Supporting information

Lanthanide complexes assembled from two flexible amide-type tripodal ligands: terminal groups effect on photoluminescence behavior

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Synthesis of ligands

Preparation of the tripodal ligand L^I: (bis-carboxymethyl-amino)-acetic acetate (3.44 g, 12.5 mmol) and benzylamine (5.36 g, 50 mmol) were warmed to ca. 120℃ for 12 h. The resulted solid was recrystallized with acetone to get tripodal ligand L^I,[1] yield 65%, m.p.145–146℃. ^{1}HNMR (CDCl$_3$, 300 MHz) δ: 3.37 (s, 6H), 4.34 (d, $J = 3.6$ Hz, 6H), 7.19–7.29 (m, Ar–H, 15H), 7.51 (s, 3H); IR (KBr, cm^{-1}) v: 3289, 1649, 1543, 1453, 1264, 1175, 977, 749, 695; Anal. Calcd. for $C_{27}H_{30}N_4O_3$: C 70.72, H 6.59, N 12.22; Found C 70.55, H 6.48, N 12.50.

Preparation of the tripodal ligand L^{II}: (bis-carboxymethyl-amino)-acetic acetate (3.44 g, 12.5 mmol) and 1-naphthalenemethylamine (7.86 g, 50 mmol) were warmed to ca. 120℃ for 12 h. The resulted solid was recrystallized with acetone to get tripodal ligand L^{II}, yield 60%, m.p.80–82℃. ^{1}HNMR (CDCl$_3$, 300 MHz) δ: 3.08 (s, 6H), 4.52 (d, $J = 5.4$ Hz, 6H), 7.22–7.81(m, Ar–H, N–H, 24H); IR (KBr, cm^{-1}) v: 3325, 1649, 1541, 1424, 1395, 1290, 1163, 1028, 794; Anal. Calcd. for $C_{39}H_{36}N_4O_3$: C 76.95, H 5.96, N 9.20; Found C 76.82, H 5.90, N 9.14.

Elemental analysis and IR spectra of the complexes and crystals

$EuL^I_2(NO_3)_3 \cdot 2H_2O$ Analytical data (%), Calcd: C, 50.23; H, 5.00; N, 11.93; Found: C, 50.55; H, 5.20; N, 12.19. IR (KBr, cm^{-1}) v: 3395, 1632, 1384, 1117, 1042, 834.

$TbL^I_2(NO_3)_3 \cdot 2H_2O$ Analytical data (%), Calcd: C, 49.97; H, 4.97; N, 11.87; Found: C, 49.89; H, 4.76; N, 12.20. IR (KBr, cm^{-1}) v: 3424, 1637, 1382, 1319, 1245, 1127, 1027, 901, 825.

$GdL^I_2(NO_3)_3 \cdot 2H_2O$ Analytical data (%), Calcd: C, 50.03; H, 4.98; N, 11.88; Found: C, 50.34; H, 4.96; N, 12.02. IR (KBr, cm^{-1}) v: 3425, 1637, 1384, 1319, 1245, 1127, 1027, 827.

$[EuL^I_2(C_3H_6O)] \cdot (NO_3)_3 \cdot (HCCl_3) \cdot (H_2O)_4$ (**1**) Analytical data (%), Calcd: C, 46.30; H, 5.02; N, 10.24; Found: C, 45.85; H, 5.22; N, 10.46.

$EuL^{II}(NO_3)_3 \cdot 2H_2O$ Analytical data (%), Calcd: C, 47.60; H, 4.10; N, 9.98; Found: C, 47.89; H, 4.18; N, 9.85. IR (KBr, cm^{-1}) v: 3294, 1705, 1658, 1639, 1593, 1480, 1385, 1332, 1294, 1033, 904, 776.

TbL^{II}(NO$_3$)$_3$·2H$_2$O   Analytical data (%),Calcd: C, 47.33; H, 4.07; N, 9.91; Found: C, 47.79; H, 4.15; N, 9.76. IR (KBr, cm^{-1}) v: 3294, 1705, 1658, 1640, 1481, 1385, 1297, 1164, 1128, 1034, 904, 777.

GdL^{II}(NO$_3$)$_3$·2H$_2$O   Analytical data (%),Calcd: C, 47.41; H, 4.08; N, 9.92; Found: C, 47.56; H, 4.23; N, 9.79. IR (KBr, cm^{-1}) v: 3294, 1705, 1657, 1638, 1385, 1297, 1164, 1128, 904, 780.

EuL^{II}(NO$_3$)$_3$ (**3**)   Analytical data (%), Calcd: C, 49.48; H, 3.83; N, 10.36; Found: C, 49.69; H, 3.65; N, 10.55.

TbL^{II}(NO$_3$)$_3$ (**4**)   Analytical data (%), Calcd: C, 49.12; H, 3.80; N, 10.28; Found: C, 49.45; H, 3.46; N, 10.78.

We also have conducted additional experiments to prove that 1:2 (M:L^I) type coordination structure is comparatively stable for L^I. The solid complex powders are obtained from mixtures under the ratio 1:1 (M:L^I) in ethyl acetate. The elemental analysis data of precipitated powders show the 1:1 type coordination structure, but the powders appear 1:2 type coordination structure when recrystallized in acetone-trichloromethane (v/v=1:3). It proves that the 1:2 (M:L^I) type coordination structure is comparatively stable for the complexes of L^I. And we couldn't obtain the solid complexes under the ratio 1:2 (M:L^{II}) in acetone for ligand L^{II}.

Table S1 Selected bond lengths (Å) and angles (°) for the complexes **1**, **3**, and **4**

1					
Eu(1)—O(1)	2.412(6)	Eu(1)—O(2)	2.414(7)	Eu(1)—O(3)	2.403(7)
Eu(1)—O(4)	2.429(6)	Eu(1)—O(5)	2.398(7)	Eu(1)—O(6)	2.412(6)
Eu(1)—O(7)	2.422(8)	Eu(1)—N(1)	2.693(8)	Eu(1)—N(5)	2.722(7)
O(1)—Eu(1)—O(2)	127.8(2)	O(1)—Eu(1)—O(3)	93.4(2)	O(2)—Eu(1)—O(3)	73.8(2)
O(1)—Eu(1)—O(6)	148.4(2)	O(2)—Eu(1)—O(6)	79.6(2)	O(3)—Eu(1)—O(6)	78.7(2)
O(1)—Eu(1)—O(5)	77.4(2)	O(2)—Eu(1)—O(5)	135.4(2)	O(3)—Eu(1)—O(5)	148.2(2)
O(6)—Eu(1)—O(5)	93.3(2)	O(1)—Eu(1)—O(7)	73.3(2)	O(2)—Eu(1)—O(7)	141.1(3)
O(3)—Eu(1)—O(7)	72.5(3)	O(6)—Eu(1)—O(7)	75.2(2)	O(5)—Eu(1)—O(7)	75.8(3)
O(1)—Eu(1)—O(4)	80.2(2)	O(2)—Eu(1)—O(4)	75.8(2)	O(3)—Eu(1)—O(4)	135.3(2)
O(6)—Eu(1)—O(4)	126.5(2)	O(5)—Eu(1)—O(4)	73.7(2)	O(7)—Eu(1)—O(4)	143.1(3)
O(1)—Eu(1)—N(1)	63.3(2)	O(2)—Eu(1)—N(1)	65.3(2)	O(3)—Eu(1)—N(1)	66.0(2)
O(6)—Eu(1)—N(1)	135.4(2)	O(5)—Eu(1)—N(1)	131.0(2)	O(7)—Eu(1)—N(1)	116.0(3)
O(4)—Eu(1)—N(1)	71.8(2)	O(1)—Eu(1)—N(5)	134.2(2)	O(2)—Eu(1)—N(5)	72.7(2)
O(3)—Eu(1)—N(5)	132.2(2)	O(6)—Eu(1)—N(5)	62.5(2)	O(5)—Eu(1)—N(5)	65.3(2)
O(7)—Eu(1)—N(5)	118.6(3)	O(4)—Eu(1)—N(5)	65.1(2)	N(1)—Eu(1)—N(5)	125.3(2)
3					
Eu(1)—O(1)	2.465(3)	Eu(1)—O(2)	2.361(3)	Eu(1)—O(3)	2.387(3)
Eu(1)—O(4)	2.482(4)	Eu(1)—O(6)	2.465(3)	Eu(1)—O(7)	2.545(3)
Eu(1)—O(9)	2.533(3)	Eu(1)—O(10)	2.512(3)	Eu(1)—O(12)	2.633(3)
Eu(1)—N(1)	2.712(3)				
O(2)—Eu(1)—O(3)	91.67(11)	O(2)—Eu(1)—O(6)	123.28(12)	O(3)—Eu(1)—O(6)	144.27(11)

O(2)—Eu(1)—O(1)	73.75(10)	O(3)—Eu(1)—O(1)	127.03(10)	O(6)—Eu(1)—O(1)	75.38(10)
O(2)—Eu(1)—O(4)	75.79(11)	O(3)—Eu(1)—O(4)	148.60(12)	O(6)—Eu(1)—O(4)	51.64(12)
O(1)—Eu(1)—O(4)	77.52(11)	O(2)—Eu(1)—O(10)	133.38(9)	O(3)—Eu(1)—O(10)	82.76(11)
O(6)—Eu(1)—O(10)	78.06(12)	O(1)—Eu(1)—O(10)	73.33(10)	O(4)—Eu(1)—O(10)	126.71(11)
O(2)—Eu(1)—O(9)	67.21(10)	O(3)—Eu(1)—O(9)	70.91(12)	O(6)—Eu(1)—O(9)	113.25(11)
O(1)—Eu(1) —O(9)	137.68(10)	O(4)—Eu(1)—O(9)	77.69(13)	O(10)—Eu(1)—O(9)	147.86(12)
O(2)—Eu(1)—O(7)	113.91(9)	O(3)—Eu(1)—O(7)	84.96(10)	O(6)—Eu(1)—O(7)	74.71(10)
O(1)—Eu(1)—O(7)	147.72(9)	O(4)—Eu(1)—O(7)	74.56(10)	O(10)—Eu(1)—O(7)	111.64(9)
O(9)—Eu(1)—O(7)	49.45(8)	O(2)—Eu(1)—O(12)	167.52(10)	O(3)—Eu(1)—O(12)	76.24(11)
O(6)—Eu(1)—O(12)	68.39(12)	O(1)—Eu(1)—O(12)	115.96(9)	O(4)—Eu(1)—O(12)	113.08(11)
O(10)—Eu(1)—O(12)	49.10(9)	O(9)—Eu(1)—O(12)	105.18(10)	O(7)—Eu(1)—O(12)	62.62(9)
O(2)—Eu(1)—N(1)	66.33(10)	O(3)—Eu(1)—N(1)	64.20(10)	O(6)—Eu(1)—N(1)	133.00(10)
O(1)—Eu(1)—N(1)	63.31(9)	O(4)—Eu(1)—N(1)	131.10(10)	O(10)—Eu(1)—N(1)	69.73(9)
O(9)—Eu(1)—N(1)	112.25(10)	O(7)—Eu(1)—N(1)	148.97(10)	O(12)—Eu(1)—N(1)	109.91(10)

4

Tb(1)—O(1)	2.444(3)	Tb(1)—O(2)	2.335(3)	Tb(1)—O(3)	2.361(3)
Tb(1)—O(4)	2.467(3)	Tb(1)—O(5)	2.441(3)	Tb(1)—O(7)	2.517(3)
Tb(1)—O(8)	2.531(3)	Tb(1)—O(10)	2.652(3)	Tb(1)—O(11)	2.483(3)
Tb(1)—N(1)	2.700(3)				
O(2)—Tb(1)—O(3)	92.14(10)	O(2)—Tb(1)—O(5)	123.67(10)	O(3)—Tb(1)—O(5)	143.31(10)
O(2)—Tb(1)—O(1)	73.96(9)	O(3)—Tb(1)—O(1)	128.02(9)	O(5)—Tb(1)—O(1)	75.28(10)
O(2)—Tb(1)—O(4)	75.57(11)	O(3)—Tb(1)—O(4)	148.10(11)	O(5)—Tb(1)—O(4)	52.21(11)
O(1)—Tb(1)—O(4)	77.35(10)	O(2)—Tb(1)—O(11)	133.44(9)	O(3)—Tb(1)—O(11)	83.02(10)
O(5)—Tb(1)—O(11)	77.65(10)	O(1)—Tb(1)—O(11)	73.22(9)	O(4)—Tb(1)—O(11)	126.76(11)
O(2)—Tb(1)—O(7)	67.11(9)	O(3)—Tb(1)—O(7)	70.72(11)	O(5)—Tb(1)—O(7)	113.24(10)
O(1)—Tb(1)—O(7)	137.63(9)	O(4)—Tb(1)—O(7)	77.39(12)	O(11)—Tb(1)—O(7)	148.12(11)
O(2)—Tb(1)—O(8)	114.45(9)	O(3)—Tb(1)—O(8)	84.33(10)	O(5)—Tb(1)—O(8)	74.20(9)
O(1)—Tb(1)—O(8)	147.25(9)	O(4)—Tb(1)—O(8)	74.74(10)	O(11)—Tb(1)—O(8)	111.09(9)
O(7)—Tb(1)—O(8)	50.05(9)	O(2)—Tb(1)—O(10)	167.46(10)	O(3)—Tb(1)—O(10)	75.74(10)
O(5)—Tb(1)—O(10)	67.98(10)	O(1)—Tb(1)—O(10)	115.95(9)	O(4)—Tb(1)—O(10)	113.17(10)
O(11)—Tb(1)—O(10)	49.29(9)	O(7)—Tb(1)—O(10)	105.11(9)	O(8)—Tb(1)—O(10)	61.90(9)
O(2)—Tb(1)—N(1)	66.69(9)	O(3)—Tb(1)—N(1)	64.73(10)	O(5)—Tb(1)—N(1)	133.01(10)
O(1)—Tb(1)—N(1)	63.78(9)	O(4)—Tb(1)—N(1)	131.33(10)	O(11)—Tb(1)—N(1)	69.54(9)
O(7)—Tb(1)—N(1)	112.41(10)	O(8)—Tb(1)—N(1)	148.95(10)	O(10)—Tb(1)—N(1)	109.71(9)

Table S2. Hydrogen bonds in crystal packing (Å, º)

Complexes	D-H…A	d(D-H)	d(H…A)	d(D…A)	∠DHA	Symmetry code
1	N(2)-H(2)…O(13)	0.90	2.43	3.0481	126	x,1+y,z
	N(3)-H(3)…O(14)	0.90	2.11	2.8301	136	1-x,1-y,1-z
	N(4)-H(4)…Cl(1)	0.90	2.82	3.6831	161	1-x,1-y,1-z
	N(6)-H(6)…O(10)	0.90	2.19	2.9411	140	
	N(7)-H(7)…Cl(6)	0.90	2.75	3.6451	176	1-x,1-y,-z

	N(8)-H(8)…O(12)	0.90	2.54	3.1441	125	
	O(17)-H(62)…O(20)	0.87	2.06	2.653	124	
	O(17)-H(62)…O(21)	0.87	2.18	2.763	124	
	O(18)-H(64)…O(19)	0.87	2.13	2.692	123	x,-1+y,z
	O(19)-H(65)…O(18)	0.87	2.13	2.692	122	x,1+y,z
	C(7)-H(7B)…O(1)	0.97	2.34	2.7001	101	
	C(12)-H(12)…Cl(4)	0.93	2.71	3.572	154	1-x,1-y,-z
	C(20)-H(20)…N(3)	0.93	2.58	2.8971	100	
	C(25)-H(25)…O(14)	0.93	2.58	3.332	138	-x,1-y,1-z
	C(31)-H(31B)…O(9)	0.97	2.51	3.4041	153	1-x,1-y,-z
	C(48)-H(48A)…O(6)	0.97	2.44	2.7831	100	
	C(51)-H(51)…Cl(2)	0.93	2.37	3.272	162	1-x,1-y,1-z
	C(55)-H(55B)…O(8)	0.96	2.50	3.432	163	-1+x,y,z
	C(57)-H(57A)…O(19)	0.96	2.50	3.162	126	
	C(58)-H(58)…O(13)	0.98	2.43	3.312	148	
	C(59)-H(59)…O(11)	0.98	2.38	3.212	142	
3	N(2)-H(2A)…O(8)	0.86	2.17	3.0138	168	
	N(3)-H(3A)…O(12)	0.86	2.19	3.0370	169	
	C(8)-H(8)…N(2)	0.93	2.44	2.8020	103	
	C(8)-H(8)…O(7)	0.93	2.59	3.4066	147'	
	C(11)-H(11B)…O(1)	0.97	2.47	2.8454	103	
	C(13)-H(13A)…O(7)	0.97	2.56	3.4237	149	
	C(13)-H(13B)…O(10)	0.97	2.43	2.9359	112	
	C(13)-H(13B)…O(9)	0.97	2.40	3.0618	125	x,1/2-y,1/2+z
	C(24)-H(24A)…O(2)	0.97	2.38	2.7976	105	
	C(24)-H(24B)…O(6)	0.97	2.55	3.5077	170	x,1/2-y,-1/2+z
	C(26)-H(26B)…O(7)	0.97	2.60	3.5354	164	
	C(34)-H(34)…N(4)	0.93	2.44	2.7842	102	
	C(37)-H(37A)…O(3)	0.97	2.41	2.7987	103	
	C(39)-H(39B)…O(5)	0.97	2.58	3.5355	167	1-x,-1/2+y,1/2-z
4	N(2)-H(2)…O(10)	0.86	2.19	3.0374	169	
	N(3)-H(3)…O(9)	0.86	2.18	3.0235	167	
	C(1)-H(1A)…O(8)	0.97	2.57	3.4401	149	
	C(1)-H(1B)…O(11)	0.97	2.42	2.9134	111	
	C(1)-H(1B)…O(7)	0.97	2.40	3.0737	126	x,1/2-y,1/2+z
	C(3)-H(3B)…O(1)	0.97	2.48	2.8553	103	
	C(5)-H(5)…N(3)	0.93	2.44	2.8045	104	
	C(14)-H(14B)…O(8)	0.97	2.60	3.5365	163	
	C(16)-H(16A)…O(2)	0.97	2.38	2.7970	105	
	C(16)-H(16B)…O(5)	0.97	2.54	3.4941	169	x,1/2-y,-1/2+z
	C(27)-H(27B)…O(6)	0.97	2.60	3.5491	166	1-x,-1/2+y,1/2-z
	C(29)-H(29A)…O(3)	0.97	2.41	2.8008	104	
	C(31)-H(31)…N(4)	0.93	2.49	2.8255	102	

Table S3. The details of the contributions of orbital transitions for some electronic transitions with large oscillator strengths for L^I and L^{II} ligands from the TD-DFT calculation.

The TD-DFT calculation of the L^I.			
Excited State 1	Percentage(%)	Excitation energy(nm)	Oscillator strength
119->123	28.99	211.54	0.0348
120->123	62.33		
120->128	3.62		
120->129	2.57		
120->130	2.49		
Excited State 2	Percentage(%)	Excitation energy(nm)	Oscillator strength
114 ->126	2.67	210.92	0.0375
114 ->127	5.04		
119 ->123	4.83		
121 ->124	28.84		
121 ->125	4.07		
121 ->126	19.41		
121 ->127	21.90		
121 ->128	10.31		
122 ->131	2.86		

The TD-DFT calculation of the L^{II}.			
Excited State 1	Percentage(%)	Excitation energy(nm)	Oscillator strength
159 ->163	18.34	284.85	0.1007
161 ->163	81.66		
Excited State 2	Percentage(%)	Excitation energy(nm)	Oscillator strength
154 ->165	2.60	276.22	0.1861
158 ->162	65.61		
160 ->164	31.78		

Intrinsic quantum yield (Φ_{Ln}).

Following the method described in literature,[2] it is possible to estimate the intrinsic quantum yield (Φ_{Ln}) of the Eu(III) complexes 1 and 3 on the basis of the luminescence data (emission spectrum and $^5D_0$ lifetimes). Assuming that only nonradiative (k_{nr}) and radiative (k_r, estimated according to the reported method) processes are involved in the depopulation of the $^5D_0$ state, (Φ_{Ln}) may be expressed as:

$$\Phi_{Ln} = \frac{k_r}{k_r + k_{nr}}$$

The lifetime (τ), radiative (k_r), and non-radiative (k_{nr}) transition rates are related through the following equation:

$$\frac{1}{\tau} = k_r + k_{nr}$$

The overall luminescence quantum yields $\Phi_{overall}$ for Eu(III) complex was determined by an absolute method using an integrating sphere, which can be calculated as follows:

$$\Phi_{overall} = \Phi_{Ln} \times \Phi_{transfer}$$

In this expression, $\Phi_{transfer}$ is the sensitization efficiency defined as the efficacy with which energy is transferred from the feeding levels of the ligands onto the Ln(III) excited states.

The intrinsic quantum yield (Φ_{Ln}), radiative (k_r), nonradiative (k_{nr}) decay rates, and the sensitization efficiency of the ligand ($\Phi_{transfer}$) are shown in Table S4.

Table S4. Photoluminescence data of the $[EuL^{I}_{2}(C_3H_6O)] \cdot (NO_3)_3 \cdot (HCCl_3) \cdot (H_2O)_4$ (**1**) and $EuL^{II}(NO_3)_3$ (**3**).

compounds	$<\tau>$(ms)	k_r (ms^{-1})	k_{nr} (ms^{-1})	Φ_{Ln}(%)	Φ_{trans}(%)
1	0.962	0.386	0.653	37.14	16.18
3	1.1376	0.526	0.353	59.86	22.27
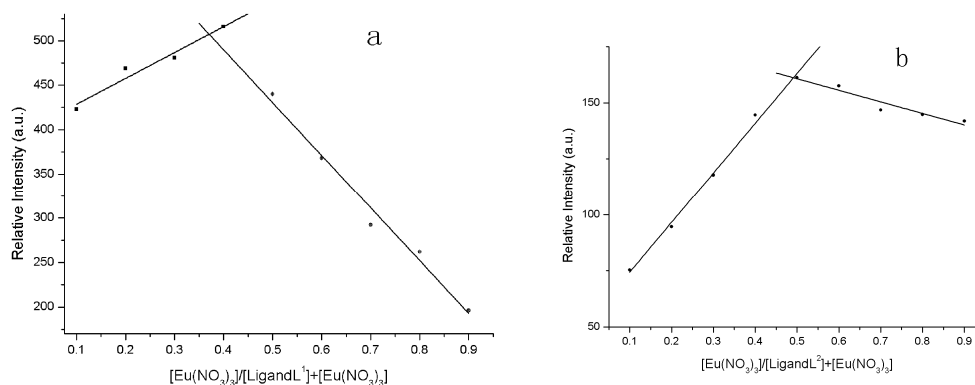
Fig. S1 Job's plots showing the 1:2 binding of L^{I} (1.0×10^{-3} molL^{-1} in ethyl acetate) to Eu(NO$_3$)$_3$ (1.0×10^{-3} molL^{-1} in ethyl acetate) (a), 1:1 binding of L^{II} (1.0×10^{-3} molL^{-1} in acetone) to Eu(NO$_3$)$_3$ (1.0×10^{-3} molL^{-1} in acetone) (b), where the difference in fluorescence intensity at 615 nm was plotted against the mole fraction of 1 at an invariant total concentration.
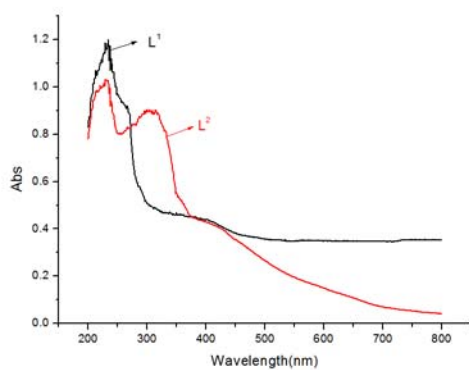
Fig. S2 The UV-vis absorbance spectra of the ligands L^I and L^{II} in the solid state.
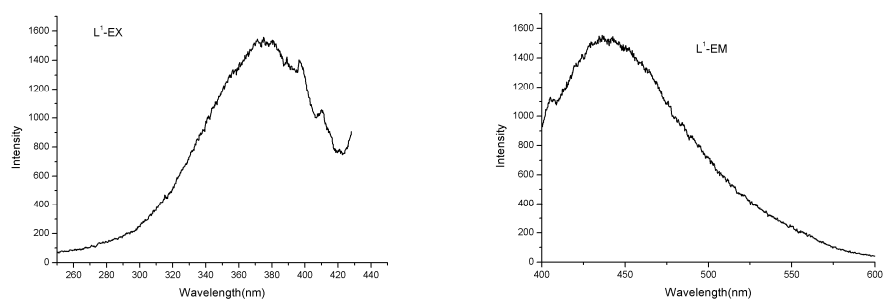
Fig. S3 Room-temperature excitation and emission spectra of L^I in the solid state.
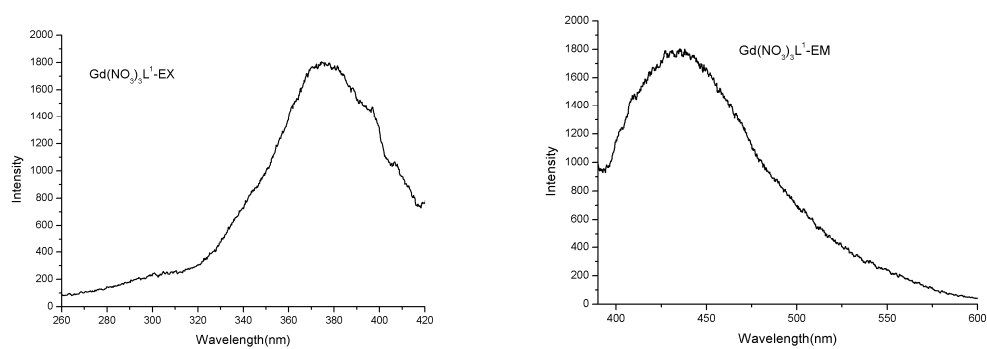

Fig. S4 Room-temperature excitation and emission spectra of $Gd(NO_3)L^I$ in the solid state.
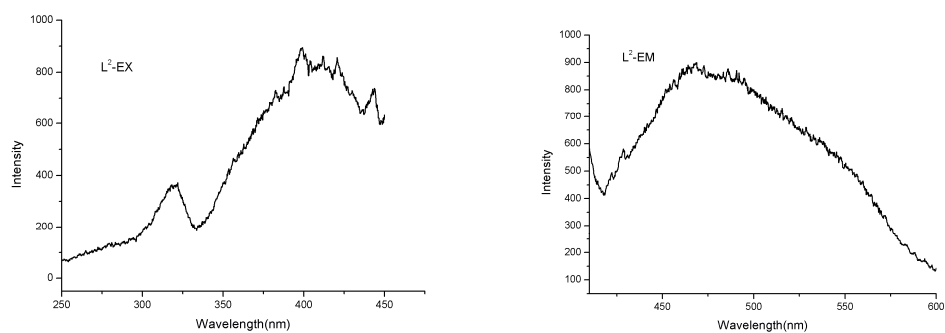
Fig. S5 Room-temperature excitation and emission spectra of L^{II} in the solid state.
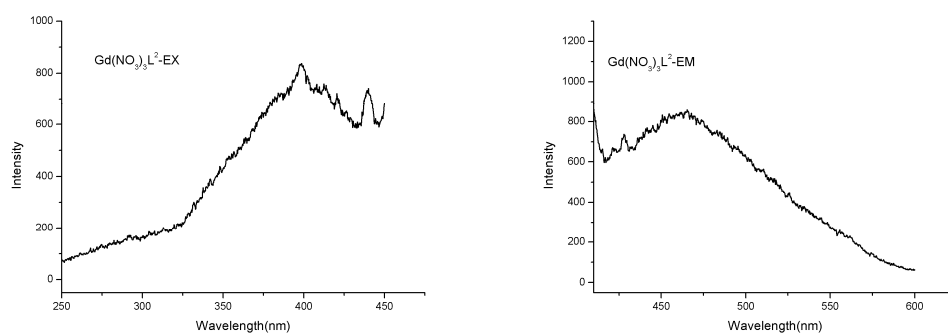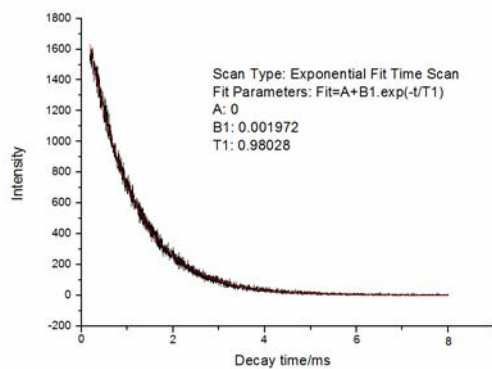

Fig. S6 Room-temperature excitation and emission spectra of $Gd(NO_3)L^{II}$ in the solid state.

Fig. S7 Luminescence decay curve of the compound **1**.
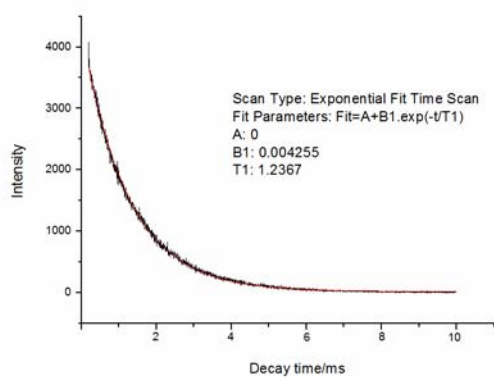
Fig. S8 Luminescence decay curve of the compound **2**.
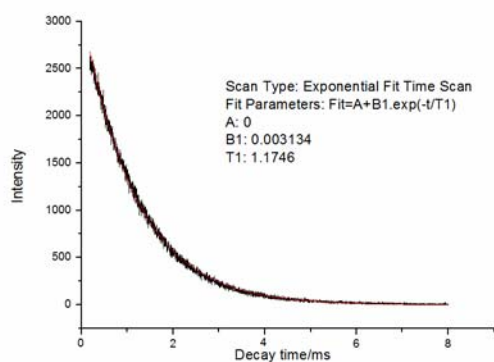
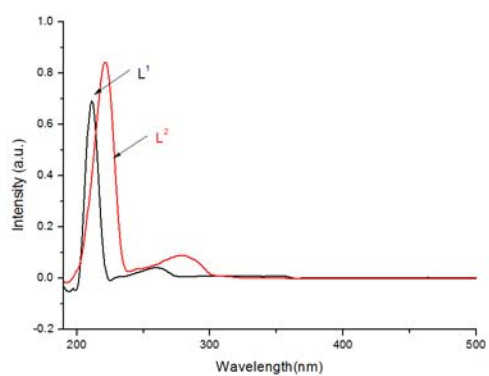**Fig. S9** Luminescence decay curve of the compound **3**.

Fig. S10 The UV-vis absorbance spectrum of the ligands L^I and L^{II} in methanol.
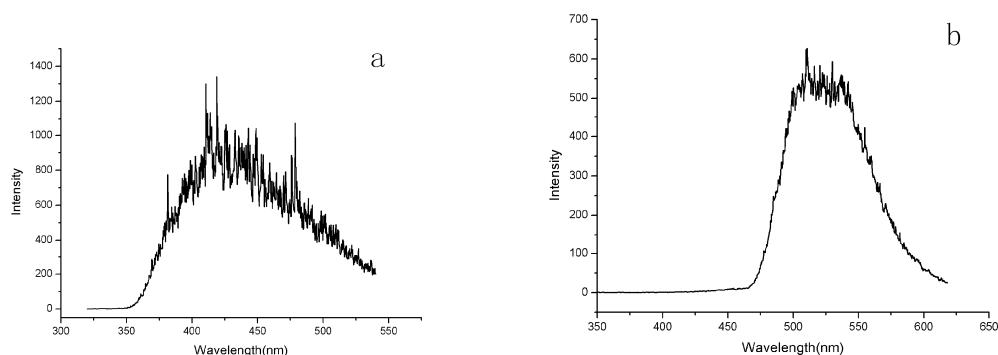
Fig. S11 Phosphorescence spectrums of the Gd complexes for the ligands L^{I} (a) and L^{II} (b) at 77K.
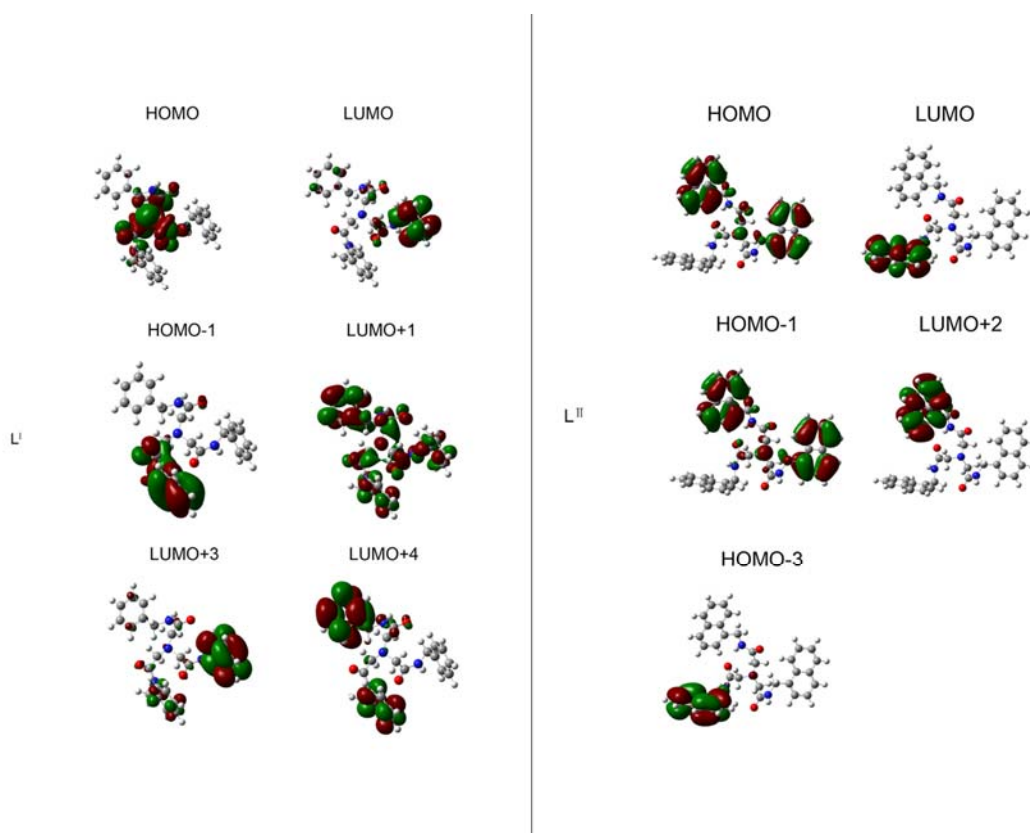

Fig. S12 Frontier molecular orbitals including HOMO and LUMO of the ligands L^{I} and L^{II}.

References

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