Supplementary Information for

Lanthanide–MOFs Constructed From Mixed Dicarboxylate Ligands As Selective Multi-responsive Luminescent Sensors

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Table S1. Selected bond lengths [Å] and angles [°] for **1**

Compound **1**			
Sm(1)-O(9)	2.409(8)	Sm(1)-O(4)#2	2.500(9)
Sm(1)-O(3)#2	2.465(8)	Sm(1)-O(7)	2.516(9)
Sm(1)-O(6)	2.471(8)	Sm(1)-O(1)	2.621(9)
Sm(1)-O(2)	2.474(10)	Sm(1)-O(8)	2.477(10)
Sm(1)-O(1)#1	2.409(9)		
O(1)#1-Sm(1)-O(9)	76.4(3)	O(2)-Sm(1)-O(7)	76.6(3)
O(1)#1-Sm(1)-O(3)#2	80.6(3)	O(8)-Sm(1)-O(7)	98.5(3)
O(9)-Sm(1)-O(3)#2	146.0(3)	O(4)#2-Sm(1)-O(7)	73.3(3)
O(1)#1-Sm(1)-O(6)	151.1(3)	O(1)#1-Sm(1)-O(1)	63.5(3)
O(9)-Sm(1)-O(6)	76.4(3)	O(9)-Sm(1)-O(1)	72.6(3)
O(3)#2-Sm(1)-O(6)	128.1(3)	O(3)#2-Sm(1)-O(1)	74.9(3)
O(1)#1-Sm(1)-O(2)	114.4(3)	O(6)-Sm(1)-O(1)	116.3(3)
O(9)-Sm(1)-O(2)	83.9(3)	O(2)-Sm(1)-O(1)	50.9(3)
O(3)#2-Sm(1)-O(2)	83.2(3)	O(8)-Sm(1)-O(1)	138.1(3)
O(6)-Sm(1)-O(2)	71.9(3)	O(4)#2-Sm(1)-O(1)	121.8(3)
O(1)#1-Sm(1)-O(8)	83.1(3)	O(7)-Sm(1)-O(1)	122.7(3)
O(9)-Sm(1)-O(8)	75.7(3)	O(3)#2-Sm(1)-O(4)#2	52.7(3)
O(3)#2-Sm(1)-O(8)	126.0(3)	O(6)-Sm(1)-O(4)#2	115.5(3)
O(6)-Sm(1)-O(8)	81.1(3)	O(2)-Sm(1)-O(4)#2	130.4(3)
O(2)-Sm(1)-O(8)	149.3(3)	O(8)-Sm(1)-O(4)#2	74.4(3)
O(1)#1-Sm(1)-O(4)#2	82.8(3)	O(1)#1-Sm(1)-O(7)	154.6(3)
O(9)-Sm(1)-O(4)#2	145.3(3)	O(9)-Sm(1)-O(7)	128.7(3)
O(6)-Sm(1)-O(7)	52.6(3)	O(3)#2-Sm(1)-O(7)	78.0(3)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z+2 #2 -x,-y,-z+2

Table S2. Selected bond lengths [Å] and angles [°] for **2**

Compound **2**			
Eu(1)-O(8)	2.382(7)	Eu(1)-O(4)#2	2.471(7)
Eu(1)-O(3)#1	2.407(7)	Eu(1)-O(1)	2.478(7)
Eu(1)-O(2)	2.436(7)	Eu(1)-O(6)	2.490(7)
Eu(1)-O(7)	2.437(8)	Eu(1)-O(3)#2	2.638(7)
Eu(1)-O(5)	2.461(7)		
O(8)-Eu(1)-O(3)#1	77.5(2)	O(7)-Eu(1)-O(1)	73.9(3)
O(8)-Eu(1)-O(2)	146.8(3)	O(5)-Eu(1)-O(1)	115.4(3)
O(3)#1-Eu(1)-O(2)	81.1(2)	O(4)#2-Eu(1)-O(1)	130.9(3)
O(8)-Eu(1)-O(7)	75.7(3)	O(8)-Eu(1)-O(6)	127.7(2)
O(3)#1-Eu(1)-O(7)	83.2(3)	O(3)#1-Eu(1)-O(6)	154.3(2)
O(2)-Eu(1)-O(7)	126.6(2)	O(2)-Eu(1)-O(6)	77.8(2)
O(8)-Eu(1)-O(5)	75.3(2)	O(7)-Eu(1)-O(6)	97.7(3)
O(3)#1-Eu(1)-O(5)	150.7(2)	O(5)-Eu(1)-O(6)	52.7(2)
O(2)-Eu(1)-O(5)	128.1(2)	O(4)#2-Eu(1)-O(6)	76.8(2)
O(7)-Eu(1)-O(5)	79.6(3)	O(1)-Eu(1)-O(6)	73.9(3)
O(8)-Eu(1)-O(4)#2	83.9(3)	O(8)-Eu(1)-O(3)#2	73.3(2)
O(3)#1-Eu(1)-O(4)#2	114.9(2)	O(3)#1-Eu(1)-O(3)#2	64.6(3)
O(2)-Eu(1)-O(4)#2	82.4(2)	O(2)-Eu(1)-O(3)#2	74.6(2)
O(7)-Eu(1)-O(4)#2	149.2(3)	O(7)-Eu(1)-O(3)#2	139.1(2)
O(5)-Eu(1)-O(4)#2	73.0(3)	O(5)-Eu(1)-O(3)#2	116.7(2)
O(8)-Eu(1)-O(1)	144.9(3)	O(4)#2-Eu(1)-O(3)#2	50.3(2)
O(3)#1-Eu(1)-O(1)	81.8(3)	O(1)-Eu(1)-O(3)#2	121.9(2)
O(2)-Eu(1)-O(1)	53.5(2)	O(6)-Eu(1)-O(3)#2	122.4(2)
Symmetry transformations used to generate equivalent atoms: #1 x-1,y,z			#2 -x+2,-y+2,-z+2

Table S3. Selected bond lengths [Å] and angles [°] for **3**

Compound **3**			
O(1)-Gd(1)	2.486(3)	Gd(1)-O(7)#4	2.426(3)
O(2)-Gd(1)	2.453(3)	Gd(1)-O(6)#1	2.452(4)
O(3)-Gd(1)	2.371(3)	Gd(1)-O(8)#4	2.485(4)
O(4)-Gd(1)	2.414(4)	Gd(1)-O(5)#1	2.648(3)
O(5)-Gd(1)	2.380(3)		
O(3)-Gd(1)-O(5)	77.03(11)	O(7)#4-Gd(1)-O(8)#4	53.06(11)
O(3)-Gd(1)-O(4)	75.79(13)	O(6)#1-Gd(1)-O(8)#4	130.49(12)
O(5)-Gd(1)-O(4)	82.89(13)	O(2)-Gd(1)-O(8)#4	115.19(13)
O(3)-Gd(1)-O(7)#4	146.38(12)	O(3)-Gd(1)-O(1)	128.21(11)
O(5)-Gd(1)-O(7)#4	80.96(11)	O(5)-Gd(1)-O(1)	154.23(11)
O(4)-Gd(1)-O(7)#4	126.30(12)	O(4)-Gd(1)-O(1)	97.45(13)
O(3)-Gd(1)-O(6)#1	84.06(13)	O(7)#4-Gd(1)-O(1)	78.17(11)
O(5)-Gd(1)-O(6)#1	115.00(11)	O(6)#1-Gd(1)-O(1)	77.11(12)

O(4)-Gd(1)-O(6)#1	149.40(13)	O(2)-Gd(1)-O(1)	52.94(11)
O(7)#4-Gd(1)-O(6)#1	82.59(12)	O(8)#4-Gd(1)-O(1)	73.55(12)
O(3)-Gd(1)-O(2)	75.59(12)	O(3)-Gd(1)-O(5)#1	73.04(12)
O(5)-Gd(1)-O(2)	150.14(11)	O(5)-Gd(1)-O(5)#1	64.47(13)
O(4)-Gd(1)-O(2)	79.07(13)	O(4)-Gd(1)-O(5)#1	138.82(11)
O(7)#4-Gd(1)-O(2)	128.88(11)	O(7)#4-Gd(1)-O(5)#1	74.64(11)
O(6)#1-Gd(1)-O(2)	73.70(12)	O(6)#1-Gd(1)-O(5)#1	50.53(10)
O(3)-Gd(1)-O(8)#4	145.01(13)	O(2)-Gd(1)-O(5)#1	117.42(12)
O(5)-Gd(1)-O(8)#4	81.88(12)	O(8)#4-Gd(1)-O(5)#1	121.62(11)
O(4)-Gd(1)-O(8)#4	74.13(13)	O(1)-Gd(1)-O(5)#1	122.94(11)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y,-z+1 #4 x-1,y,z

Table S4. Selected bond lengths [Å] and angles [°] for **4**

Compound **4**			
Tb(1)-O(5)#1	2.353(7)	Tb(1)-O(2)	2.447(8)
Tb(1)-O(7)	2.378(8)	Tb(1)-O(4)	2.461(9)
Tb(1)-O(3)	2.383(8)	Tb(1)-O(1)	2.480(7)
Tb(1)-O(6)#2	2.418(8)	Tb(1)-O(5)#2	2.656(8)
Tb(1)-O(8)	2.428(9)		
O(5)#1-Tb(1)-O(7)	77.8(3)	O(6)#2-Tb(1)-O(4)	131.2(3)
O(5)#1-Tb(1)-O(3)	81.4(3)	O(8)-Tb(1)-O(4)	74.2(3)
O(7)-Tb(1)-O(3)	147.3(3)	O(2)-Tb(1)-O(4)	114.9(3)
O(5)#1-Tb(1)-O(6)#2	114.9(3)	O(5)#1-Tb(1)-O(1)	154.0(3)
O(7)-Tb(1)-O(6)#2	83.9(3)	O(7)-Tb(1)-O(1)	127.6(3)
O(3)-Tb(1)-O(6)#2	82.3(3)	O(3)-Tb(1)-O(1)	77.7(3)
O(5)#1-Tb(1)-O(8)	83.2(3)	O(6)#2-Tb(1)-O(1)	77.6(3)
O(7)-Tb(1)-O(8)	74.9(3)	O(8)-Tb(1)-O(1)	97.2(3)
O(3)-Tb(1)-O(8)	127.3(3)	O(2)-Tb(1)-O(1)	53.4(3)
O(6)#2-Tb(1)-O(8)	148.6(3)	O(4)-Tb(1)-O(1)	73.2(3)
O(5)#1-Tb(1)-O(2)	149.9(3)	O(5)#1-Tb(1)-O(5)#2	64.2(3)
O(7)-Tb(1)-O(2)	74.5(3)	O(7)-Tb(1)-O(5)#2	74.0(3)
O(3)-Tb(1)-O(2)	128.7(3)	O(3)-Tb(1)-O(5)#2	74.3(3)
O(6)#2-Tb(1)-O(2)	73.8(3)	O(6)#2-Tb(1)-O(5)#2	50.7(2)
O(8)-Tb(1)-O(2)	78.4(3)	O(8)-Tb(1)-O(5)#2	138.7(3)
O(5)#1-Tb(1)-O(4)	82.0(3)	O(2)-Tb(1)-O(5)#2	117.8(3)
O(7)-Tb(1)-O(4)	144.7(3)	O(4)-Tb(1)-O(5)#2	121.8(3)
O(3)-Tb(1)-O(4)	53.9(3)	O(1)-Tb(1)-O(5)#2	123.3(3)

Symmetry transformations used to generate equivalent atoms: #1 x-1,y,z #2 -x+2,-y+1,-z+1

Table S5. Selected bond lengths [Å] and angles [°] for **5**

Compound **5**

Dy(1)-O(8)	2.337(6)	Dy(1)-O(2)#1	2.344(6)
Dy(1)-O(3)#2	2.376(6	Dy(1)-O(1	2.400(7)
Dy(1)-O(5)	2.430(6)	Dy(1)-O(7)	2.432(7)
Dy(1)-O(6)	2.449(6)	Dy(1)-O(4)#2	2.467(7)
Dy(1)-O(2)	2.660(6)		
O(8)-Dy(1)-O(2)#1	76.4(3)	O(1)-Dy(1)-O(6)	76.6(3)
O(8)-Dy(1)-O(3)#2	80.6(3)	O(5)-Dy(1)-O(6)	98.5(3)
O(2)#1-Dy(1)-O(3)#2	146.0(3)	O(7)-Dy(1)-O(6)	73.3(3)
O(8)-Dy(1)-O(1)	151.1(3)	O(8)-Dy(1)-O(4)#2	63.5(3)
O(2)#1-Dy(1)-O(1)	76.4(3)	O(2)#1-Dy(1)-O(4)#2	72.6(3)
O(3)#2-Dy(1)-O(1)	128.1(3)	O(3)#2-Dy(1)-O(4)#2	74.9(3)
O(8)-Dy(1)-O(5)	114.4(3)	O(1)-Dy(1)-O(4)#2	116.3(3)
O(2)#1-Dy(1)-O(5)	83.9(3)	O(5)-Dy(1)-O(4)#2	50.9(3)
O(3)#2-Dy(1)-O(5)	83.2(3)	O(7)-Dy(1)-O(4)#2	138.1(3)
O(1)-Dy(1)-O(5)	71.9(3)	O(6)-Dy(1)-O(4)#2	121.8(3)
O(8)-Dy(1)-O(7)	83.1(3)	O(8)-Dy(1)-O(2)	122.7(3)
O(2)#1-Dy(1)-O(7)	75.7(3)	O(2)#1-Dy(1)-O(2)	52.7(3)
O(3)#2-Dy(1)-O(7)	126.0(3)	O(3)#2-Dy(1)-O(2)	115.5(3)
O(1)-Dy(1)-O(7)	81.1(3)	O(1)-Dy(1)-O(2)	130.4(3)
O(5)-Dy(1)-O(7)	149.3(3)	O(5)-Dy(1)-O(2)	74.4(3)
O(8)-Dy(1)-O(6)	82.8(3)	O(7)-Dy(1)-O(2)	154.6(3)
O(2)#1-Dy(1)-O(6)	145.3(3)	O(6)-Dy(1)-O(2)	128.7(3)
O(3)#2-Dy(1)-O(6)	52.6(3)	O(4)#2-Dy(1)-O(2)	78.0(3)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+1 #2 -x+2,-y+1,-z+1

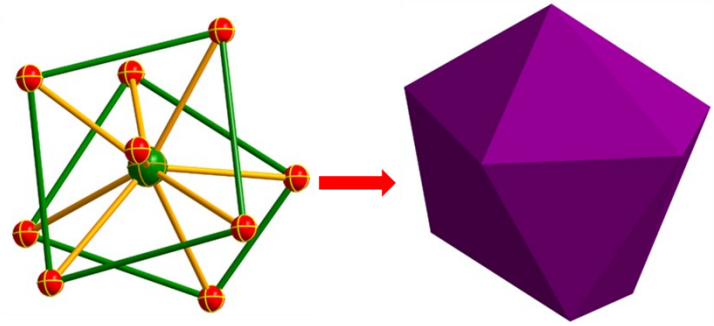

Fig. S1 The monocapped square antiprism coordination geometry of Tb^{3+} ion.

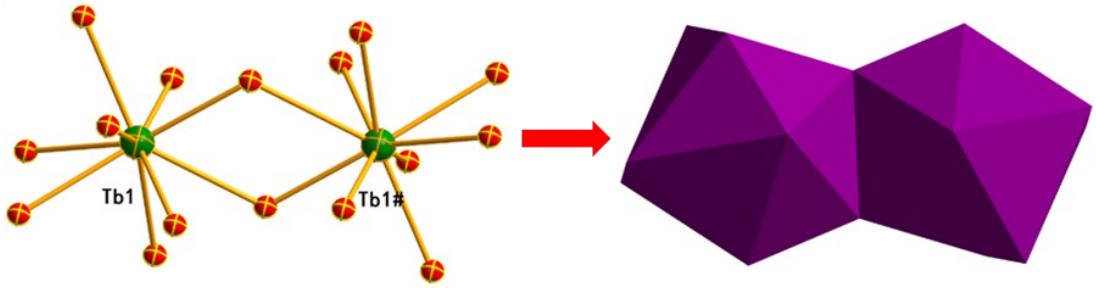

Fig. S2 The binuclear constituted by Tb^{3+} ions.

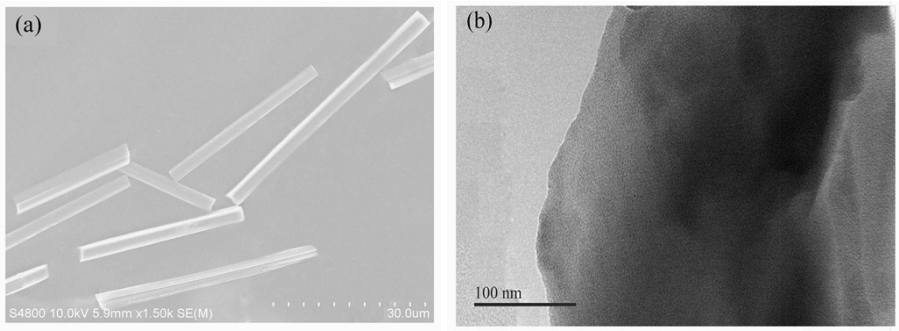

Fig.S3 The SEM (a) and TEM (b) image of compound **4**.

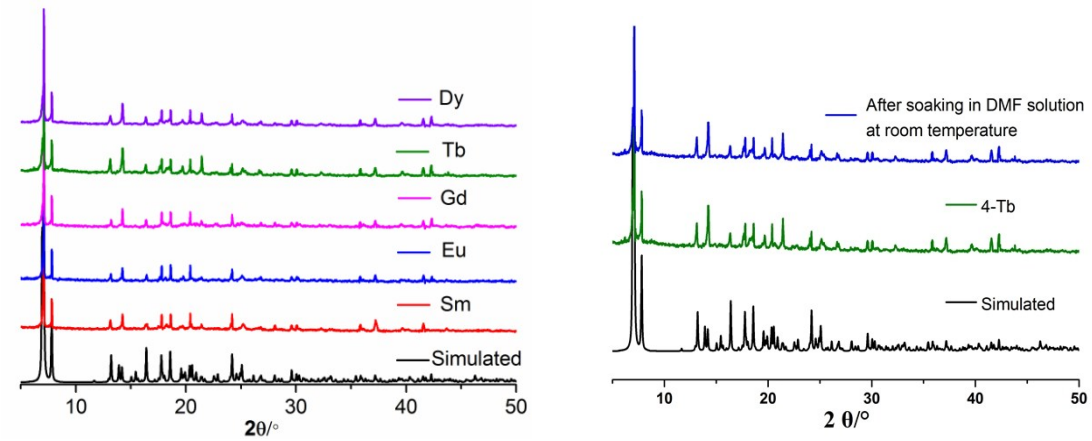

Fig. S4 PXRD patterns of compound 4 simulated from the X-ray single-crystal structure and as-synthesized samples of compound 1-5.

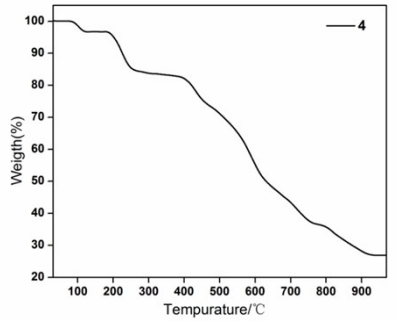

Fig. S5 View of the TG analysis profile of compound **4**.

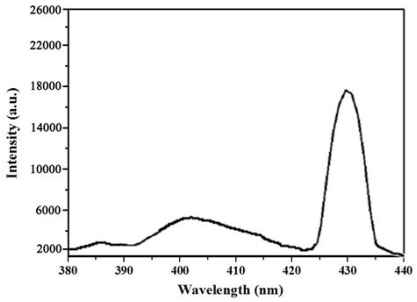

Fig. S6 The phosphorescence spectrum of complex **3**

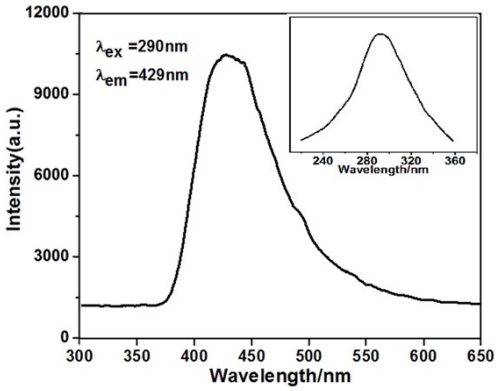

Fig. S7 The emission spectrum of H_2ppda ligand. Insets: The excitation spectrum of H_2ppda ligand.

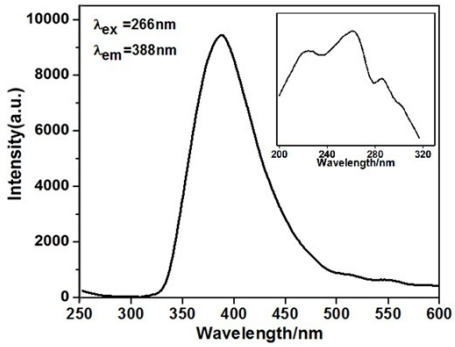

Fig. S8 The emission spectrum of H_2bdc ligand. Insets: The excitation spectrum of H_2bdc ligand.

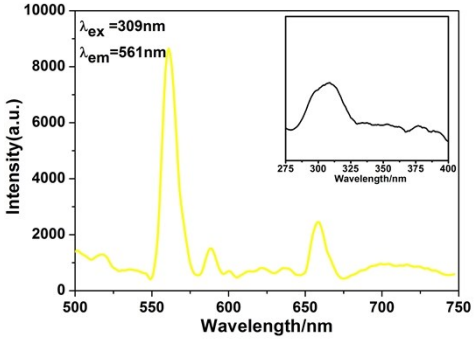

Fig. S9 The emission spectrum of compound **1**. Insets: The excitation spectrum of compound **1**.

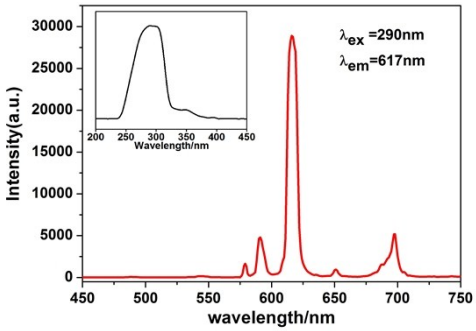

Fig. S10 The emission spectrum of compound **2**. Insets: The excitation spectrum of compound **2**.

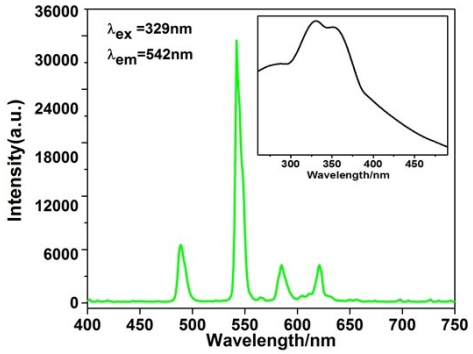

Fig. S11 The emission spectrum of compound **4**. Insets: The excitation spectrum of compound **4**.

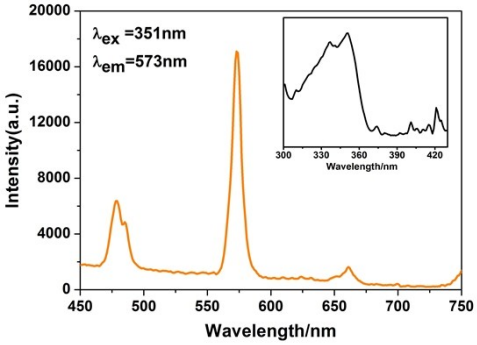

Fig. S12 The emission spectrum of compound **5**. Insets: The excitation spectrum of compound **5**.

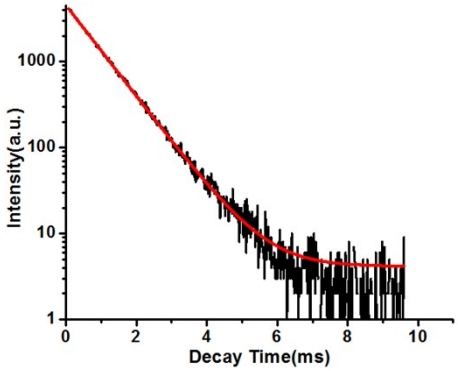

Fig. S13 The decay curve and fit curve for compound **1**.

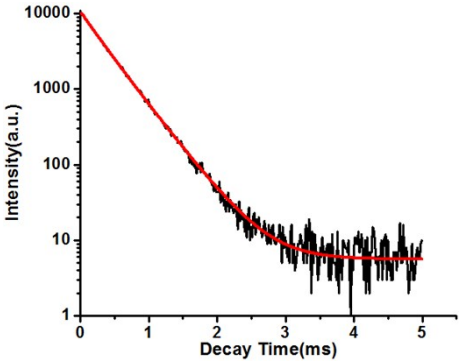

Fig. S14 The decay curve and fit curve for compound **2**.

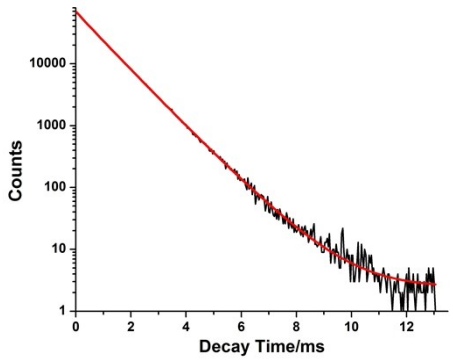

Fig. S15 The decay curve and fit curve for compound **4**.

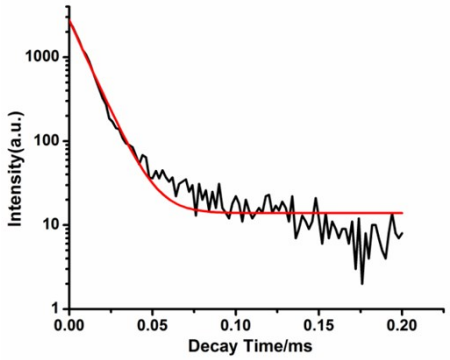

Fig. S16 The decay curve and fit curve for compound **5**.

Table S6 Fluorescent quantum yield data of compound **2**

The luminescence quantum yield η of the $^5D_0$ emission lever in the ternary Eu(III) complex could be calculated based on the measurements: Eq. (1) is a means to determine the η values from experimental spectroscopic data,

η = Ar /(Ar +Anr) Eq. (1)

where Ar and Anr are radiative and non-radiative transition rates, respectively. The denominator in Eq. (1) is calculated from the lifetime of the emitting level ($1/\tau$ = Ar +Anr, where τ stands for fluorescence lifetime).

In the case of europium luminescence, value of Ar could be obtained from the Eq. (2),

$Ar = \Sigma A_{0J} = A_{00}+A_{01}+A_{02}+A_{03}+A_{04}$ Eq. (2)

where J represents the final $^7F_{0\text{-}4}$ levers. The values of A_{0J} could be calculated by the Eq. (3) and Eq. (4) ,

$A_{0J} = A_{01}(I_{0J}/I_{01})(\nu_{01}/\nu_{0J})$ Eq. (3)

$\nu_{0J} = 1/\lambda_J$ Eq. (4)

Where λ stands for wavelength correspondingly, A_{01} is the Einstein coefficient of spontaneous emission between the $^5D_0$ and the $^7F_1$ Stark levels, which may be used as a reference for the whole spectrum in vacuum, A_{01} = 50 s^{-1} [1]. Finally, fluorescent quantum yield η of compound 1 was 17.52% by calculated with above equations, which is moderate among the reported complexes [2]. The needed calculated responding data are shown in Table S6.

Compound **2**			
ν_{00} (cm^{-1})	17271	A_{01}	50
ν_{01} (cm^{-1})	16920	A_{02}	294.583
ν_{02} (cm^{-1})	16207	A_{03}	10.764

ν_{03} (cm^{-1})	15361	A_{04}	48.606
ν_{04} (cm^{-1})	14347	Ar	422.285
I_{01} (a.u)	470082	τ(ms)	0.415
I_{02} (a.u)	2891393	$1/\tau$	2.410
I_{02}/I_{01}	6.151	η %	17.52
A_{00}	18.332		

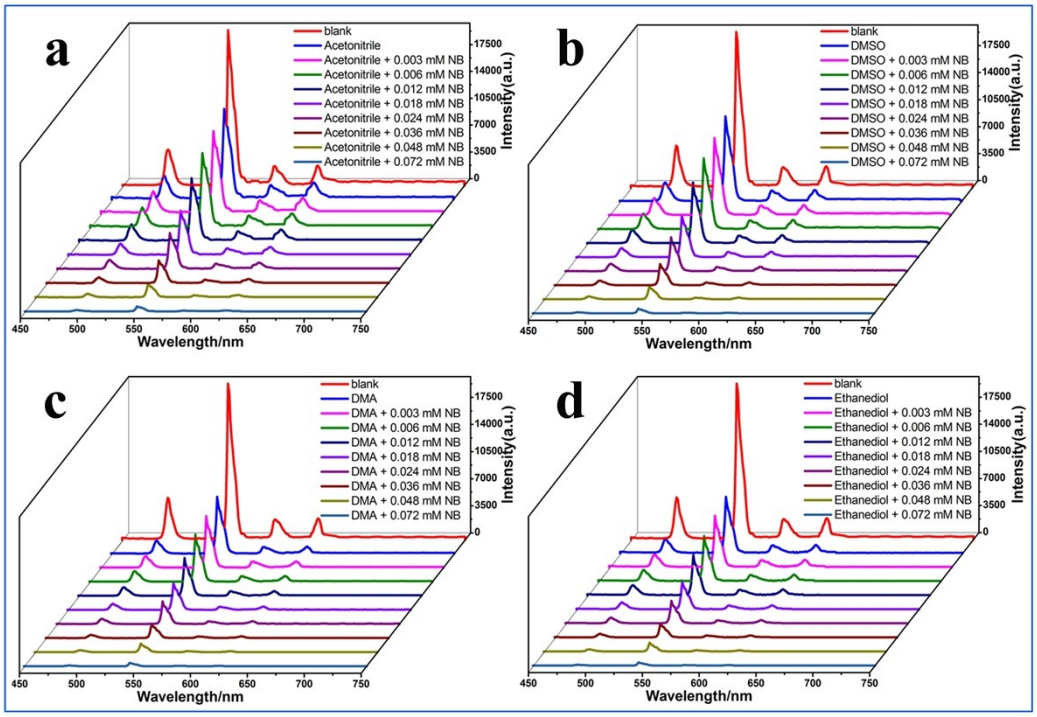

Fig. S17 Fluorescence emission spectra of **4** in the DMF solutions with the concentration of 7.2 mM competing analytes: (a) acetonitrile, (b) DMSO, (c) DMA, (d) phenylcarbinol followed by incremental addition of NB when excited at 329 nm.

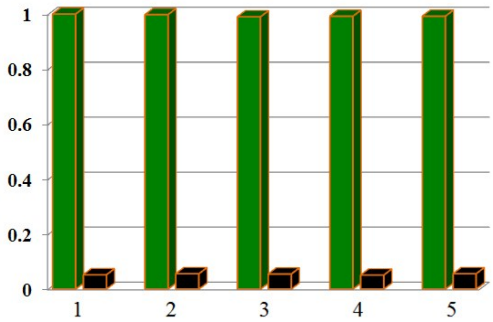

Fig. S18 Quenching and recovery test of **4** in DMF solution. The green columns represent the initial relative luminescent intensity and the black columns represent the relative intensity on addition of NB.

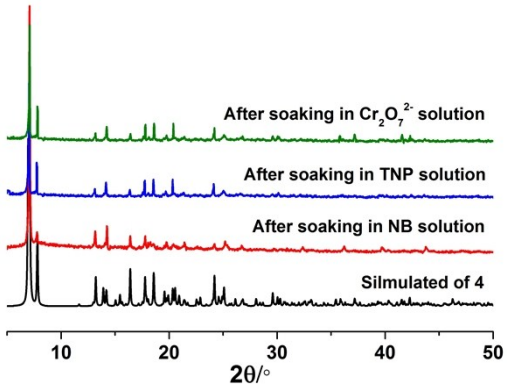

Fig. S19 Power X-ray diffraction patterns of **4** after five recyclable experiments.

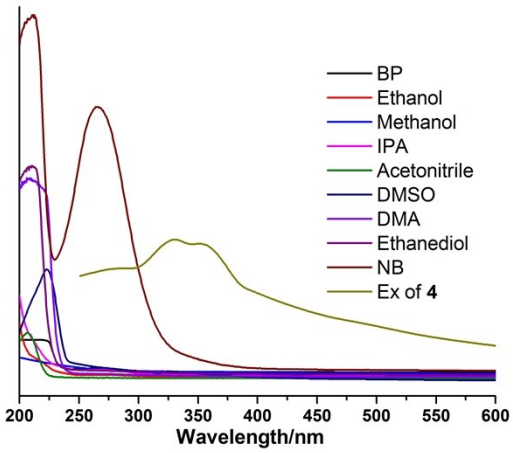

Fig. S20 The UV-Vis adsorption spectra of different inorganic solutions and the excitation spectrum of **4**.

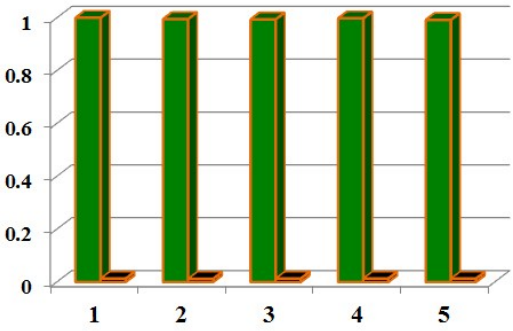

Fig. S21 Quenching and recovery test of **4** in DMF solution. The green columns represent the initial relative luminescent intensity and the black columns represent the relative intensity on addition of TNP.

Table S7. HOMO and LUMO energies calculated for nitroaromatic explosives at B3LYP/6-31G** level of theory.

Analytes	HOMO (eV)	LUMO (eV)	Band gap
NB[3]	-7.5912	-2.4283	5.1629
1,3-DNB[3]	-7.9855	-3.4311	4.5544

1,4-DNB[4]	-8.3525	-3.4967	4.8557
2,4-DNT[3]	-7.7645	-3.2174	4.5471
1,3,5-TNB[5]	-8.9338	-3.6831	5.2507
TNT[3]	-8.2374	-3.8978	4.3396
TNP[3]	-8.4592	-3.4926	4.9666

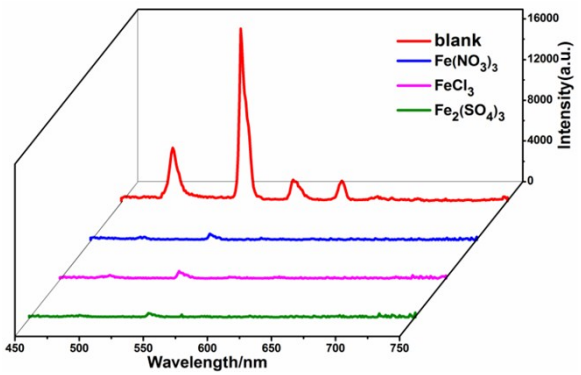

Fig. S22 The fluorescence emission spectra of **4** in the DMF solutions upon addition of Fe^{3+} salt aqueous solutions.

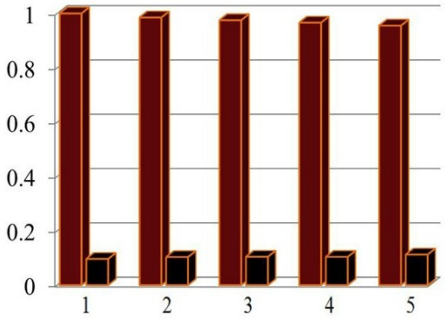

Fig. S23 Quenching and recovery test of **4** in DMF solution. The red columns represent the initial relative luminescent intensity and the black columns represent the relative intensity on addition of Fe^{3+}.

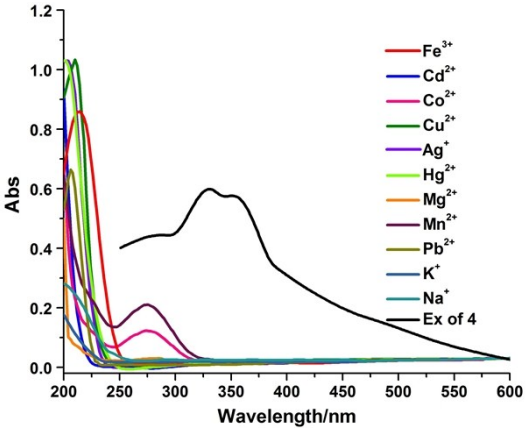

Fig. S24 The UV-Vis adsorption spectra of $M(NO_3)_X$ DMF solutions and the excitation spectrum of **4**.

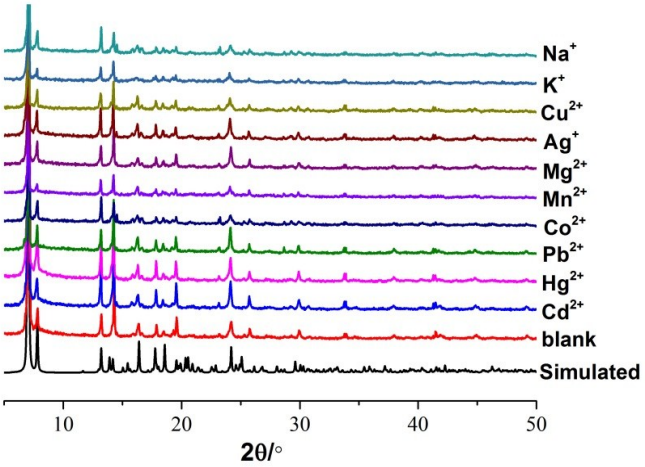

Fig. S25 PXRD patterns of compound **4** treated by different $M(NO_3)_x$ DMF solutions. It indicated that compound **4** retains its framework after immersed in DMF solution containing different metal ions.

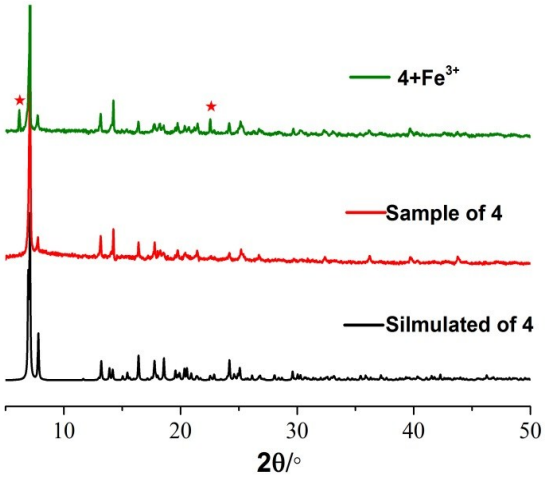

Fig. S26 PXRD patterns of compound **4** and compound **4** after treatment with Fe^{3+} solution for 48 h; stars denote the new peaks.

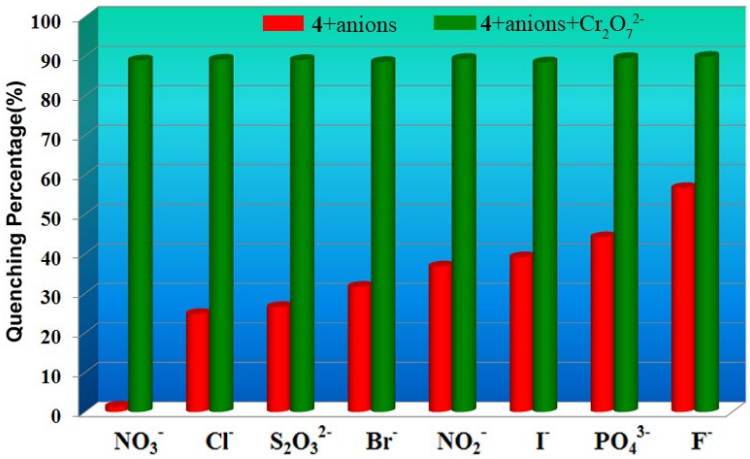

Fig. S27 Quenching efficiency of the fluorescence intensity for **4** exposed to single anions and mixed anions in DMF solutions.

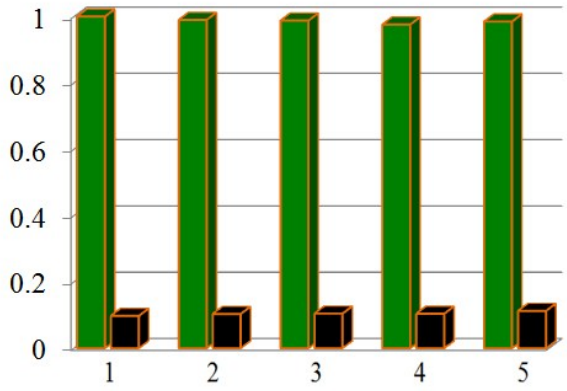

Fig. S28 Quenching and recovery test of **4** in DMF solution. The green columns represent the initial relative luminescent intensity and the black columns represent the relative intensity on addition of $Cr_2O_7^{2-}$.

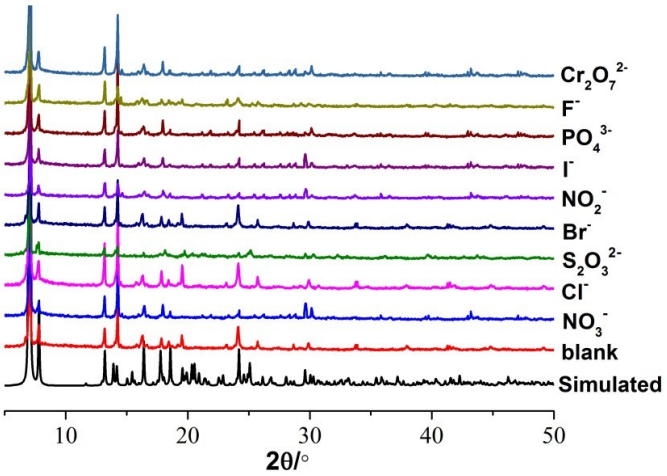

Fig. S29 PXRD patterns of compound **4** treated by different K(anion)x DMF solutions. It indicated that compound **4** retains its framework after immersed in DMF solution containing different metal ions.

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