Electronic Supplementary Information (ESI)

Lanthanide metal-organic frameworks constructed by asymmetric 2-nitro-biphenyl-4,4′-dicarboxylate ligand: syntheses, structures, luminescence and magnetic investigations

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Table S1 Selected bond lengths (Å) and angles (°) for complexes **1-8**[a]

1					
Eu1-O2C	2.172(18)	Eu1-O11	2.474(15)	N1-O6	1.230(20)
Eu1-O7	2.290(20)	Eu1-O1W	2.540(30)	N2-C20	1.462(6)
Eu1-O4B	2.401(17)	Eu1-O1D	2.560(20)	N2-O9	1.251(8)
Eu1-O3	2.431(17)	N1-C13	1.482(19)	N2-O10	1.271(9)
Eu1-O8A	2.460(30)	N1-O5	1.260(20)		
O2C-Eu1-O7	61.8(7)	O7-Eu1-O11	78.4(6)	O3-Eu1-O1W	76.7(11)
O2C-Eu1-O4B	93.8(6)	O7-Eu1-O1W	130.2(14)	O3-Eu1-O1D	76.9(7)
O2C-Eu1-O3	153.0(5)	O7-Eu1-O1D	85.7(7)	O8A-Eu1-O11	143.3(9)
O2C-Eu1-O8A	77.5(8)	O4B-Eu1-O3	90.5(6)	O8A-Eu1-O1W	68.4(11)
O2C-Eu1-O11	137.1(6)	O4B-Eu1-O8A	145.0(7)	O8A-Eu1-O1D	82.5(8)
O2C-Eu1-O1W	78.4(11)	O4B-Eu1-O11	60.3(5)	O11-Eu1-O1W	121.5(10)
O2C-Eu1-O1D	119.0(6)	O4B-Eu1-O1W	76.6(11)	O11-Eu1-O1D	70.1(6)
O7-Eu1-O4B	77.3(7)	O4B-Eu1-O1D	129.7(6)	O1W-Eu1-O1D	142.4(13)
O7-Eu1-O3	144.7(7)	O3-Eu1-O8A	83.7(7)		
O7-Eu1-O8A	124.5(6)	O3-Eu1-O11	66.9(5)		
2					
Gd1-O2C	2.109(17)	Gd1-O3	2.459(15)	N1-O6	1.180(30)
Gd1-O7	2.320(17)	Gd1-O11	2.603(18)	N2-C20	1.464(6)
Gd1-O4B	2.388(15)	Gd1-O1D	2.671(19)	N2-O9	1.255(8)
Gd1-O1W	2.400(30)	N1-C13	1.480(20)	N2-O10	1.266(8)
Gd1-O8A	2.391(19)	N1-O5	1.300(30)		
O2C-Gd1-O7	60.6(6)	O7-Gd1-O3	139.8(6)	O1W-Gd1-O11	124.8(9)
O2C-Gd1-O4B	90.0(6)	O7-Gd1-O11	76.4(6)	O1W-Gd1-O1D	145.3(7)
O2C-Gd1-O1W	79.9(7)	O7-Gd1-O1D	82.7(6)	O8A-Gd1-O3	85.0(6)
O2C-Gd1-O8A	80.3(7)	O4B-Gd1-O1W	79.1(7)	O8A-Gd1-O11	140.0(7)
O2C-Gd1-O3	159.6(6)	O4B-Gd1-O8A	149.8(6)	O8A-Gd1-O1D	82.1(6)
O2C-Gd1-O11	134.9(7)	O4B-Gd1-O3	89.5(5)	O3-Gd1-O11	64.3(5)
O2C-Gd1-O1D	117.2(6)	O4B-Gd1-O11	59.6(6)	O3- Gd1-O1D	74.4(5)
O7-Gd1-O4B	77.0(5)	O4B-Gd1-O1D	124.9(6)	O11-Gd1-O1D	66.0(6)
O7-Gd1-O1W	130.5(7)	O1W-Gd1-O8A	70.8(8)		
O7-Gd1-O8A	124.3(5)	O1W-Gd1-O3	81.9(7)		
3					
Nd1-O2C	2.208(16)	Nd1-O8A	2.423(18)	N1-O6	1.150(20)
Nd1-O7	2.384(15)	Nd1-O11	2.592(12)	N2-C20	1.463(6)
Nd1-O4B	2.467(13)	Nd1-O1D	2.677(16)	N2-O9	1.255(8)
Nd1-O3	2.467(14)	N1-C13	1.500(20)	N2-O10	1.264(8)
Nd1-O1W	2.454(15)	N1-O5	1.290(30)		
O2C-Nd1-O7	60.9(5)	O7-Nd1-O8A	124.9(5)	O3-Nd1-O11	66.7(4)
O2C-Nd1-O4B	93.8(5)	O7-Nd1-O11	74.9(5)	O3-Nd1-O1D	75.8(5)
O2C-Nd1-O3	157.9(5)	O7-Nd1-O1D	83.7(5)	O1W-Nd1-O8A	71.8(5)
O2C-Nd1-O1W	77.7(5)	O4B-Nd1-O3	91.0(5)	O1W-Nd1-O11	123.4(5)
O2C-Nd1-O8A	78.7(6)	O4B-Nd1-O1W	76.2(5)	O1W-Nd1-O1D	148.3(5)
O2C-Nd1-O11	133.4(5)	O4B-Nd1-O8A	148.0(5)	O8A-Nd1-O11	144.2(6)
O2C-Nd1-O1D	117.5(6)	O4B-Nd1-O11	59.0(4)	O8A-Nd1-O1D	83.6(5)
O7-Nd1-O4B	74.8(5)	O4B-Nd1-O1D	126.4(5)	O11-Nd1-O1D	68.2(4)
O7-Nd1-O3	140.9(6)	O3-Nd1-O1W	82.6(5)		
O7-Nd1-O1W	126.7(6)	O3-Nd1-O8A	85.8(5)		
4					
La1-O2C	2.370(20)	La1-O1W	2.611(12)	N1-O6	1.150(20)
La1-O7	2.400(20)	La1-O11	2.608(17)	N2-C20	1.463(6)
La1-O3	2.494(16)	La1-O1D	2.640(20)	N2-O9	1.252(8)
La1-O4B	2.540(18)	N1-C13	1.460(20)	N2-O10	1.271(9)
La1-O8A	2.550(30)	N1-O5	1.290(20)		
O2C-La1-O7	61.8(7)	O7-La1-O1W	123.9(7)	O4B-La1-O11	61.9(6)

O2C-La1-O3	153.4(5)	O7-La1-O11	78.3(7)	O4B-La1-O1D	130.4(5)
O2C-La1-O4B	93.1(6)	O7-La1-O1D	86.3(7)	O8A-La1-O1W	68.9(12)
O2C-La1-O8A	76.8(7)	O3-La1-O4B	91.3(5)	O8A-La1-O11	143.7(8)
O2C-La1-O1W	74.5(8)	O3-La1-O8A	83.8(7)	O8A-La1-O1D	84.9(7)
O2C-La1-O11	137.7(6)	O3-La1-O1W	81.7(7)	O1W-La1-O11	122.9(12)
O2C-La1-O1D	118.3(7)	O3-La1-O11	66.3(5)	O1W-La1-O1D	147.8(8)
O7-La1-O3	144.3(6)	O3-La1-O1D	77.2(6)	O11-La1-O1D	69.4(6)
O7-La1-O4B	75.6(6)	O4B-La1-O8A	142.4(6)		
O7-La1-O8A	126.4(5)	O4B-La1-O1W	73.5(11)		
5					
Ce1-O2C	2.190(20)	Ce1-O11	2.690(30)	N1-O6	1.160(30)
Ce1-O7	2.420(20)	Ce1-O1W	2.563(12)	N2-C20	1.462(6)
Ce1-O3	2.548(17)	Ce1-O1D	2.740(20)	N2-O9	1.257(8)
Ce1-O4B	2.520(20)	N1-C13	1.4250(30)	N2-O10	1.266(8)
Ce1-O8A	2.450(30)	N1-O5	1270(30)		
O2C-Ce1-O7	61.5(8)	O7-Ce1-O11	75.4(8)	O4B-Ce1-O1W	77.8(6)
O2C-Ce1-O3	159.5(7)	O7-Ce1-O1W	128.8(7)	O4B-Ce1-O1D	124.4(6)
O2C-Ce1-O4B	96.5(7)	O7-Ce1-O1D	83.8(7)	O8A-Ce1-O11	140.9(9)
O2C-Ce1-O8A	79.9(8)	O3-Ce1-O4B	89.1(6)	O8A-Ce1-O1W	70.4(7)
O2C-Ce1-O11	135.3(8)	O3-Ce1-O8A	85.0(7)	O8A-Ce1-O1D	84.0(7)
O2C-Ce1-O1W	79.9(6)	O3-Ce1-O11	63.9(7)	O11-Ce1-O1W	123.5(8)
O2C-Ce1-O1D	117.2(7)	O3-Ce1-O1W	82.1(6)	O11-Ce1-O1D	66.0(8)
O7-Ce1-O3	138.8(7)	O3-Ce1-O1D	74.4(7)	O1W-Ce1-O1D	146.5(6)
O7-Ce1-O4B	74.9(6)	O4B-Ce1-O8A	148.1(7)		
O7-Ce1-O8A	127.5(5)	O4B-Ce1-O11	59.1(8)		
6					
Pr1-O2C	2.180(20)	Pr1-O11	2.660(20)	N1-O6	1.130(30)
Pr1-O7	2.400(20)	Pr1-O1W	2.529(11)	N2-C20	1.463(6)
Pr1-O3	2.505(17)	Pr1-O1D	2.710(20)	N2-O9	1.256(8)
Pr1-O4B	2.505(19)	N1-C13	1.410(20)	N2-O10	1.266(8)
Pr1-O8A	2.420(30)	N1-O5	1.360(30)		
O2C-Pr1-O7	60.2(8)	O7-Pr1-O11	76.5(8)	O4B-Pr1-O1W	77.0(5)
O2C-Pr1-O3	159.5(6)	O7-Pr1-O1W	127.8(7)	O4B-Pr1-O1D	125.3(6)
O2C-Pr1-O4B	95.0(7)	O7-Pr1-O1D	84.4(8)	O8A-Pr1-O11	140.0(10)
O2C-Pr1-O8A	81.5(10)	O3-Pr1-O4B	89.7(6)	O8A-Pr1-O1W	71.9(8)
O2C-Pr1-O11	134.7(7)	O3-Pr1-O8A	84.2(8)	O8A-Pr1-O1D	82.3(9)
O2C-Pr1-O1W	79.3(6)	O3-Pr1-O11	64.2(6)	O11-Pr1-O1W	123.2(6)
O2C-Pr1-O1D	117.8(8)	O3-Pr1-O1W	82.3(5)	O11-Pr1-O1D	66.6(7)
O7-Pr1-O3	140.1(7)	O3-Pr1-O1D	74.4(7)	O1W-Pr1-O1D	146.8(6)
O7-Pr1-O4B	75.4(7)	O4B-Pr1-O8A	148.9(8)		
O7-Pr1-O8A	126.5(6)	O4B-Pr1-O11	59.5(6)		
7					
Sm1-O2C	2.070(20)	Sm1-O1W	2.481(12)	N1-O6	1.150(30)
Sm1-O7	2.350(20)	Sm1-O11	2.648(18)	N2-C20	1.464(6)
Sm1-O4B	2.465(17)	Sm1-O1D	2.690(20)	N2-O9	1.257(8)
Sm1-O8A	2.370(30)	N1-C13	1.470(20)	N2-O10	1.265(8)
Sm1-O3	2.474(19)	N1-O5	1.340(30)		
O2C-Sm1-O7	59.9(8)	O7-Sm1-O1W	128.4(7)	O8A-Sm1-O11	139.4(9)
O2C-Sm1-O4B	95.8(6)	O7-Sm1-O11	76.4(7)	O8A-Sm1-O1D	81.8(8)
O2C-Sm1-O8A	81.9(9)	O7-Sm1-O1D	84.8(8)	O3-Sm1-O1W	81.5(6)
O2C-Sm1-O3	160.1(6)	O4B-Sm1-O8A	150.5(7)	O3-Sm1-O11	63.8(6)
O2C-Sm1-O1W	80.5(6)	O4B-Sm1-O3	88.9(7)	O3-Sm1-O1D	73.9(7)
O2C-Sm1-O11	134.5(7)	O4B-Sm1-O1W	78.0(5)	O1W-Sm1-O11	122.7(6)
O2C-Sm1-O1D	118.2(7)	O4B-Sm1-O11	58.5(6)	O1W-Sm1-O1D	146.0(6)
O7-Sm1-O4B	74.9(6)	O4B-Sm1-O1D	123.7(6)	O11-Sm1-O1D	65.9(6)
O7-Sm1-O8A	126.4(6)	O8A-Sm1-O3	84.6(8)		
O7-Sm1-O3	139.7(8)	O8A-Sm1-O1W	72.6(8)		

8					
Tb1-O2C	1.930(30)	Tb1-O1W	2.513(16)	N1-O6	1.180(40)
Tb1-O8A	2.260(50)	Tb1-O11	2.610(20)	N2-C20	1.461(6)
Tb1-O7	2.340(30)	Tb1-O1D	2.720(30)	N2-O9	1.259(8)
Tb1-O4B	2.370(20)	N1-C13	1.460(30)	N2-O10	1.267(8)
Tb1-O3	2.480(20)	N1-O5	1.260(40)		
O2C-Tb1-O8A	86.4(14)	O8A-Tb1-O1W	75.4(14)	O4B-Tb1-O11	55.4(8)
O2C-Tb1-O7	60.6(10)	O8A-Tb1-O11	135.8(15)	O4B-Tb1-O1D	120.2(8)
O2C-Tb1-O4B	97.3(9)	O8A-Tb1-O1D	78.6(15)	O3-Tb1-O1W	81.4(8)
O2C-Tb1-O3	162.8(8)	O7-Tb1-O4B	74.9(8)	O3-Tb1-O11	63.4(7)
O2C -Tb1-O1W	82.8(9)	O7-Tb1-O3	136.4(9)	O3-Tb1-O1D	73.3(8)
O2C-Tb1-O11	132.2(9)	O7-Tb1-O1W	131.8(10)	O1W-Tb1-O11	122.7(9)
O2C-Tb1-O1D	117.9(9)	O7-Tb1-O11	73.8(9)	O1W-Tb1-O1D	145.5(9)
O8A-Tb1-O7	127.0(8)	O7-Tb1-O1D	82.3(10)	O11-Tb1-O1D	65.3(8)
O8A-Tb1-O4B	155.0(12)	O4B-Tb1-O3	86.8(7)		
O8A-Tb1-O3	83.1(12)	O4B-Tb1-O1W	80.5(8)		

[a] Symmetry codes: A: -x + 2, -y + 1, -z + 2; B: -x + 1, -y + 1, -z + 2; C: x, y, z + 1; D: -x + 2, -y + 1, -z + 1.

Table S2 Continuous Shape Measures (CShMs) of the coordination sphere of Ln(III) in complexes **1**-**8**

CShMs / Complexes	Octagon (D_{8h})	Heptagonal pyramid (C_{7v})	Hexagonal bipyramid (D_{6h})	Cube (O_h)	Square antiprism (D_{4d})	Triangular dodecahedron (D_{2d})	Delta Δ (path)
4 (La-NO_2)	30.06019	22.34302	15.60951	10.98305	**2.44744**	**2.10040**	**0.784**
5 (Ce-NO_2)	30.36443	21.92258	15.78234	11.41003	**2.76238**	**2.37483**	**0.874**
6 (Pr-NO_2)	30.40270	22.09121	15.76218	11.12154	**2.66028**	**2.34942**	**0.845**
3 (Nd-NO_2)	30.32569	22.16273	15.93143	11.30358	**2.49645**	**2.35991**	**0.916**
7 (Sm-NO_2)	30.62776	21.94864	15.72264	11.17153	**2.80056**	**2.49586**	**0.927**
1 (Eu-NO_2)	30.62828	21.34102	16.17977	11.34817	**2.29691**	**2.32081**	**0.799**
2 (Gd-NO_2)	30.55985	21.82165	16.20503	11.42644	**2.66203**	**2.43395**	**0.890**
8 (Tb-NO_2)	30.82879	22.50488	16.05152	11.23072	**3.04076**	**2.66603**	**1.001**

Table S3 The Ln-O-C(-O^-) angles (°) of complexes **1**-**8**

4		**5**		**6**	
C1-O1-La1D	101.0(20)	C1-O1-Ce1D	99.0(20)	C1-O1-Pr1D	105.9(13)
C1-O2-La1E	170.0(30)	C1-O2-Ce1E	172.0(30)	C1-O2-Pr1E	172.9(14)
C14-O3-La1	146.0(8)	C14-O3-Ce1	140.9(9)	C14-O3-Pr1	142.3(8)
C14-O4-La1B	129.3(12)	C14-O4-Ce1B	126.9(12)	C14-O4-Pr1B	127.7(12)
C15-O7-La1	150.8(17)	C15-O7-Ce1	150.0(17)	C15-O7-Pr1	150.0(20)
C15-O8-La1A	136.9(15)	C15-O8-Ce1A	136.6(16)	C15-O8-Pr1A	136.0(20)
3		**7**		**1**	
C1-O1-Nd1D	103.1(19)	C1-O1-Sm1D	100.7(16)	C1-O1-Eu1D	105.5(15)
C1-O2-Nd1E	172.0(20)	C1-O2-Sm1E	177.0(20)	C1-O2-Eu1E	175.3(17)
C14-O3-Nd1	143.3(9)	C14-O3-Sm1	141.8(9)	C14-O3-Eu1	145.4(8)
C14-O4-Nd1B	126.9(12)	C14-O4-Sm1B	126.8(12)	C14-O4-Eu1B	130.1(11)
C15-O7-Nd1	152.3(15)	C15-O7-Sm1	148.5(19)	C15-O7-Eu1	152.5(18)
C15-O8-Nd1A	139.5(14)	C15-O8-Sm1A	135.3(18)	C15-O8-Eu1A	136.4(15)

2		**8**	
C1-O1-Gd1D	103.0(17)	C1-O1-Tb1D	98.0(20)
C1-O2-Gd1E	177.0(20)	C1-O2-Tb1E	175.0(30)
C14-O3-Gd1	142.3(9)	C14-O3-Tb1	139.2(11)
C14-O4-Gd1B	128.1(12)	C14-O4-Tb1B	126.4(14)
C15-O7-Gd1	153.1(16)	C15-O7-Tb1	147.0(20)
C15-O8-Gd1A	137.0(15)	C15-O8-Tb1A	135.0(30)

[a] Symmetry codes: A: -x + 2, -y + 1, -z + 2; B: -x + 1, -y + 1, -z + 2; C: x, y, z + 1; D: -x + 2, -y + 1, -z + 1; E: x, y, z – 1.

Table S4 The integral intensities of $^5D_0 \rightarrow {}^7F_J$ (J = 0, 1, 2, 3, 4) transitions for complex **1***

Integral ranges	$^5D_0 \rightarrow {}^7F_J$ **transitions**	**Integral intensities**	**Integral ratio**	I_{tot}/I_{MD}
577-581 nm	J = 0	1.64×10^4	0.003	1/0.139 = 7.19
583-603 nm	J = 1	77.60×10^4	0.139	
605-638 nm	J = 2	298.13×10^4	0.534	
647-657 nm	J = 3	6.53×10^4	0.012	
666-715 nm	J = 4	174.61×10^4	0.312	

*This table was compiled acoording to the corrected emission spectrum of **1** shown in Fig. S6.

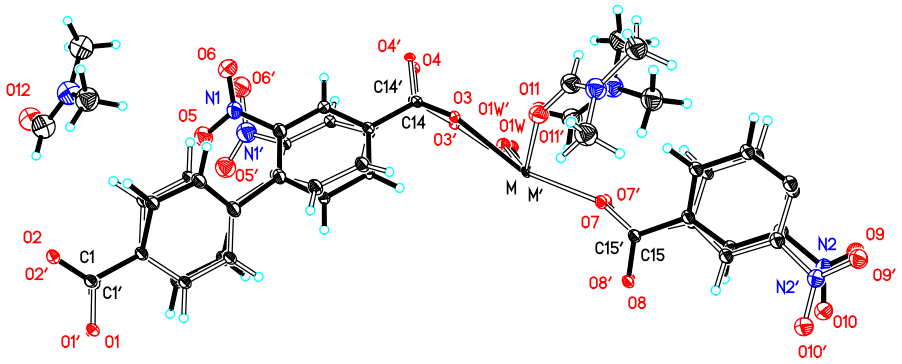
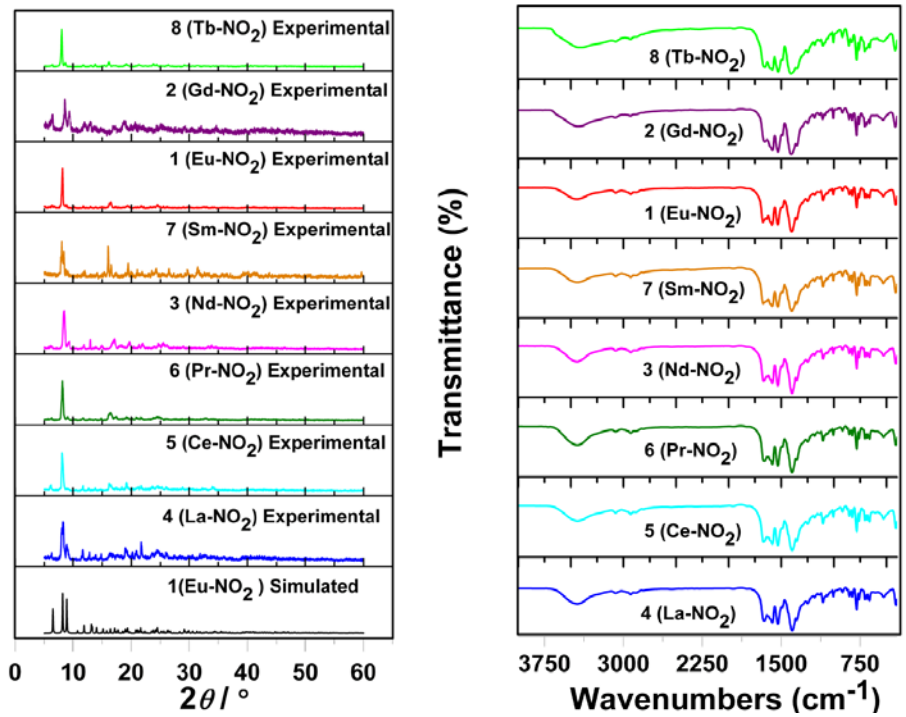
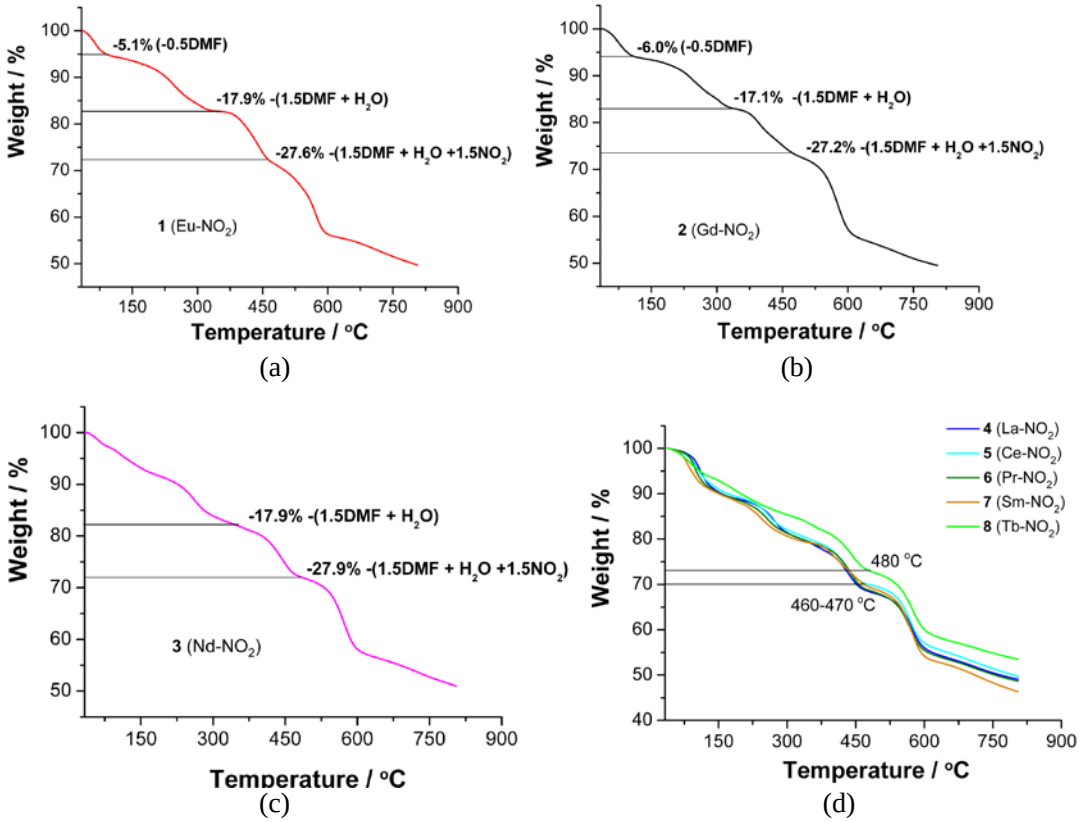


Fig. S1 The least asymmetric unit of complexes **1**-**8**, in which the two sets of positions were presented clearly. The M and M′ represent the same lanthanide ions [Ln^{3+} = Eu^{3+}(**1**), Gd^{3+}(**2**), Nd^{3+}(**3**), La^{3+}(**4**), Ce^{3+}(**5**), Pr^{3+}(**6**), Sm^{3+}(**7**), and Tb^{3+}(**8**)] located at different positions.



(a) (b)

Fig. S2 The PXRD patterns (a) and IR spectra (b) of complexes **1**-**8**.



(a) (b) (c) (d)

Fig. S3 TGA curves of complexes **1**-**8**.

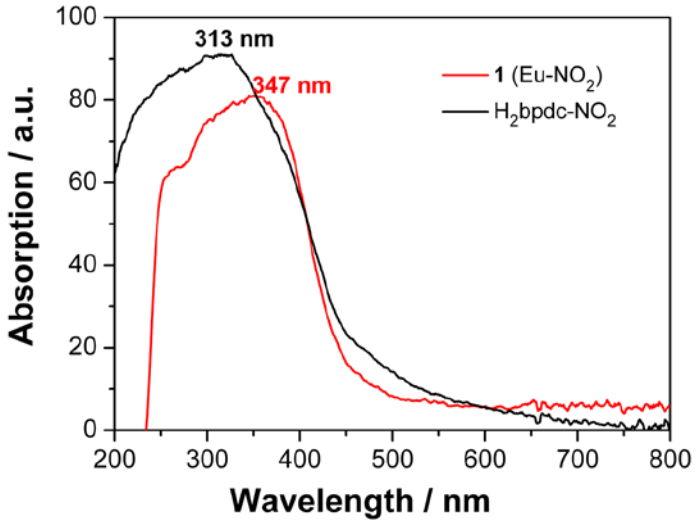


Fig. S4 The room-temperature UV-Vis spectra of H_2bpdc-NO_2 and complex **1** measured in the solid state.

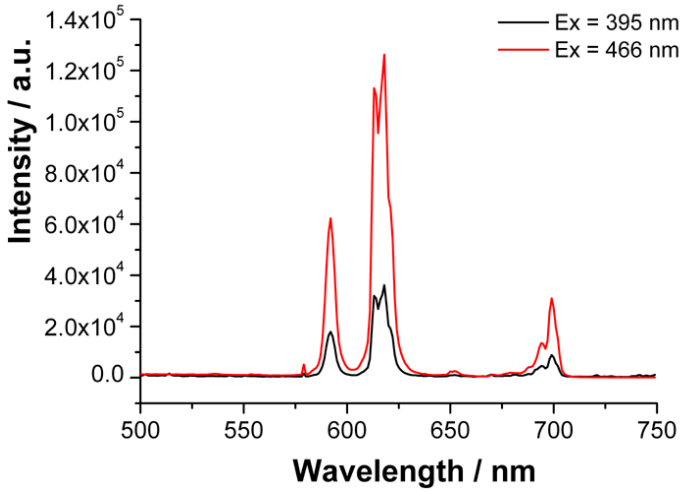


Fig. S5 The solid-state emission spectra of complex **1** excited at 395 nm and 466 nm at room temperature, respectivly (Ex slit = Em slit = 0.6 nm).

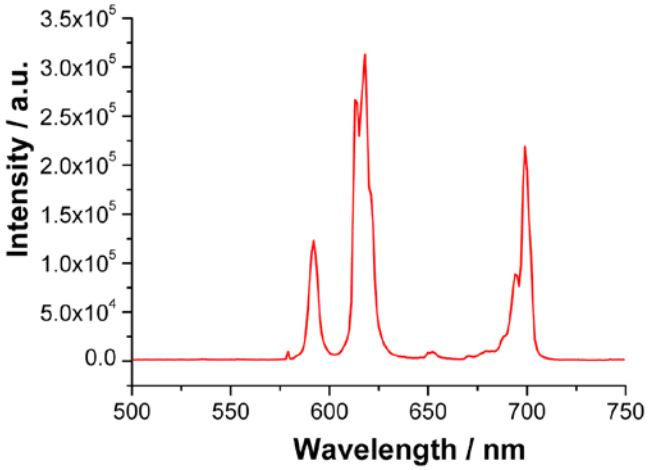


Fig. S6 The solid-state **corrected** emission spectra of complex **1** excited at 466 nm at room temperature (Ex slit = Em slit = 0.6 nm).

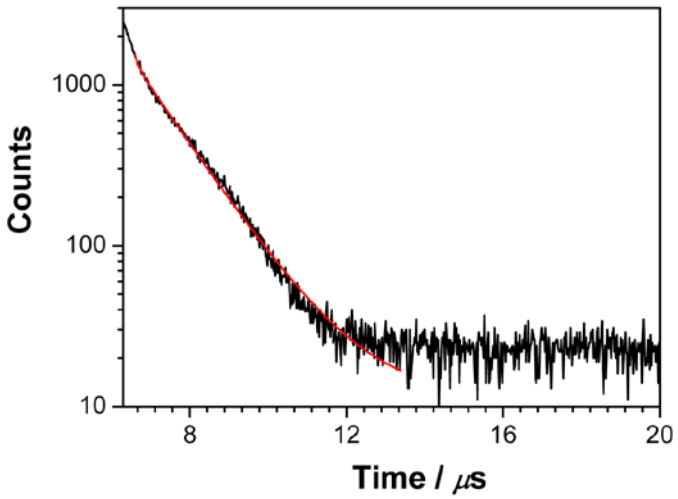


Fig. S7 The decay curve of **3** monitored at 1055 nm and detected at room temperature (λ_{ex} = 582 nm). The fitting curve with a monoexponential function is presented as the solid line.