Electronic Supplementary Information

Excitation wavelength-induced color tunable and white-light emissions in lanthanide(III) coordination polymers constructed by an environment-dependent luminescent tetrazolate-dicarboxylate ligand

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Table S1 Selected bond lengths (Å) and angles (°) for compounds **1-4**

1			
Sm(1)–O(2)#1	2.344(2)	Sm(1)–O(3)	2.406(2)
Sm(1)–O(1)#2	2.353(2)	Sm(1)–O(2W)	2.445(3)
Sm(1)–O(1W)	2.383(3)	Sm(1)–O(4)#3	2.490(2)
Sm(1) –O(3W)	2.389(3)	Sm(1) –O(3)#3	2.616(2)
O(2)#1–Sm(1)–O(1)#2	88.14(9)	O(3)–Sm(1)–O(2W)	88.41(9)
O(2)#1–Sm(1)–O(1W)	97.65(11)	O(2)#1–Sm(1)–O(4)#3	78.34(8)
O(1)#2–Sm(1)–O(1W)	141.75(10)	O(1)#2–Sm(1)–O(4)#3	145.61(10)
O(2)#1–Sm(1)–O(3W)	85.46(11)	O(1W)–Sm(1)–O(4)#3	72.02(10)
O(1)#2–Sm(1)–O(3W)	71.22(10)	O(3W)–Sm(1)–O(4)#3	76.25(9)
O(1W) Sm(1)–O(3W)	146.70(10)	O(3)–Sm(1)–O(4)#3	117.72(8)

O(2)#1–Sm(1)–O(3)	163.16(9)	O(2W)–Sm(1)–O(4)#3	132.28(8)
O(1)#2–Sm(1)–O(3)	80.77(9)	O(2)#1–Sm(1)–O(3)#3	128.19(8)
O(1W)–Sm(1)–O(3)	83.67(10)	O(1)#2–Sm(1)–O(3)#3	126.77(8)
O(3W)–Sm(1)–O(3)	102.71(10)	O(1W)–Sm(1)–O(3)#3	77.84(10)
O(2)#1–Sm(1)–O(2W)	76.12(9)	O(3W)–Sm(1)–O(3)#3	74.45(9)
O(1)#2–Sm(1)–O(2W)	72.54(9)	O(3)–Sm(1)–O(3)#3	68.57(9)
O(1W)–Sm(1)–O(2W)	72.31(10)	O(2W)–Sm(1)–O(3)#3	144.06(9)
O(3W)–Sm(1)–O(2W)	139.62(10)	O(4)#3–Sm(1)–O(3)#3	50.86(8)

Symmetry transformations used to generate equivalent atoms: for **1**: (#1) x, y – 1, z; (#2) –x + 1, –y + 2, –z; (#3) –x, –y + 1, –z.

2

Eu(1)–O(3)#1	2.335(2)	Eu(1)-O(1)	2.392(2)
Eu(1)–O(4)#2	2.347(3)	Eu(1)–O(2W)	2.436(2)
Eu(1)–O(3W)	2.368(3)	Eu(1)–O(2)#3	2.480(2)
Eu(1)–O(1W)	2.372(3)	Eu(1)–O(1)#3	2.609(2)
O(3)#1–Eu(1)–O(4)#2	88.27(8)	O(1)–Eu(1)–O(2W)	88.52(9)
O(3)#1–Eu(1)–O(3W)	72.39(9)	O(3)#1–Eu(1)–O(2)#3	146.43(10)
O(4)#2–Eu(1)–O(3W)	85.60(10)	O(4)#2–Eu(1)–O(2)#3	78.46(8)
O(3)#1–Eu(1)–O(1W)	140.88(10)	O(3W)–Eu(1)–O(2)#3	75.92(9)
O(4)#2–Eu(1)–O(1W)	97.59(10)	O(1W)–Eu(1)–O(2)#3	72.06(9)
O(3W)–Eu(1)–O(1W)	146.41(9)	O(1)–Eu(1)–O(2)#3	117.50(8)
O(3)#1–Eu(1)–O(1)	80.59(8)	O(2W)–Eu(1)–O(2)#3	132.16(8)
O(4)#2–Eu(1)–O(1)	163.23(8)	O(3)#1–Eu(1)–O(1)#3	126.82(8)
O(3W)–Eu(1)–O(1)	102.71(10)	O(4)#2–Eu(1)–O(1)#3	128.45(7)
O(1W)–Eu(1)–O(1)	83.61(10)	O(3W)–Eu(1)–O(1)#3	73.90(9)
O(3)#1–Eu(1)–O(2W)	72.00(9)	O(1W)–Eu(1)–O(1)#3	78.23(10)
O(4)#2–Eu(1)–O(2W)	76.07(9)	O(1)–Eu(1)–O(1)#3	68.24(8)

O(3W)–Eu(1)–O(2W)	140.16(9)	O(2W)–Eu(1)–O(1)#3	144.06(8)
O(1W)–Eu(1)–O(2W)	72.04(9)	O(2)#3–Eu(1)–O(1)#3	51.06(8)

Symmetry transformations used to generate equivalent atoms: for **2**: (#1) –x + 1, –y + 2, –z; (#2) x, y – 1, z; (#3) –x, –y + 1, –z.

3

Gd(1)–O(3)#1	2.318(3)	Gd(1)–O(1)#3	2.365(3)
Gd(1)–O(4)#2	2.322(2)	Gd(1)–O(1W)	2.407(2)
Gd(1)–O(2W)	2.339(3)	Gd(1)–O(2)	2.460(2)
Gd(1)–O(3W)	2.347(3)	Gd(1)–O(1)	2.599(2)
O(3)#1–Gd(1)–O(4)#2	88.04(9)	O(1)#3–Gd(1)–O(1W)	88.30(9)
O(3)#1–Gd(1)–O(2W)	85.29(10)	O(3)#1–Gd(1)–O(2)	78.46(8)
O(4)#2–Gd(1)–O(2W)	71.76(9)	O(4)#2–Gd(1)–O(2)	145.66(9)
O(3)#1–Gd(1)–O(3W)	97.76(11)	O(2W)–Gd(1)–O(2)	75.74(9)
O(4)#2–Gd(1)–O(3W)	141.80(10)	O(3W)–Gd(1)–O(2)	71.93(9)
O(2W)–Gd(1)–O(3W)	146.14(10)	O(1)#3–Gd(1)–O(2)	117.55(8)
O(3)#1–Gd(1)–O(1)#3	163.23(8)	O(1W)–Gd(1)–O(2)	132.24(9)
O(4)#2–Gd(1)–O(1)#3	80.86(9)	O(3)#1–Gd(1)–O(1)	128.67(8)
O(2W)–Gd(1)–O(1)#3	102.90(11)	O(4)#2–Gd(1)–O(1)	126.33(9)
O(3W)–Gd(1)–O(1)#3	83.65(11)	O(2W)–Gd(1)–O(1)	74.02(9)
O(3)#1–Gd(1)–O(1W)	76.36(9)	O(3W)–Gd(1)–O(1)	78.05(10)
O(4)#2–Gd(1)–O(1W)	72.72(9)	O(1)#3–Gd(1)–O(1)	68.04(9)
O(2W)–Gd(1)–O(1W)	140.31(9)	O(1W)–Gd(1)–O(1)	143.73(9)
O(3W)–Gd(1)–O(1W)	72.12(9)	O(2)–Gd(1)–O(1)	51.29(8)

Symmetry transformations used to generate equivalent atoms: for **3**: (#1) –x, –y + 2, –z; (#2) x + 1, y + 1, z; (#3) –x, –y + 3, –z.

4

Gd(1)–O(3)#1	2.324(2)	Gd(1)–O(1)#3	2.374(2)
Gd(1)–O(4)#2	2.330(2)	Gd(1)–O(1W)	2.414(2)

Gd(1)–O(2W)	2.350(2)	Gd(1)–O(2)	2.467(2)
Gd(1)–O(3W)	2.347(3)	Gd(1)–O(1)	2.609(2)
Eu(1)–O(3)#1	2.324(2)	Eu(1)–O(1)#3	2.374(2)
Eu(1)–O(4)#2	2.330(2)	Eu(1)–O(1W)	2.414(2)
Eu(1)–O(2W)	2.350(2)	Eu(1)–O(2)	2.467(2)
Eu(1)–O(3W)	2.347(3)	Eu(1)–O(1)	2.609(2)
O(3)#1–Gd(1)–O(4)#2	87.86(8)	O(1)#3-Gd(1)-O(1W)	88.44(8)
O(3)#1-Gd(1)-O(2W)	85.58(9)	O(3)#1-Gd(1)-O(2)	78.46(7)
O(4)#2-Gd(1)-O(2W)	71.65(8)	O(4)#2-Gd(1)-O(2)	145.66(8)
O(3)#1-Gd(1)-O(3W)	97.70(9)	O(2W)-Gd(1)-O(2)	75.97(8)
O(4)#2-Gd(1)-O(3W)	141.71(9)	O(3W)-Gd(1)-O(2)	71.96(9)
O(2W)-Gd(1)-O(3W)	146.32(9)	O(1)#3-Gd(1)-O(2)	117.72(7)
O(3)#1-Gd(1)-O(1)#3	163.08(8)	O(1W)-Gd(1)-O(2)	131.97(8)
O(4)#2-Gd(1)-O(1)#3	80.83(8)	O(3)#1-Gd(1)-O(1)	128.53(7)
O(2W)-Gd(1)-O(1)#3	102.55(9)	O(4)#2-Gd(1)-O(1)	126.57(7)
O(3W)-Gd(1)-O(1)#3	83.82(9)	O(2W)-Gd(1)-O(1)	73.90(8)
O(3)#1-Gd(1)-O(1W)	76.14(8)	O(3W)-Gd(1)-O(1)	78.14(9)
O(4)#2-Gd(1)-O(1W)	72.80(8)	O(1)#3-Gd(1)-O(1)	68.34(8)
O(2W)-Gd(1)-O(1W)	140.37(8)	O(1W)-Gd(1)-O(1)	143.86(8)
O(3W)-Gd(1)-O(1W)	71.92(9)	O(2)-Gd(1)-O(1)	51.16(7)
O(3)#1–Eu(1)–O(4)#2	87.86(8)	O(1)#3-Eu(1)-O(1W)	88.44(8)
O(3)#1-Eu(1)-O(2W)	85.58(9)	O(3)#1-Eu(1)-O(2)	78.46(7)
O(4)#2-Eu(1)-O(2W)	71.65(8)	O(4)#2-Eu(1)-O(2)	145.66(8)
O(3)#1-Eu(1)-O(3W)	97.70(9)	O(2W)-Eu(1)-O(2)	75.97(8)
O(4)#2-Eu(1)-O(3W)	141.71(9)	O(3W)-Eu(1)-O(2)	71.96(9)
O(2W)-Eu(1)-O(3W)	146.32(9)	O(1)#3-Eu(1)-O(2)	117.72(7)
O(3)#1-Eu(1)-O(1)#3	163.08(8)	O(1W)-Eu(1)-O(2)	131.97(8)

O(4)#2-Eu(1)-O(1)#3	80.83(8)	O(3)#1-Eu(1)-O(1)	128.53(7)
O(2W)-Eu(1)-O(1)#3	102.55(9)	O(4)#2-Eu(1)-O(1)	126.57(7)
O(3W)-Eu(1)-O(1)#3	83.82(9)	O(2W)-Eu(1)-O(1)	73.90(8)
O(3)#1-Eu(1)-O(1W)	76.14(8)	O(3W)-Eu(1)-O(1)	78.14(9)
O(4)#2-Eu(1)-O(1W)	72.80(8)	O(1)#3-Eu(1)-O(1)	68.34(8)
O(2W)-Eu(1)-O(1W)	140.37(8)	O(1W)-Eu(1)-O(1)	143.86(8)
O(3W)-Eu(1)-O(1W)	71.92(9)	O(2)-Eu(1)-O(1)	51.16(7)

Symmetry transformations used to generate equivalent atoms: for 4**:** (#1) –x, –y, –z**;** (#2) x + 1; y + 1, z; (#3) –x, –y + 1, –z; (#4) x – 1, y – 1, z.

Table S2 CIE coordinates (x, y), CRI and CCT for compound **1**

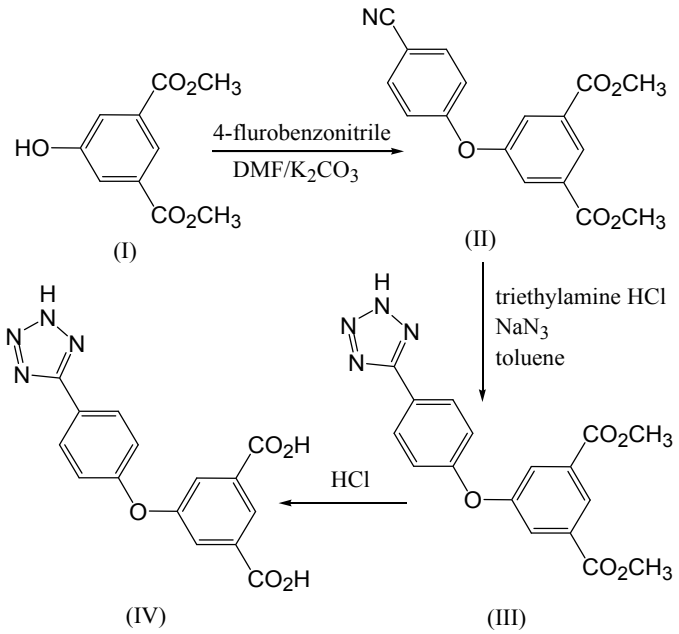
λ_{ex}/nm	(x, y)	CRI	CCT/K
340	(0.53, 0.36)	33	1728
345	(0.49, 0.35)	43	1833
350	(0.44, 0.34)	65	2301
352	(0.41, 0.33)	73	2739
354	(0.38, 0.32)	79	3480
356	(0.35, 0.32)	84	4454
358	(0.33, 0.31)	87	5748
360	(0.31, 0.31)	90	7000
365	(0.29, 0.30)	94	8716
370	(0.26, 0.30)	87	10958
384	(0.25, 0.30)	78	11849

Table S3 CIE coordinates (x, y), CRI and CCT for compound **4**

λ_{ex}/nm	(x, y)	CRI	CCT/K
340	(0.48, 0.34)	56	1915
345	(0.45, 0.35)	67	2301
350	(0.41, 0.34)	75	3025
355	(0.36, 0.34)	84	4177
360	(0.33, 0.33)	89	5489
365	(0.31, 0.32)	92	6957
370	(0.29, 0.31)	94	8206

Table S4 CIE coordinates(x, y) for the Eu(III)-doped Gd(III) frameworks

λ_{ex}/nm	**$Eu_{0.009}Gd_{0.991}$ (x, y)**	**$Eu_{0.02}Gd_{0.98}$ (x,y)**	**$Eu_{0.04}Gd_{0.96}$ (x, y)**	**$Eu_{0.06}Gd_{0.94}$ (x, y)**	**$Eu_{0.07}Gd_{0.93}$ (x, y)**	**$Eu_{0.11}Gd_{0.89}$ (x, y)**
340	(0.40, 0.47)	(0.42, 0.45)	(0.43, 0.43)	(0.45, 0.39)	(0.43, 0.41)	(0.48, 0.33)
345	(0.39, 0.47)	(0.40, 0.45)	(0.42, 0.43)	(0.43, 0.40)	(0.41, 0.40)	(0.45, 0.34)
350	(0.38, 0.46)	(0.39, 0.44)	(0.40, 0.43)	(0.40, 0.39)	(0.39, 0.39)	(0.40, 0.33)
355	(0.36, 0.44)	(0.36, 0.42)	(0.37, 0.41)	(0.37, 0.38)	(0.35, 0.37)	(0.36, 0.32)
360	(0.34, 0.41)	(0.34, 0.39)	(0.34, 0.38)	(0.33, 0.36)	(0.32, 0.34)	(0.32, 0.31)
365	(0.31, 0.38)	(0.31, 0.37)	(0.30, 0.35)	(0.31, 0.34)	(0.29, 0.32)	(0.30, 0.30)
370	(0.28, 0.35)	(0.28, 0.34)	(0.28, 0.33)	(0.29, 0.32)	(0.27, 0.30)	(0.28, 0.30)



Scheme S1 The synthetic route of H_3TPIA

Synthesis of dimethyl 5-(4-cyanophenoxy)isophthalate (II). The mixture of 4-flurobenzonitrile (12.1 g, 0.1 mol), dimethyl 5-hydroxyisophthalate **I** (10.5 g, 0.05 mol) and K_2CO_3 (13.8 g, 0.1 mol) in 500 mL DMF was refluxed for overnight under N_2 atmosphere and then poured into cold water. Pure product of **II** was obtained from recrystallization in EtOH with a yield of 95%. Anal. Calcd for $C_{17}H_{13}NO_5$: C, 65.59; H, 4.21; N, 4.50%. Found: C, 65.42; H, 4.15; N, 4.33%.

Synthesis of dimethyl 5-(4-(2H-tetrazol-5-yl)phenoxy)isophthalate (III). The mixture of **II** (3.1 g, 0.01 mol), NaN_3 (2.0 g, 0.03 mol), and triethylamine hydrochloride (4.1 g, 0.03 mol) in 100 mL toluene was refluxed for 3 days under N_2 atmosphere and then 100 mL 0.1 M NaOH was dropped. The water solution was separated and acidified with dilute hydrochloric acid. White solid was obtained and recrystallized in EtOH with a yield of 90%. ESI−MS: m/z $[M - H]^-$, 353.3 (calcd for $C_{17}H_{14}N_4O_5$, 354.3). Anal. Calcd for $C_{17}H_{14}N_4O_5$: C, 57.63; H, 3.98; N, 15.81%. Found: C, 57.52; H, 3.90; N, 15.83%.

Synthesis of 5-(4-(tetrazol-5-yl)phenoxy) isophthalic acid IV (H_3TPIA). The mixture of **III** (1.8 g, 0.005 mol) and 2 mL concentrated hydrochloric acid in 100 mL H_2O was refluxed for 1 day and then filtrated. The white solid was recrystallized in EtOH with a yield of 92%. ESI−MS: m/z $[M - H]^-$, 325.4 (calcd for $C_{15}H_{10}N_4O_5$, 326.3). Anal. Calcd for $C_{15}H_{10}N_4O_5$: C, 55.22; H, 3.09; N, 17.17%. Found: C, 55.15; H, 2.96; N, 17.05%.

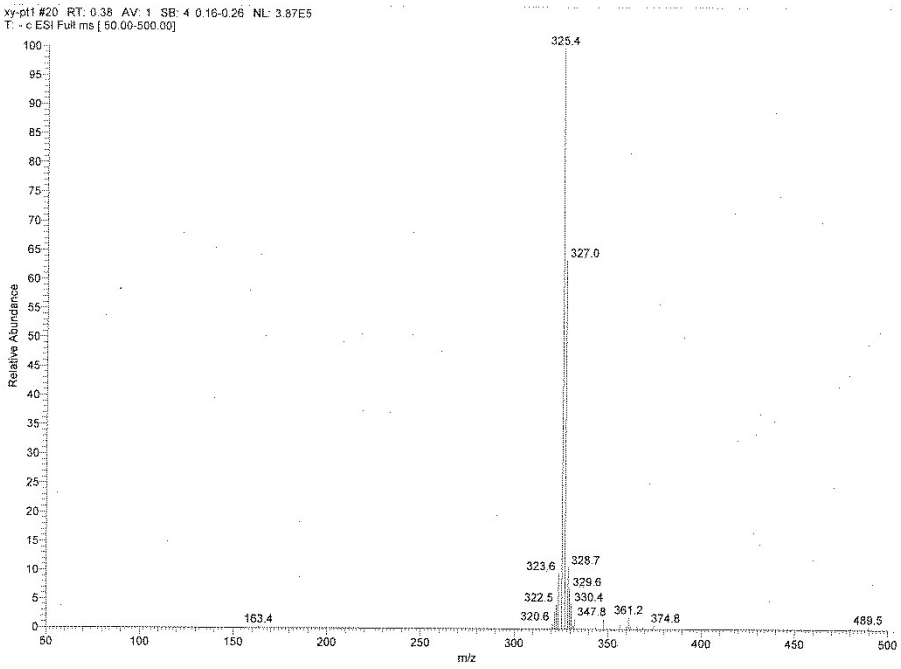


Fig. S1 ESI-MS of H_3TPIA

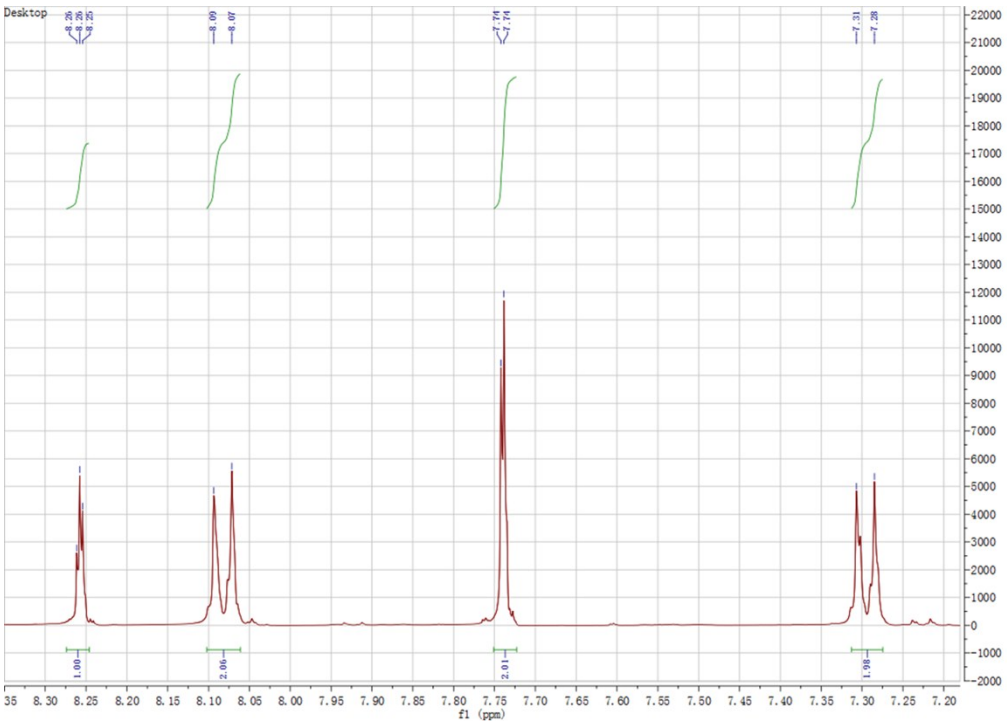


Fig. S2 ^{1}H NMR spectrum of H_3TPIA in DMSO-d_6

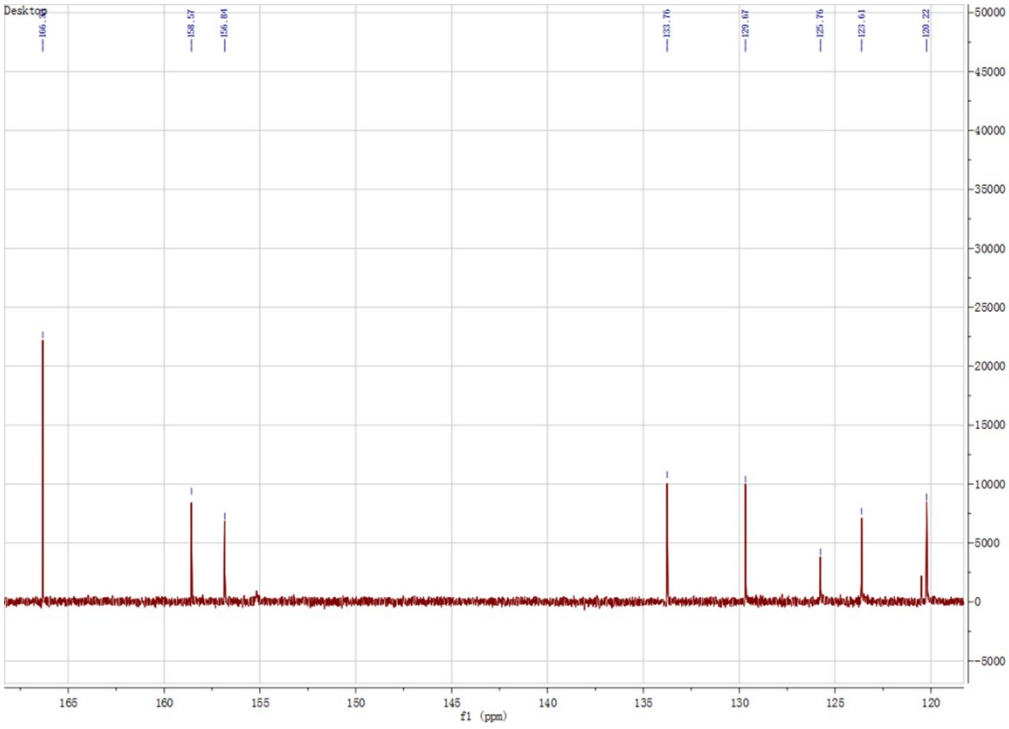


Fig. S3 ^{13}C NMR spectrum of H_3TPIA in DMSO-d_6

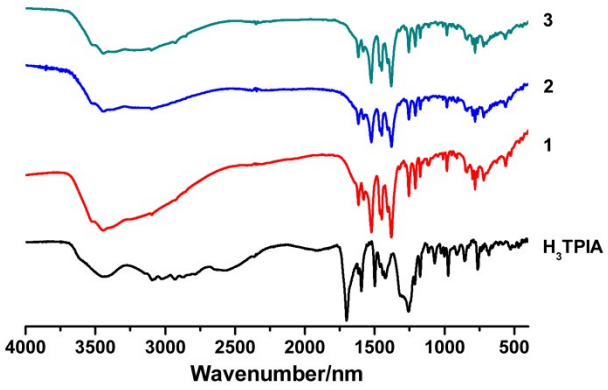


Fig. S4 FT-IR of H_3TPIA and **1**–**3**.

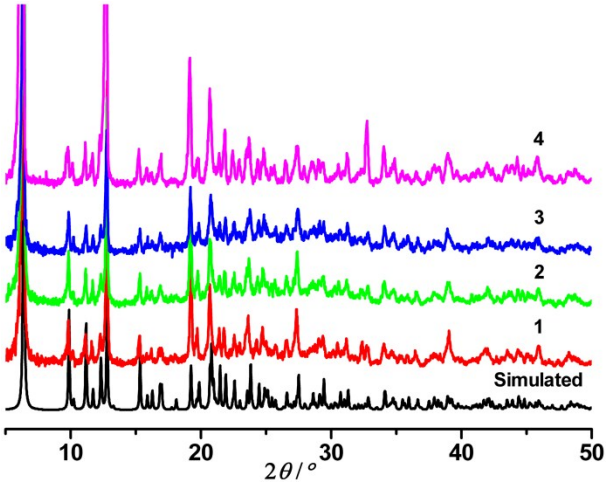


Fig. S5 PXRD patterns for the as-synthesized compounds **1**–**4** and the simulated one from single-crystal X-ray diffraction data.

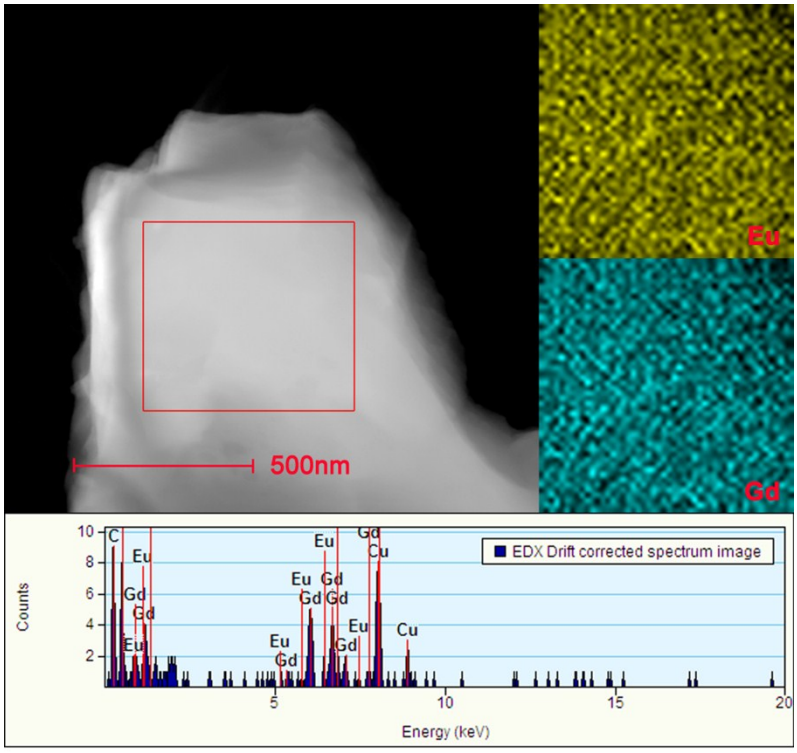


Fig. S6 Electron microscopy mapping studies of a portion of the $[(Eu_{0.12}Gd_{0.88})(TPIA)(H_2O)_3]\cdot 5.5H2O$ (**4**).

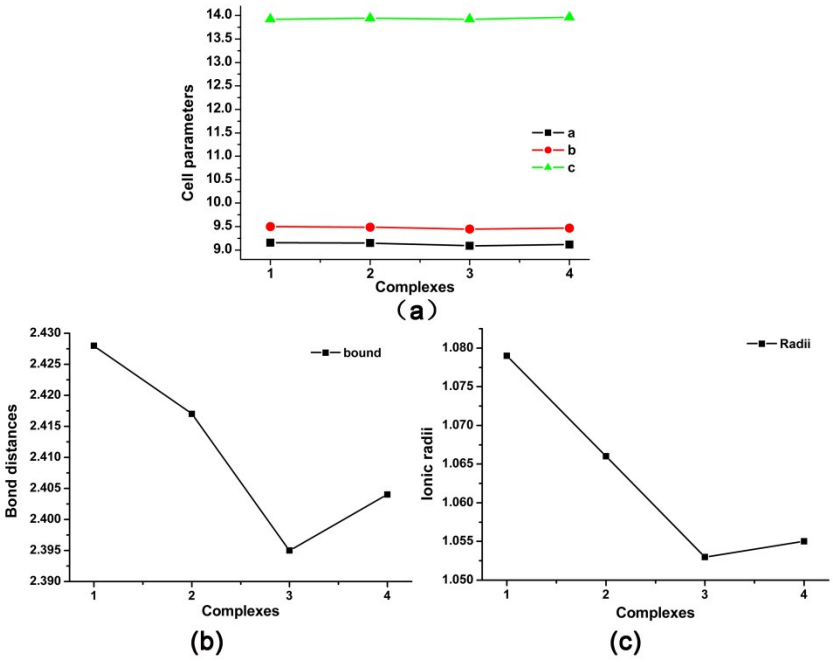


Fig. S7 (a) Cell parameters. (b) Crystallographicall identified Ln−O bond distances. (c) Ideal Ln(III) ionic radii in mono- and bimetallic Ln-MOFs (normalized for mixed Ln(III) ions according to corresponding Ln(III) ion content in mixed-Ln-MOFs **4**).

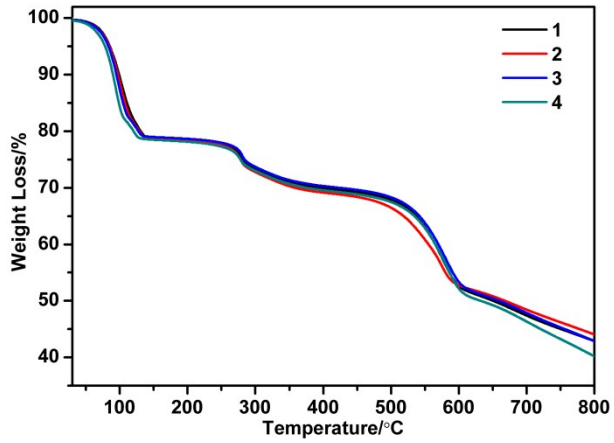


Fig. S8 The TGA curves of compounds **1**–**4**.

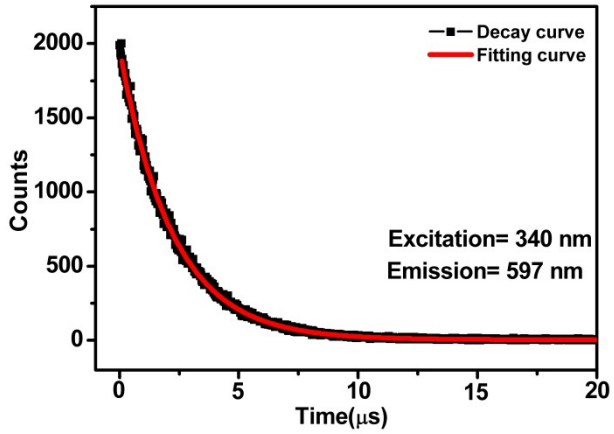


Fig. S9 The fluorescent decay curves for **1**

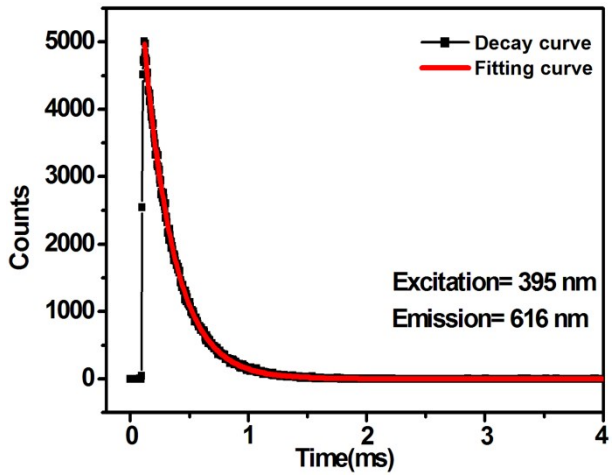


Fig. S10 The fluorescent decay curves for **2**

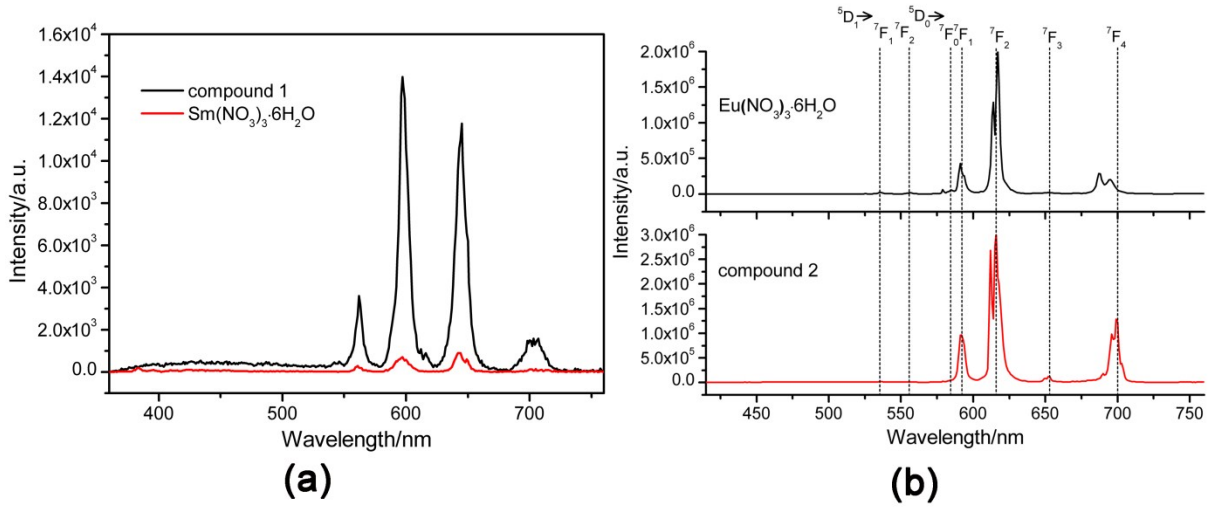


Fig. S11 (a) Emission spectra of compound **1** and $Sm(NO_3)_3 \cdot 6H_2O$ when excited at 340 nm; (b) Emission spectra of compound **2** and $Eu(NO_3)_3 \cdot 6H_2O$ when excited at 395 nm.

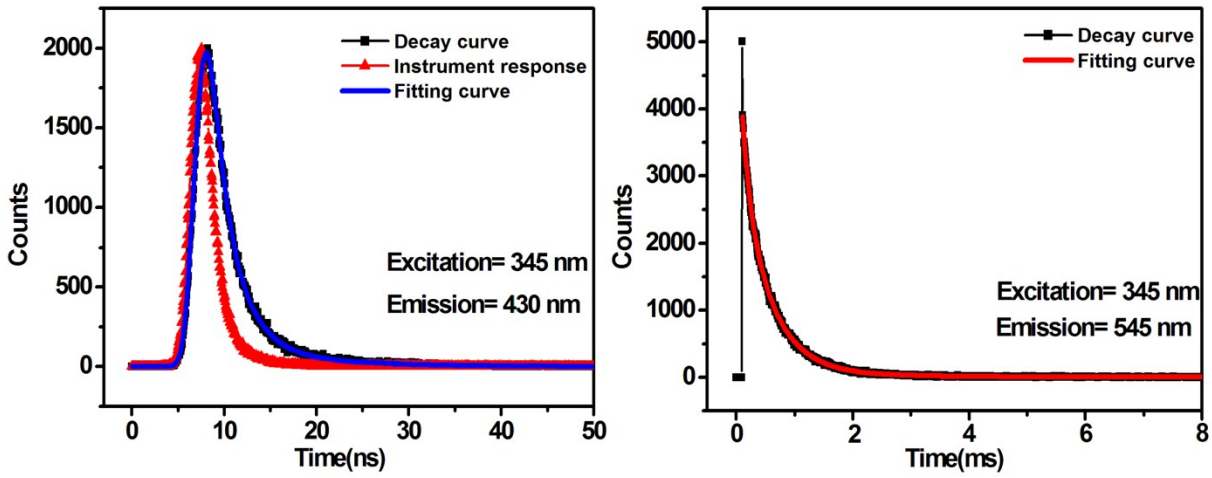


Fig. S12 The fluorescent decay curves for **3**

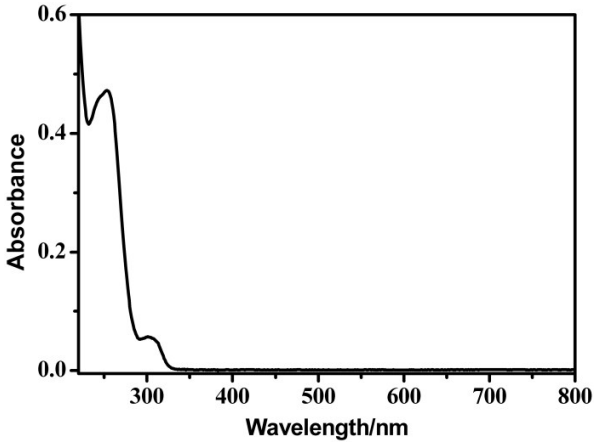


Fig. S13 UV-Vis absorption spectra of the free ligand H_3TPIA in methanol solution.

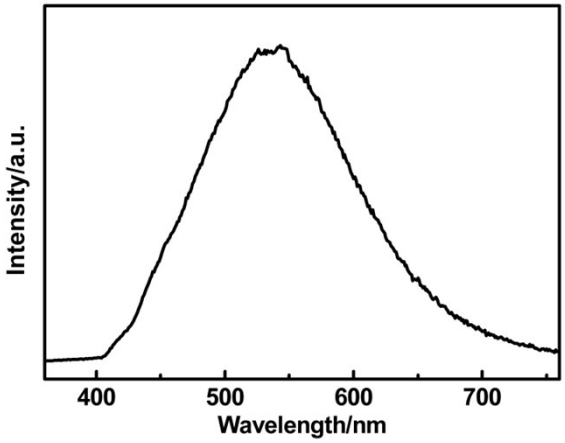


Fig. S14 The emission spectrum of **3** at 77K

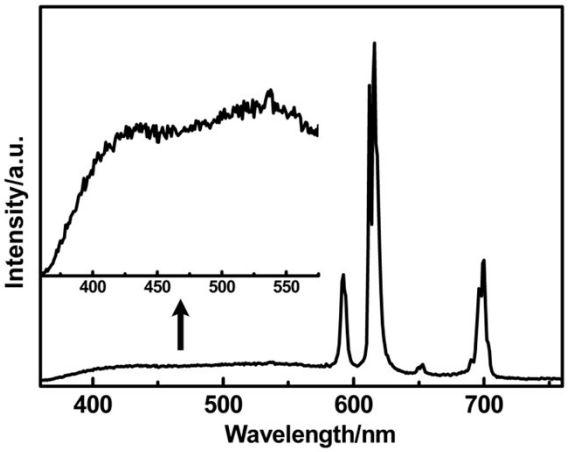


Fig. S15 The emission spectrum of **4** excited at 340 nm

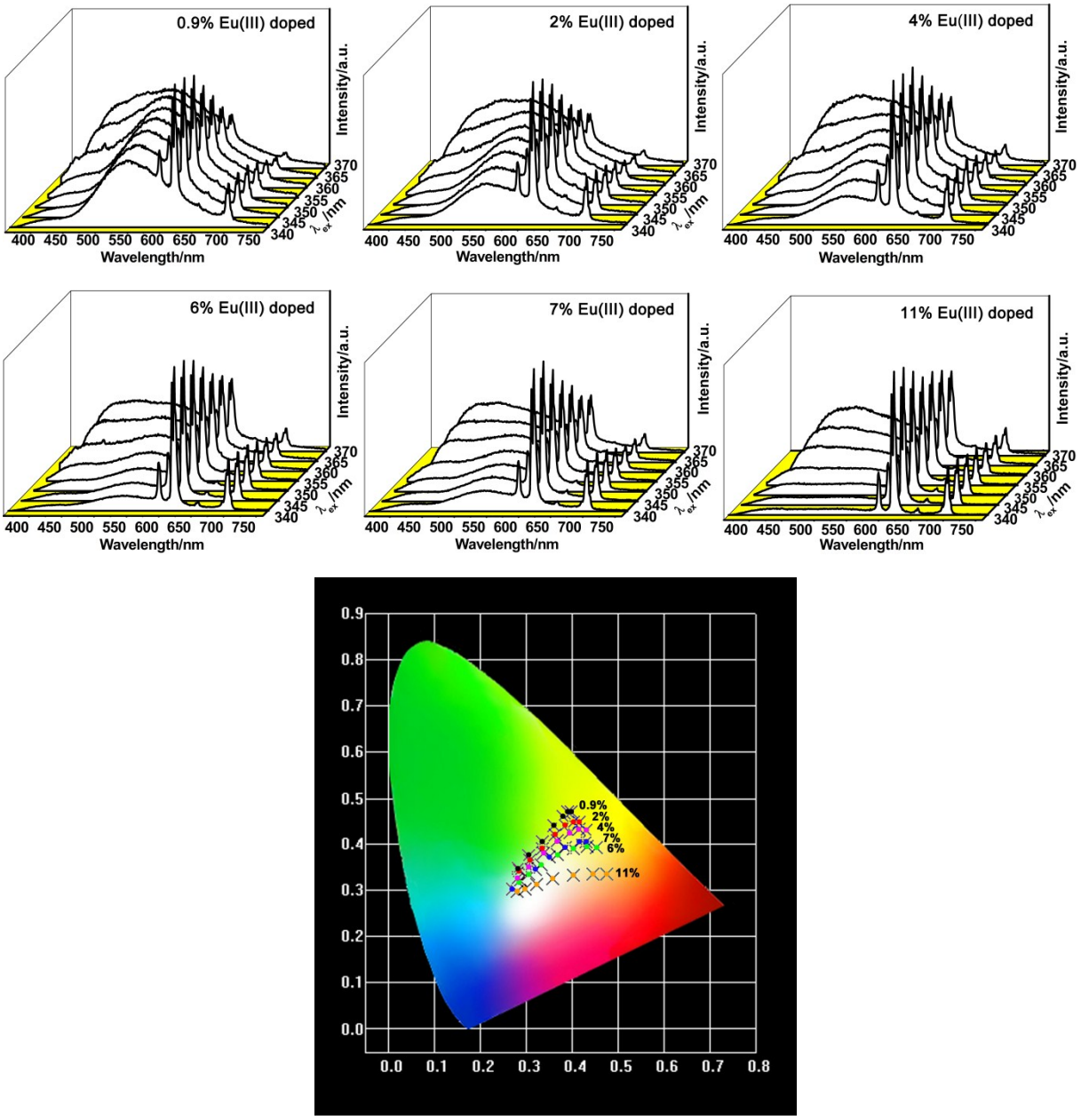


Fig. S16 The emission spectra (upper) and 1931 CIE chromaticity diagrams (lower) of different doping concentrations of Eu(III) ion embedded in **3** excited at different wavelengths.