

Support information for Dalton Trans.

Multi-functional Lanthanide-CPs based on tricarboxyl phenyl terpyridyl ligand as ratiometric luminescent thermometer and highly sensitive ion sensor with turn on/off effect

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Experimental details

Materials and preparation of series compounds

The organic ligand H₃tcptpy was synthesized with the help of Jinan Camolai Trading Company of Shandong, China. EDTA (>98% purity), was purchased from TCI chemicals. Lanthanide nitrate was prepared by the reaction of lanthanide oxide (purchased from J & K Chemical Limited) with nitric acid (10 mol / L⁻¹). Elemental analyses (C, H and N) were performed on an Elementar Vario ELIII analyzer. The FT-IR spectra (KBr pellet) were recorded in the range of 500-4000 cm⁻¹ on a Nicolet Magna 750 FTIR spectrometer.

The thermal gravimetric (TG) and difference thermal analysis (DTA) measurements were performed on a STA449C integration thermal analyzer at a heating rate of 10 °C min⁻¹ from room temperature to 850 °C in N₂ atmosphere with a heating rate of 10 °C min⁻¹. Powder X-ray diffraction patterns (PXRD) were carried out on a Bruker D8 Advance powder diffractometer for Cu K α radiation (λ = 1.5406 Å). The powder X-ray diffraction (PXRD) patterns were measured using a Bruker D8 Advance powder diffractometer at 40 kV, 40 mA with Cu K α radiation (λ = 1.5418 Å), with a scan speed of 0.2 s per step and a step size of 0.02 (2 θ).

For series of Tb-Eu mixed compounds {Tb_{1-x}Eu_xtcptpy }_n, in situ doped compounds were prepared by reaction lanthanides with ligand according to corresponding molar ratio. Series of

binary co-doped $\text{Tb}_x\text{Eu}_{1-x}\text{tcptpy}$ are built by a solvothermal in situ reaction: the procedure was similar to **1**, as a typical doping experiment, the total molar amounts of Tb^{3+} and Eu^{3+} equal to 100%, and the molar ratio amounts of doped Eu^{3+} ranges from 10-90%, respectively. All kinds of metal elemental analysis for doped compounds and normalization formula are reported in Table S3, ESI.

Additional Results and Discussion

$[\text{Eu}(\text{tcptpy})(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]_n$ (**2**): Yield: 54% (based on H_3tcptpy). Elemental analysis (%): calcd. for $\text{C}_{24}\text{H}_{20}\text{N}_3\text{O}_{10}\text{Eu}$ (Mr = 662.39): C 43.52, H 3.04, N 6.34; found: C 43.57, H 3.09, N 6.28. IR (cm^{-1}): 3535(s), 1746(w), 1595(s), 1533(s), 1464(m), 1430(m), 1401(m), 1348(s), 1316(s), 1209(w), 1062(m), 1005(m), 920(w), 823(m), 788(m), 730(m), 709(s).

$[\text{Gd}(\text{tcptpy})(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]_n$ (**3**): Yield: 58% (based on H_3tcptpy). Elemental analysis (%): calcd. for $\text{C}_{24}\text{H}_{20}\text{N}_3\text{O}_{10}\text{Gd}$ (Mr = 667.68): C 43.17, H 3.02, N 6.29; found: C 43.25, H 3.05, N 6.35. IR (cm^{-1}): 3535(s), 1750(w), 1595(s), 1537(m), 1468(w), 1430(w), 1404(w), 1354(s), 1318(s), 1206(w), 1066(m), 1008(m), 923(w), 824(m), 788(m), 734(m), 710(s).

$[\text{Tb}(\text{tcptpy})(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]_n$ (**4**): Yield: 52% (based on H_3tcptpy). Elemental analysis (%): calcd. for $\text{C}_{24}\text{H}_{20}\text{N}_3\text{O}_{10}\text{Tb}$ (Mr = 669.35): C 43.07, H 3.01, N 6.28; found: C 43.10, H 3.09, N 6.21. IR (cm^{-1}): 3535(s), 1748(w), 1595(s), 1537(m), 1467(m), 1430(m), 1405(w), 1352(s), 1316(s), 1209(w), 1062(m), 1008(m), 922(w), 824(m), 785(m), 731(m), 710(s).

$[\text{Dy}(\text{tcptpy})(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]_n$ (**5**): Yield: 55% (based on H_3tcptpy). Elemental analysis (%): calcd. for $\text{C}_{24}\text{H}_{20}\text{N}_3\text{O}_{10}\text{Dy}$ (Mr = 672.93): C 42.84, H 3.00, N 6.24; found: C 42.96, H 3.03, N 6.31. IR (cm^{-1}): 3535(s), 1746(w), 1599(s), 1537(m), 1470(m), 1430(m), 1405(w), 1356(s), 1316(s), 1206(w), 1070(m), 1005(m), 921(w), 827(m), 785(m), 734(m), 709(s).

Sensing properties measurement

The **4** solvent emulsions were prepared by introducing 2.75 mg of **4** as-powder into 3.00 mL of water. For sensing properties with respect to various solvents, different kinds of organic solvents and amounts of reagents were added into a standard **4** emulsion, while the concentration of Tb^{3+} was kept constant. Fluorometric titration of cation using dehydrated MOF to test the effect of Al^{3+}

and Na^+ , K^+ , Ag^+ , Mg^{2+} , Zn^{2+} , Cd^{2+} , Pb^{2+} , Co^{2+} , Sr^{2+} , Ni^{2+} , Cu^{2+} , Hg^{2+} , Fe^{3+} on the fluorescence Tb^{3+} ion, fluorometric titration were done by adding a few microliters of a working solution to 2.5 mL 0.3M HAc–NaAc (pH=5.5) buffer solution containing with a quartz cell.

EDTA (>90% purity), was purchased from TCI chemicals (Japan), and dissolved in ultra pure water. And then the solution's pH was adjusted to 4 by concentrated hydrochloric acid. Buffer solution of ammonium chloride-ammonia, and then made up to 5ml with pure water. One hundred microlitres of the new prepared sample of EDTA (0.20 g, 1.38 mol) was added to the heated distilled water and stirring continued for about 1 h.

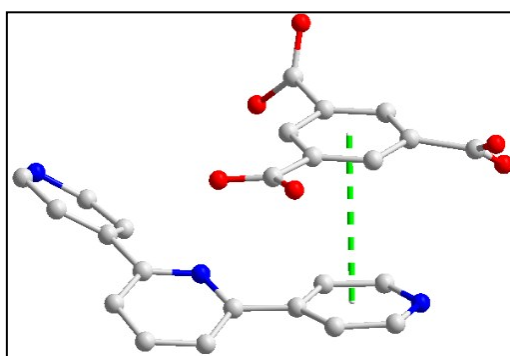


Fig. S1. π - π interaction of **4** (centroid-centroid separation distance: 3.758 Å).

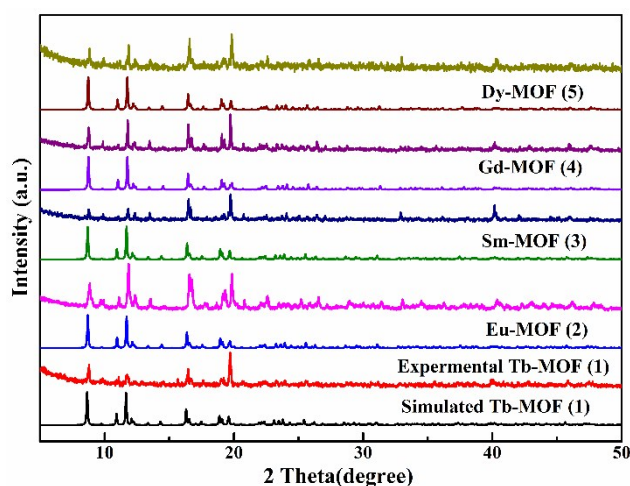


Fig. S2. Comparing the experiment and sample PXRD patterns of **1-5**.

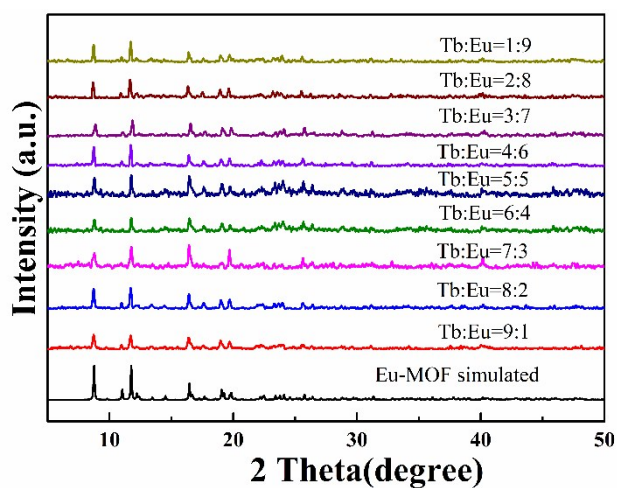


Fig. S3. PXRD patterns of series of $\text{Tb}_{1-x}\text{Eu}_x\text{tcptpy}$.

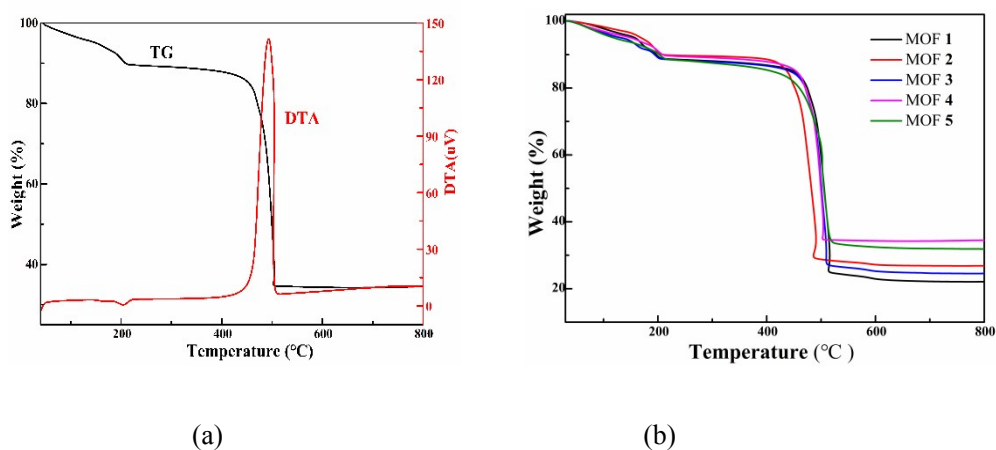


Fig. S4. (a) The TG and DTA curves for CPS **4**; (b) The TG curves for CPs **1-5**.

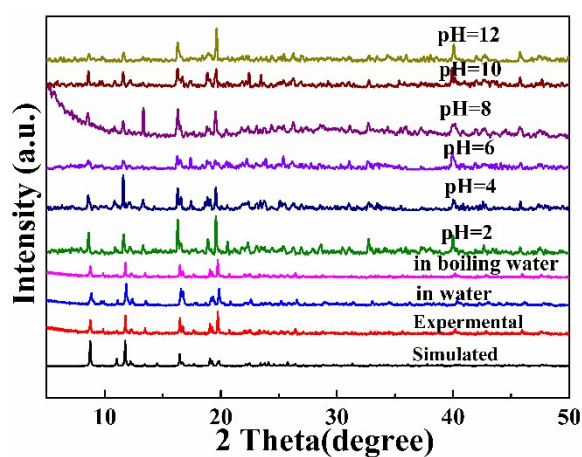


Fig. S5. PXRD patterns of **4** in water, boiling water and under various pH values (pH=2, 4, 6, 8, 10, 12) in aqueous media.

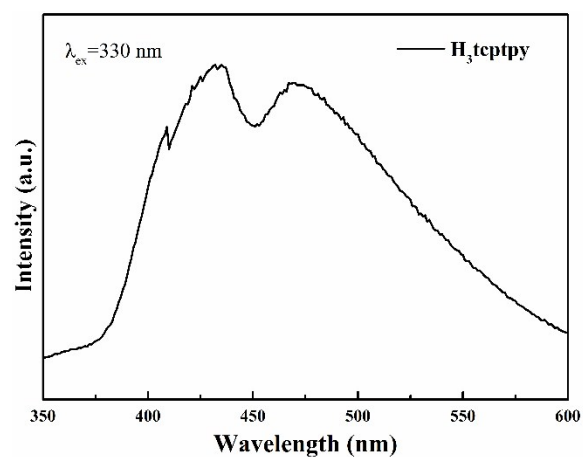


Fig. S6. Solid state emission spectra of free H₃tcptpy ligand.

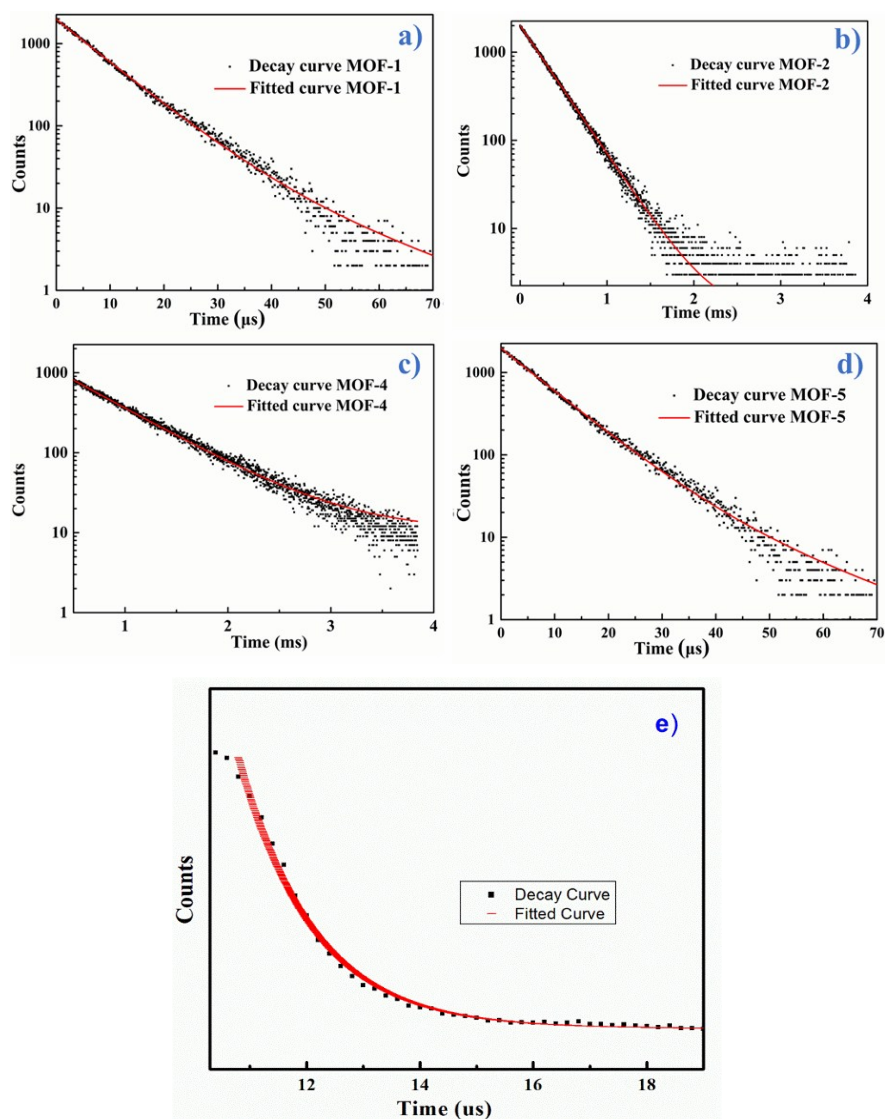


Fig. S7. Luminescence decay lifetimes of **4-Tb** (a), **2-Eu** (b), **1-Sm** (c), **5-Dy** (d) and **3-Gd** (e) measured at the excitation/emission maxima.

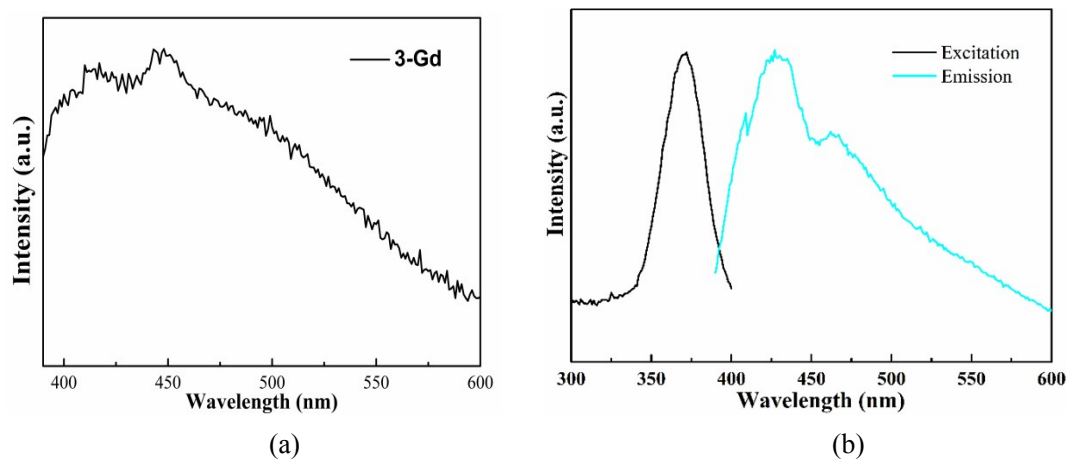


Fig. S8. (a) Solid state phosphorescence emission spectra of Gd compound **3** at 77 K; (b) Solid state emission spectra of compound **3** at room temperature.

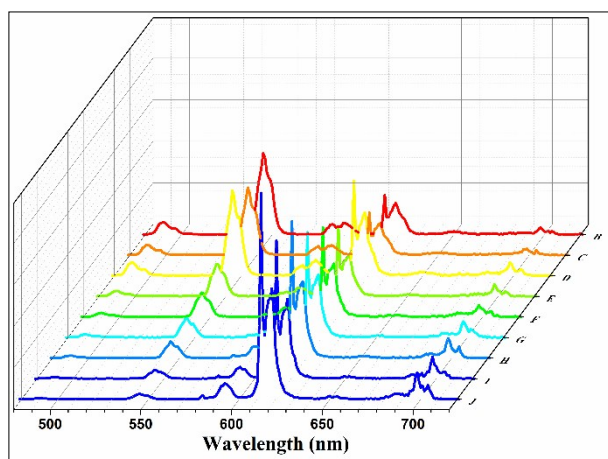


Fig. S9. Solid state emission spectra of $\text{Tb}_{1-x}\text{Eu}_x\text{tcptpy}$ (from B to J, Tb:Eu molar ratio is 9:1, 8:2, 7:3.....2:8, 1:9 respectively)

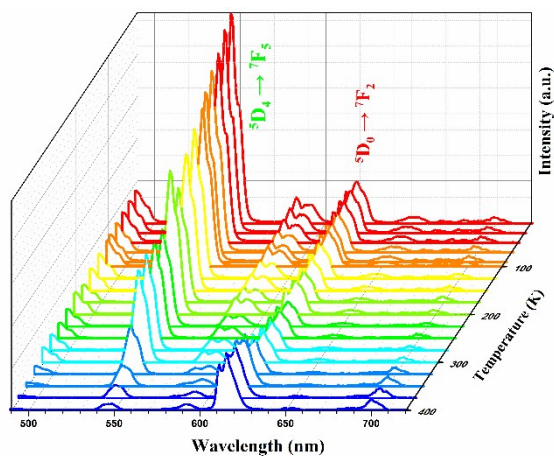


Fig. S10. Temperature dependent solid state emission spectra of $\text{Tb}_{0.897}\text{Eu}_{0.103}\text{tcptpy}$

from 10 to 400 K.

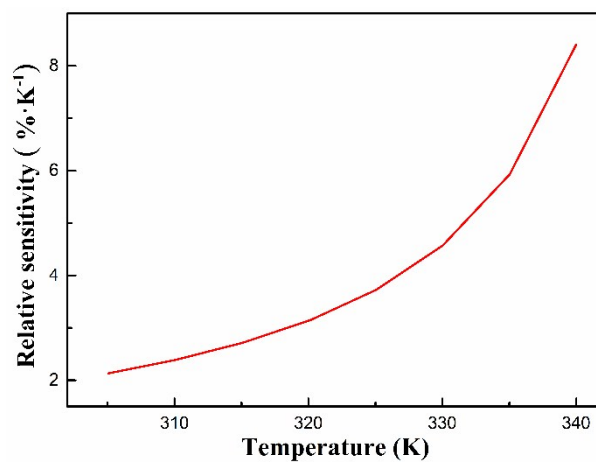


Fig. S11. The relative sensitivity values (S_m) of Tb_{0.897}Eu_{0.103}tcptpy from 300 K to 340 K.

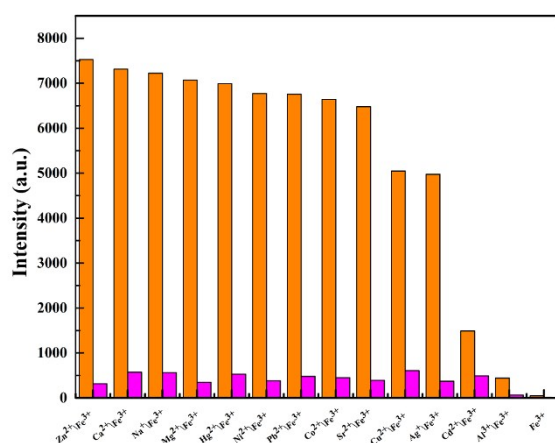


Fig. S12. Luminescence intensities of the $^5D_4 \rightarrow ^7F_5$ transition of **4** dispersed in H₂O in presence of different metal ions ($10^{-2} \text{ mol} \cdot \text{L}^{-1}$) (in orange) or a mixture of Fe³⁺ ions ($10^{-2} \text{ mol} \cdot \text{L}^{-1}$) (in purple).

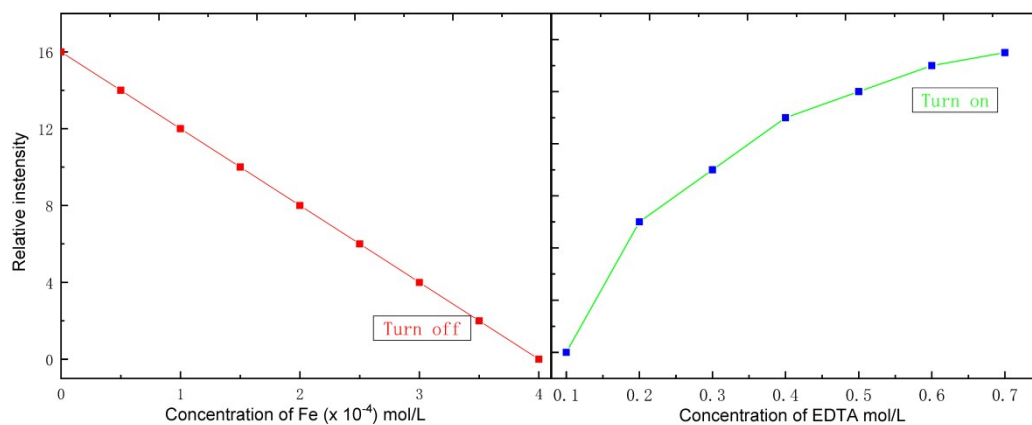


Fig. S13. Scheme illustration the recovery of Tb luminescence from turn off to turn on

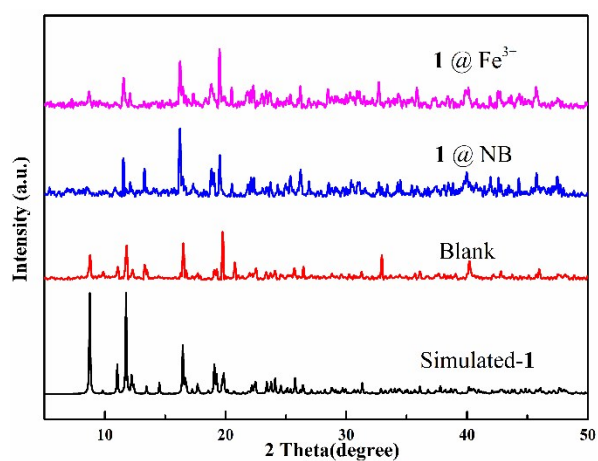


Fig. S14. PXRD patterns of **1** before and after treatment with NB in methanol and Fe³⁺ ions in water

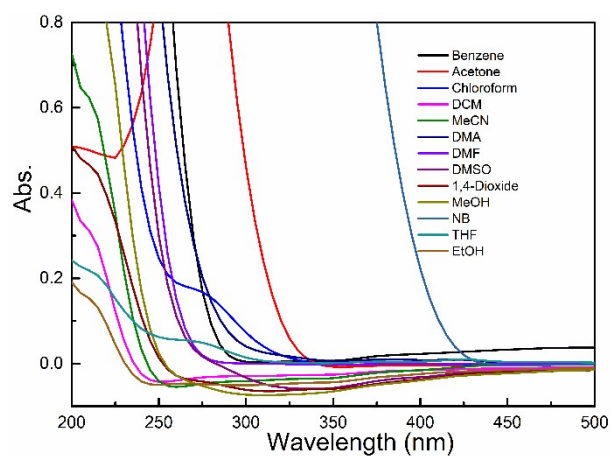


Fig. S15. UV-vis absorption spectra of Tb-MOFs soaked in some kinds solvent molecules.

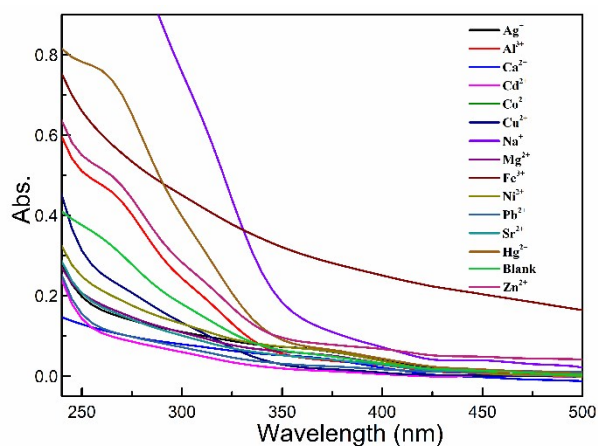


Fig. S16. UV-vis absorption spectra of Tb-MOFs soaked in solution containing different cation ions.

Table S1. Selected bond lengths (Å) and angles (deg) for compounds **1-5**.

Compound 1					
Bond	Å	Bond	Å	Bond	Å
Sm(1)-O(1)	2.255(3)	Sm(1)-O(3)#1	2.480(3)	Sm(1)-O(4)#1	2.465(3)
Sm(1)-O2W	2.390(3)	Sm(1)-O1W	2.410(3)	Sm(1)-O(5)#2	2.517(3)
Sm(1)-O(6)#2	2.468(3)	Sm(1)-N(3)#3	2.646(4)	O(3)-Sm(1)#4	2.480(3)
angle	deg	angle	deg	angle	deg
O(1)-Sm(1)-O(3)#1	97.63(11)	O(1)-Sm(1)-O(4)#1	93.22(12)	O(1)-Sm(1)-O(8)	151.41(11)
O(1)-Sm(1)-O(7)	87.99(12)	O(1)-Sm(1)-O(5)#2	82.35(11)	O(1)-Sm(1)-O(6)#2	134.82(11)
O(1)-Sm(1)-N(3)#3	77.28(12)	O(3)#1-Sm(1)-O(5)#2	125.73(10)	O(3)#1-Sm(1)-N(3)#3	75.00(11)
O(4)#1-Sm(1)-O(3)#1	52.61(9)	O(4)#1-Sm(1)-O(5)#2	73.15(10)	O(4)#1-Sm(1)-O(6)#2	74.48(12)
O(4)#1-Sm(1)-N(3)#3	125.16(12)	O(8)-Sm(1)-O(3)#1	80.94(11)	O(8)-Sm(1)-O(4)	107.72(11)
O(8)-Sm(1)-O(7)	82.21(12)	O(8)-Sm(1)-O(5)#2	121.77(11)	O(8)-Sm(1)-O(6)#2	71.22(11)
Compound 2					
Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Eu(1)-O(1)	2.243(3)	Eu(1)-O(3)#1	2.469(3)	N(3)-Eu(1)#6	2.621(4)
Eu(1)-O(6)#2	2.502(3)	Eu(1)-O(5)#2	2.452(3)	Eu(1)-O(8)	2.365(3)
Eu(1)-O(7)	2.392(3)	Eu(1)-N(3)#3	2.621(4)	O(3)-Eu(1)#4	2.469(3)
O(4)-Eu(1)#4	2.451(3)	O(6)-Eu(1)#5	2.502(3)	O(5)-Eu(1)#5	2.452(3)
Angle	Degree (°)	Angle	Degree (°)	Angle	Degree (°)
O(1)-Eu(1)-O(3)#1	98.14(11)	O(1)-Eu(1)-O(4)#1	92.39(11)	O(1)-Eu(1)-O(6)#2	81.72(11)
O(1)-Eu(1)-O(5)#2	134.60(11)	O(1)-Eu(1)-O(8)	151.40(11)	O(1)-Eu(1)-O(7)	88.29(12)
O(1)-Eu(1)-N(3)#3	77.36(11)	O(3)#1-Eu(1)-O(6)#2	125.82(10)	O(3)#1-Eu(1)-N(3)#3	75.19(11)
O(8)-Eu(1)-O(4)#1	108.48(11)	O(8)-Eu(1)-O(6)#2	122.38(11)	O(8)-Eu(1)-O(5)#2	71.53(10)
O(8)-Eu(1)-O(7)	82.22(12)	O(8)-Eu(1)-N(3)#3	74.68(11)	O(7)-Eu(1)-O(3)#1	154.59(10)
O(7)-Eu(1)-O(4)#1	152.06(11)	O(7)-Eu(1)-O(6)#2	79.34(10)	O(7)-Eu(1)-O(5)#2	85.05(11)
Compound 3					
Bond	Å	Bond	Å	Bond	Å
Gd(1)-O(1)	2.245(4)	Gd(1)-O3#1	2.452(4)	Gd(1)-O(4)#1	2.441(4)
Gd(1)-O(5)#2	2.488(4)	Gd(1)-O(6)#2	2.439(4)	Gd(1)-O(7)	2.353(4)
Gd(1)-O(8)	2.374(4)	Gd(1)-N(2)#3	2.613(5)	O(3)-Gd(1)#4	2.452(4)
O(4)-Gd(14)	2.441(4)	O(5)-Gd(15)	2.487(4)	O(6)-Gd(15)	2.439(4)
Angle	Angle	Angle	Angle	Angle	Angle
O(1)-Gd(1)-O(3)#1	98.21(15)	O(1)-Gd(1)-O(4)#1	92.44(16)	O(1)-Gd(1)-O(5)#2	81.82(15)
O(1)-Gd(1)-O(6)#2	134.66(14)	O(1)-Gd(1)-O(7)	151.29(15)	O(1)-Gd(1)-O(8)	87.86(15)
O(1)-Gd(1)-N(2)#3	77.33(15)	O(3)#1-Gd(1)-O(5)#2	125.83(14)	O(3)#1-Gd(1)-N(2)#3	75.17(15)
O(4)#1-Gd(1)-O(3)#1	52.97(13)	O(4)#1-Gd(1)-O(5)#2	72.87(13)	O(4)#1-Gd(1)-N(2)#3	125.24(16)
O(5)#2-Gd(1)-N(2)#3	152.59(15)	O(6)#2-Gd(1)-O(3)#1	106.56(14)	O(6)#2-Gd(1)-O(4)#1	74.35(15)

O(6)#2-Gd(1)-O(5)#2	52.87(14)	O(6)#2-Gd(1)-N(2)#3	145.25(15)	O(7)-Gd(1)-O(3)#1	80.65(15)
O(7)-Gd(1)-O(4)#1	108.77(15)	O(7)-Gd(1)-O(5)#2	122.23(15)	O(7)-Gd(1)-O(6)#2	71.53(14)
O(7)-Gd(1)-O(8)	81.89(16)	O(7)-Gd(1)-N(2)#3	74.65(15)	O(8)-Gd(1)-O(3)#1	153.70(14)
O(8)-Gd(1)-O(4)#1	152.81(14)	O(8)-Gd(1)-O(5)#2	80.28(15)	O(8)-Gd(1)-O(6)#2	86.19(15)

Compound 4

Bond Length	Å	Bond	Å	Bond	Å
Tb(1)-O(1)	2.222(5)	Tb(1)-O(3)#1	2.441(4)	Tb(1)-O(4)#1	2.423(4)
Tb(1)-O(5)#2	2.422(5)	Tb(1)-O(6)#2	2.465(5)	Tb(1)-O1W	2.356(4)
Tb(1)-O2W	2.334(5)	Tb(1)-N(2)#3	2.575(6)	O(3)-Tb(1)#4	2.441(4)
N(2)-Tb(1)#6	2.575(6)	O(5)-Tb(1)#5	2.422(5)	O(6)-Tb(1)#5	2.465(5)
Bond Angle	deg	angle	deg	angle	deg
O(1)-Tb(1)-O(3)#1	98.34(18)	O(1)-Tb(1)-O(4)#1	92.22(18)	O(1)-Tb(1)-O(5)#2	135.00(17)
O(1)-Tb(1)-O(6)#2	81.93(17)	O(1)-Tb(1)-O(7)	88.87(18)	O(1)-Tb(1)-O2W	151.62(17)
O(7)-Tb(1)-O(4)#1	152.31(17)	O(7)-Tb(1)-O(5)#2	85.29(18)	O(7)-Tb(1)-O(6)#2	80.06(16)
O(7)-Tb(1)-N(2)#3	81.66(19)	O2W-Tb(1)-O(3)#1	79.97(18)	O2W-Tb(1)-O(4)#1	108.44(18)
O2W-Tb(1)-O(5)#2	71.06(16)	O(8)-Tb(1)-O(6)#2	122.15(17)	O2W-Tb(1)-O(7)	81.71(18)

Compound 5

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Dy(1)-O(1)	2.209(3)	Dy(1)-O(3)#1	2.426(3)	N(2)-Dy(1)#6	2.576(4)
Dy(1)-O(5)#2	2.414(3)	Dy(1)-O(6)#2	2.468(3)	Dy(1)-O(7)	2.337(3)
Dy(1)-O(8)	2.327(3)	Dy(1)-N(2)#3	2.576(4)	O(3)-Dy(1)#4	2.426(3)
O(4)-Dy(1)#4	2.412(3)	O(5)-Dy(1)#5	2.414(3)	O(6)-Dy(1)#5	2.468(3)
Angle	Degree (°)	Angle	Degree (°)	Angle	Degree (°)
O(1)-Dy(1)-O(3)#1	98.93(13)	O(1)-Dy(1)-O(4)#1	91.25(12)	O(1)-Dy(1)-O(5)#2	134.72(12)
O(1)-Dy(1)-O(6)#2	81.29(12)	O(1)-Dy(1)-O(7)	88.21(13)	O(1)-Dy(1)-O(8)	151.71(12)
O(1)-Dy(1)-N(2)#3	77.64(13)	O(3)#1-Dy(1)-N(2)#3	75.20(12)	O(4)#1-Dy(1)-O(3)#1	53.48(11)
O(4)#1-Dy(1)-O(5)#2	74.56(12)	O(4)#1-Dy(1)-O(6)#2	72.80(11)	O(4)#1-Dy(1)-N(2)#3	125.15(13)
O(5)#2-Dy(1)-O(3)#1	105.54(12)	O(5)#2-Dy(1)-O(6)#2	53.51(12)	O(5)#2-Dy(1)-N(2)#3	145.16(13)
O(6)#2-Dy(1)-N(2)#3	152.24(12)	O(7)-Dy(1)-O(3)#1	153.27(11)	O(7)-Dy(1)-O(4)#1	152.70(12)
O(7)-Dy(1)-O(5)#2	86.57(13)	O(7)-Dy(1)-O(6)#2	80.15(11)	O(7)-Dy(1)-N(2)#3	81.33(13)
O(8)-Dy(1)-O(3)#1	80.52(12)	O(8)-Dy(1)-O(4)#1	110.03(12)	O(8)-Dy(1)-O(5)#2	71.02(12)
O(8)-Dy(1)-O(6)#2	122.01(12)	O(8)-Dy(1)-O(7)	81.17(13)	O(8)-Dy(1)-N(2)#3	74.88(13)

Symmetry Codes:

1#1+X,3/2-Y,-1/2+Z; #21-X,-1/2+Y,3/2-Z; #3-1+X,+Y,+Z; #4+X,3/2-Y,1/2+Z; #51-X,1/2+Y,3/2-Z; #61+X,+Y,+Z;
2#1+X,3/2-Y,-1/2+Z; #21-X,-1/2+Y,3/2-Z; #3-1+X,+Y,+Z; #4+X,3/2-Y,1/2+Z; #51-X,1/2+Y,3/2-Z; #61+X,+Y,+Z; **3**#1+X,3/2-Y,-1/2+Z;
#21-X,-1/2+Y,3/2-Z; #3-1+X,+Y,+Z; #4+X,3/2-Y,1/2+Z; #51-X,1/2+Y,3/2-Z; #61+X,+Y,+Z; **4**#1+X,3/2-Y,1/2+Z; #21-X,-1/2+Y,1/2-Z;
#31+X,+Y,+Z;#4+X,3/2-Y,-1/2+Z; #51-X,1/2+Y,1/2-Z; #6-1+X,+Y,+Z;
5#1+X,1/2-Y,1/2+Z; #21-X,1/2+Y,1/2-Z; #31+X,+Y,+Z;#4+X,1/2-Y,-1/2+Z; #51-X,-1/2+Y,1/2-Z; #6-1+X,+Y,+Z;

Table S2. Hydrogen bond lengths (Å) and angles (deg) for compounds **1-5**.

Compound 1

D-H-A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O8-H8B-O3 ¹	0.85	2.40	2.672(4)	99.3
O7-H7A-O2 ¹	0.91	1.89	2.742(5)	153.8
Compound 2				
D-H-A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O8-H8B-O3 ¹	0.85	2.40	2.661(4)	98.2
O7-H7A-O21	0.85	1.96	2.738(5)	151.6
O7-H7B-N12	0.85	2.24	2.709(6)	114.8
Compound 3				
D-H-A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O7-H7B-O3 ¹	0.85	2.32	2.683(5)	106.1
O8-H8B-O2 ¹	0.86	2.08	2.752(7)	134.0
Compound 4				
D-H-A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O7-H7A-N3 ¹	0.85	2.15	2.717(8)	123.7
Compound 5				
D-H-A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O7-H7B-N3 ¹	0.91	1.81	2.713(6)	172.6

Symmetry Codes:

1#1+X,3/2-Y,1/2+Z; **2**#1-X,-1/2+Y,3/2-Z; **2**+X,3/2-Y,1/2+Z; **3**#1-X,-1/2+Y,3/2-Z; **4**#1 2-X,-1/2+Y,1/2-Z; **5**#1+X,1/2-Y,-1/2+Z.

Table S3.
Metal elemental analysis for doped compounds and normalization formula

Design Formula	Wt% Calcu.	Eu Found	Wt% Calcu.	Tb Found	Normalization Formula
Tb _{0.9} Eu _{0.1} tcptpy	9.61	10.26	90.4	89.74	Tb _{0.897} Eu _{0.103} tcptpy
Tb _{0.8} Eu _{0.2} tcptpy	19.29	20.02	81.71	79.98	Tb _{0.800} Eu _{0.200} tcptpy
Tb _{0.6} Eu _{0.4} tcptpy	38.93	39.37	61.07	60.63	Tb _{0.606} Eu _{0.394} tcptpy
Tb _{0.4} Eu _{0.6} tcptpy	58.92	58.57	41.08	41.43	Tb _{0.414} Eu _{0.586} tcptpy
Tb _{0.2} Eu _{0.8} tcptpy	79.27	78.96	20.73	21.04	Tb _{0.210} Eu _{0.790} tcptpy
Tb _{0.3} Eu _{0.2} Gd _{0.5} tcptpy	19.43	20.37	30.43	31.15	Tb _{0.312} Eu _{0.204} Gd _{0.484} tcptpy