Supporting Information

Lanthanide Metal-Organic Frameworks Assembled from Fluorene-based Ligand: Selective Sensing of Pb^{2+} and Fe^{3+} Ions

Liang Li,[a] Qiang Chen,[a] Zhigang Niu,[b] Xinhui Zhou,*[a] Tao Yang[a] and Wei Huang*[a,c]

[a.] *Key Laboratory for Organic Electronics and Information Displays & Institute of Advanced Materials, National Jiangsu Syngerstic Innovation Center for Advanced Materials (SICAM), Nanjing University of Posts & Telecommunications, Nanjing 210023, China*

[b.] *College of Chemistry and Chemical Engineering, Hainan Normal University, Haikou 571158, China.*

[c.] *Key Laboratory of Flexible Electronics (KLOFE) & Institute of Advanced Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing Tech University (NanjingTech), Nanjing 211816, China*

Table S1. Crystallographic data for **1-4**.

	1	**2**	**3**	**4**
Empirical formula	$Sm_4C_{118}H_{138}N_4O_{43}$	$Eu_4C_{118}H_{138}N_4O_{43}$	$Gd_4C_{118}H_{138}N_4O_{43}$	$Tb_4C_{118}H_{138}N_4O_{43}$
Formula weight	2901.72	2908.16	2929.32	2936.00
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	*P*-1	*P*-1	*P*-1	*P*-1
a/Å	11.4087(8)	11.4422(4)	11.4957(4)	11.4646(4)
b/Å	13.6584(8)	13.6499(5)	13.6804(4)	13.6288(5)
c/Å	24.023(1)	23.9769(8)	23.9693(8)	23.7978(7)
α/°	93.171(4)	92.915(3)	76.328(3)	92.929(3)
β/°	103.627(5)	103.671(3)	76.214(3)	103.548(3)
γ/°	112.671(6)	112.821(3)	66.917(3)	112.494(3)
V/Å^3	3312.0(3)	3311.2(2)	3324.5(2)	3298.6(2)
Z	1	1	1	1
ρ_{calc} g/cm^3	1.455	1.458	1.463	1.478
μ/mm^{-1}	1.827	1.949	2.049	2.198

F(000)	1466.0	1470.0	1474.0	1478.0
Reflections collected	26109	26254	25537	26114
Independent reflections	11677	11675	11710	11622
R_{int}, R_{sigma}	0.0617, 0.0806	0.0494, 0.0617	0.0512, 0.0843	0.0307, 0.0427
GOF (F^2)	1.225	1.224	1.030	1.230
$R_1{}^a$, $wR_2{}^b$ [I>=2σ (I)]	0.0899, 0.2464	0.1089, 0.2970	0.0455, 0.1085	0.0503, 0.1269
$R_1{}^a$, $wR_2{}^b$ [all data]	0.1113, 0.2595	0.1221, 0.3022	0.0781, 0.1189	0.0617, 0.1314

$R_1{}^a = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR_2{}^b = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)]^{1/2}$.

Table S2. Selected bond lengths (Å) and angles (°) for **1**.

Sm1 - O4	2.354(8)	Sm2 - O6$^{\#4}$	2.361(10)
Sm1 - O14	2.356(10)	Sm2 - O1$^{\#5}$	2.395(10)
Sm1 - O3$^{\#1}$	2.378(10)	Sm2 - O12	2.422(9)
Sm1 - O7	2.415(9)	Sm2 - O11	2.504(10)
Sm1 - O13	2.433(11)	Sm2 - O19	2.61(4)
Sm1 - O8	2.444(11)	O1 - Sm2$^{\#6}$	2.395(9)
Sm1 - O9	2.461(9)	O2 - Sm2$^{\#2}$	2.343(11)
Sm1 - O10	2.463(9)	O3 - Sm1$^{\#1}$	2.378(10)
Sm2 - O2$^{\#2}$	2.343(11)	O5 - Sm2$^{\#7}$	2.348(10)
Sm2 - O5$^{\#3}$	2.348(10)	O6 - Sm2$^{\#4}$	2.361(10)
Sm2 - O20	2.35(3)		
O4 - Sm1 - O14	79.1(3)	O2$^{\#2}$ - Sm2 - O5$^{\#3}$	76.8(4)
O4 - Sm1 - O3$^{\#1}$	83.8(3)	O2$^{\#2}$ - Sm2 - O20	157.4(7)
O14 - Sm1 - O3$^{\#1}$	79.4(4)	O5$^{\#3}$ - Sm2 - O20	93.4(8)
O4 - Sm1 - O7	76.2(3)	O2$^{\#2}$ - Sm2 - O6$^{\#4}$	73.6(4)
O14 - Sm1 - O7	121.8(4)	O5$^{\#3}$ - Sm2 - O6$^{\#4}$	127.7(4)
O3$^{\#1}$ - Sm1 - O7	146.4(3)	O20 - Sm2 - O6$^{\#4}$	126.9(8)
O4 - Sm1 - O13	77.0(3)	O2$^{\#2}$ - Sm2 - O1$^{\#5}$	123.6(4)
O14 - Sm1 - O13	146.3(4)	O5 $^{\#3}$ - Sm2 - O1$^{\#5}$	78.5(4)
O3$^{\#1}$ - Sm1 - O13	74.7(4)	O20 - Sm2 - O1$^{\#5}$	72.9(7)
O7 - Sm1 - O13	74.6(3)	O6$^{\#4}$ - Sm2 - O1$^{\#5}$	83.3(4)
O4 - Sm1 - O8	96.0(3)	O2$^{\#2}$ - Sm2 - O12	82.2(4)
O14 - Sm1 - O8	78.4(4)	O5$^{\#3}$ - Sm2 - O12	82.0(4)
O3$^{\#1}$ - Sm1 - O8	157.4(4)	O20 - Sm2 - O12	76.3(7)
O7 - Sm1 - O8	53.4(3)	O6$^{\#4}$ - Sm2 - O12	133.7(4)

O13 - Sm1 - O8	127.3(3)	O1$^{\#5}$ - Sm2 - O12	142.1(4)
O4 - Sm1 - O9	151.4(3)	O2$^{\#2}$ - Sm2 - O11	87.7(4)
O14 - Sm1 - O9	128.3(3)	O5$^{\#3}$ - Sm2 - O11	134.4(3)
O3$^{\#1}$ - Sm1 - O9	107.0(4)	O20 - Sm2 - O11	84.8(7)
O7 - Sm1 - O9	81.0(3)	O6$^{\#4}$ - Sm2 - O11	86.3(4)
O13 - Sm1 - O9	80.5(3)	O1$^{\#5}$ - Sm2 - O11	142.0(4)
O8 - Sm1 - O9	83.9(4)	O12 - Sm2 - O11	53.3(3)
O4 - Sm1 - O10	155.0(3)	O2$^{\#2}$ - Sm2 - O19	147.2(9)
O14 - Sm1 - O10	79.9(3)	O5$^{\#3}$ - Sm2 - O19	136.0(9)
O3$^{\#1}$ - Sm1 - O10	79.0(3)	O20 - Sm2 - O19	47.1(6)
O7 - Sm1 - O10	127.1(3)	O6$^{\#4}$ - Sm2 - O19	80.8(8)
O13 - Sm1 - O10	115.2(3)	O1$^{\#5}$ - Sm2 - O19	72.1(9)
O8 - Sm1 - O10	93.0(3)	O12 - Sm2 - O19	101.9(9)
O9 - Sm1 - O10	52.8(3)	O11 - Sm2 - O19	70.2(9)

#1 -x+1, -y+1, -z+1; #2 -x, -y, -z+1; #3 x+1, y, z+1; #4 -x, -y-1, -z+1; #5 x+1, y-1, z+1; #6 x-1, y+1, z-1; #7 x-1, y, z-1.

Table S3. Selected bond lengths (Å) and angles (^{o}) for **2**.

Eu1 - O14	2.340(16)	Eu2 - O1$^{\#5}$	2.380(13)
Eu1 - O3$^{\#1}$	2.357(14)	Eu2 - O20	2.40(4)
Eu1 - O4	2.361(12)	Eu2 - O12	2.406(14)
Eu1 - O7	2.406(13)	Eu2 - O11	2.490(15)
Eu1 - O10	2.435(12)	Eu2 - O19	2.55(5)
Eu1 - O13	2.444(14)	O1 - Eu2$^{\#6}$	2.380(13)
Eu1 - O8	2.449(14)	O2 - Eu2$^{\#3}$	2.329(14)
Eu1 - O9	2.455(13)	O3 - Eu1$^{\#1}$	2.357(14)
Eu2 - O6$^{\#2}$	2.326(14)	O5 - Eu2$^{\#7}$	2.355(17)
Eu2 - O2$^{\#3}$	2.329(14)	O6 - Eu2$^{\#2}$	2.326(14)
Eu2 - O5$^{\#4}$	2.355(17)		
O14 - Eu1 - O3$^{\#1}$	78.8(6)	O6$^{\#2}$ - Eu2 - O2$^{\#3}$	74.9(6)
O14 - Eu1 - O4	77.9(5)	O6$^{\#2}$ - Eu2 - O5$^{\#4}$	128.6(6)
O3$^{\#1}$ - Eu1 - O4	84.0(5)	O2$^{\#3}$ - Eu2 - O5$^{\#4}$	76.5(6)
O14 - Eu1 - O7	121.7(6)	O6$^{\#2}$ - Eu2 - O1$^{\#5}$	82.9(6)
O3$^{\#1}$ - Eu1 - O7	147.1(5)	O2$^{\#3}$ - Eu2 - O1$^{\#5}$	124.2(6)
O4 - Eu1 - O7	76.8(4)	O5$^{\#4}$ - Eu2 - O1$^{\#5}$	79.3(6)
O14 - Eu1 - O10	79.7(5)	O6$^{\#2}$ - Eu2 - O20	124.8(10)
O3$^{\#1}$ - Eu1 - O10	79.0(5)	O2$^{\#3}$ - Eu2 - O20	157.4(10)
O4 - Eu1 - O10	154.0(5)	O5$^{\#4}$ - Eu2 - O20	95.2(11)
O7 - Eu1 - O10	126.9(5)	O1$^{\#5}$ - Eu2 - O20	73.4(10)
O14 - Eu1 - O13	145.4(6)	O6$^{\#2}$ - Eu2 - O12	133.3(5)

O3$^{\#1}$ - Eu1 - O13	75.0(6)	O2$^{\#3}$ - Eu2 - O12	81.2(6)
O4 - Eu1 - O13	77.3(5)	O5$^{\#4}$ - Eu2 - O12	81.8(5)
O7 - Eu1 - O13	74.9(5)	O1$^{\#5}$ - Eu2 - O12	142.7(6)
O10 - Eu1 - O13	116.3(5)	O20 - Eu2 - O12	76.8(10)
O14 - Eu1 - O8	79.2(6)	O6$^{\#2}$ - Eu2 - O11	85.8(5)
O3$^{\#1}$ - Eu1 - O8	157.3(5)	O2$^{\#3}$ - Eu2 - O11	87.9(6)
O4 - Eu1 - O8	97.0(5)	O5$^{\#4}$ - Eu2 - O11	134.4(5)
O7 - Eu1 - O8	53.4(4)	O1$^{\#5}$ - Eu2 - O11	141.0(6)
O10 - Eu1 - O8	91.4(5)	O20 - Eu2 - O11	83.1(10)
O13 - Eu1 - O8	127.5(5)	O12 - Eu2 - O11	53.4(5)
O14 - Eu1 - O9	129.4(5)	O6$^{\#2}$ - Eu2 - O19	77.7(11)
O3$^{\#1}$ - Eu1 - O9	106.4(5)	O2$^{\#3}$ - Eu2 - O19	146.3(12)
O4 - Eu1 - O9	151.8(5)	O5$^{\#4}$ - Eu2 - O19	136.9(12)
O7 - Eu1 - O9	81.1(5)	O1$^{\#5}$ - Eu2 - O19	70.4(14)
O10 - Eu1 - O9	53.5(5)	O20 - Eu2 - O19	47.6(7)
O13 - Eu1 - O9	80.3(5)	O12 - Eu2 - O19	104.4(13)
O8 - Eu1 - O9	83.3(5)	O11 - Eu2 - O19	70.8(13)

#1 -x+1, -y+1, -z+1; #2 -x, -y-1, -z+1; #3 -x, -y, -z+1; #4 x+1, y, z+1; #5 x+1, y-1, z+1; #6 x-1, y+1, z-1; #7 x-1, y, z-1.

Table S4. Selected bond lengths (Å) and angles (^{o}) for **3**.

Gd1 - O14	2.324(5)	Gd2 - O20	2.359(9)
Gd1 - O4	2.336(4)	Gd2 - O1$^{\#5}$	2.381(5)
Gd1 - O3$^{\#1}$	2.350(5)	Gd2 - O12	2.410(5)
Gd1 - O7	2.399(4)	Gd2 - O11	2.483(5)
Gd1 - O10	2.435(5)	Gd2 - O19	2.570(7)
Gd1 - O13	2.436(4)	O1 - Gd2$^{\#6}$	2.381(5)
Gd1 - O9	2.437(5)	O2 - Gd2$^{\#2}$	2.304(5)
Gd1 - O8	2.442(5)	O3 - Gd1$^{\#1}$	2.350(5)
Gd2 - O2$^{\#2}$	2.304(5)	O5 - Gd2$^{\#7}$	2.334(5)
Gd2 - O6$^{\#3}$	2.320(5)	O6 - Gd2$^{\#3}$	2.320(5)
Gd2 - O5$^{\#4}$	2.334(5)		
O14 - Gd1 - O4	78.10(17)	O2$^{\#2}$ - Gd2 - O6$^{\#3}$	74.39(19)
O14 - Gd1 - O3$^{\#1}$	78.32(19)	O2$^{\#2}$ - Gd2 - O5$^{\#4}$	76.66(19)
O4 - Gd1 - O3$^{\#1}$	83.35(17)	O6$^{\#3}$ - Gd2 - O5$^{\#4}$	127.41(17
O14 - Gd1 - O7	121.78(17	O2$^{\#2}$ - Gd2 - O20	152.7(4)
O4 - Gd1 - O7	77.05(16)	O6$^{\#3}$ - Gd2 - O20	131.8(5)
O3$^{\#1}$ - Gd1 - O7	147.31(15	O5$^{\#4}$ - Gd2 - O20	88.8(5)
O14 - Gd1 - O10	80.05(17)	O2$^{\#2}$ - Gd2 - O1$^{\#5}$	123.55(18
O4 - Gd1 - O10	154.43(16	O6$^{\#3}$ - Gd2 - O1$^{\#5}$	82.96(19)

O3$^{\#1}$ - Gd1 - O10	79.36(16)	O5$^{\#4}$ - Gd2 - O1$^{\#5}$	77.9(2)
O7 - Gd1 - O10	126.45(16	O20 - Gd2 - O1$^{\#5}$	74.2(2)
O14 - Gd1 - O13	145.42(18	O2$^{\#2}$ - Gd2 - O12	81.3(2)
O4 - Gd1 - O13	77.41(17)	O6$^{\#3}$ - Gd2 - O12	133.06(17
O3$^{\#1}$ - Gd1 - O13	74.93(17)	O5$^{\#4}$ - Gd2 - O12	83.09(18)
O7 - Gd1 - O13	75.42(16)	O20 - Gd2 - O12	74.0(3)
O10 - Gd1 - O13	115.44(17	O1$^{\#5}$ - Gd2 - O12	143.06(19
O14 - Gd1 - O9	129.76(16	O2$^{\#2}$ - Gd2 - O11	87.80(19)
O4 - Gd1 - O9	151.33(15	O6$^{\#3}$ - Gd2 - O11	85.72(17)
O3$^{\#1}$ - Gd1 - O9	106.69(19	O5$^{\#4}$ - Gd2 - O11	135.7(2)
O7 - Gd1 - O9	80.93(16)	O20 - Gd2 - O11	86.8(3)
O10 - Gd1 - O9	53.40(15)	O1$^{\#5}$ - Gd2 - O11	141.7(2)
O13 - Gd1 - O9	79.45(17)	O12 - Gd2 - O11	53.41(18)
O14 - Gd1 - O8	78.63(18)	O2$^{\#2}$ - Gd2 - O19	146.4(4)
O4 - Gd1 - O8	96.96(17)	O6$^{\#3}$ - Gd2 - O19	78.2(4)
O3$^{\#1}$ - Gd1 - O8	156.35(17	O5$^{\#4}$ - Gd2 - O19	136.5(4)
O7 - Gd1 - O8	53.65(14)	O20 - Gd2 - O19	54.4(5)
O10 - Gd1 - O8	91.56(17)	O1$^{\#5}$ - Gd2 - O19	70.8(3)
O13 - Gd1 - O8	128.36(16	O12 - Gd2 - O19	104.5(3)
O9 - Gd1 - O8	84.32(19)	O11 - Gd2 - O19	71.1(3)

#1 -x+1, -y+1, -z+1; #2 -x+2, -y, -z+1; #3 -x+2, -y-1, -z+1; #4 x, y, z-1; #5 x, y-1, z-1; #6 x, y+1, z+1; #7 x, y, z+1.

Table S5. Selected bond lengths (Å) and angles (^{o}) for **4**.

Tb1 - O14	2.310(6)	Tb2 - O20	2.326(13)
Tb1 - O4	2.329(5)	Tb2 - O1$^{\#5}$	2.354(6)
Tb1 - O3$^{\#1}$	2.340(6)	Tb2 - O12	2.392(6)
Tb1 - O7	2.378(5)	Tb2 - O11	2.443(6)
Tb1 - O13	2.416(6)	Tb2 - O19	2.69(4)
Tb1 - O10	2.425(5)	O1 - Tb2$^{\#6}$	2.354(6)
Tb1 - O9	2.425(6)	O2 - Tb2$^{\#3}$	2.293(6)
Tb1 - O8	2.435(6)	O3 - Tb1$^{\#1}$	2.340(6)
Tb2 - O6$^{\#2}$	2.290(6)	O5 - Tb2$^{\#7}$	2.297(7)
Tb2 - O2$^{\#3}$	2.293(6)	O6 - Tb2$^{\#2}$	2.290(6)
Tb2 - O5$^{\#4}$	2.297(7)		
O14 - Tb1 - O4	77.9(2)	O6$^{\#2}$ - Tb2 - O2$^{\#3}$	75.5(2)
O14 - Tb1 - O3$^{\#1}$	79.0(2)	O6$^{\#2}$ - Tb2 - O5$^{\#4}$	129.7(2)
O4 - Tb1 - O3$^{\#1}$	84.93(19)	O2$^{\#3}$ - Tb2 - O5$^{\#4}$	77.6(3)
O14 - Tb1 - O7	122.2(2)	O6$^{\#2}$ - Tb2 - O20	123.6(5)
O4 - Tb1 - O7	77.09(19)	O2$^{\#3}$ - Tb2 - O20	157.0(4)

O3$^{\#1}$ - Tb1 - O7	147.5(2)	O5$^{\#4}$ - Tb2 - O20	95.5(5)
O14 - Tb1 - O13	145.1(2)	O6$^{\#2}$ - Tb2 - O1$^{\#5}$	82.9(2)
O4 - Tb1 - O13	77.3(2)	O2$^{\#3}$ - Tb2 - O1$^{\#5}$	125.6(3)
O3$^{\#1}$ - Tb1 - O13	74.7(2)	O5$^{\#4}$ - Tb2 - O1$^{\#5}$	79.4(3)
O7 - Tb1 - O13	75.0(2)	O20 - Tb2 - O1$^{\#5}$	73.3(4)
O14 - Tb1 - O10	79.2(2)	O6$^{\#2}$ - Tb2 - O12	132.8(2)
O4 - Tb1 - O10	154.1(2)	O2$^{\#3}$ - Tb2 - O12	81.9(3)
O3$^{\#1}$ - Tb1 - O10	78.8(2)	O5$^{\#4}$ - Tb2 - O12	83.2(2)
O7 - Tb1 - O10	126.2(2)	O20 - Tb2 - O12	75.4(4)
O13 - Tb1 - O10	116.9(2)	O1$^{\#5}$ - Tb2 - O12	142.3(3)
O14 - Tb1 - O9	129.8(2)	O6$^{\#2}$ - Tb2 - O11	84.2(2)
O4 - Tb1 - O9	151.5(2)	O2$^{\#3}$ - Tb2 - O11	88.3(3)
O3$^{\#1}$ - Tb1 - O9	105.0(2)	O5$^{\#4}$ - Tb2 - O11	136.4(2)
O7 - Tb1 - O9	80.93(19)	O20 - Tb2 - O11	81.7(4)
O13 - Tb1 - O9	79.7(2)	O1$^{\#5}$ - Tb2 - O11	138.7(3)
O10 - Tb1 - O9	53.85(19)	O12 - Tb2 - O11	53.8(2)
O14 - Tb1 - O8	78.7(2)	O6$^{\#2}$ - Tb2 - O19	77.9(6)
O4 - Tb1 - O8	97.3(2)	O2$^{\#3}$ - Tb2 - O19	146.8(7)
O3$^{\#1}$ - Tb1 - O8	156.6(2)	O5$^{\#4}$ - Tb2 - O19	135.4(7)
O7 - Tb1 - O8	54.24(19)	O20 - Tb2 - O19	46.0(5)
O13 - Tb1 - O8	128.5(2)	O1$^{\#5}$ - Tb2 - O19	69.4(8)
O10 - Tb1 - O8	90.1(2)	O12 - Tb2 - O19	102.5(8)
O9 - Tb1 - O8	84.2(2)	O11 - Tb2 - O19	69.6(8)

#1 -x+1, -y+1, -z+1; #2 -x, -y-1, -z+1; #3 -x, -y, -z+1; #4 x+1, y, z+1; #5 x+1, y-1, z+1; #6 x-1, y+1, z-1; #7 x-1, y, z-1

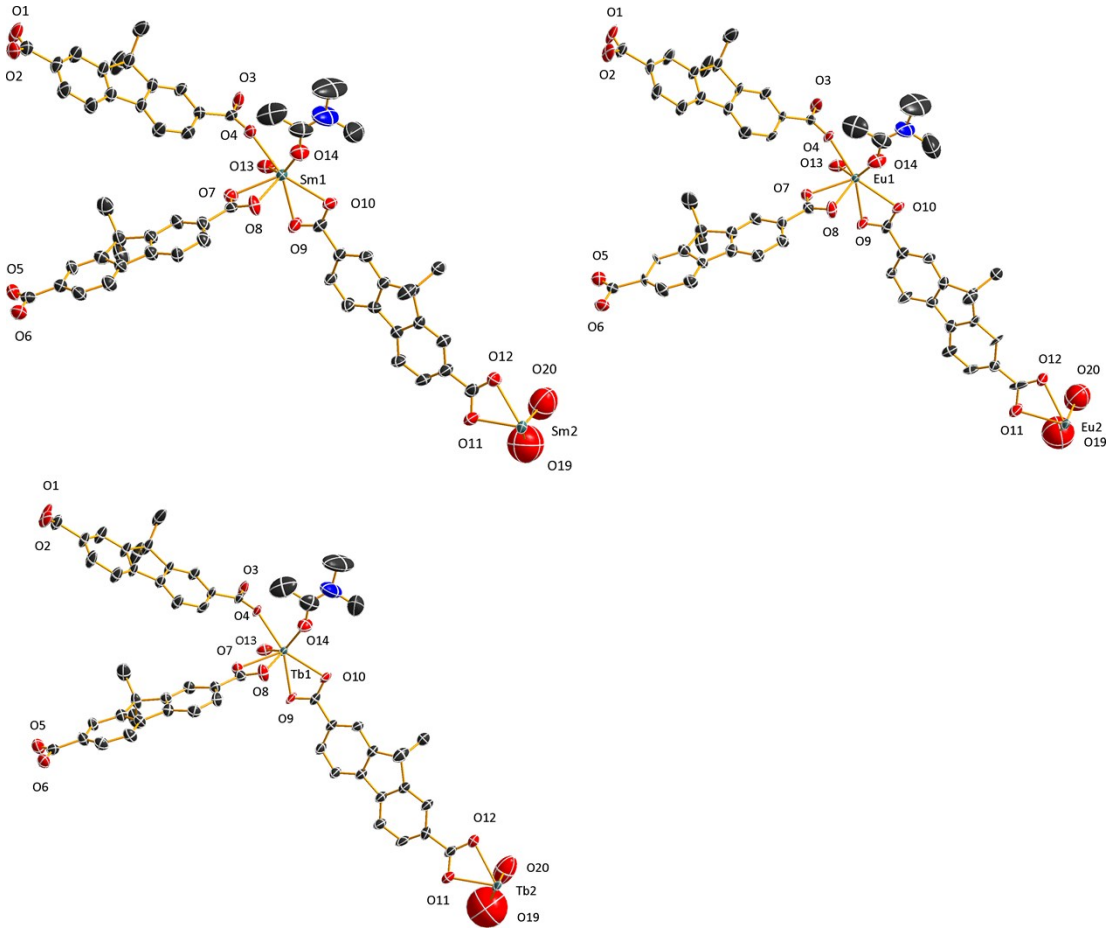

Fig. S1 View of the asymmetric units of **1, 2** and **4** with the thermal ellipsoids drawn at the 50% probability level.

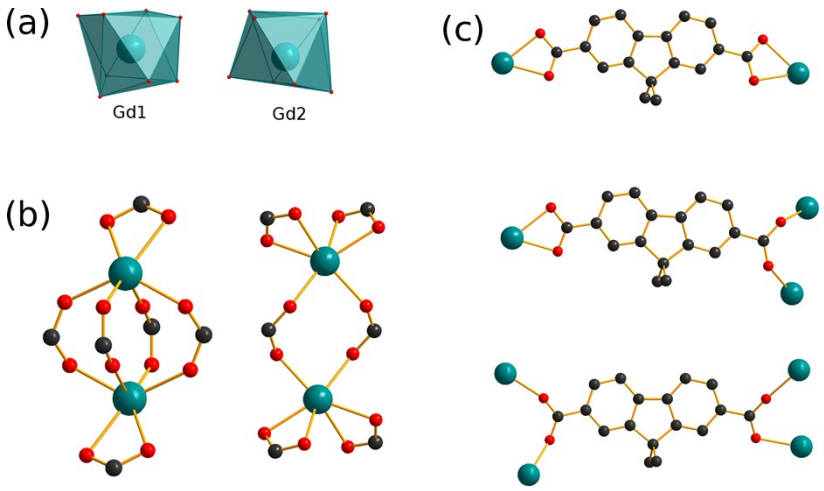

Fig. S2 View of coordination geometries of Gd1 and Gd2 ions (a), SBUs (b) and ligand modes (c) in **3**.

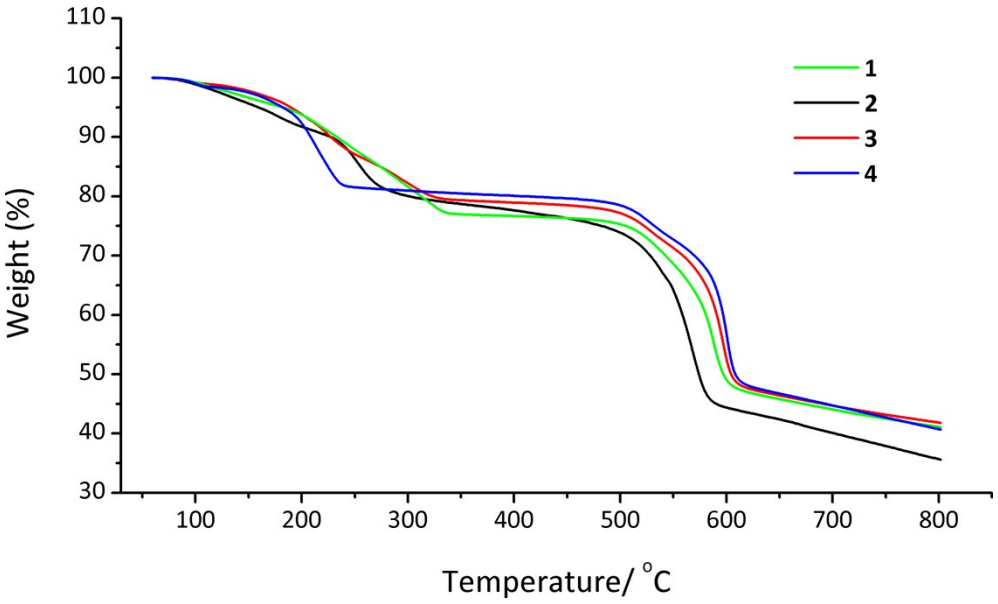

Fig. S3. Thermogravimetric curves of **1-4**.

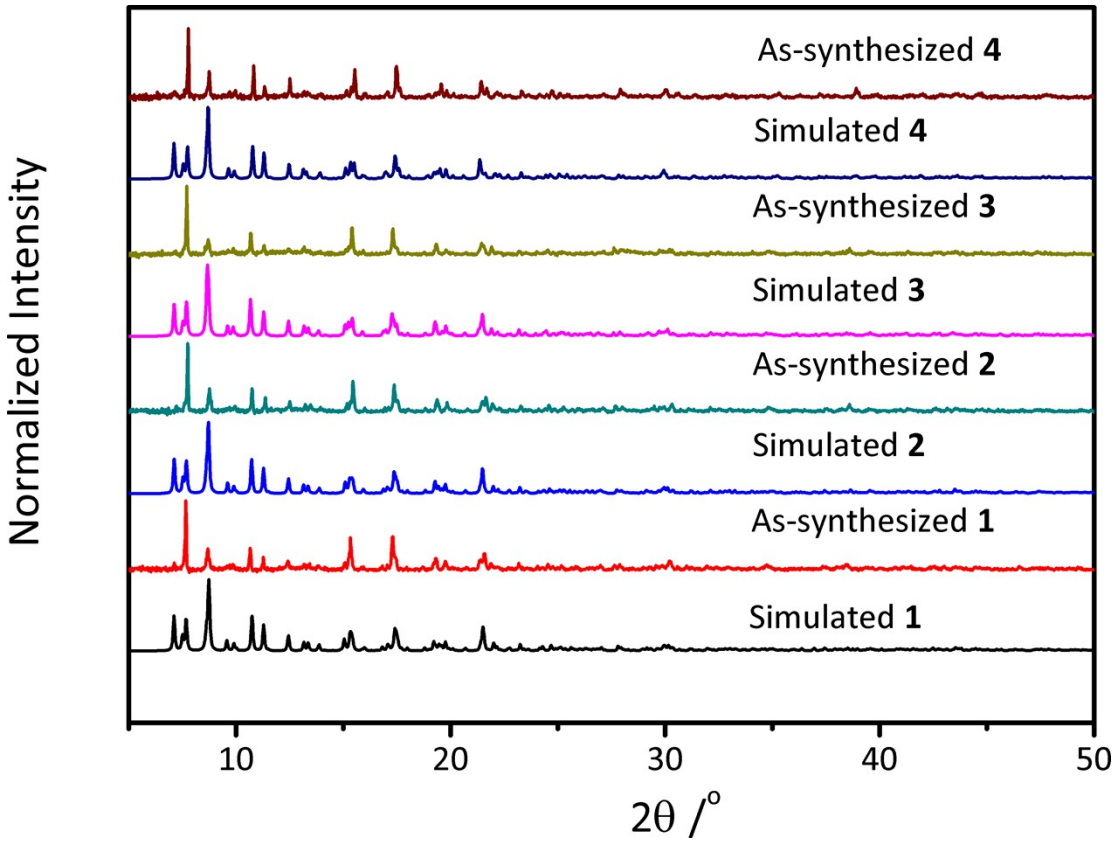

Fig. S4. The simulated and as-synthesized powder X-ray diffraction patterns of **1-4**.

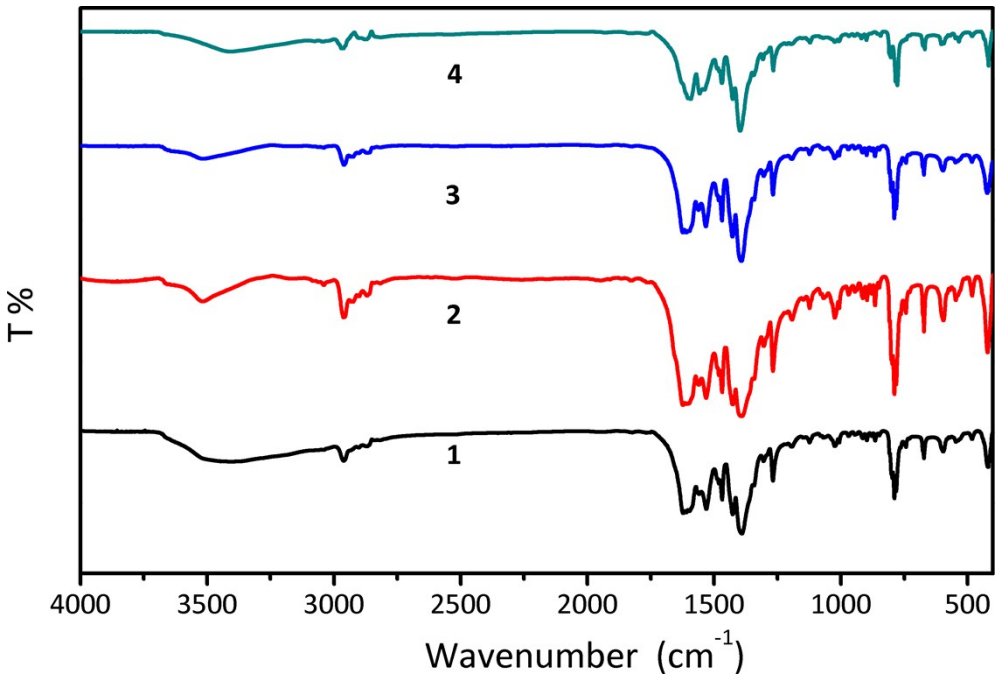

Fig. S5. The IR spectra of **1-4**.

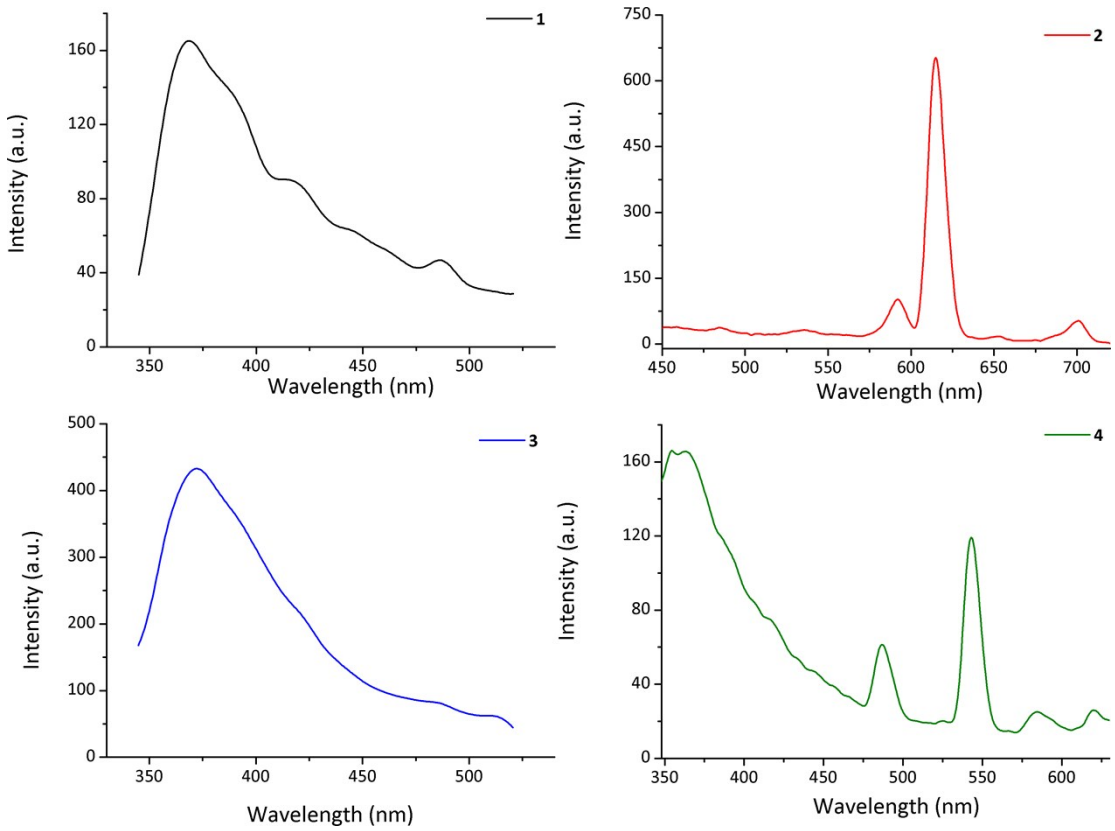

Fig. S6 Solid-state emission spectra for **1-4** at room temperature.

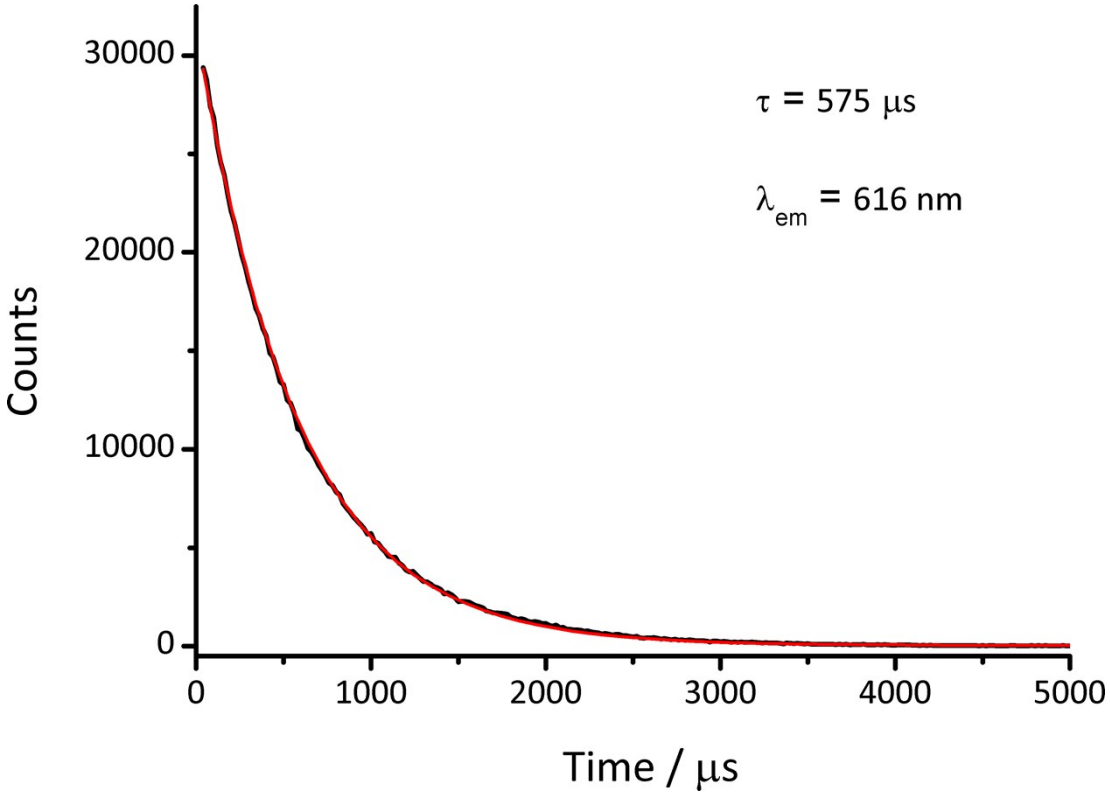

Fig. S7. The fluorescence decay curve for **2** in solid state.

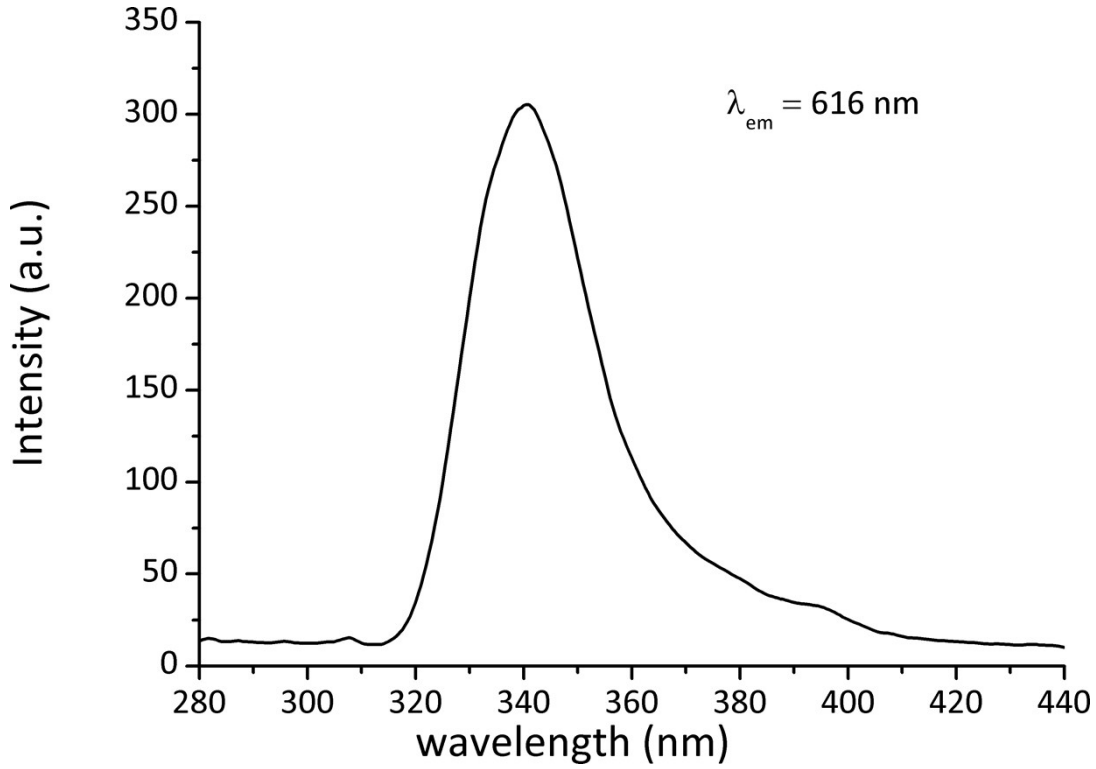

Fig. S8. The excitation spectrum of **2** in Tris-HCl.

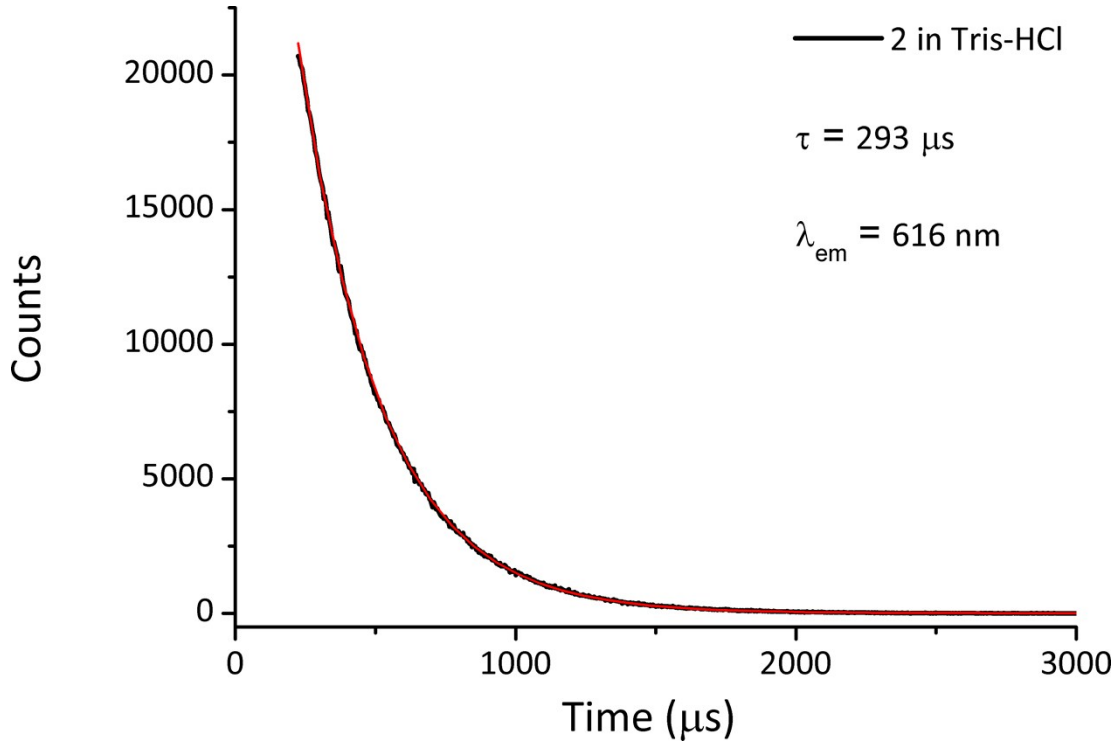

Fig. S9. The fluorescence decay curve for **2** in Tris-HCl and is 293 μs.

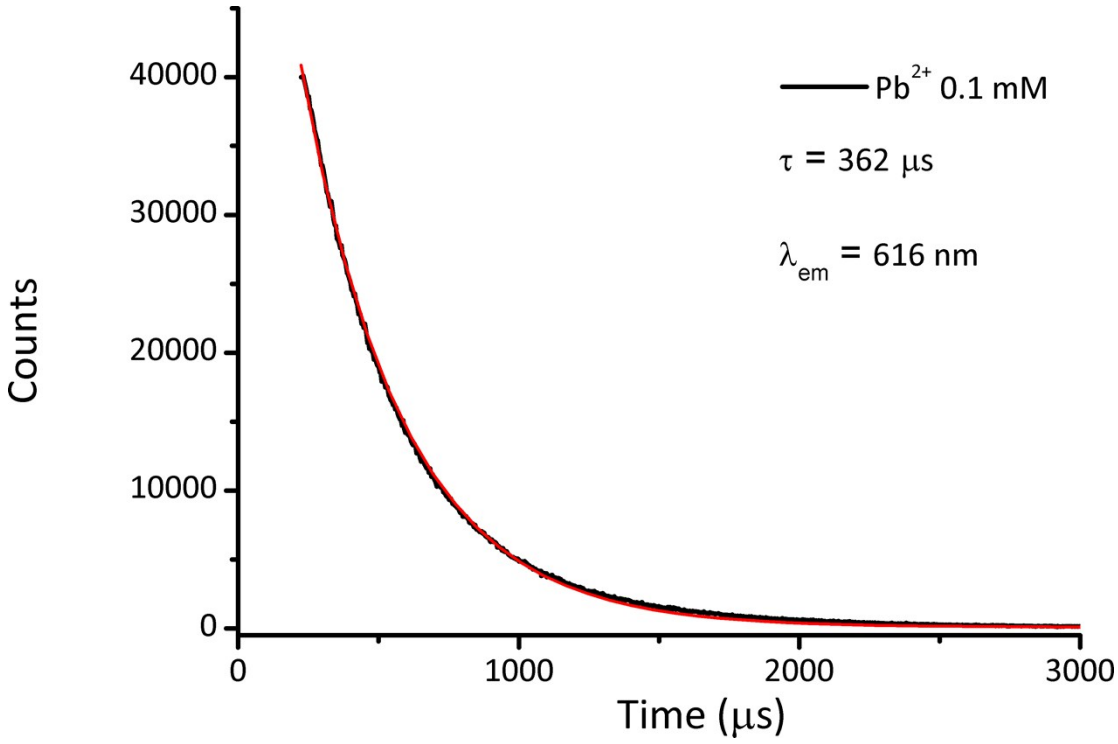

Fig. S10. The fluorescence decay curve for **2** in Pb^{2+} solution (0.1 mM).

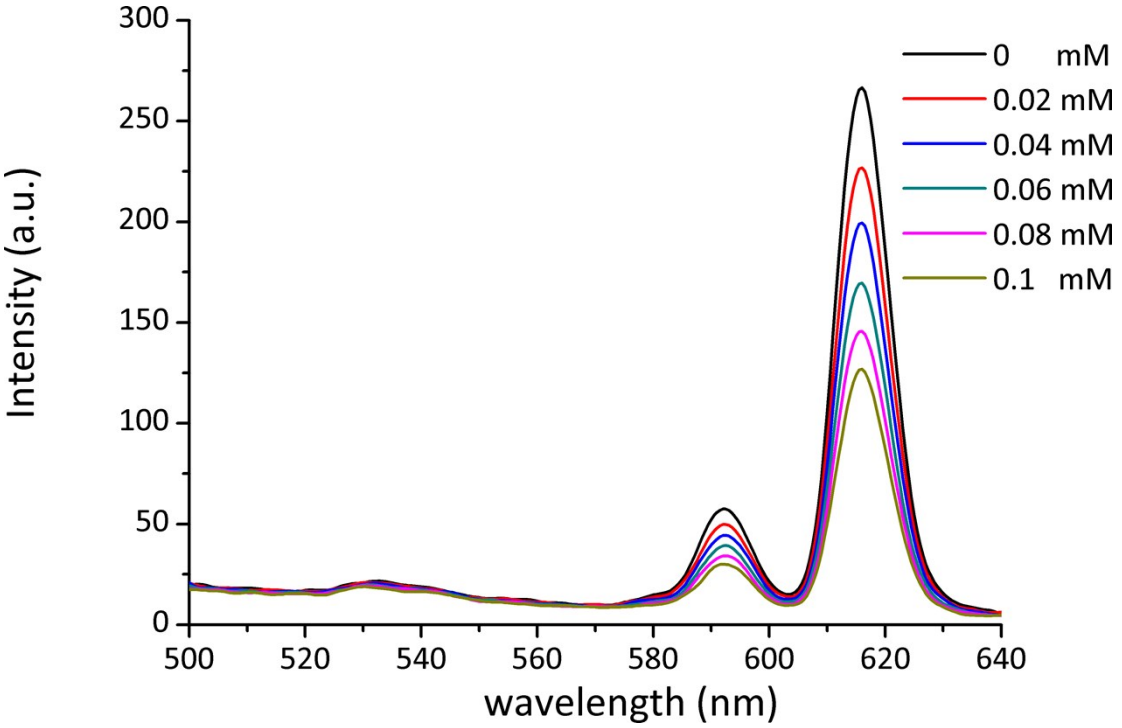

Fig. S11. Emission spectra of **2** in Fe^{3+} solution in the concentration of 0-0.1 mM.

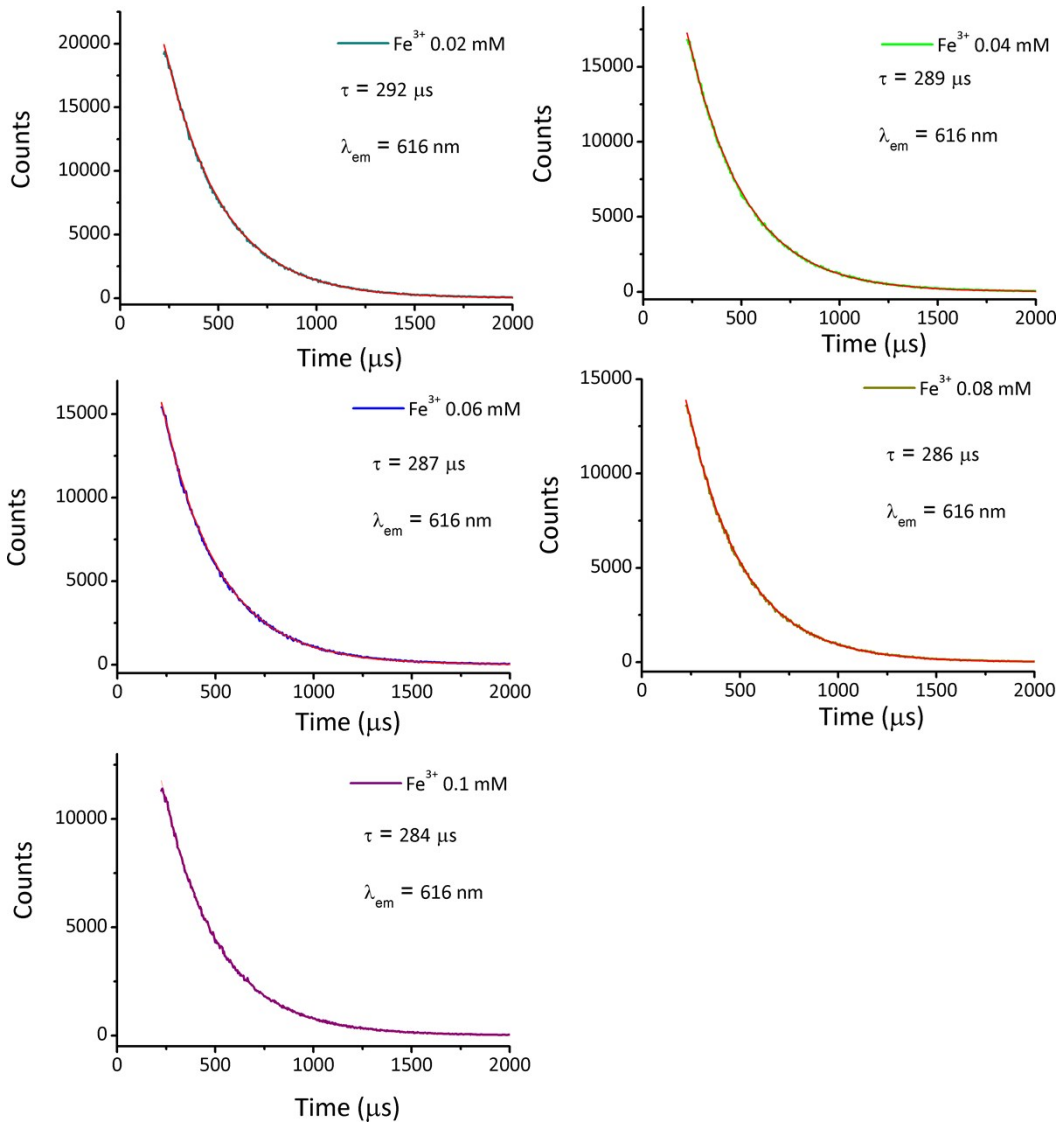

Fig. S12. The fluorescence decay curves for **2** in Fe^{3+} solution.

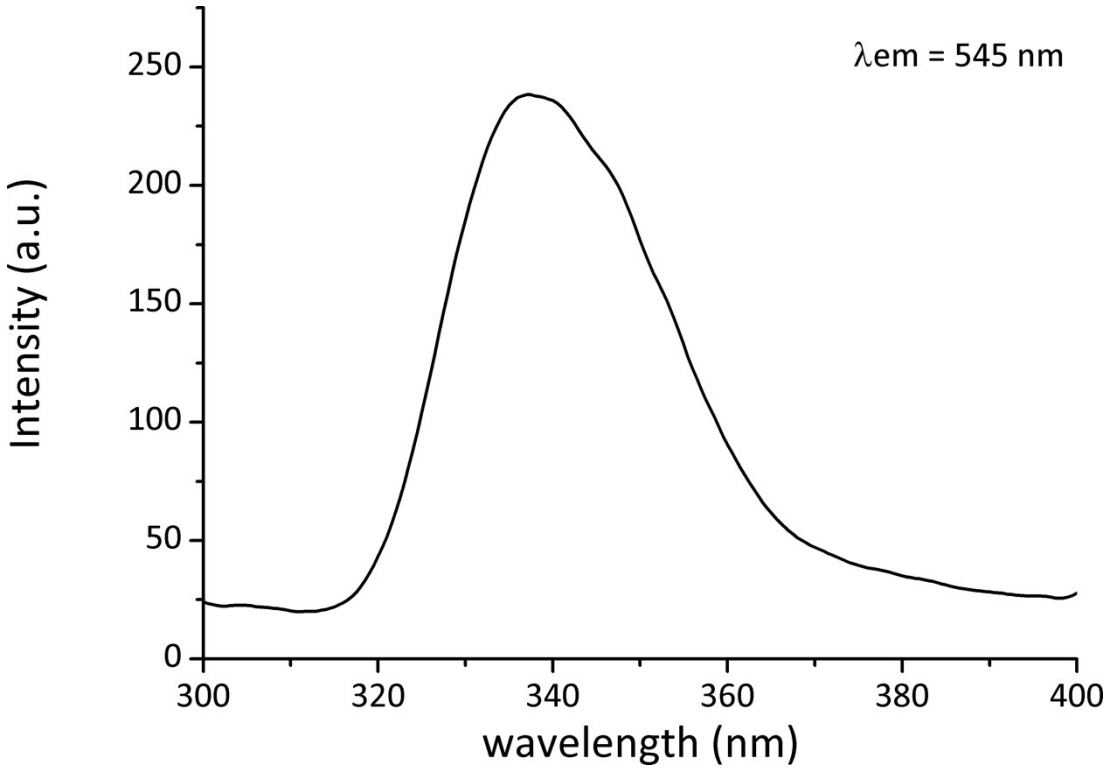

Fig. S13. The excitation spectrum of **4** in Tris-HCl.

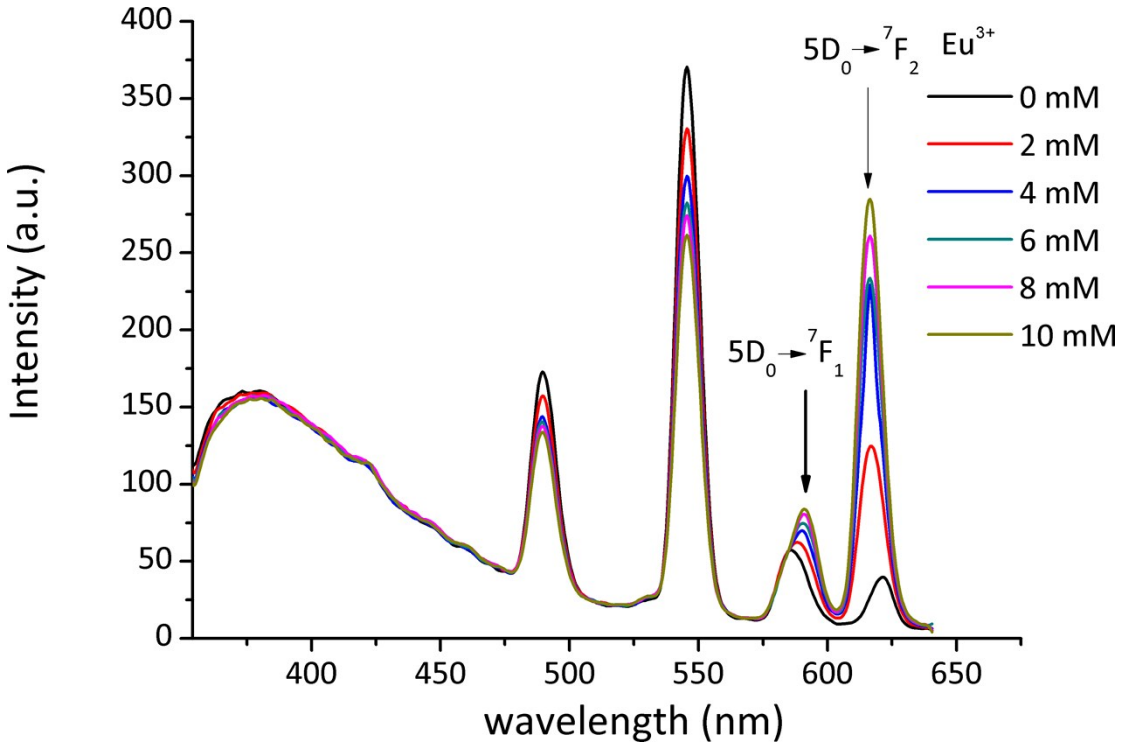

Fig. S14. Emission spectra of **4** in $Eu(NO_3)_3$ solution.

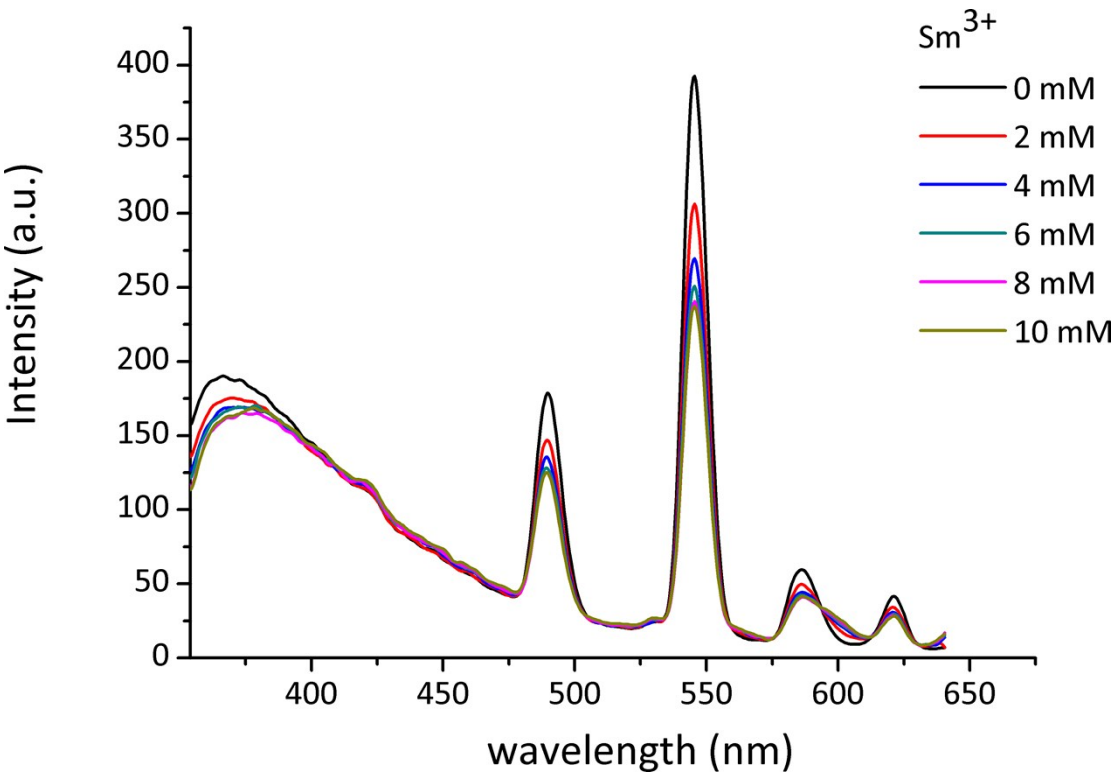

Fig. S15. Emission spectra of **4** in $Sm(NO_3)_3$ solution.