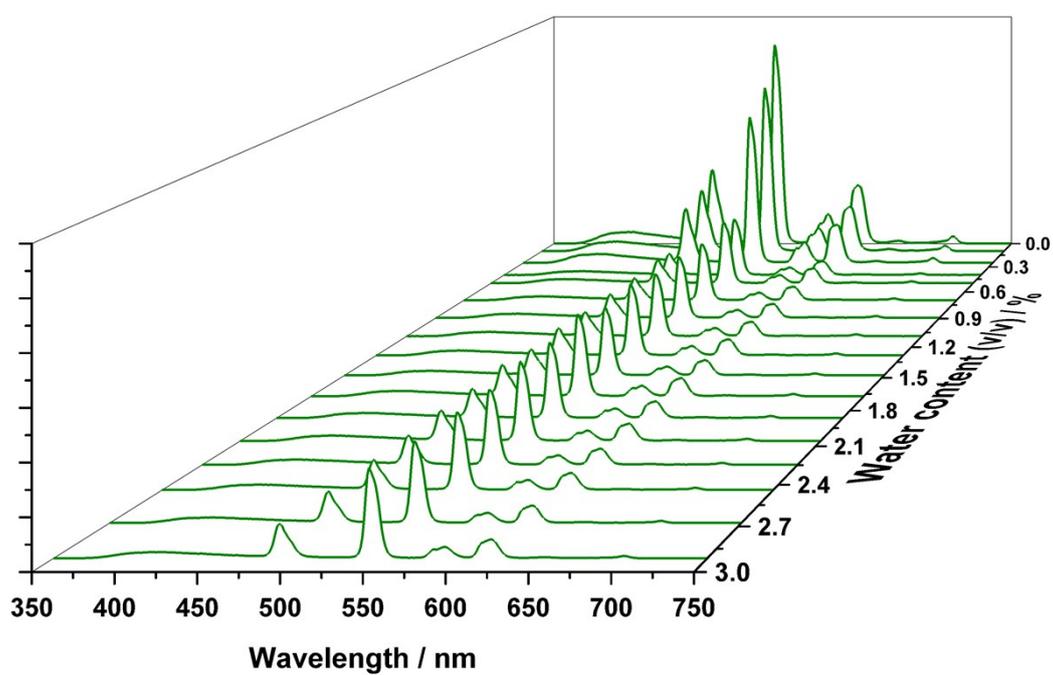
Figure S18. The fluorescence spectra of **Tb₉₇.₁₁Eu₂.₈₉-L1** for different amounts of water in DMSO
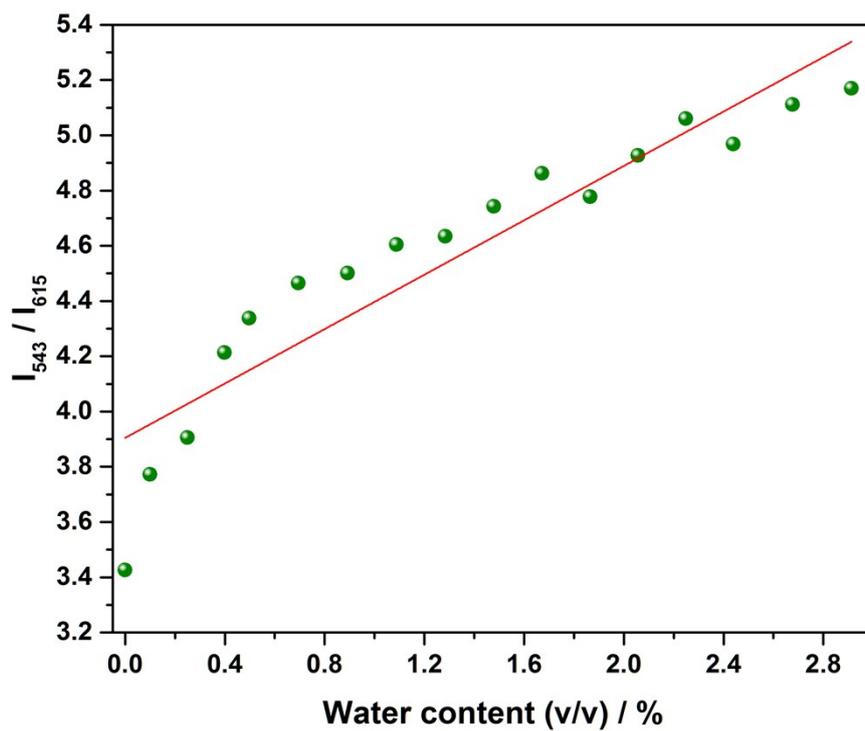
Figure S19. The fluorescence spectra of **Tb$_{97.11}$Eu$_{2.89}$-L1** for different amounts of water in DMSO
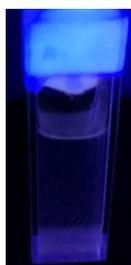
Figure S20. Optical images of **Tb$_{97.11}$Eu$_{2.89}$-L1** under a 254 nm UV lamp in acetone
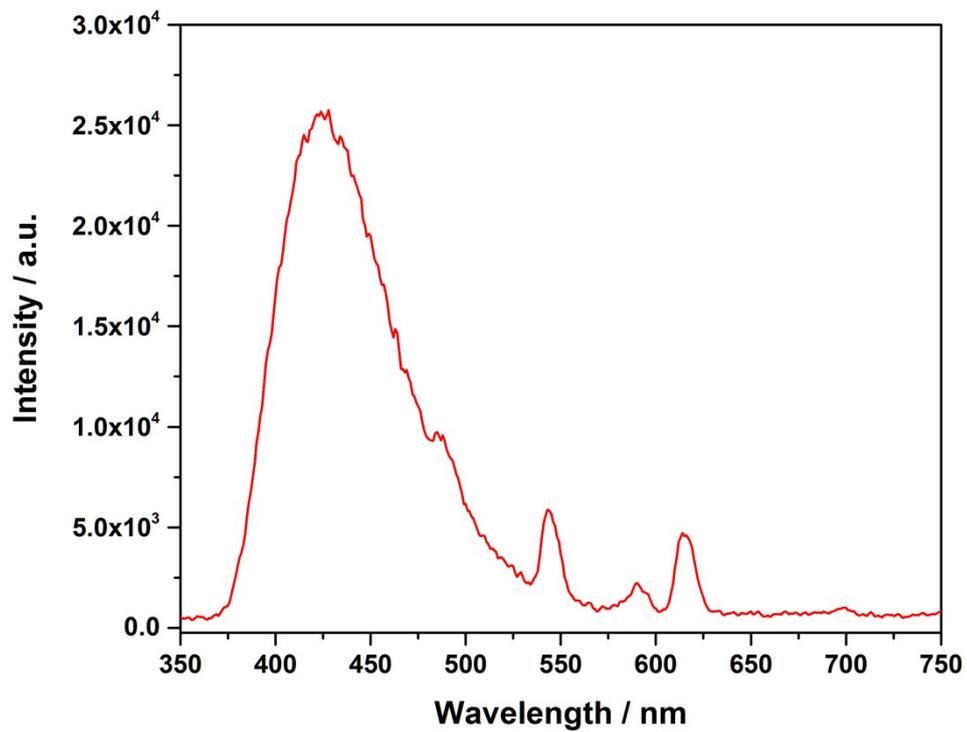
Figure S21. The fluorescence spectra of $\mathbf{Tb_{97.11}Eu_{2.89}\text{-}L1}$ in acetone
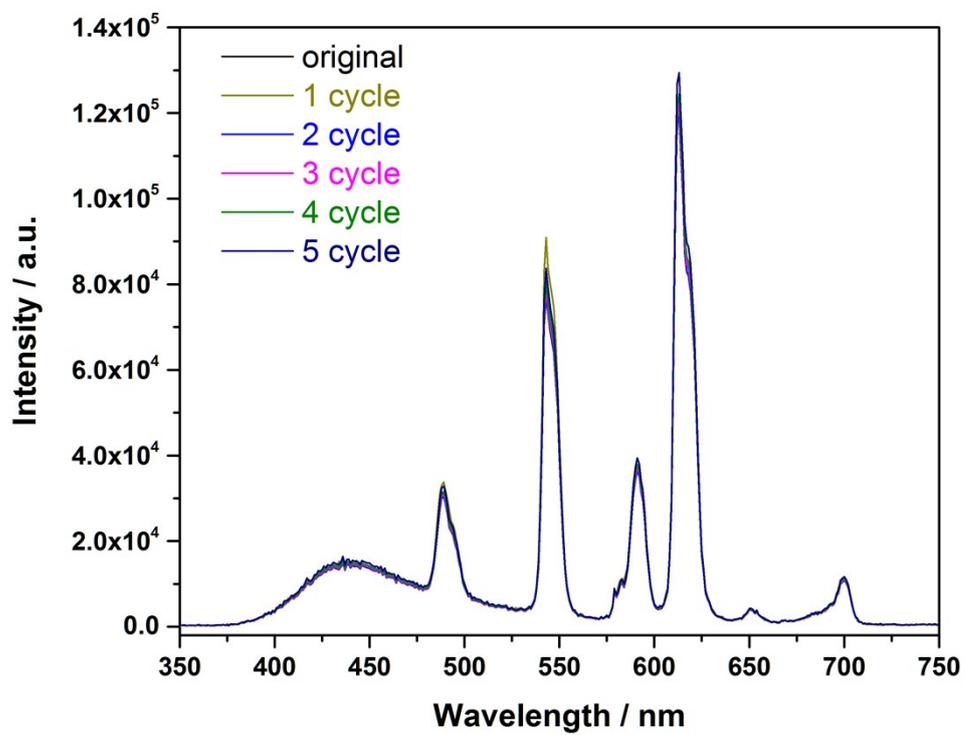
Figure S22. The fluorescence spectra of dry $\mathbf{Tb_{97.11}Eu_{2.89}\text{-}L1}$ after five dry-wet cycles
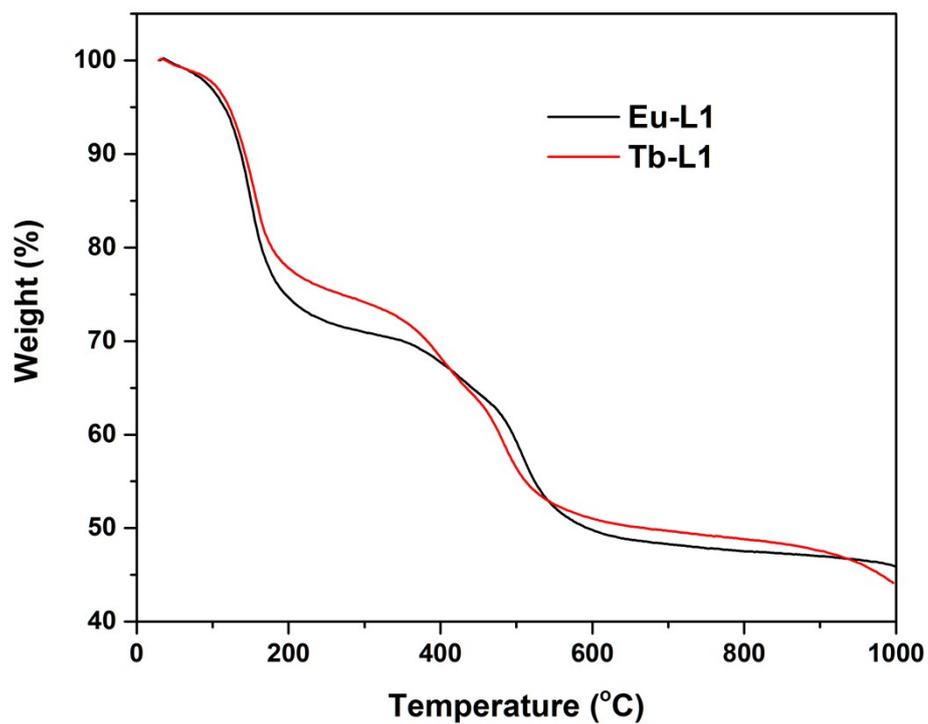
Figure S23. TGA curves of freshly prepared **Eu-L1** (black) and **Tb-L1** (red) the 25 - 1000 °C range.

Reference

1.   B. Bai-Chun, L. Bin and G. He, *Chinesis J. Appl. Chem.*, 2009, **26**, 4.
2.   G. M. Sheldrick, *Acta Crystallogr A*, 2008, **64**, 112-122.
3.   A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7-13.