

*Reversible trans-to-cis* Photoisomerization and Unreversible  
Photocyclization Reactions of a Co-coordinated Stilbene Derivative on  
the Chiral di- $\beta$ -Diketonate Lanthanide Complexes

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**Table S1. Selected bond lengths (Å) for complexes 1 and 2.**

<b>Complex 1</b>		<b>Complex 2</b>	
<b>[La(<i>d</i>-fbc)<sub>2</sub>(L)(CF<sub>3</sub>COO)]·H<sub>2</sub>O</b>		<b>[La(<i>l</i>-fbc)<sub>2</sub>(L)(CF<sub>3</sub>COO)]·H<sub>2</sub>O</b>	
<b>Bond</b>	<b>lengths (Å)</b>	<b>Bond</b>	<b>lengths (Å)</b>
La1–O1	2.535(3)	La1–O1	2.547(7)
La1–O2	2.549(3)	La1–O2	2.525(7)
La1–O3	2.436(3)	La1–O3	2.449(7)
La1–O4	2.533(3)	La1–O4	2.503(7)
La1–O5	2.479(3)	La1–O5	2.498(7)
La1–O6	2.428(3)	La1–O6	2.445(8)
La1–N1	2.718(4)	La1–N1	2.684(9)
La1–N2	2.853(4)	La1–N2	2.841(10)
La1–N3	2.697(3)	La1–N3	2.730(8)
La2–O9	2.538(3)	La2–O9	2.533(7)
La2–O10	2.459(3)	La2–O10	2.445(6)
La2–O11	2.529(3)	La2–O11	2.545(7)
La2–O12	2.485(3)	La2–O12	2.480(7)
La2–O13	2.499(3)	La2–O13	2.531(7)
La2–O14	2.442(3)	La2–O14	2.421(7)
La2–N5	2.681(4)	La2–N5	2.733(8)
La2–N6	2.839(4)	La2–N6	2.845(9)
La2–N7	2.719(4)	La2–N7	2.711(8)

\* O2, O3 and O4, O5 are from the two *d*-fbc, O6 is from trifluoroacetate, O1 and N2 are from benzohydazide and N1, N3 are from pyridines of ligand L.

**Table S2. Selected bond lengths (Å) for complexes 3 and 4.**

<b>Complex 3</b> <b>[Sm(<i>d</i>-fbc)<sub>2</sub>(L)(CF<sub>3</sub>COO)]·H<sub>2</sub>O</b>		<b>Complex 4</b> <b>[Eu(<i>d</i>-fbc)<sub>2</sub>(L)(CF<sub>3</sub>COO)]·H<sub>2</sub>O</b>	
<b>Bond</b>	<b>lengths (Å)</b>	<b>Bond</b>	<b>lengths (Å)</b>
Sm1–O1	2.460(6)	Eu1–O1	2.448(4)
Sm1–O2	2.471(6)	Eu1–O2	2.461(4)
Sm1–O3	2.375(6)	Eu1–O3	2.358(4)
Sm1–O4	2.461(6)	Eu1–O4	2.444(4)
Sm1–O5	2.393(6)	Eu1–O5	2.386(4)
Sm1–O6	2.360(6)	Eu1–O6	2.344(4)
Sm1–N1	2.645(8)	Eu1–N1	2.609(5)
Sm1–N2	2.770(9)	Eu1–N2	2.772(6)
Sm1–N3	2.621(8)	Eu1–N3	2.626(6)
Sm2–O9	2.443(7)	Eu2–O9	2.446(5)
Sm2–O10	2.362(7)	Eu2–O10	2.364(5)
Sm2–O11	2.462(7)	Eu2–O11	2.430(4)
Sm2–O12	2.398(7)	Eu2–O12	2.398(4)
Sm2–O13	2.427(7)	Eu2–O13	2.414(5)
Sm2–O14	2.343(7)	Eu2–O14	2.346(5)
Sm2–N5	2.612(8)	Eu2–N5	2.625(5)
Sm2–N6	2.767(11)	Eu2–N6	2.751(7)
Sm2–N7	2.627(8)	Eu2–N7	2.589(6)

\*\* O2, O3 and O4, O5 are from the two *d*-fbc, O6 is from trifluoroacetate, O1 and N2 are from benzohydazide and N1, N3 are from pyridines of ligand L.

**Table S3. Selected angles (deg) of complexes 1 and 2.**

<b>Complex 1</b> <b>[La(<i>d</i>-fbc)<sub>2</sub>(L)(CF<sub>3</sub>COO)]·H<sub>2</sub>O</b> <b>Angles(Å)</b>				<b>Complex 2</b> <b>[La(<i>l</i>-fbc)<sub>2</sub>(L)(CF<sub>3</sub>COO)]·H<sub>2</sub>O</b> <b>Angles(Å)</b>			
O2-La1-N2	111.78(10)	N7-La2-N6	61.08(11)	O1-La1-N3	71.8(2)	O11-La2-N6	112.5(2)
O2-La1-N1	134.26(10)	O9-La2-N7	71.78(10)	O1-La1-N2	60.0(2)	O11-La2-N5	134.4(2)
O2-La1-N3	72.79(10)	O9-La2-N6	60.11(10)	O1-La1-N1	82.1(3)	O11-La2-N7	72.9(2)
O6-La1-O2	74.62(10)	O9-La2-N5	82.42(11)	O4-La1-N3	68.1(3)	O14-La2-O11	74.4(2)
O6-La1-O3	95.23(11)	O13-La2-N7	68.50(11)	O4-La1-O1	131.4(2)	O14-La2-O10	95.5(3)
O6-La1-N2	135.02(10)	O13-La2-O9	131.61(10)	O4-La1-O2	126.9(3)	O14-La2-N6	135.3(2)
O6-La1-O4	76.14(11)	O13-La2-O11	126.85(11)	O4-La1-N2	117.6(3)	O14-La2-O13	75.9(2)
O6-La1-O1	141.78(11)	O13-La2-N6	118.19(11)	O4-La1-N1	143.3(2)	O14-La2-O9	142.0(2)
O6-La1-O5	81.55(11)	O13-La2-N5	143.12(10)	O5-La1-N3	81.8(2)	O14-La2-O12	81.0(3)
O6-La1-N1	144.80(11)	O12-La2-N7	82.08(10)	O5-La1-O1	129.0(3)	O14-La2-N5	144.7(3)
O6-La1-N3	81.16(11)	O12-La2-O9	129.34(12)	O5-La1-O4	70.5(2)	O14-La2-N7	81.8(3)
O3-La1-O2	69.99(9)	O12-La2-O13	70.61(11)	O5-La1-O2	138.9(2)	O10-La2-O11	69.7(2)
O3-La1-N2	129.38(10)	O12-La2-O11	139.01(10)	O5-La1-N2	69.0(3)	O10-La2-N6	128.9(2)
O3-La1-O4	70.19(9)	O12-La2-N6	69.32(11)	O5-La1-N1	76.1(3)	O10-La2-O13	70.5(2)
O3-La1-O1	77.54(10)	O12-La2-N5	76.17(11)	O3-La1-N3	81.5(3)	O10-La2-O9	77.4(2)
O3-La1-O5	139.98(10)	O10-La2-N7	81.32(11)	O3-La1-O1	75.8(2)	O10-La2-O12	140.6(2)
O3-La1-N1	81.36(11)	O10-La2-O9	75.75(11)	O3-La1-O4	72.3(2)	O10-La2-N5	81.3(3)
O3-La1-N3	142.18(10)	O10-La2-O13	72.01(10)	O3-La1-O5	142.7(2)	O10-La2-N7	141.8(2)
O4-La1-O2	127.31(10)	O10-La2-O12	142.46(10)	O3-La1-O2	69.8(2)	O13-La2-O11	126.8(3)
O4-La1-N2	119.94(10)	O10-La2-O11	69.96(9)	O3-La1-N2	128.2(2)	O13-La2-N6	119.8(2)
O4-La1-O1	132.66(9)	O10-La2-N6	128.23(10)	O3-La1-N1	140.3(2)	O13-La2-O9	132.9(2)
O4-La1-N1	69.73(11)	O10-La2-N5	140.41(10)	O2-La1-N3	137.6(2)	O13-La2-N5	69.9(3)
O4-La1-N3	142.45(9)	O11-La2-N7	137.19(10)	O2-La1-O1	71.3(2)	O13-La2-N7	142.9(2)
O1-La1-O2	67.60(10)	O11-La2-O9	70.83(11)	O2-La1-N2	114.9(3)	O9-La2-O11	68.1(2)
O1-La1-N2	59.70(10)	O11-La2-N6	114.34(11)	O2-La1-N1	72.0(2)	O9-La2-N6	59.5(2)
O1-La1-N1	71.98(10)	O11-La2-N5	71.83(11)	O6-La1-N3	143.0(3)	O9-La2-N5	71.9(2)
O1-La1-N3	82.41(10)	O14-La2-N7	143.48(11)	O6-La1-O1	143.6(3)	O9-La2-N7	81.7(2)
O5-La1-O2	143.89(10)	O14-La2-O9	143.34(11)	O6-La1-O4	76.0(3)	O12-La2-O11	143.3(2)
O5-La1-N2	68.10(10)	O14-La2-O13	76.13(11)	O6-La1-O5	78.2(3)	O12-La2-N6	68.3(2)
O5-La1-O4	70.34(10)	O14-La2-O12	77.82(12)	O6-La1-O3	96.0(3)	O12-La2-O13	70.6(2)
O5-La1-O1	127.50(11)	O14-La2-O10	96.54(12)	O6-La1-O2	72.6(3)	O12-La2-O9	127.6(3)
O5-La1-N1	79.21(11)	O14-La2-O11	72.86(11)	O6-La1-N2	135.6(3)	O12-La2-N5	79.9(2)
O5-La1-N3	77.09(10)	O14-La2-N6	134.97(11)	O6-La1-N1	82.6(3)	O12-La2-N7	77.0(2)
N1-La1-N2	61.52(11)	O14-La2-N5	81.71(12)	N1-La1-N3	122.2(3)	N5-La2-N6	61.2(3)
N3-La1-N2	60.72(10)	N5-La2-N7	122.49(13)	O1-La1-N3	61.4(3)	N7-La2-N6	60.6(2)
N3-La1-N1	122.15(12)	N5-La2-N6	61.46(11)	O1-La1-N2	71.8(2)	N7-La2-N5	121.8(3)

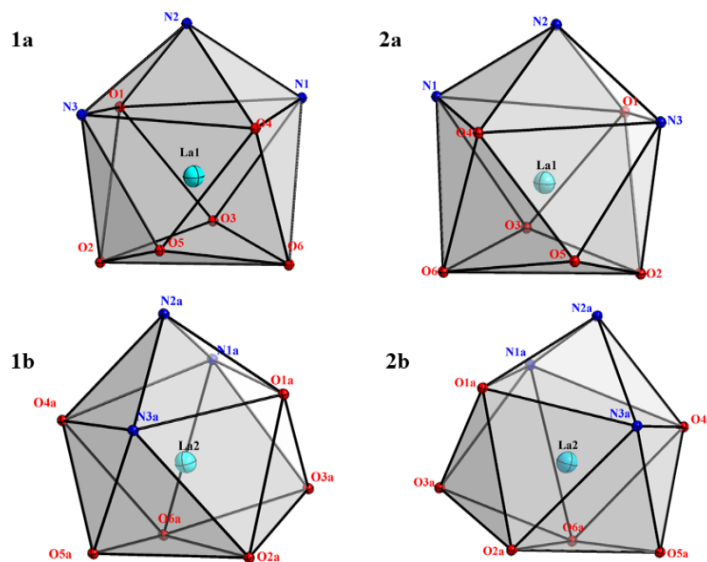
**Table S4. Selected angles (deg) of complexes 3 and 4**

<b>Complex 3</b> <b>[Sm(<i>d</i>-fbc)<sub>2</sub>(L)(CF<sub>3</sub>COO)]·H<sub>2</sub>O</b>				<b>Complex 4</b> <b>[Eu(<i>d</i>-fbc)<sub>2</sub>(L)(CF<sub>3</sub>COO)]·H<sub>2</sub>O</b>			
<b>Angles(Å)</b>				<b>Angles(Å)</b>			
O6–Sm1–O3	95.0(3)	N7–Sm2–N6	62.4(3)	O1–Eu1–N2	61.46(15)	N5–Eu2–N6	62.72(18)
O6–Sm1–O2	73.9(2)	O9–Sm2–N7	72.7(2)	O1–Eu1–N3	72.15(16)	O10–Eu2–N5	79.73(17)
O6–Sm1–O5	80.6(3)	O9–Sm2–N6	62.1(2)	O1–Eu1–N1	85.13(15)	O10–Eu2–O13	70.26(15)
O6–Sm1–O1	141.6(2)	O9–Sm2–O11	70.4(2)	O6–Eu1–O1	141.21(16)	O10–Eu2–O11	71.93(15)
O6–Sm1–O4	75.1(2)	O9–Sm2–N5	84.8(3)	O6–Eu1–O2	73.74(16)	O10–Eu2–O9	74.50(17)
O6–Sm1–N3	80.1(2)	O13–Sm2–N7	68.8(3)	O6–Eu1–N2	135.32(16)	O10–Eu2–O12	142.57(17)
O6–Sm1–N2	135.3(2)	O13–Sm2–N6	119.7(3)	O6–Eu1–O5	80.69(17)	O10–Eu2–N7	141.36(16)
O6–Sm1–N1	144.3(3)	O13–Sm2–O9	131.2(2)	O6–Eu1–O4	75.35(16)	O10–Eu2–N6	128.56(16)
O3–Sm1–O2	71.49(19)	O13–Sm2–O11	125.7(3)	O6–Eu1–O3	94.68(17)	O13–Eu2–N5	68.59(18)
O3–Sm1–O5	141.1(2)	O13–Sm2–N5	142.4(2)	O6–Eu1–N3	144.15(17)	O13–Eu2–O11	125.97(19)
O3–Sm1–O1	76.4(2)	O11–Sm2–N7	138.1(2)	O6–Eu1–N1	79.71(16)	O13–Eu2–O9	131.03(15)
O3–Sm1–O4	69.0(2)	O11–Sm2–N6	114.1(3)	O2–Eu1–N2	111.50(16)	O13–Eu2–N7	142.01(16)
O3–Sm1–N3	142.4(2)	O11–Sm2–N5	70.4(2)	O2–Eu1–N3	134.75(15)	O13–Eu2–N6	119.90(17)
O3–Sm1–N2	129.5(2)	O12–Sm2–N7	83.0(2)	O2–Eu1–N1	71.00(15)	O11–Eu2–N5	137.95(15)
O3–Sm1–N1	79.8(3)	O12–Sm2–N6	69.0(3)	O5–Eu1–O1	129.43(17)	O11–Eu2–O9	70.31(16)
O2–Sm1–N3	71.4(2)	O12–Sm2–O9	131.0(3)	O5–Eu1–O2	140.67(15)	O11–Eu2–N7	70.28(17)
O2–Sm1–N2	111.8(2)	O12–Sm2–O13	72.2(3)	O5–Eu1–N2	68.17(16)	O11–Eu2–N6	113.70(17)
O2–Sm1–N1	134.7(2)	O12–Sm2–O11	137.2(2)	O5–Eu1–O4	72.20(16)	O14–Eu2–N5	142.63(18)
O5–Sm1–O2	140.7(2)	O12–Sm2–N5	75.2(3)	O5–Eu1–N3	82.01(17)	O14–Eu2–O10	95.67(19)
O5–Sm1–O1	129.0(3)	O10–Sm2–N7	80.3(2)	O5–Eu1–N1	75.45(16)	O14–Eu2–O13	74.93(17)
O5–Sm1–O4	72.5(2)	O10–Sm2–N6	129.0(2)	O4–Eu1–O1	131.75(14)	O14–Eu2–O11	71.97(17)
O5–Sm1–N3	75.3(2)	O10–Sm2–O9	74.8(2)	O4–Eu1–O2	126.93(16)	O14–Eu2–O9	142.24(17)
O5–Sm1–N2	68.0(2)	O10–Sm2–O13	70.3(2)	O4–Eu1–N2	120.87(16)	O14–Eu2–O12	78.45(18)
O5–Sm1–N1	82.0(2)	O10–Sm2–O11	71.5(2)	O4–Eu1–N3	69.52(17)	O14–Eu2–N7	80.2(2)
O1–Sm1–O2	67.9(2)	O10–Sm2–O12	142.3(2)	O4–Eu1–N1	141.68(15)	O14–Eu2–N6	135.55(17)
O1–Sm1–O4	131.9(2)	O10–Sm2–N5	141.0(2)	O3–Eu1–O1	76.32(15)	O9–Eu2–N5	72.61(16)
O1–Sm1–N3	84.7(2)	N5–Sm2–N7	124.9(3)	O3–Eu1–O2	71.86(14)	O9–Eu2–N7	85.49(18)
O1–Sm1–N2	61.1(2)	N5–Sm2–N6	62.6(3)	O3–Eu1–N2	129.71(15)	O9–Eu2–N6	61.99(16)
O1–Sm1–N1	71.9(2)	O14–Sm2–N7	142.9(3)	O3–Eu1–O5	140.69(15)	O12–Eu2–N5	83.15(16)
O4–Sm1–O2	126.5(2)	O14–Sm2–N6	135.5(2)	O3–Eu1–O4	68.90(14)	O12–Eu2–O13	72.55(17)
O4–Sm1–N3	141.9(2)	O14–Sm2–O9	142.0(2)	O3–Eu1–N3	79.48(17)	O12–Eu2–O11	137.11(15)
O4–Sm1–N2	121.0(2)	O14–Sm2–O13	75.0(2)	O3–Eu1–N1	142.52(15)	O12–Eu2–O9	130.75(19)
O4–Sm1–N1	70.0(3)	O14–Sm2–O11	71.6(3)	N3–Eu1–N2	63.14(18)	O12–Eu2–N7	74.68(18)
N3–Sm1–N2	62.1(2)	O14–Sm2–O12	78.4(3)	N1–Eu1–N2	62.35(16)	O12–Eu2–N6	68.84(17)
N3–Sm1–N1	124.7(3)	O14–Sm2–O10	95.3(3)	N1–Eu1–N3	125.4(2)	N7–Eu2–N5	125.6(2)
N1–Sm1–N2	62.7(3)	O14–Sm2–N5	80.7(3)	O1–Eu1–N2	61.46(15)	N7–Eu2–N6	63.00(18)

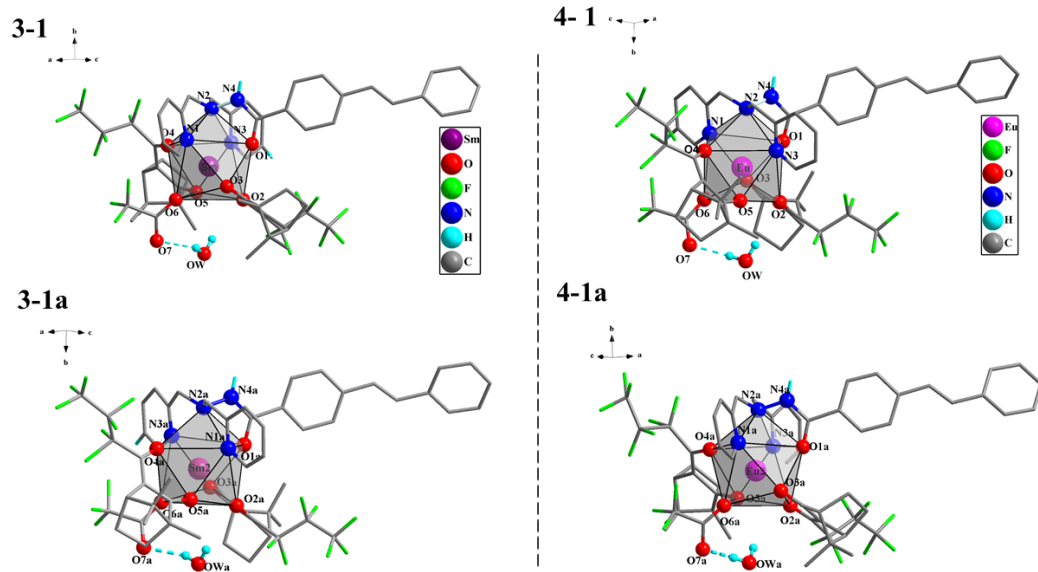
**Table S5. Hydrogen-bonding Geometry (Å and °)**

Compounds	Donor-H···accepter	D-H	H···A	D···A	D-H···A
<b>1</b>	Ow-H···O(7)	0.87	1.88	2.746(5)	171.7
	N(4)-H···Ow <sup>i</sup>	0.95	2.33	2.917(11)	119.2
<b>2</b>	Ow-H···O(7)	0.87	1.92	2.767(12)	165.2
	N(4)-H···Ow <sup>ii</sup>	0.88	2.11	2.852(13)	141.4
<b>3</b>	Ow-H···O(7)	0.85	1.96	2.725(12)	149.0
	N(4)-H···Ow <sup>iii</sup>	0.88	2.17	2.906(13)	140.6
<b>4</b>	Ow-H···O(7)	0.87	1.91	2.731(8)	155.9
	N(4)-H···Ow <sup>iv</sup>	0.88	2.16	2.899(9)	140.9

Symmetry code: (i) 1/2-X,-1/2+Y,1-Z; (ii) -1/2-X,-1/2+Y,-2-Z; (iii) 1/2-X,-1/2+Y,1-Z; (iv) 3/2-X,-1/2+Y,1-Z



**Figure S1. The polyhedron geometry of center La(III) of complex 1 (1a, 1b, left) and 2 (2a, 2b, right).**



**Figure S2. The Crystal structure and coordination polyhedron geometry of the two independent molecules of complexes 3 (3-1, 3-1a in left) and 4 (4-1, 4-1a in right) in the unit cell.**



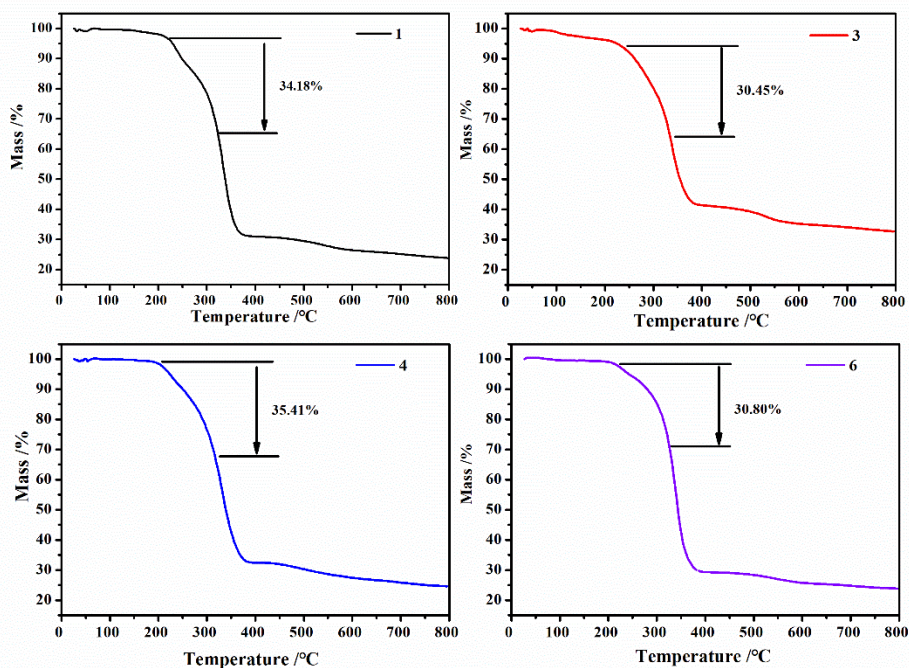


Figure S3. Thermogravimetric analysis (TGA) curves of complexes 1 (black), 3 (red), 4 (blue) and 5 (magenta).

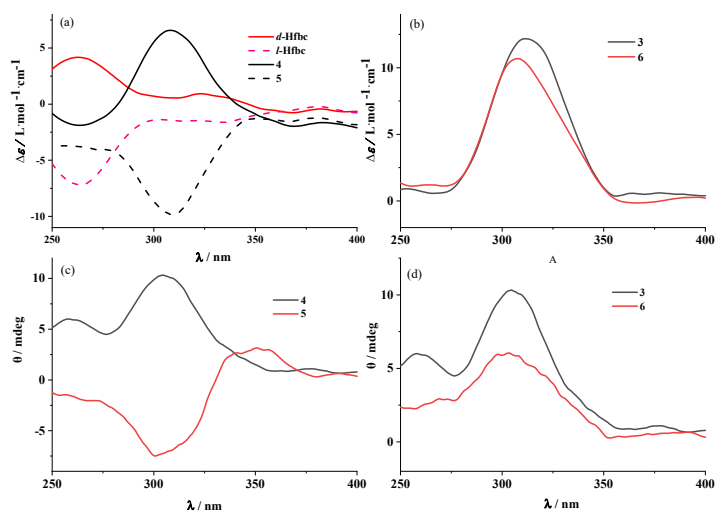
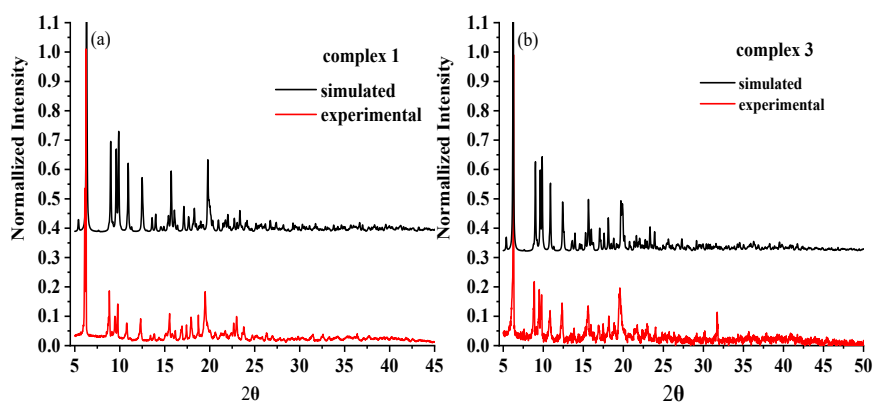
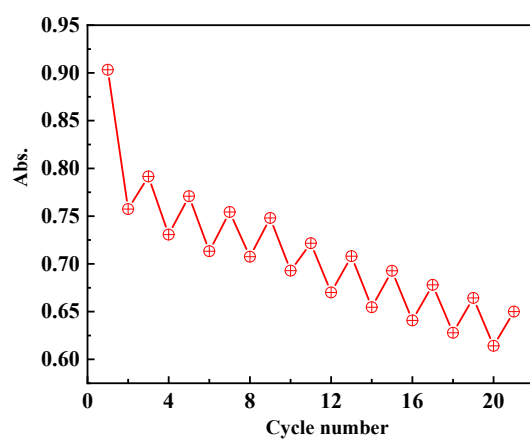


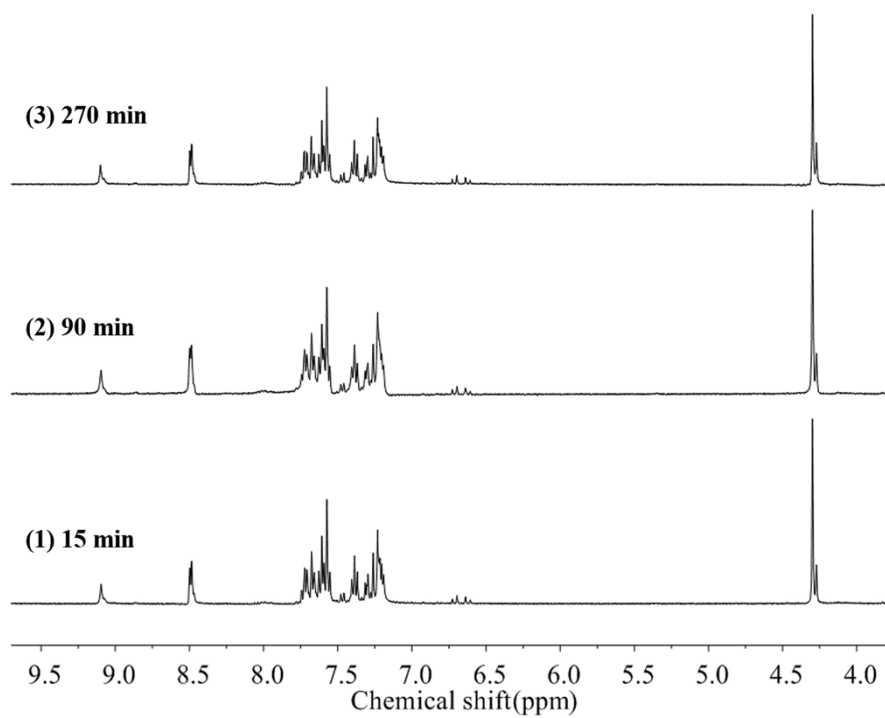
Figure S4. ECD spectra of *d/l*-Hfbc, complexes 4, 5 (a) and complexes 3, 6 (b) in acetonitrile solution, and complexes 4, 5 (c) and 3, 6 (d) in solid state, respectively.



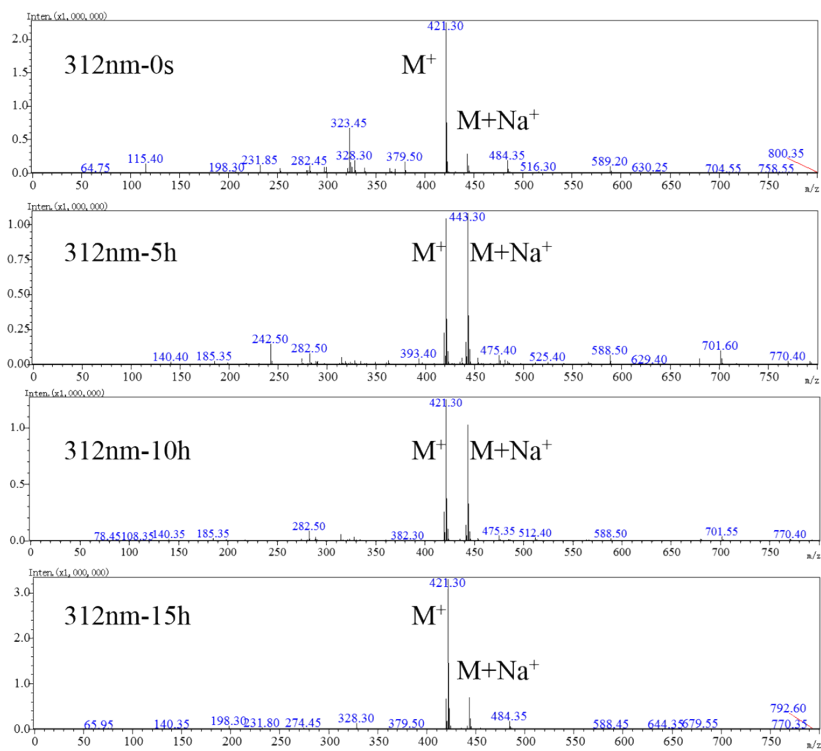
**Figure S5. Observed (Red) and calculated (Black) X-ray powder diffraction patterns of complexes 1 (a) and 3 (b).**



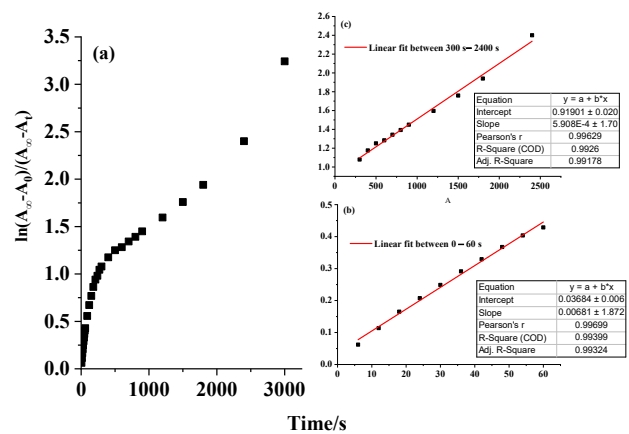
**Figure S6. Cycles of maximum absorption intensity at 319 nm of ligand L in acetonitrile solutions are modulated by the irradiation of UV light at 365 nm for 10 min and 254 nm for 5 min, alternatively.**



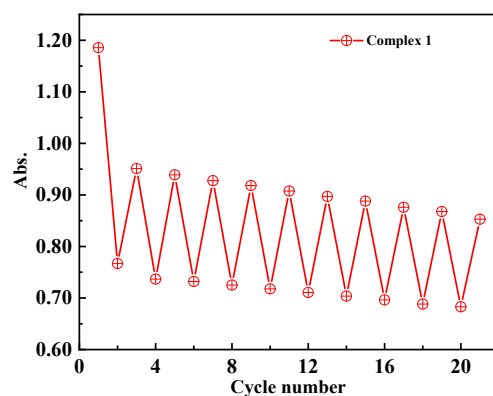
**Figure S7. Evolution of  $^1\text{H-NMR}$  spectra of L in acetonitrile- $d_3$  solution (after 365 nm light irradiation for 2 h) at 254 nm light with increasing irradiation time.**



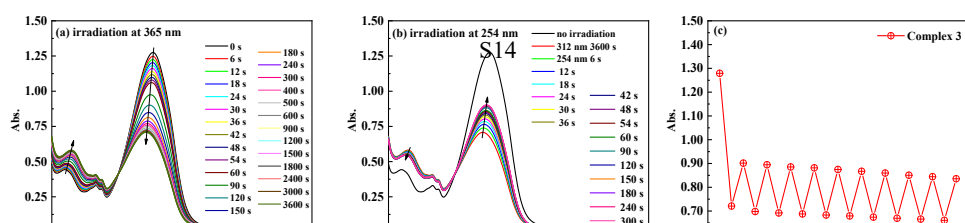
**Figure S8. Mass spectra of L in methanol solution exposed to 312 nm UV light in different irradiation time.**



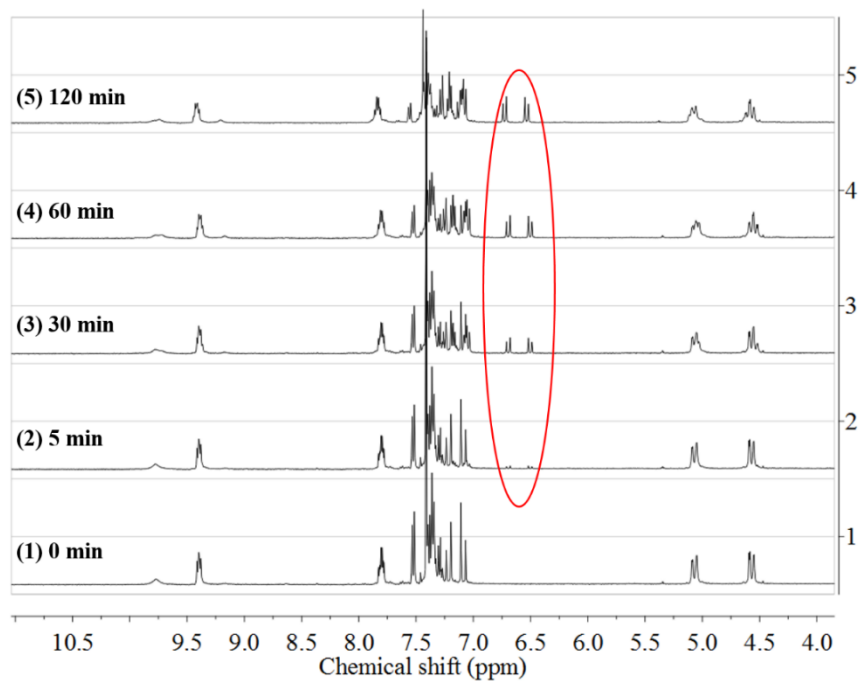
**Figure S9. The *trans* to *cis* photoisomerization and photocyclization reactional kinetics of  $\ln(A_{\infty}-A_0)/(A_{\infty}-A_t)$  as a function of time for L in acetonitrile solution.**



**Figure S10. Cycles of maximum absorption intensity at 324 nm of complex 1 in acetonitrile solution are modulated by the irradiation of UV light at 365 nm for 3 min and 254 nm for 5 min, alternatively.**

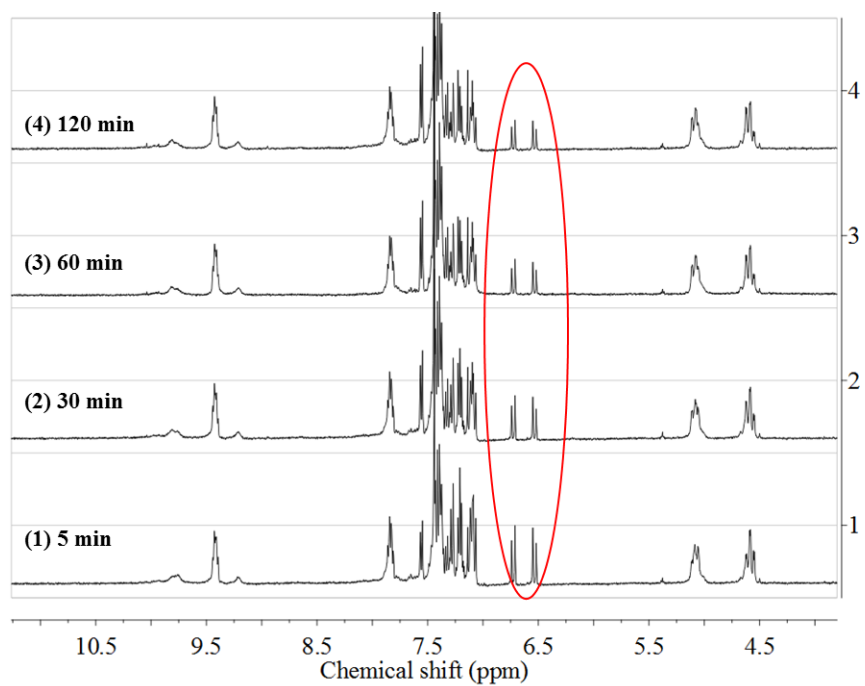


**Figure S11. UV-Vis spectral change of complexes 3 (a, b), 4 (e, f), 6 (h, j) in acetonitrile solutions ( $2.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ ) upon irradiation at UV-365 nm and recoverable irradiation at UV-254 nm as a function of time and cycles of maximum absorption intensity at 324 nm are modulated by the irradiation of UV light at 365 nm for 3 min and 254 nm for 5 min, alternatively (c for complex 3, g for complex 4, k for complex 6).**



**Figure S12. Evolution of  $^1\text{H-NMR}$  spectra of complex 1 in acetonitrile- $d_3$  solution at 365 nm light with increasing irradiation time.**





**Figure S13. Evolution of  $^1\text{H-NMR}$  spectra of complex 1 in acetonitrile- $d_3$  solution (after 365 nm light irradiation for 2 h) at 254 nm light with increasing irradiation time.**

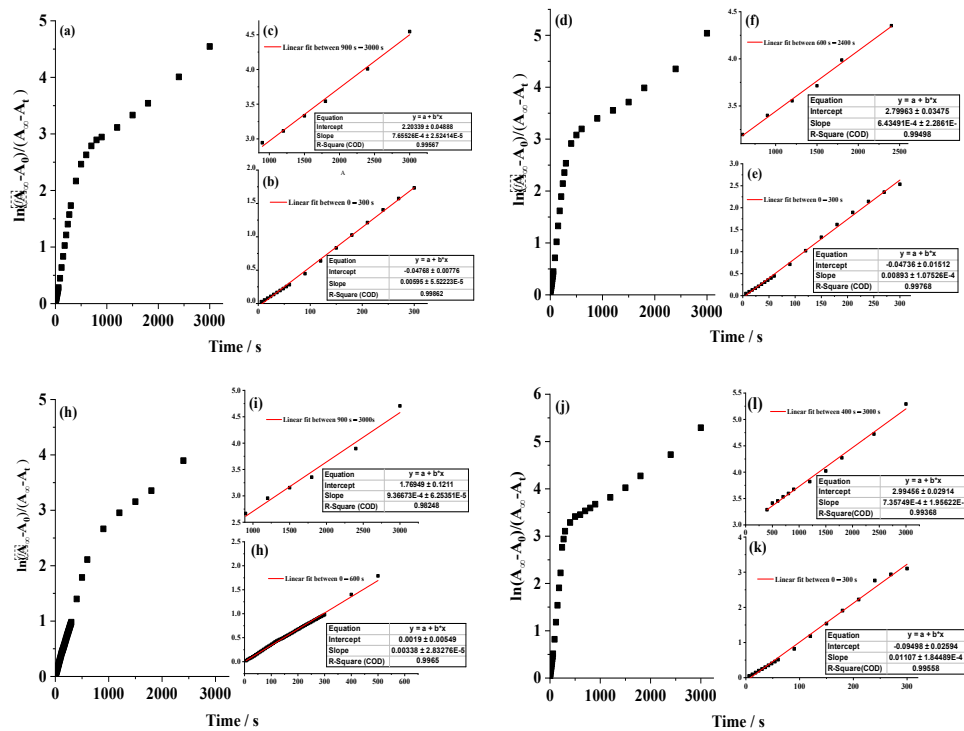
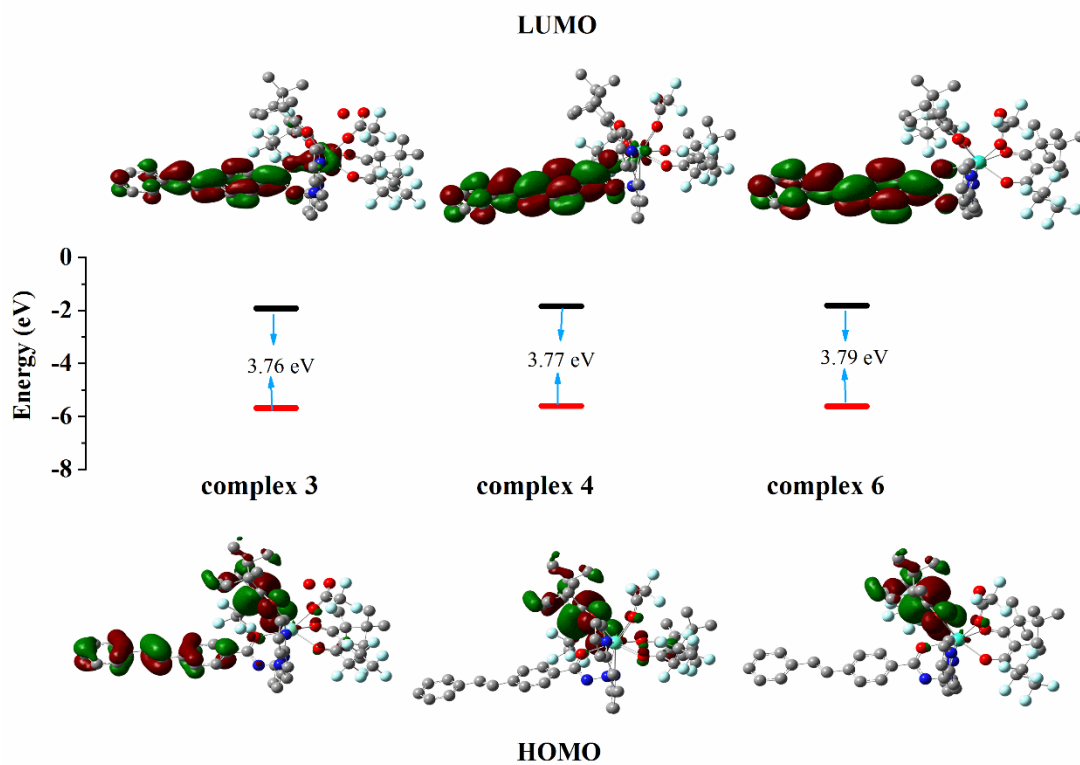


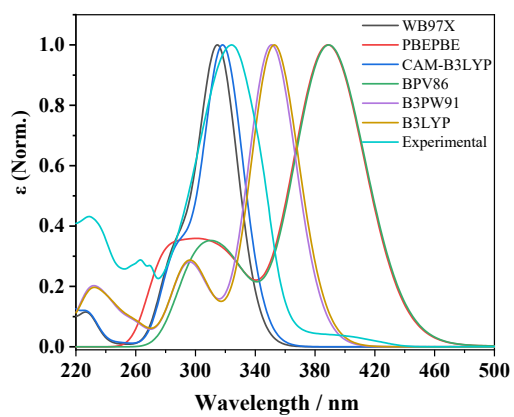
Figure S14. The *trans* to *cis* photoisomerization kinetics of  $\ln(A_{\infty} - A_0)/(A_{\infty} - A_t)$  as a function of time for complexes 1 (a, b, c), 3 (d, e, f), 4 (g, h, i), and 6 (j, k, l) in acetonitrile solutions.

**Table S6. The main structural geometric parameters obtained by the RB3LYP functional method for the optimization of complex 3 and the crystallographic data measured by single crystal X-ray diffractometer.**

Bond	Bond lengths (Å)		Bond	Bond angle (°)	
	measured	RB3LYP		measured	RB3LYP
Sm <sub>1</sub> -O <sub>1</sub>	2.460	2.495	O <sub>2</sub> -Sm <sub>1</sub> -N <sub>2</sub>	111.8	118.6
Sm <sub>1</sub> -O <sub>2</sub>	2.471	2.484	O <sub>6</sub> -Sm <sub>1</sub> -O <sub>2</sub>	73.9	71.6
Sm <sub>1</sub> -O <sub>3</sub>	2.375	2.353	O <sub>6</sub> -Sm <sub>1</sub> -O <sub>3</sub>	95.0	105.8
Sm <sub>1</sub> -O <sub>4</sub>	2.461	2.460	O <sub>6</sub> -Sm <sub>1</sub> -O <sub>4</sub>	75.1	76.9
Sm <sub>1</sub> -O <sub>5</sub>	2.393	2.392	O <sub>6</sub> -Sm <sub>1</sub> -O <sub>5</sub>	80.6	77.1
Sm <sub>1</sub> -O <sub>6</sub>	2.360	2.348	O <sub>6</sub> -Sm <sub>1</sub> -N <sub>2</sub>	135.3	128.7
Sm <sub>1</sub> -N <sub>1</sub>	2.645	2.724	O <sub>2</sub> -Sm <sub>1</sub> -N <sub>1</sub>	71.4	73.8
Sm <sub>1</sub> -N <sub>2</sub>	2.770	2.870	O <sub>3</sub> -Sm <sub>1</sub> -N <sub>2</sub>	129.5	125.3
Sm <sub>1</sub> -N <sub>3</sub>	2.621	2.728	O <sub>6</sub> -Sm <sub>1</sub> -N <sub>3</sub>	144.3	147.8
<i>Trans</i> C=C	1.310	1.351	N <sub>1</sub> -Sm <sub>1</sub> -N <sub>3</sub>	124.7	121.3



**Figure S15. HOMO and LUMO energy levels and orbital distributions of complexes 3, 4 and 6.**



**Figure S16. Overlay of calculated and experimental absorption spectra of the complex 1 in acetonitrile solutions.**

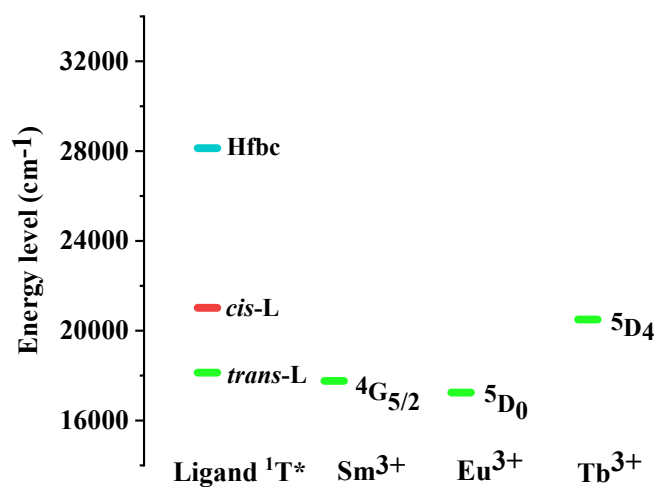


Figure S17. The energy levels of the first excited states of ligands *trans*-L, *cis*-L, Hfbc and the related energy levels of the Sm<sup>3+</sup>, Eu<sup>3+</sup> and Tb<sup>3+</sup>.

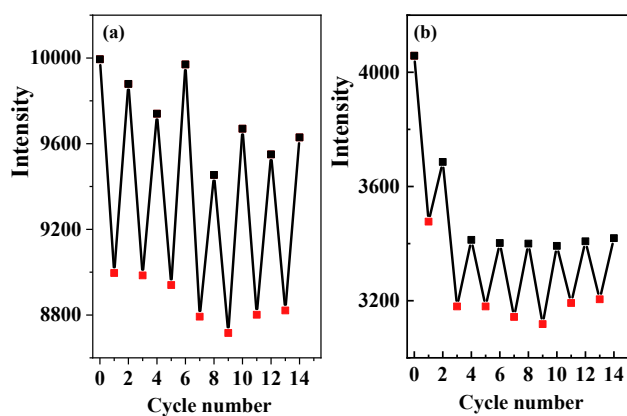


Figure S18. Cycles of maximum luminescence intensity at 420 nm are modulated by the irradiation of UV light at 365 nm for 2 min and 254 nm for 2 min, alternatively (a for complex 3, b for complex 4).