Achieving Colour Tuneable and White-Light Luminescence in a Large Family of Dual-Emission Lanthanide Coordination Polymers

Junfeng Qian,[a,‡] Huangjie Lu,[b,c,‡] Zhaofa Zheng,[b,c] Miaomiao Xu,[a,b] Yuan Qian,[b,c] Zhi-Hui Zhang,[a] Jian-Qiang Wang,[b,c] and Ming-Yang He,[a] Jian Lin[b,c,*]

[a] Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, Changzhou University, Changzhou 213164, P. R. China,

[b] Shanghai Institute of Applied Physics, Chinese Academy of Sciences, 2019 Jia Luo Road, Shanghai 201800, P. R. China. E-mail: linjian@sinap.ac.cn,

[c] University of Chinese Academy of Sciences, No.19(A) Yuquan Road, Shijingshan District, Beijing, 100049, P. R. China

‡ These authors contributed equally to this work.

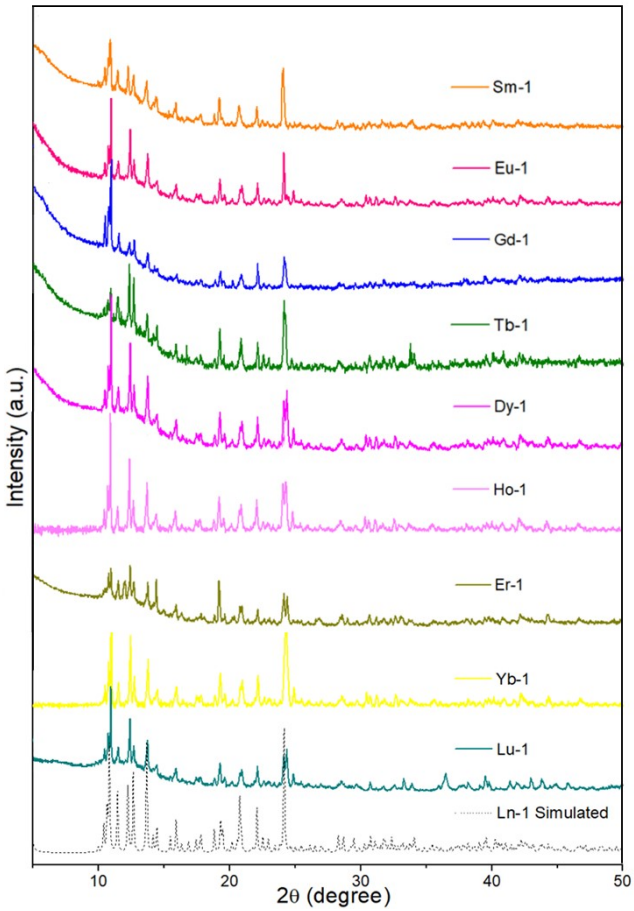

Fig. S1 The Powder X-ray diffraction (PXRD) patterns of **Ln-1** (Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, and Lu). Dashed line simulated patterns; solid line: experimental patterns.

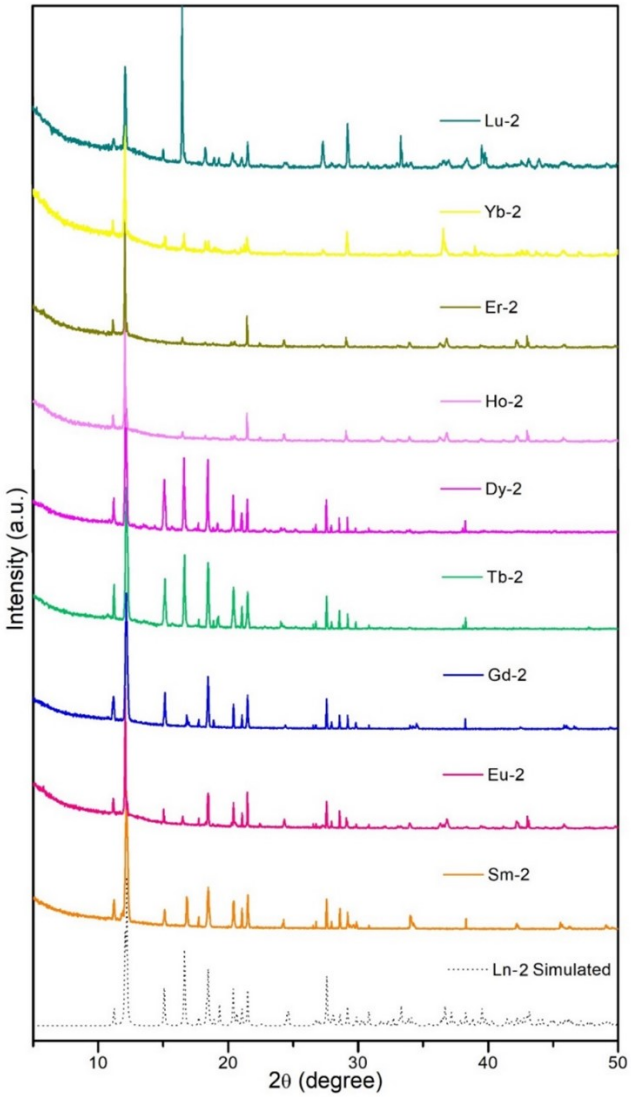

Fig. S2 The Powder X-ray diffraction (PXRD) patterns of **Ln-2** (Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, and Lu). Dashed line simulated patterns; solid line: experimental patterns.

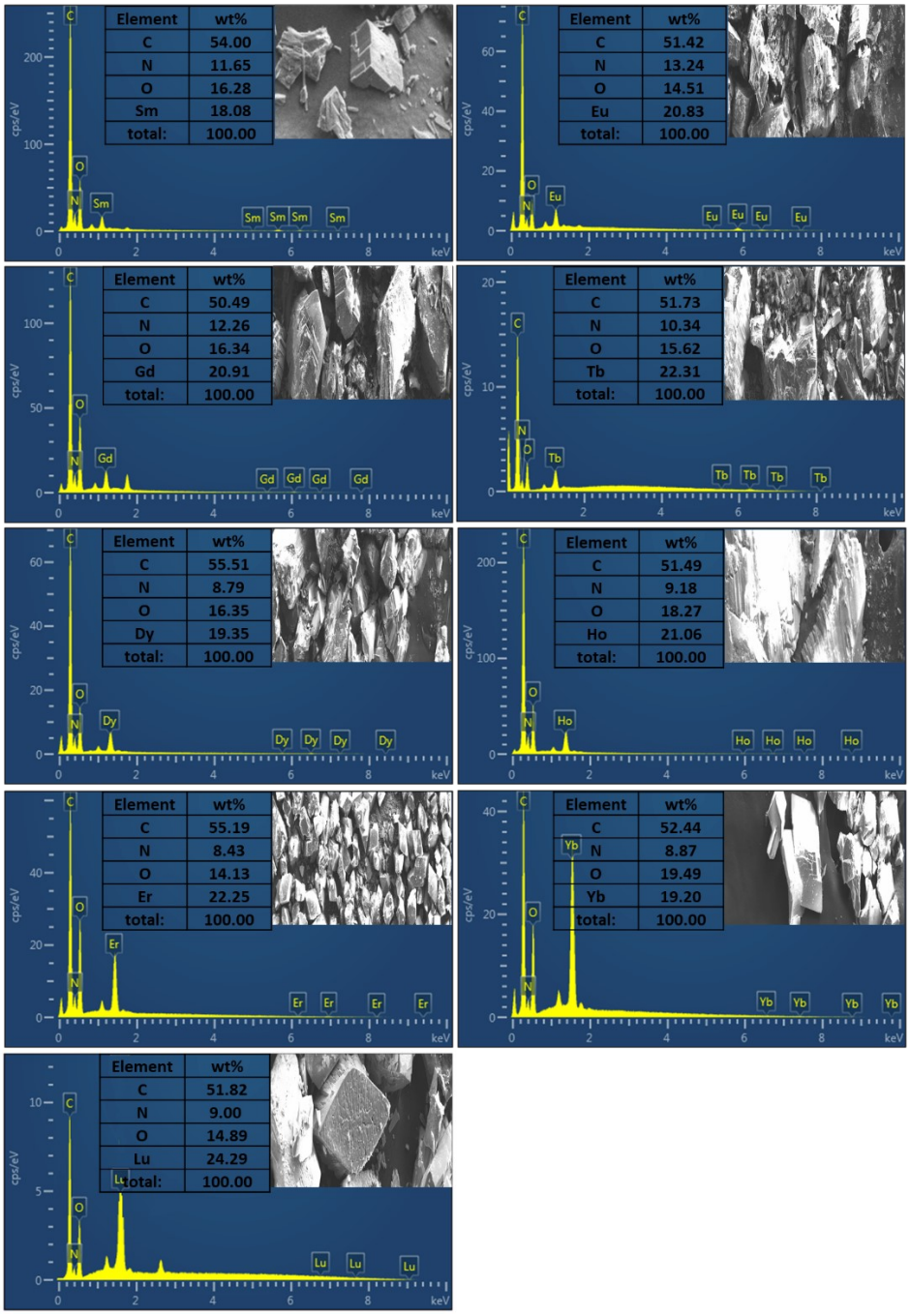

Fig. S3 SEM images and EDS spectra of **Ln-1** (Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb and Lu).

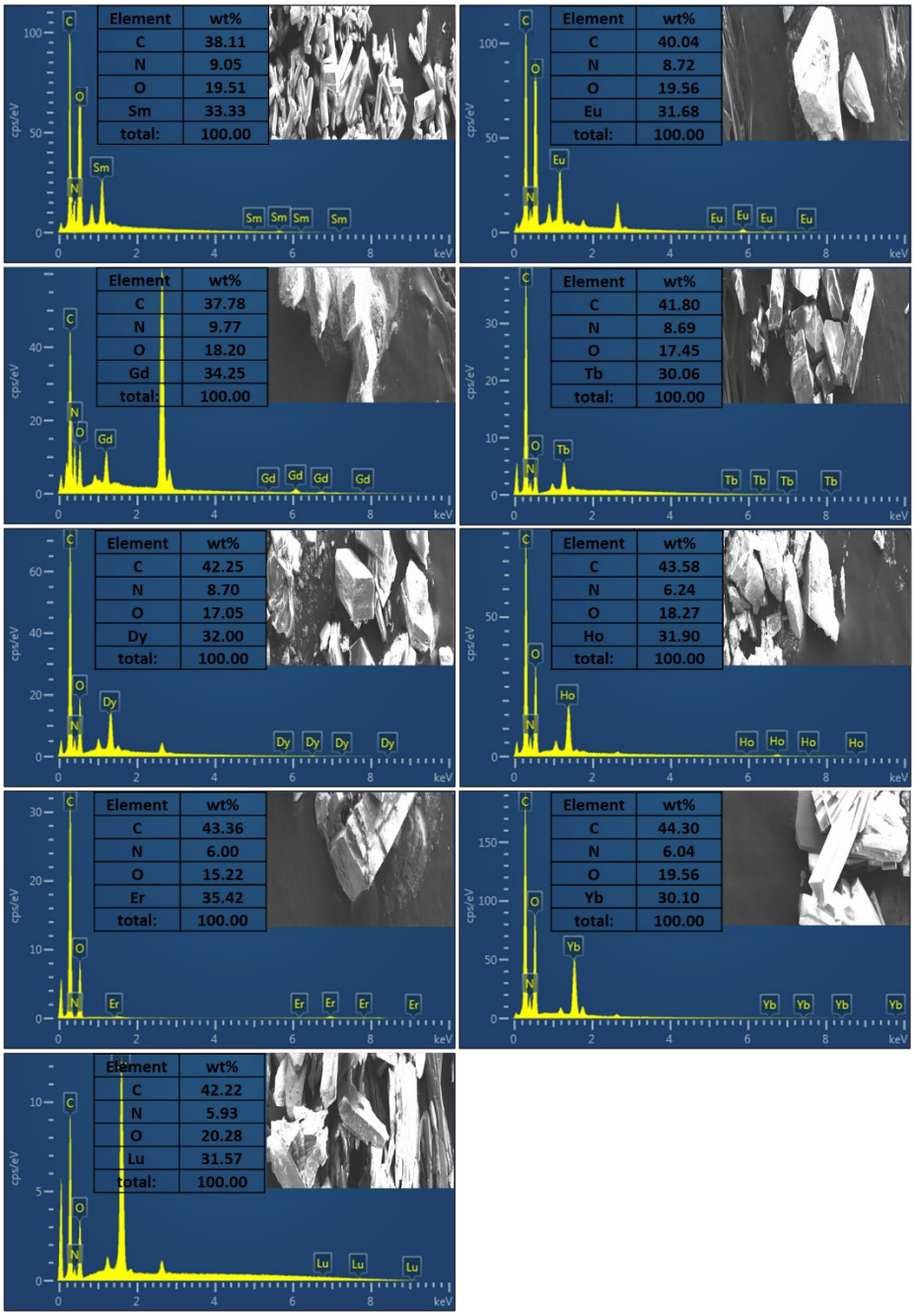

Fig. S4 SEM images and EDS spectra of **Ln-2** (Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb and Lu).

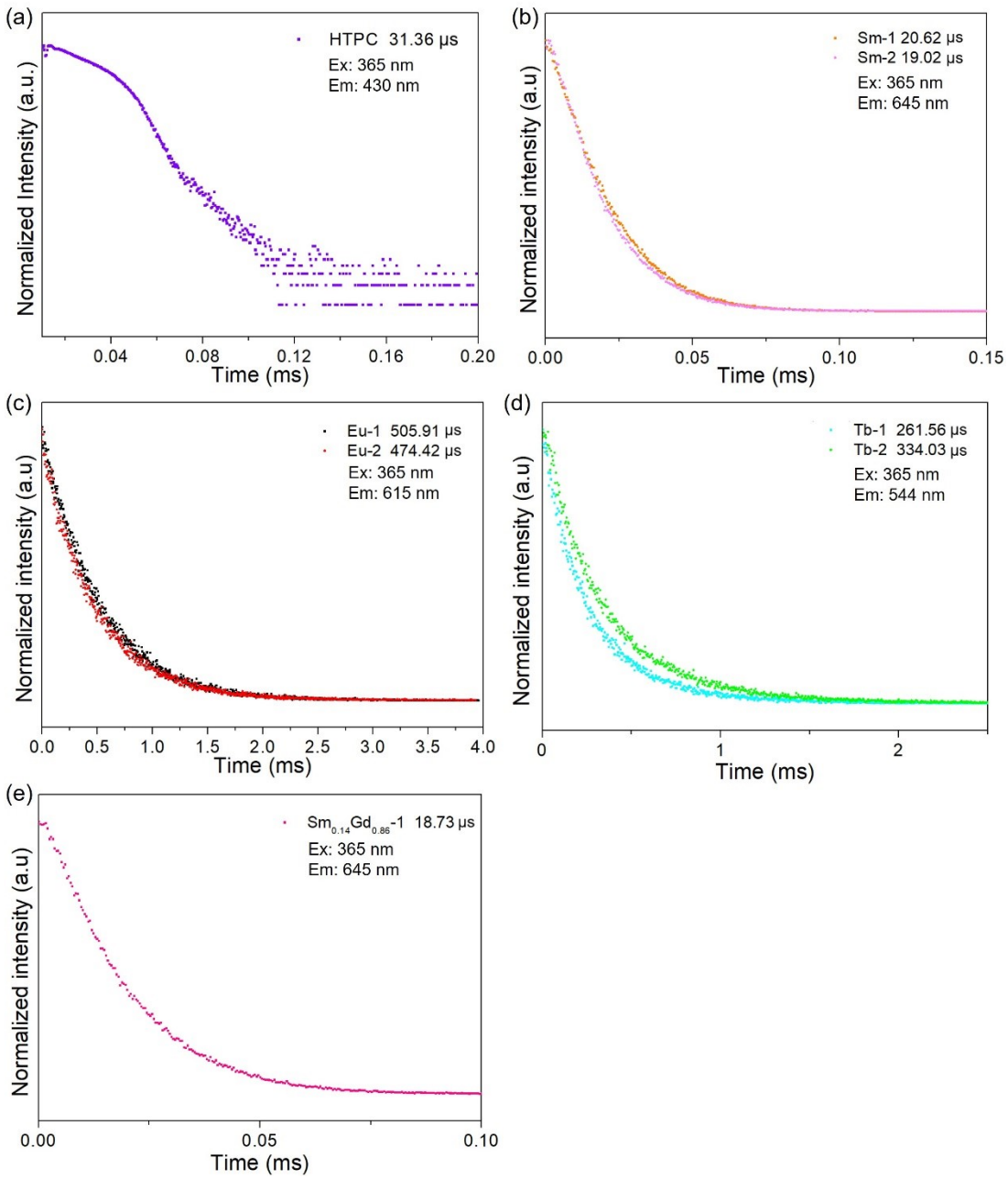

Fig. S5 Photoluminescence decay spectra of (a) HTPC, (b) **Sm-1**/**Sm-2**, (c) **Eu-1**/**Eu-2**, (d) **Tb-1**/**Tb-2**, and (e) $\mathbf{Sm_{0.14}Gd_{0.86}}$**-1**.

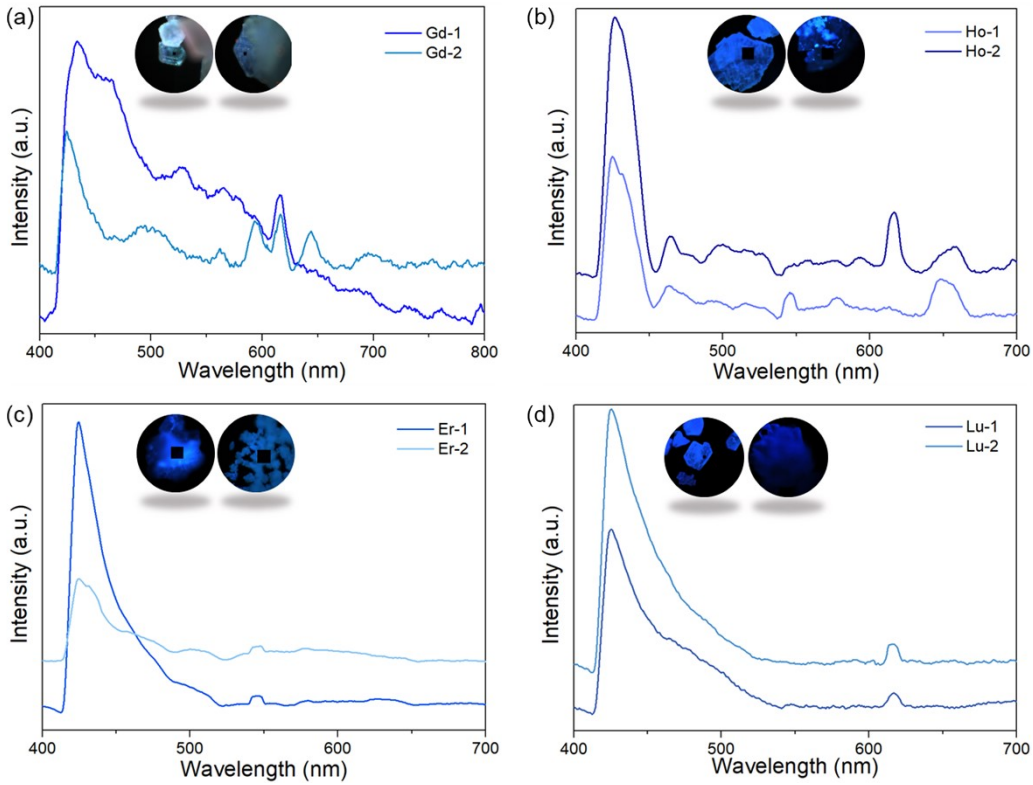

Fig. S6 Photoluminescent spectra and photographs of (a) **Gd-1** and **Gd-2**, (b) **Ho-1** and **Ho-2**, (c) **Er-1** and **Er-2**, and (d) **Lu-1** and **Lu-2**.

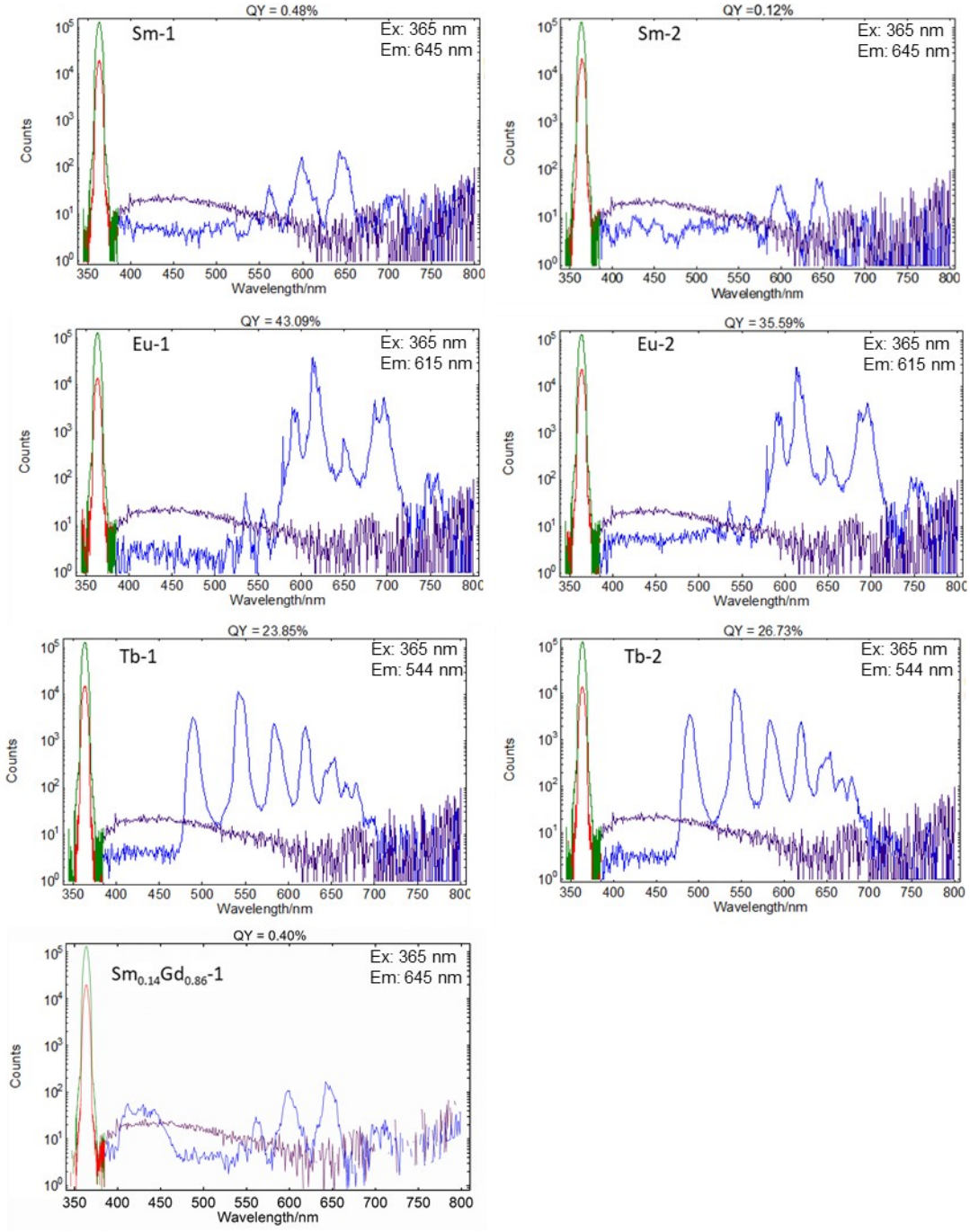

Fig. S7 The photoluminescence quantum yields (PLQYs) of **Sm-1/Sm-2**, **Eu-1/Eu-2**, **Tb-1/Tb-2**, and **$Sm_{0.14}Gd_{0.86}$-1**.

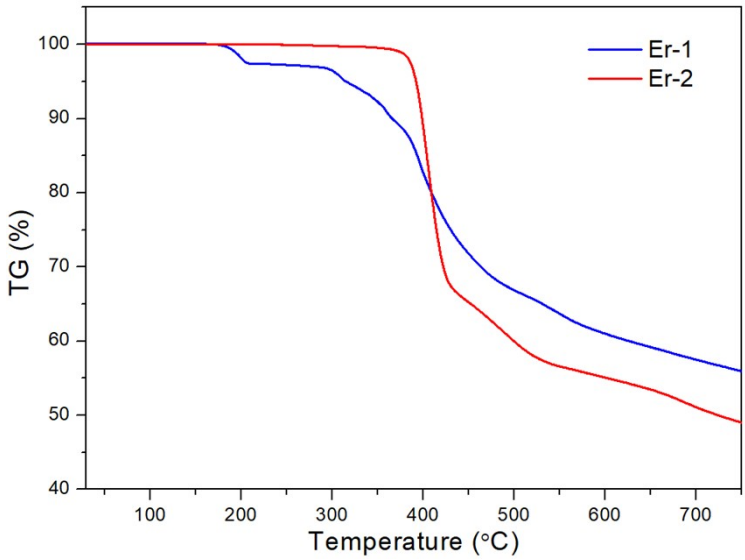

Fig. S8 The thermogravimetric analysis data showing that **Er-1** and **Er-2** are thermally stable up to 275 and 380 °C, respectively.

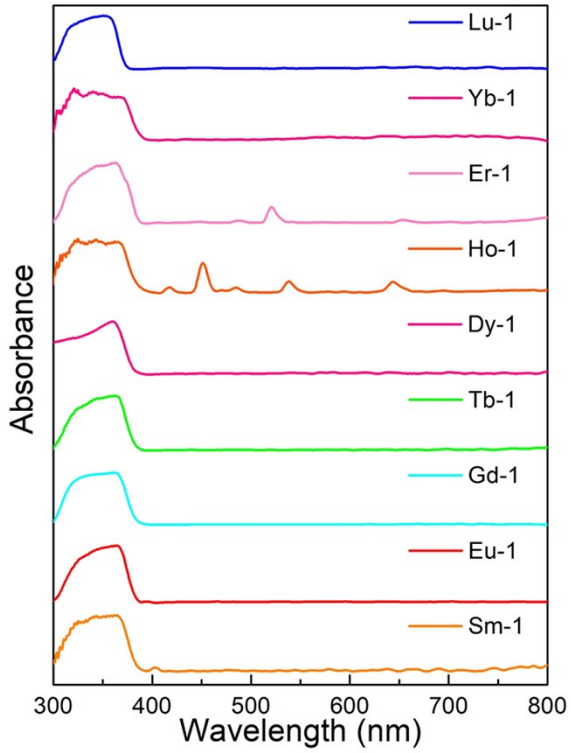

Fig. S9 UV-Vis spectra of **Ln-1** (Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb and Lu).

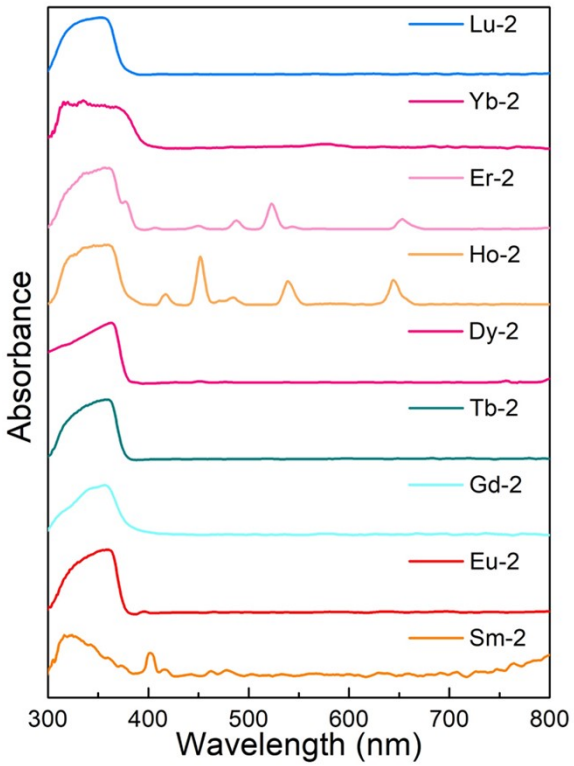

Fig. S10 UV-Vis spectra of **Ln-2** (Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb and Lu).

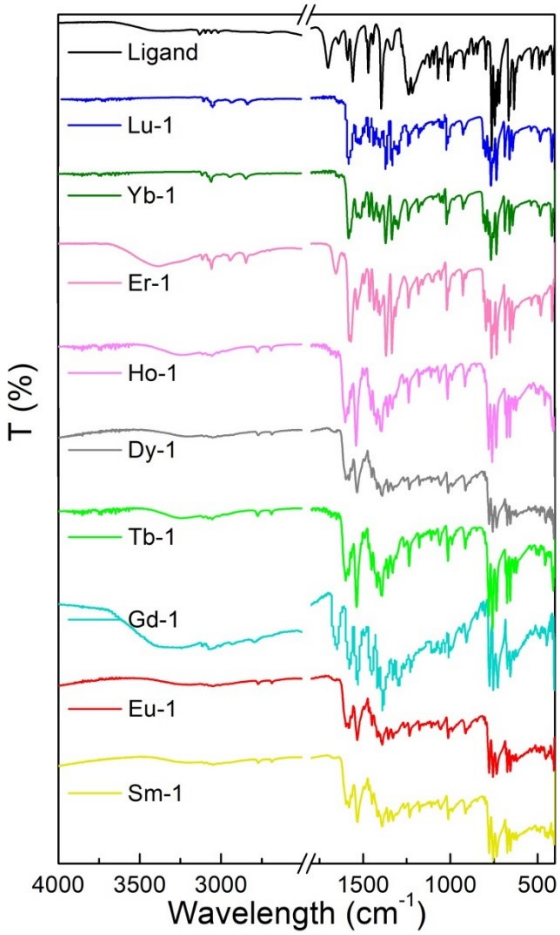

Fig. S11 FTIR spectra of **Ln-1** (Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, and Lu) and HTPC ligand.

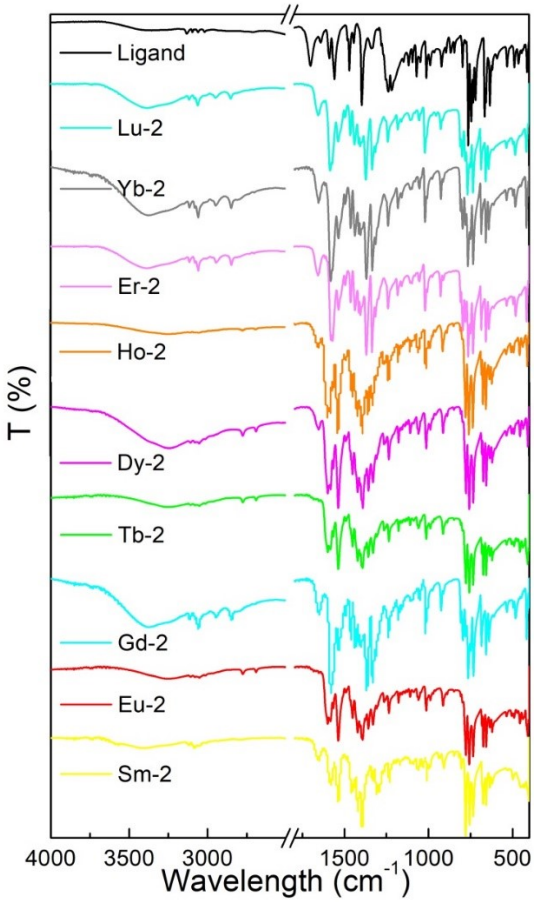

Fig. S12 FTIR spectra of **Ln-2** (Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, and Lu) and HTPC ligand.

Table S1 Crystallographic data of **Ln-1** and **Ln-2**.

Compound	**Sm-1**	**Eu-1**	**Gd-1**	**Tb-1**	**Dy-1**	**Ho-1**	**Er-1**	**Yb-1**	**Lu-1**
Formula Mass	742.74	744.35	749.64	751.31	754.89	757.32	759.65	765.43	767.36
Color	Colorless	Colorless	Colorless	Colorless	Colorless	Orange	Pink	Colorless	Colorless
Habit	Block	Block	Block	Block	Block	Block	Block	Block	Block
Space Group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	8.9331(3)	8.8826(3)	8.9185(5)	8.8962(7)	8.8872(5)	8.8861(7)	8.8673(15)	8.8478(13)	8.8308(5)
b (Å)	37.0448(10)	36.7385(11)	37.0181(18)	37.022(3)	36.989(3)	36.999(2)	37.153(8)	36.887(6)	36.9771(18)
c (Å)	9.5587(3)	9.5138(3)	9.5210(5)	9.4944(8)	9.4668(6)	9.4549(7)	9.4413(19)	9.4061(11)	9.3896(5)
α (°)	90	90	90	90	90	90	90	90	90
β (°)	106.753(1)	106.717(1)	106.664(2)	106.503(3)	106.421(2)	106.468(2)	106.228(7)	106.100(6)	106.119(2)
γ (°)	90	90	90	90	90	90	90	90	90
V (Å^3)	3028.95(16)	2973.46(16)	3011.3(3)	2998.2(4)	2985.1(3)	2981.0(4)	2986.5(10)	2949.5(7)	2945.5(3)
Z	4	4	4	4	4	4	4	4	4
T (K)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Maximum 2θ (°)	55.058	55.080	55.012	55.080	55.130	55.032	54.948	49.998	55.108
ρ_{calcd} (g cm^{-3})	1.629	1.663	1.654	1.664	1.680	1.687	1.690	1.724	1.730
μ (Mo Kα) (mm^{-1})	1.997	2.169	2.261	2.418	2.563	2.714	2.870	3.231	3.412
R_1	0.0371	0.0451	0.0378	0.0379	0.0413	0.0380	0.0677	0.0462	0.0389
wR_2	0.1009	0.1032	0.1017	0.1012	0.1062	0.1001	0.1988	0.1075	0.1420
R_{int}	0.0616	0.0346	0.0697	0.0610	0.0853	0.0773	0.0584	0.0484	0.0597
GoF on F^2	1.030	1.354	1.021	1.083	1.047	1.008	1.167	1.129	1.064

Compound	**Sm-2**	**Eu-2**	**Gd-2**	**Tb-2**	**Dy-2**	**Ho-2**	**Er-2**	**Yb-2**	**Lu-2**
Formula Mass	504.56	506.17	511.46	513.13	516.71	519.14	521.47	527.25	529.18
Color	Colorless	Colorless	Colorless	Colorless	Colorless	Orange	Pink	Colorless	Colorless
Habit	Block	Block	Block	Block	Block	Block	Block	Block	Block
Space Group	C_2/c	C_2/c	C_2/c	C_2/c	C_2/c	C_2/c	C_2/c	C_2/c	C_2/c
a (Å)	17.9643(15)	17.9743(10)	17.9534(12)	17.9568(8)	17.9267(15)	17.943(3)	17.9251(3)	17.945(2)	17.8020(9)
b (Å)	9.4713(6)	9.4752(5)	9.4710(7)	9.4586(4)	9.5160(8)	9.4929(16)	9.4654(2)	9.4044(10)	9.3809(5)
c (Å)	11.8804(9)	11.8779(6)	11.8781(9)	11.8830(5)	11.8585(9)	11.8703(19)	11.8816(2)	11.9566(14)	11.7938(6)
α (°)	90	90	90	90	90	90	90	90	90
β (°)	125.099(2)	125.097(2)	125.100(2)	125.126(1)	125.021(2)	125.173(5)	125.1780(10)	124.353(4)	125.478(1)
γ (°)	90	90	90	90	90	90	90	90	90
V (Å^3)	1653.8(2)	1655.12(16)	1652.4(2)	1650.73(12)	1656.7(2)	1652.7(5)	1647.75(5)	1665.8(3)	1603.88(14)
Z	4	4	4	4	4	4	4	4	4
T (K)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Maximum 2θ (°)	55.058	55.004	55.036	55.086	55.064	55.154	55.008	55.044	55.062
ρ_{calcd} (g cm^{-3})	2.026	2.031	2.056	2.065	2.072	2.086	2.102	2.102	2.191
μ (Mo Kα) (mm^{-1})	3.594	3.833	4.057	4.328	4.554	4.831	5.137	5.657	6.200
R_1	0.0275	0.0227	0.0240	0.0225	0.0195	0.0189	0.0181	0.0299	0.0286
wR_2	0.0756	0.0629	0.0650	0.0676	0.0569	0.0546	0.0536	0.0828	0.0781
R_{int}	0.0541	0.0398	0.0606	0.0495	0.0418	0.0402	0.0374	0.0409	0.0403
GoF on F^2	1.094	1.096	1.058	1.111	1.096	1.095	1.157	1.097	1.075

Table S2 Molar ratios of Eu^{3+} and CIE chromaticity coordinates (x, y) of $\mathbf{Eu_xTb_{1-x}}$ **−1** and $\mathbf{Eu_xTb_{1-x}}$ **−2** (x = 0−1).

Eu^{3+} molar ratios of $\mathbf{Eu_xTb_{1-x}}$ **-1** before reaction	Eu^{3+} molar ratio $\mathbf{Eu_xTb_{1-x}}$ **-1** after reaction	CIE coordinates (x, y)
0	0	(0.33,0.58)
0.001	0.0007	(0.35,0.58)
0.002	0.0016	(0.36,0.57)
0.005	0.0040	(0.40,0.54)
0.01	0.008	(0.49,0.47)
0.05	0.043	(0.60,0.38)
0.1	0.095	(0.63,0.36)
0.2	0.363	(0.66,0.34)
Eu^{3+} molar ratios of $\mathbf{Eu_xTb_{1-x}}$ **-2** before reaction	Eu^{3+} molar ratio $\mathbf{Eu_xTb_{1-x}}$ **-2** after reaction	CIE coordinates (x, y)
0	0	(0.34,0.59)
0.001	0.0008	(0.35,0.58)
0.002	0.0014	(0.36,0.57)
0.005	0.0036	(0.39,0.55)
0.01	0.007	(0.45,0.50)
0.02	0.010	(0.53,0.44)
0.05	0.069	(0.63,0.36)
0.1	0.104	(0.65,0.34)

Table S3 Molar ratios of Eu^{3+} and CIE chromaticity coordinates (x, y) of $\mathbf{Eu_xHo_{1-x}}$ **−1** and $\mathbf{Sm_xGd_{1-x}}$ **−1** (x = 0−1).

Eu^{3+} molar ratios of $\mathbf{Eu_xHo_{1-x}}$ **-1** before reaction	Eu^{3+} molar ratio $\mathbf{Eu_xHo_{1-x}}$ **-1** after reaction	CIE coordinates (x, y)
0	0	(0.22,0.12)
0.0001	0.0003	(0.28,0.24)
0.001	0.0007	(0.43,0.28)
0.002	0.0012	(0.59,0.32)
0.005	0.0042	(0.63,0.33)
0.01	0.0085	(0.65,0.33)
0.02	0.015	(0.66,0.33)
0.05	0.047	(0.66,0.34)
Sm^{3+} molar ratios of $\mathbf{Sm_xGd_{1-x}}$ **-1** before reaction	Sm^{3+} molar ratio $\mathbf{Sm_xGd_{1-x}}$ **-1** after reaction	CIE coordinates (x, y)
0	0	(0.20,0.14)
0.01	0.01	(0.25,0.20)
0.1	0.14	(0.32,0.24)
0.2	0.23	(0.38,0.28)
0.4	0.50	(0.46,0.35)
1.0	1.00	(0.58,0.37)

Table S4 Element analyses showing the C, H, and N contents of **Ln-1** and **Ln-2**.

		Calculated			Measured		
		C (%)	H (%)	N (%)	C (%)	H (%)	N (%)
Ln-1	**Sm-1**	51.74	3.01	10.98	51.32	2.98	10.88
	Eu-1	51.63	3.00	10.95	51.89	3.02	10.86
	Gd-1	51.28	2.98	10.88	50.78	3.00	10.78
	Tb-1	51.17	2.97	10.85	50.84	2.96	10.75
	Dy-1	50.93	2.96	10.80	50.54	2.93	10.73
	Ho-1	50.77	2.95	10.77	50.35	2.96	10.7
	Er-1	50.62	2.94	10.74	50.44	2.91	10.7
	Tm-2	50.51	2.93	10.72	50.11	2.90	10.65
	Yb-1	50.25	2.92	10.66	49.83	2.89	10.75
	Lu-1	50.13	2.91	10.63	49.86	2.89	10.55
Ln-2	**Sm-2**	41.83	2.32	8.13	41.53	2.34	8.10
	Eu-2	41.70	2.32	8.11	41.24	2.30	8.14
	Gd-2	41.28	2.29	8.03	40.98	2.27	7.96
	Tb-2	41.15	2.29	8.00	40.76	2.28	8.05
	Dy-2	40.87	2.27	7.95	40.46	2.29	7.89
	Ho-2	40.68	2.26	7.91	40.31	2.28	7.87
	Er-2	40.51	2.25	7.88	40.52	2.26	7.97
	Tm-2	40.38	2.24	7.85	40.12	2.23	7.89
	Yb-2	40.07	2.22	7.76	39.91	2.23	7.82
	Lu-2	39.93	2.22	7.76	39.65	2.21	7.83