

## Supporting Information

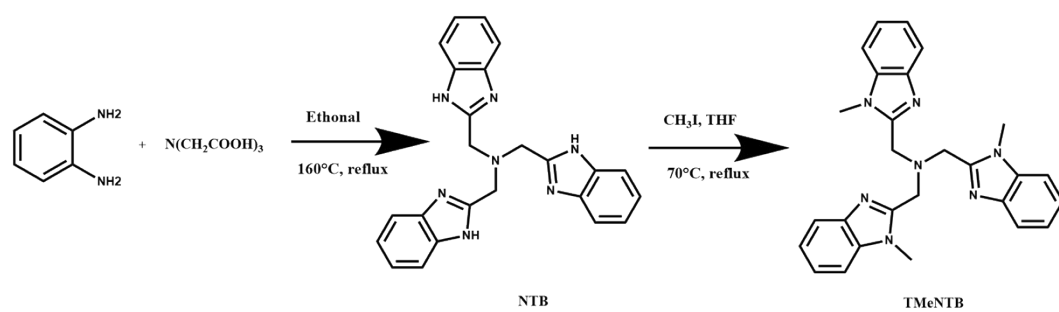
### 1. Crystal structures

**Table S1.** Crystal data and structure refinement for Eu-1, Eu-2, Tb-2 and Gd-2.

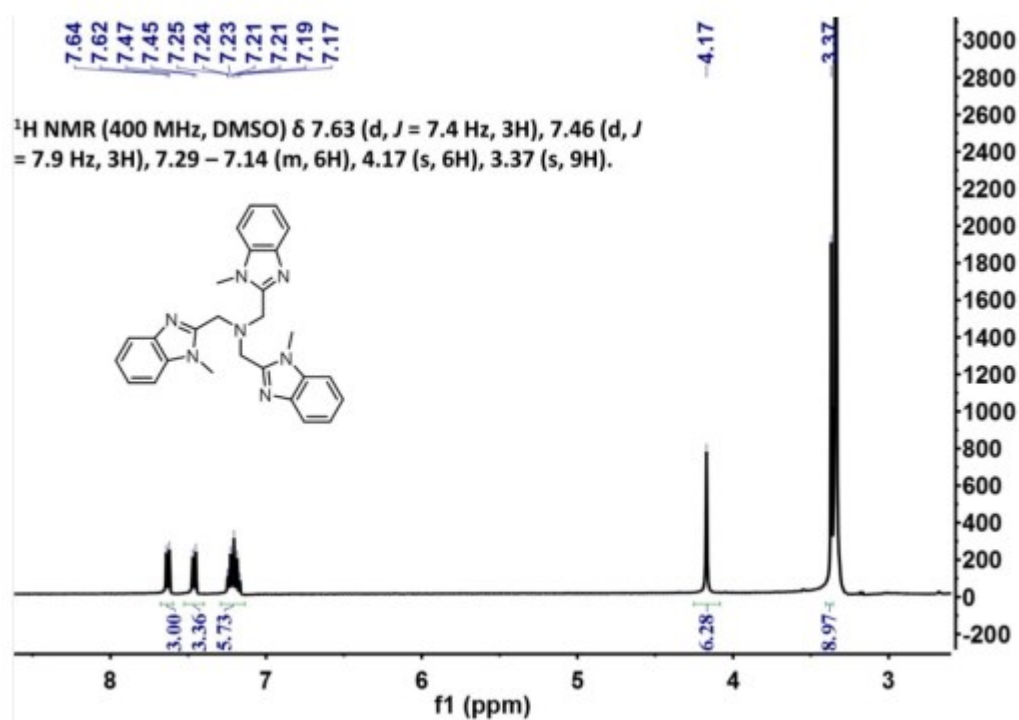
Complex	Eu-1	Eu-2	Tb-2	Gd-2
Empirical formula	$C_{56}H_{60}N_{14}O_{14}Cl_3Eu$	$C_{57}H_{61}Cl_3EuN_{15}O_{13}$	$C_{57}H_{61}Cl_3N_{15}O_{13}Tb$	$C_{57}H_{61}Cl_3GdN_{15}O_{13}$
Formula weight	1411.49	1422.51	1428.47	1427.80
Temperature/K	293(2)	150.15	293(2)	150.00(10)
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a/Å	12.7639(5)	12.7697(5)	12.7866(3)	12.7306(7)
b/Å	21.0583(8)	20.9395(8)	21.0103(5)	20.959(2)
c/Å	22.859(3)	22.6567(12)	22.6401(6)	22.596(3)
$\alpha/^\circ$	90	90	90	90
$\beta/^\circ$	90	90	90	90
$\gamma/^\circ$	90	90	90	90
Volume/Å <sup>3</sup>	6144.1(8)	6058.2(5)	6082.3(2)	6029.1(11)
Z	4	4	4	4
$\rho_{calc}/g/cm^3$	1.526	1.560	1.560	1.573
$\mu/mm^{-1}$	9.145	1.244	1.371	8.985
F(000)	2880.0	2904.0	2908.0	2908.0
Reflections collected	11327	22808	13436	15018
Independent reflections	8494	10479	9416	9726
Data/restraints /parameters	8494/297/802	10479/80/828	9416/1382/817	9726/844/811
Goof	1.111	1.040	1.027	1.020
Final R indexes [I>>=2 $\sigma$ (I)]	R <sub>1</sub> = 0.1488, wR <sub>2</sub> = 0.3210	R <sub>1</sub> = 0.0451, wR <sub>2</sub> = 0.1012	R <sub>1</sub> = 0.0923, wR <sub>2</sub> = 0.2346	R <sub>1</sub> = 0.0784, wR <sub>2</sub> = 0.1898
Final R indexes [all data]	R <sub>1</sub> = 0.2317, wR <sub>2</sub> = 0.3790	R <sub>1</sub> = 0.0573, wR <sub>2</sub> = 0.1089	R <sub>1</sub> = 0.1087, wR <sub>2</sub> = 0.2534	R <sub>1</sub> = 0.0954, wR <sub>2</sub> = 0.2145

**Table S2.** Selected Bond Lengths (Å) of Eu-1, Eu-2, Tb-2 and Gd-2.

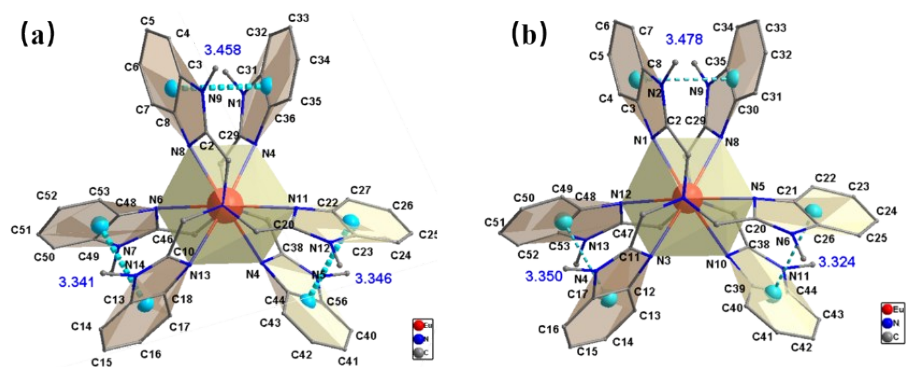
Eu-1					
Eu1	N2	2.460(11)	Eu1	N11	2.617(10)
Eu1	N3	2.702(10)	Eu1	N13	2.497(12)
Eu1	N4	2.457(8)	Eu1	N8	2.501(12)
Eu1	N6	2.540(10)	Eu1	N10	2.706(10)
Eu-2					
Eu1	N1	2.488(7)	Eu1	N10	2.478(7)
Eu1	N3	2.470(7)	Eu1	N12	2.492(7)
Eu1	N5	2.495(7)	Eu1	N14	2.675(7)
Eu1	N7	2.694(7)	Eu1	N8	2.477(7)
Tb-2					
Tb1	N1	2.446(13)	Tb1	N8	2.445(13)
Tb1	N3	2.457(13)	Tb1	N10	2.439(14)
Tb1	N4	2.468(13)	Tb1	N12	2.470(13)
Tb1	N6	2.675(13)	Tb1	N14	2.666(13)
Gd-2					
Gd1	N1	2.468(13)	Gd1	N8	2.466(12)
Gd1	N3	2.665(12)	Gd1	N10	2.702(12)
Gd1	N4	2.445(11)	Gd1	N11	2.480(13)
Gd1	N6	2.494(12)	Gd1	N13	2.479(12)



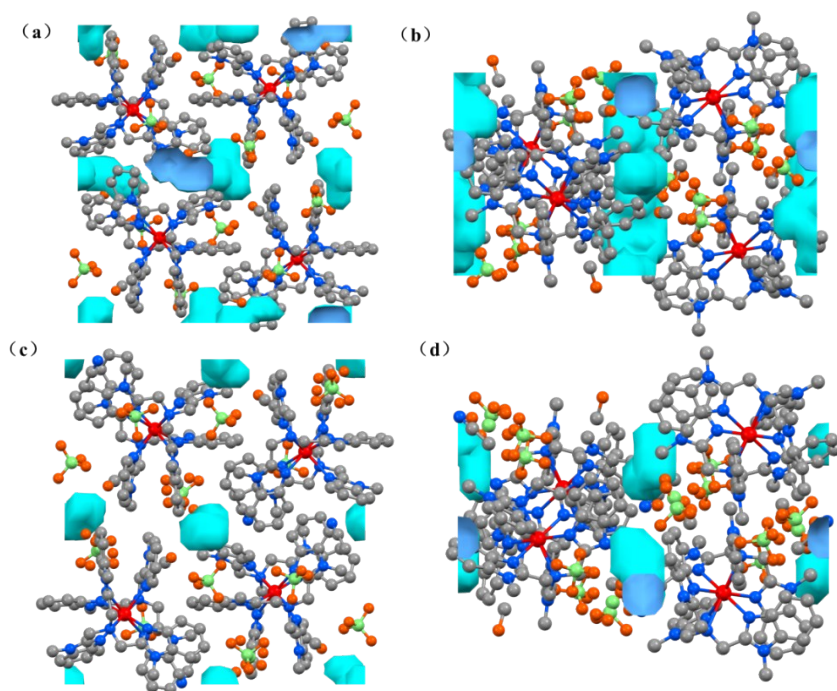
**Scheme S1.** Synthetic route of TMeNTB ligand.



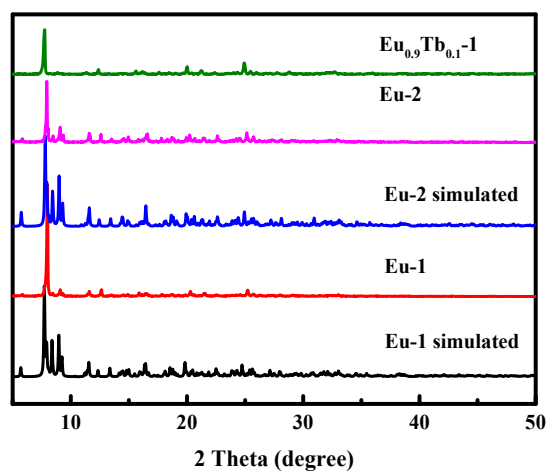
**Fig. S1** The <sup>1</sup>H NMR spectra of TMeNTB ligand.



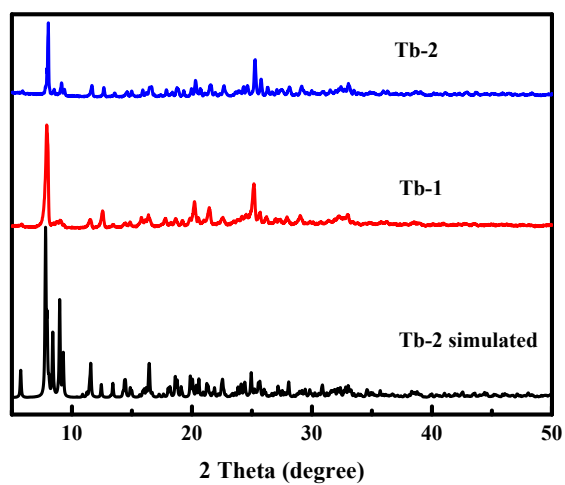
**Fig. S2** Structure of the cationic unit in Eu-1 (a) and Eu-2 (b). Eu red, N blue, C gray, the teal dash lines showing the  $\pi$ - $\pi$  interactions between the BLMs, the light yellow box showing the distorted cubic coordination geometry around the Eu(III) ion.



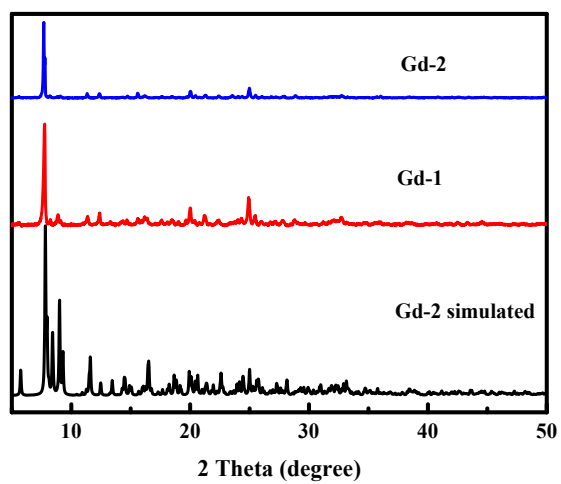
**Fig. S3** The structure of Eu-1 viewed along *a* axis (a) and *b* axis (b). The structure of Eu-2 viewed from *a* axis (c) and *b* axis (d). Eu red, N blue, C gray, O orange, Cl green, and the cyan polyhedron showing the cavities between coordination units.



(a)



(b)



(c)

Fig. S4 PXRD patterns of the Ln-1 and Ln-2 series compared with the simulated.

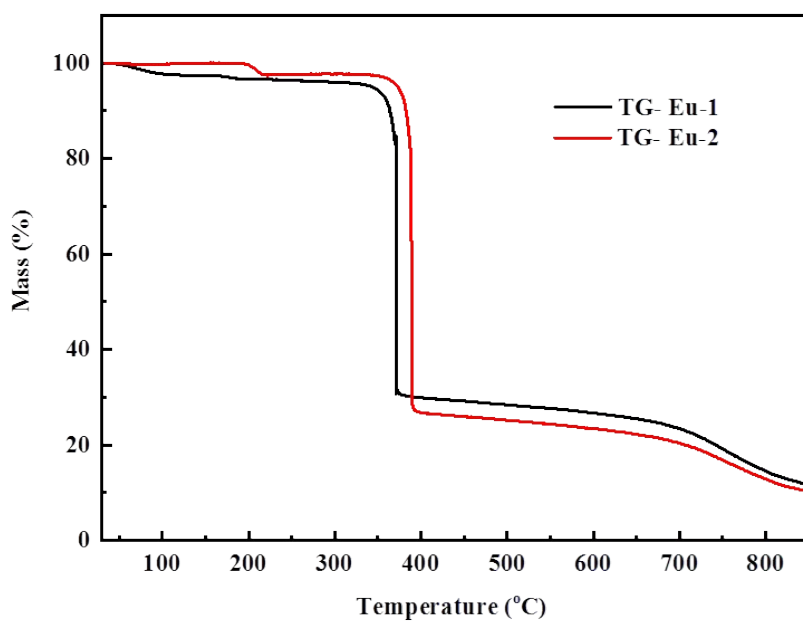


Fig. S5 TG curves of Eu-1 and Eu-2.

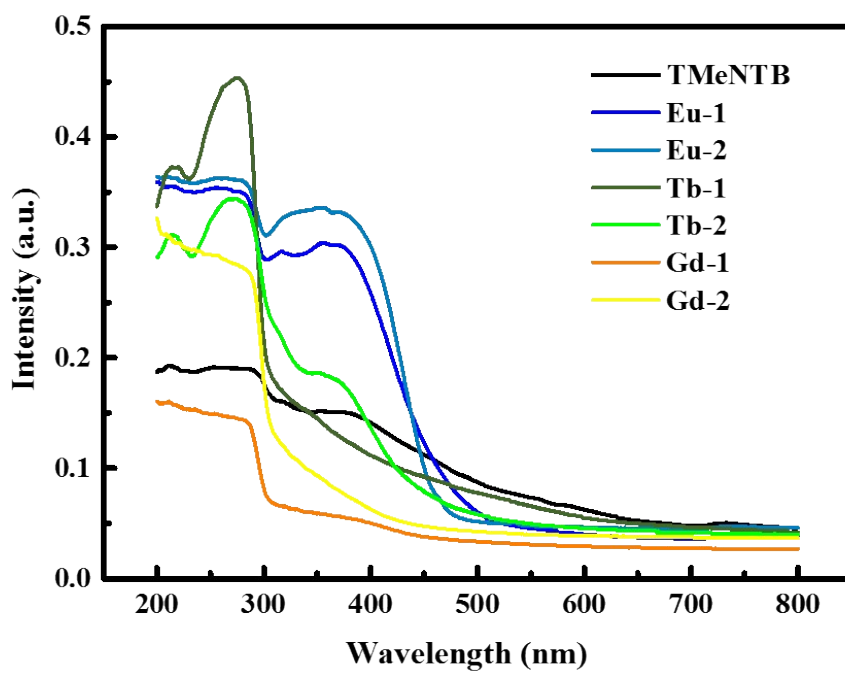
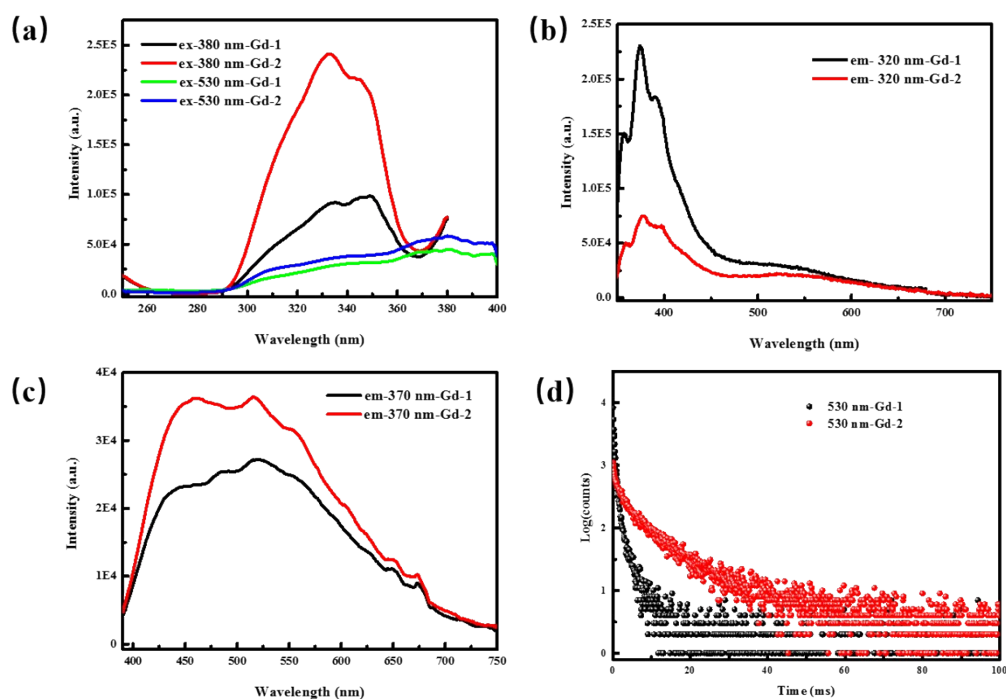
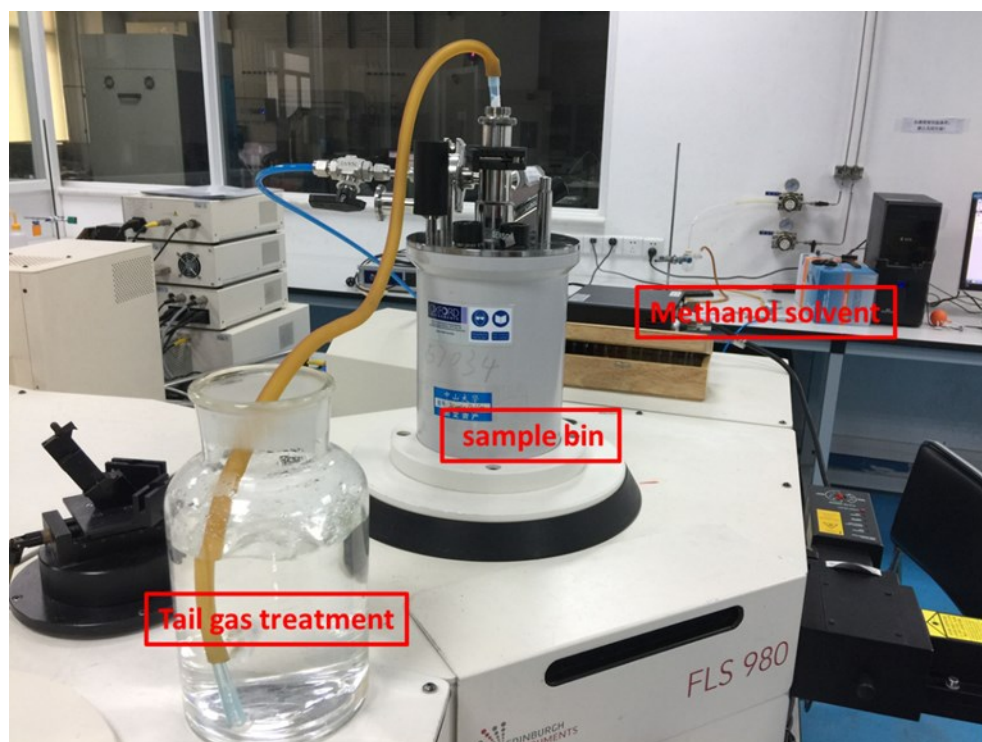


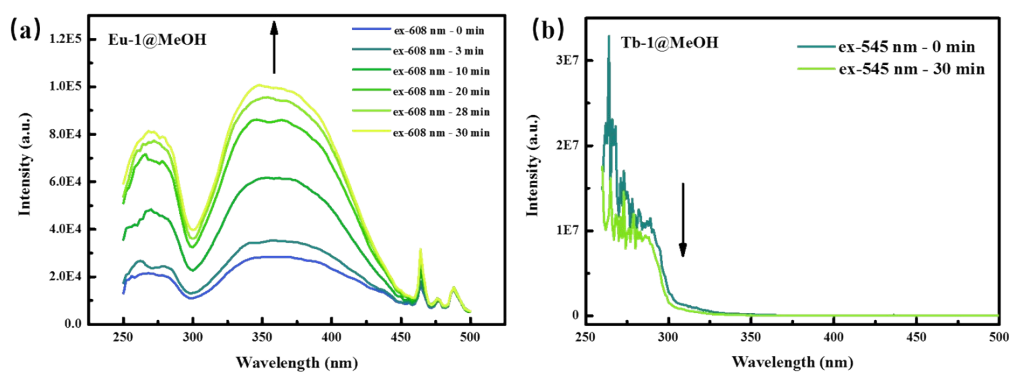
Fig. S6 Solid state UV-visible absorption spectra of TMeNTB, Ln-1 and Ln-2 series.



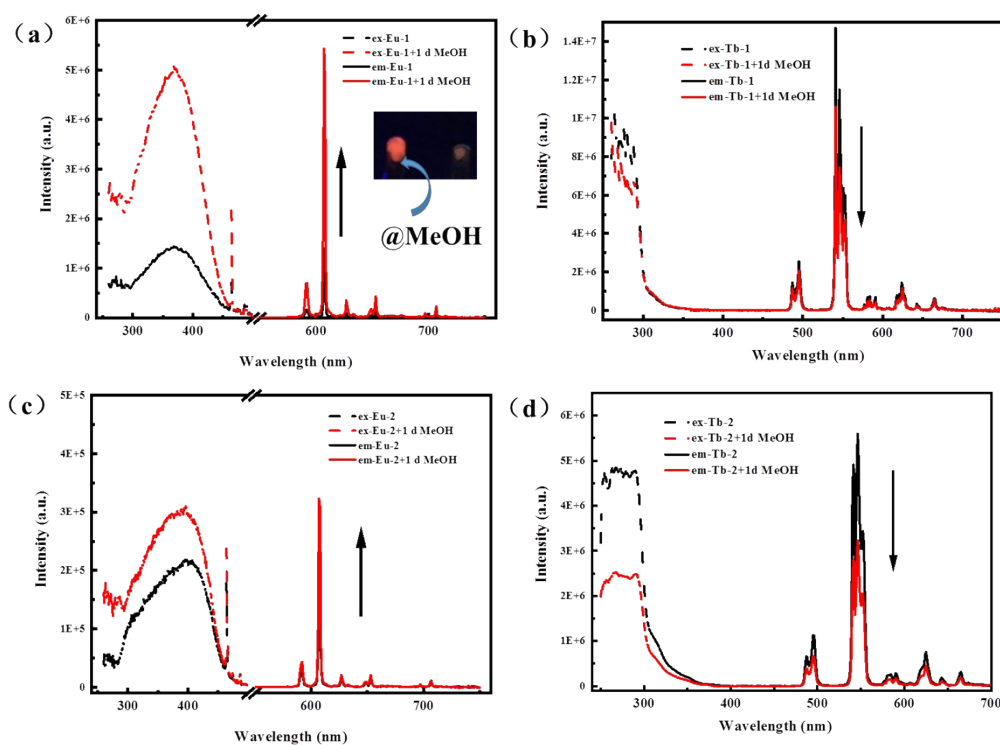
**Fig. S7** (a) The excitation spectra of Gd-1 and Gd-2 ( $\lambda_{em} = 380$  or  $530$  nm); (b) The emission spectra of Gd-1 and Gd-2 ( $\lambda_{ex} = 320$  nm); (c) The emission spectra of Gd-1 and Gd-2 ( $\lambda_{ex} = 370$  nm); (d) The lifetime decay curves of Gd-1 and Gd-2 ( $\lambda_{ex} = 370$  nm,  $\lambda_{em} = 530$  nm).



**Fig. S8** Device diagram of sample response to methanol vapor.

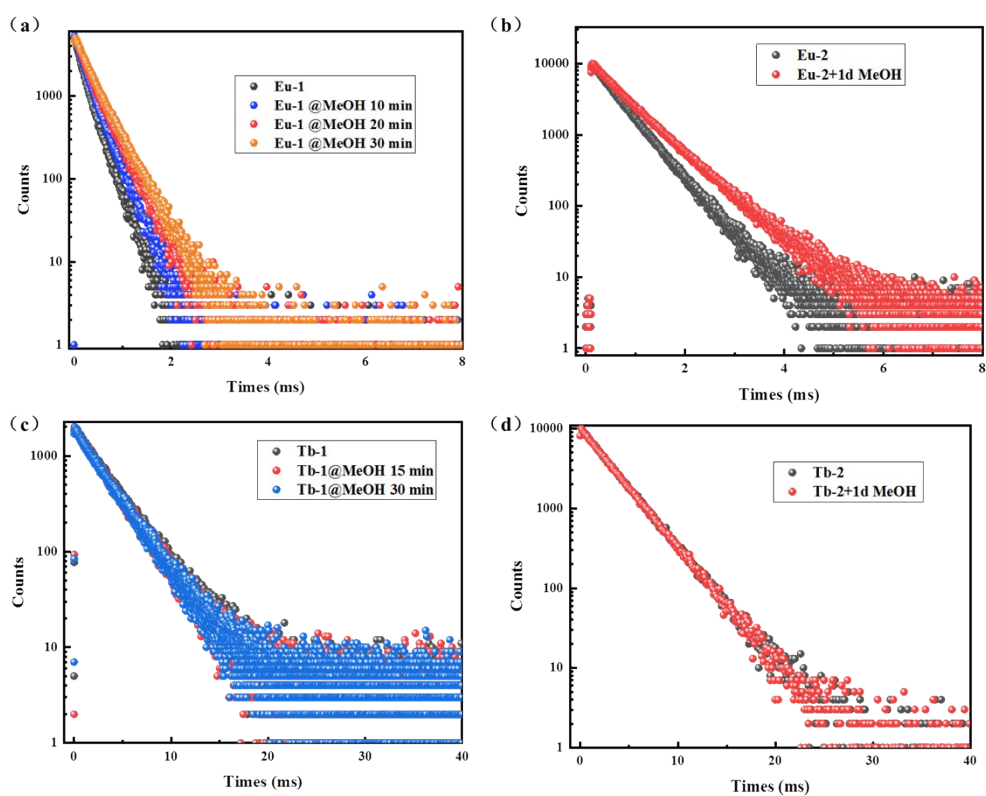


**Fig. S9** The fluorescent excitation spectra of (a) Eu-1, and (b) Tb-1 in the atmosphere of MeOH/N<sub>2</sub> with time at room temperature.

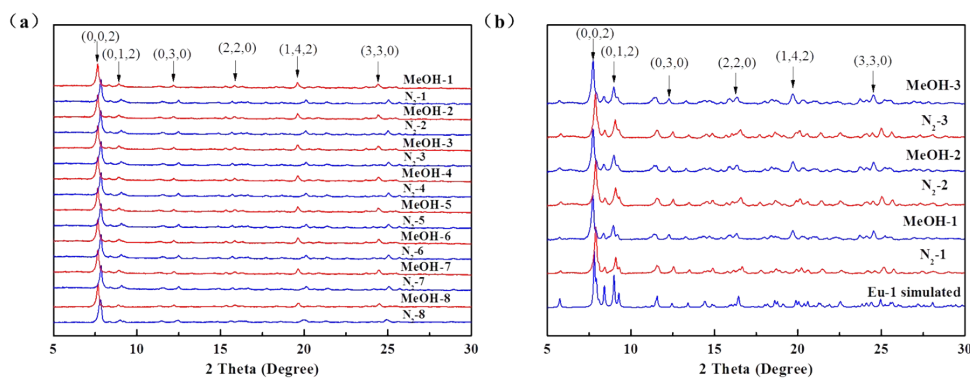


**Fig. S10** The fluorescent excitation and emission spectra of (a) Eu-1, (b) Tb-1, (c) Eu-2, and (d) Tb-2 microcrystalline samples before and after adding one drop of MeOH liquid.

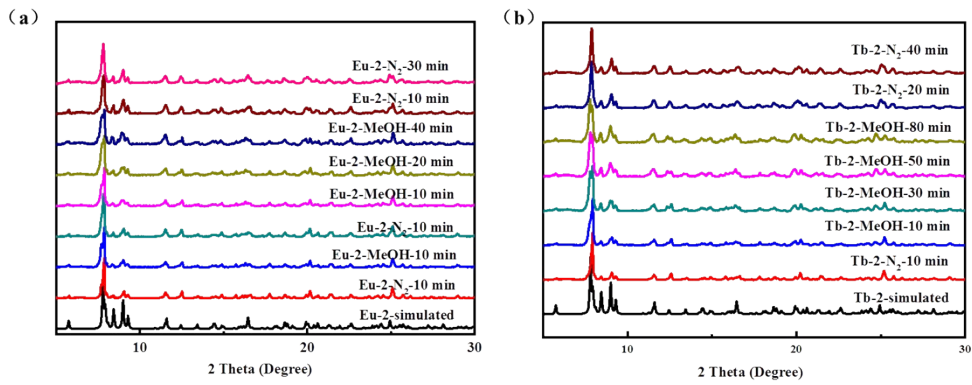




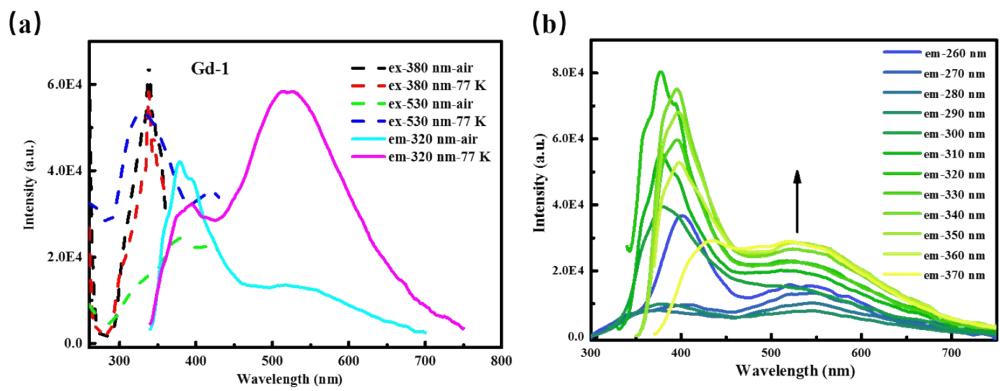
**Fig. S11** The decay curves of Ln-1 and Ln-2 before and after treated with methanol vapor or liquid.



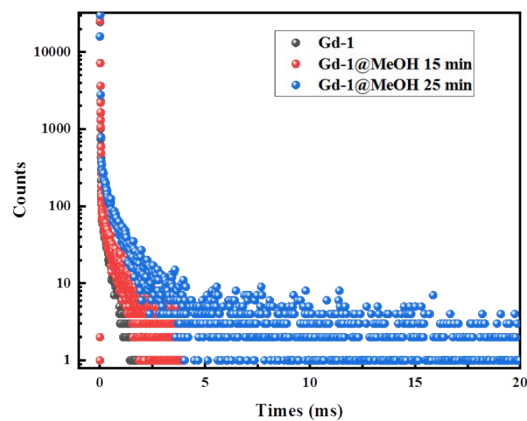
**Fig. S12** The X-ray powder diffraction (PXRD) patterns of (a) Eu-1, and (b) Tb-1 under MeOH/N<sub>2</sub> steam cycles (the number of 1-8 or 1-3 means the cycle number).



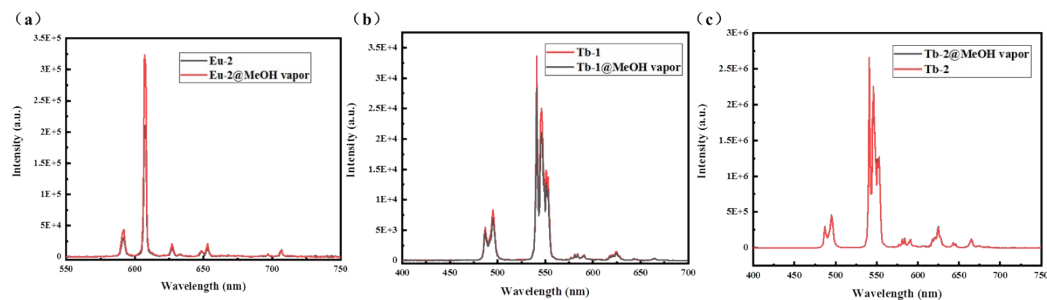
**Fig. S13** The PXRD patterns of (a) Eu-2, and (b) Tb-2 under MeOH/N<sub>2</sub> steam cycle.



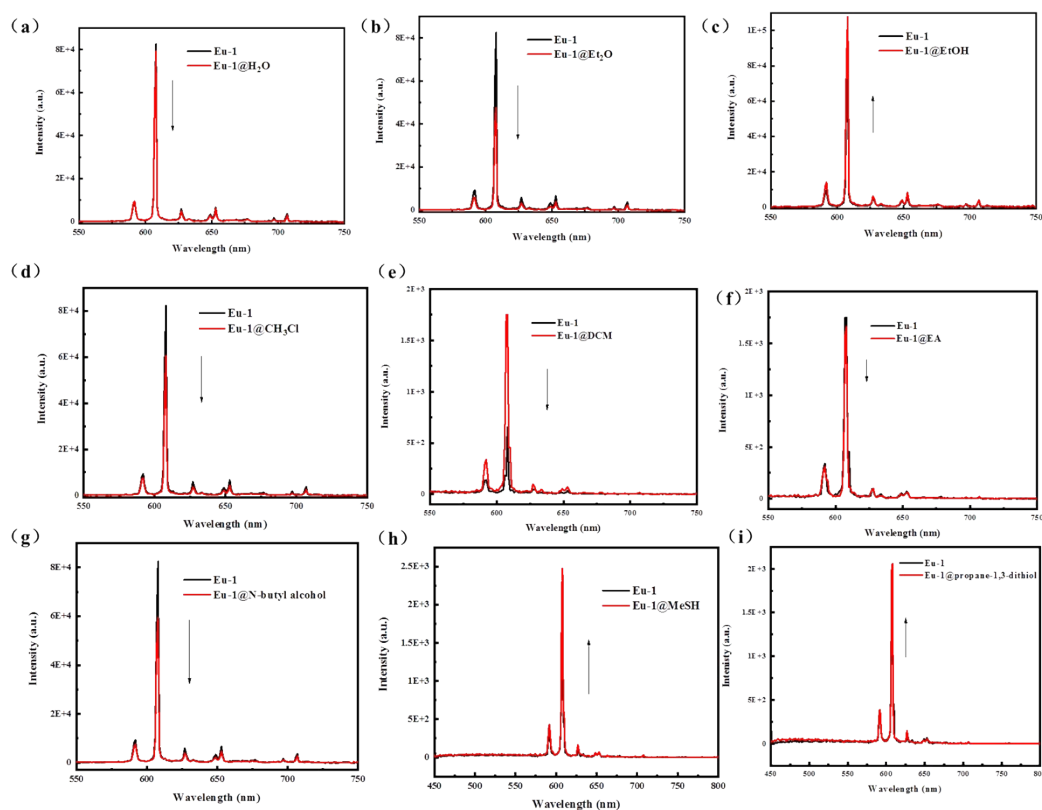
**Fig. S14** (a) The emission spectra and excitation spectra of Gd-1 at r.t. in air and 77 K; (b) The emission spectra of Gd-1 excited by different excitation wavelength.



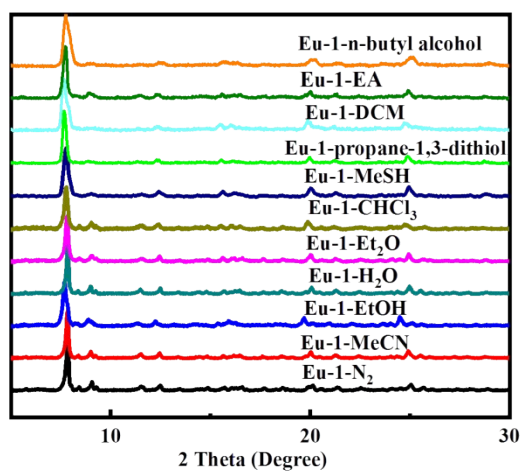
**Fig. S15** The decay curves of Gd-1 before and after treated with methanol vapor.



**Fig. S16** The emission spectra of (a) Eu-2, (b) Tb-1 and (c) Tb-2 film before and after treated with MeOH vapor for 30 min.



**Fig. S17** The emission spectra of Eu-1 before and after treated with (a) H<sub>2</sub>O, (b) Et<sub>2</sub>O, (c) EtOH, (d) CH<sub>3</sub>Cl, (e) DCM, (f) EA, (g) *n*-butyl alcohol, (h) MeSH, (i) propane-1,3-dithiol vapors.



**Fig. S18** The PXRD of Eu-1 before and after treated with H<sub>2</sub>O, Et<sub>2</sub>O, EtOH, CH<sub>3</sub>Cl, DCM, EA, n-butyl alcohol, MeSH, propane-1,3-dithiol vapors.

Table S3 The absolute photoluminescence quantum yield of Ln-1 and Ln-2 (Ln=Eu, Tb, Gd).

<b>Sample</b>	<b><math>\lambda_{\text{ex}}</math> (nm)</b>	<b>PLQY (%)</b>
Eu-1	370	10
Eu-2	370	28
Tb-1	280	72
Tb-2	280	87
Gd-1	370	4.3
Gd-2	370	5.3

Table S4 The lifetime of Gd-1 in the atmosphere of MeOH at different times.

<b>Sample</b>	<b>530 nm</b>	<b>Lifetime (<math>\mu\text{s}</math>)</b>	<b>Rel. (%)</b>
Gd-1@MeOH-0 min	$\tau_1$	3.80	12.9
	$\tau_2$	332.38	87.1
	$\tau$	336.18	
Gd-1@MeOH-15 min	$\tau_1$	16.50	15.94
	$\tau_2$	512.92	84.06
	$\tau$	529.41	
Gd-1@MeOH-25 min	$\tau_1$	99.70	46.53
	$\tau_2$	612.98	53.47
	$\tau$	712.68	