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Self-assembled Lanthanide-based Helixes: Synthetic Control of the Helical Handedness by Chirality of the Ligand

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Supporting Information

Experimental

X-ray Crystallographic Studies

Single crystals of complexes **1-6** suitable for X-ray diffraction measurements were mounted on an Oxford Xcalibur Sapphire-3 CCD Gemini diffractometer employing graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å), and intensity data were collected with ω scans. The data collection and reduction were performed with the CrysAlisPro software, and the absorptions were corrected by the SCALE3 ABSPACK multiscan method. The space-group determination was based on a check of the Laue symmetry and systematic absences, and it was confirmed using the structure solution. The structure was solved and refined with the Olex2 1.2-ac21 package. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms.

Circular Dichroism(CD), FT-IR spectroscopy and NMR Spectroscopy

The CD spectrum was recorded by Jasco J-815 Circular Dichroism (CD) Spectropolarimeter. Infrared spectra were recorded on all samples in the solid state under ambient conditions on a Nicolet iS5 FT-IR spectrometer in the 4000-400 cm^{-1} region. The background of the environment was eliminated by OMNIC software. ^1H NMR spectra were recorded on a Varian Mercury-400 (400 MHz for ^1H) spectrometer

Measurements of triboluminescence

The luminescence was measured by a photomultiplier (PMT R94-03, Hamamatsu) in analog mode at room temperature. While grinding the crystal of samples in a glass tube using a stainless-steel rod, the emitted photons were recorded by a digital oscilloscope (LeCroy, WaveRunner 610Zi) with 1 GS/s sampling rate in a darkroom without any pre-amplification (Figure S13). The time-resolved profile indicated the intensity of the emission decayed in 1000 ns.

Synthesis of ligand and complexes 1-6

(2R,4S)-2-(2-hydroxy-3,5-dinitrophenyl)thiazolidine-4-carboxylic acid (L^{RS}/L^{SS})

The methanol (30 ml) solution contained D-cysteine (0.001 mol, 0.121 g) was mixed with a solution of 3,5-dinitrosalicylaldehyde (0.001 mol, 0.195 g) in methanol (30 ml). After stirred 6 hr, the product, a yellow powder, was filtered, washed with methanol and dried in vacuo. The product contains two diastereomers (L^{RS}/L^{SS}). NMR (DMSO-d6, 400 MHz): 8.57 (d, 1H), 8.27 (d, 1H), 5.98 (s, 1H), 4.72(t,1H), 3.53-3.45(m, 2H). Select IR data (cm^{-1}):1735.53(m), 1615.83(m), 1575.40(w), 1537.19(m), 1495.83(m), 1424.82(m), 1394.11(m), 1334.84(w), 1312.03(w), 1276.83(w), 1224.64(w), 1201.66(w), 1171.19(w), 1094.34(m), 1061.08(m), 1028.60(s), 995.32(s), 929.42(m), 914.86(m), 846.70(s), 833.29(s), 795.72(w), 763.07(m), 742.60(m), 719.26(m), 709.08(m), 685.11(s), 648.56(s), 630.08(m), 600.24(m), 567.23(m).

(2S,4R)-2-(2-hydroxy-3,5-dinitrophenyl)thiazolidine-4-carboxylic acid (L^{SR}/L^{RR})

The methanol (30 ml) solution contained L-cysteine (0.001 mol, 0.121 g) was mixed with a solution of 3,5-dinitrosalicylaldehyde (0.001 mol, 0.195 g) in methanol (30 ml). After stirred 6 hr, the product, a yellow powder, was filtered, washed with methanol and dried in vacuo. The product contains two diastereomers (L^{SR}/L^{RR}). NMR (DMSO-d6, 400 MHz): 8.57 (d, 1H), 8.27 (d, 1H), 5.98 (s, 1H), 4.73(t,1H), 3.53-3.45(m, 2H). Select IR data (cm^{-1}): 1737.43(m), 1614.95(m), 1574.80(m), 1537.76(m), 1495.57(m), 1471.25(s), 1425.24(m), 1392.63(m), 1334.75(w), 1311.60(w), 1276.42(w), 1224.57(w), 1201.42(w), 1170.88(w), 1094.39(m), 1060.93(m), 1028.83(s), 995.28(s), 929.46(m), 914.77(m), 795.73(w), 763.12(s), 742.58(m), 719.15(m), 708.95(m), 684.96(s), 647.57(s), 630.35(s), 598.49(s), 567.11(m).

$[Sm_2(L^{RS})_3(H_2O)_5]\cdot 3H_2O$ (Complex $1\cdot 3H_2O$)

To a solution of $SmCl_3\bullet 6H_2O$ (0.125 mmol) in EtOH (15 mL) was added to a solution of 3,5-dinitrosalicylaldehyde (0.125 mmol) and D-cysteine (0.125 mmol) in EtOH/H_2O (15 ml/5 ml) was treated with 1 equivalents of pyridine. The resulting yellow solution yielded rectangular, yellow crystals of the helical chain complex after one night. (yield: 31.7%) The structure of the helical chain complex, Δ-Form $[Sm_2(L^{RS})_3(H_2O)_5]_\infty\cdot 3H_2O$, crystallized in the Orthorhombic $P2_12_12_1$ space group. This complex also can be synthesized by added L^{RS}/L^{SS} (0.125 mmol) as a ligand. To a solution of $SmCl_3\bullet 6H_2O$ (0.125 mmol) in EtOH (15 mL) was added a solution of L^{RS}/L^{SS} (0.125 mmol) and 1 equivalents of pyridine in EtOH/H_2O (15 ml/5 ml). The resulting yellow solution gave well-formed rectangular, yellow crystals of the helical chain complex after one night. (yield: 28.6%) Select IR data (cm^{-1}): 1593.41(s), 1574.12(s), 1520.86(s), 1490.67(m), 1469.94(m), 1431.39(w), 1403.71(w), 1359.92(m), 1317.98(s), 1276.13(s), 1169.89(m), 1149.11(w), 1074.02(m), 1002.14(w), 934.86(m), 924.39(w), 907.32(m), 893.67(m), 841.84(m), 806.28(w),

790.14(m), 747.68(m), 731.72(m), 707.05(s), 629.24(m), 578.18(w), 559.36(w). Anal. Calcd. for $C_{30}H_{36}N_9O_{29}S_3Sm_2$: C, 26.02; H, 2.69; N, 9.10. Found: C, 26.07; H, 2.69; N, 9.05. CCDC reference number: 2092895

$[Eu_2(L^{RS})_3(H_2O)_5]\cdot 3H_2O$ (Complex 2·3H_2O)

To a solution of $EuCl_3$•6H_2O (0.125 mmol) in EtOH (15 mL) was added to a solution of 3,5-dinitrosalicylaldehyde (0.125 mmol) and D-cysteine (0.125 mmol) in EtOH/H_2O (15 ml/5 ml) was treated with 1 equivalents of pyridine. The resulting yellow solution yielded rectangular, yellow crystals of the helical chain complex after one night. (yield: 34.1%) The structure of the helical chain complex, Δ-Form $[Eu_2(L^{RS})_3(H_2O)_5]_\infty\cdot 3H_2O$, crystallized in the Orthorhombic $P2_12_12_1$ space group. This complex also can be synthesized by added L^{RS}/L^{SS} (0.125 mmol) as a ligand. To a solution of $EuCl_3$•6H_2O (0.125 mmol) in EtOH (15 mL) was added a solution of L^{RS}/L^{SS} (0.125 mmol) and 1 equivalents of pyridine in EtOH/H_2O (15 ml/5 ml). The resulting yellow solution gave well-formed rectangular, yellow crystals of the helical chain complex after one night. (yield: 33.1%) Select IR data (cm^{-1}): 1594.10(w),1573.96(w), 1520.18(w), 1493.99(m), 1470.47(m), 1455.36(s), 1432.55(s), 1403.07(s), 1360.14(s), 1317.63(w), 1276.16(w), 1248.26(m), 1170.12(m), 1149.46(s), 1074.12(m), 1002.57(s), 956.07(s), 934.78(m), 924.36(m), 907.57(m), 893.93(m), 841.89(m), 806.64(s), 790.30(m), 747.84 (m), 732.02(m), 706.90(w), 657.85(m), 628.51(m), 564.24(s). Anal. Calcd. for $C_{30}H_{34}N_9O_{29}S_3Eu_2$: C, 25.96; H, 2.69; N, 9.08. Found: C, 25.97; H, 2.73; N, 8.95. . CCDC reference number: 2092896.

$[Tb_2(L^{RS})_3(H_2O)_5]\cdot 3H_2O$ (Complex 3·3H_2O)

To a solution of $TbCl_3$•6H_2O (0.125 mmol) in EtOH (15 mL) was added to a solution of 3,5-dinitrosalicylaldehyde (0.125 mmol) and D-cysteine (0.125 mmol) in EtOH/H_2O (15 ml/5 ml) was treated with 1 equivalents of pyridine. The resulting yellow solution yielded rectangular, yellow crystals of the helical chain complex after one night. (yield: 20.3%) The structure of the helical chain complex, Δ-Form $[Tb_2(L^{RS})_3(H_2O)_5]_\infty\cdot 3H_2O$, crystallized in the Orthorhombic $P2_12_12_1$ space group. This complex also can be synthesized by added L^{RS}/L^{SS} (0.125 mmol) as a ligand. To a solution of $TbCl_3$•6H_2O (0.125 mmol) in EtOH (15 mL) was added a solution of L^{RS}/L^{SS} (0.125 mmol) and 1 equivalents of pyridine in EtOH/H_2O (15 ml/5 ml). The resulting yellow solution gave well-formed rectangular, yellow crystals of the helical chain complex after one night. (yield: 12.5%) Select IR data (cm^{-1}): 1596.83(w), 1576.55(w), 1523.02(w), 1491.74(w), 1471.81(m), 1432.52(m), 1404.81(m), 1319.08(w), 1277.87(w), 1171.56(m), 1150.49(s), 1082.94(m), 1004.41(s), 936.32(m), 897.04(m), 868.40(m), 843.80(m), 808.30(s), 791.35(m), 748.21(m), 732.76(m), 708.35(w), 653.61(m), 644.66(m), 635.19(w), 627.57(m), 618.59(m), 608.99(m), 601.03(s), 591.15(s), 582.77(m), 572.28(s), 563.42(s). Anal. Calcd. for $C_{30}H_{34}N_9O_{29}S_3Tb_2$: C, 25.71; H, 2.66; N, 8.99. Found: C, 26.02; H, 2.80; N, 8.68. CCDC reference number: 2116474.

$[Sm_2(L^{SR})_3(H_2O)_5]\cdot 3H_2O$ (Complex 4·$3H_2O$)

To a solution of $SmCl_3$•$6H_2O$ (0.125 mmol) in EtOH (15 mL) was added to a solution of 3,5-dinitrosalicylaldehyde (0.125 mmol) and L-cysteine (0.125 mmol) in EtOH/H_2O (15 ml/5 ml) was treated with 1 equivalents of pyridine. The resulting yellow solution yielded rectangular, yellow crystals of the helical chain complex after one night. (yield: 33.7%) The structure of the helical chain complex, Λ-Form $[Sm_2(L^{SR})_3(H_2O)_5]_\infty\cdot 3H_2O$, crystallized in the Orthorhombic $P2_12_12_1$ space group. This complex also can be synthesized by added L^{SR}/L^{RR} (0.125 mmol) as a ligand. To a solution of $SmCl_3$•$6H_2O$ (0.125 mmol) in EtOH (15 mL) was added a solution of L^{SR}/L^{RR} (0.125 mmol) and 1 equivalents of pyridine in EtOH/H_2O (15 ml/5 ml). The resulting yellow solution gave well-formed rectangular, yellow crystals of the helical chain complex after one night. (yield: 31.4%) Select IR data (cm^{-1}): 1592.44(s), 1574.38(s), 1520.18(s), 1494.51(m), 1470.27(m), 1455.48(w), 1432.05(w), 1403.31(w), 1360.14(m), 1317.49(s), 1276.52(s), 1248.46(m), 1169.86(m), 1149.57(w), 1074.09(m), 1001.85(w), 955.43(w), 934.61(w), 924.50(w), 907.88(m), 893.73(m), 841.72(m), 806.35(m), 790.08(m), 747.62(m), 731.83(m), 706.43(s), 625.43(s), 592.68(m), 574.58(m). Anal. Calcd. for $C_{30}H_{36}N_9O_{29}S_3Sm_2$: C, 26.02; H, 2.69; N, 9.10. Found: C, 26.01; H, 2.67; N, 9.04. CCDC reference number: 2092897.

$[Eu_2(L^{SR})_3(H_2O)_5]\cdot 3H_2O$ (Complex 5·$3H_2O$)

To a solution of $EuCl_3$•$6H_2O$ (0.125 mmol) in EtOH (15 mL) was added to a solution of 3,5-dinitrosalicylaldehyde (0.125 mmol) and L-cysteine (0.125 mmol) in EtOH/H_2O (15 ml/5 ml) was treated with 1 equivalents of pyridine. The resulting yellow solution yielded rectangular, yellow crystals of the helical chain complex after one night. (yield: 38.7%) The structure of the helical chain complex, Λ-Form $[Eu_2(L^{SR})_3(H_2O)_5]_\infty\cdot 3H_2O$, crystallized in the Orthorhombic $P2_12_12_1$ space group. This complex also can be synthesized by added L^{SR}/L^{RR} (0.125 mmol) as a ligand. To a solution of $EuCl_3$•$6H_2O$ (0.125 mmol) in EtOH (15 mL) was added a solution of L^{SR}/L^{RR} (0.125 mmol) and 1 equivalents of pyridine in EtOH/H_2O (15 ml/5 ml). The resulting yellow solution gave well-formed rectangular, yellow crystals of the helical chain complex after one night. (yield: 36.5%) Select IR data (cm^{-1}): 1595.25(w)1576.06(w), 1521.59(w), 1490.78(m), 1471.63(m), 1457.40(s), 1431.73(s), 1404.61(m), 1317.83(w), 1276.19(w), 1248.94(w), 1170.64(m), 1150.15(s), 1075.04(w), 1003.37(s), 935.45(m), 924.83(m), 907.96(m), 894.18(m), 842.26(m), 807.06(m), 790.40(m), 748.03(m), 732.43(m), 707.08(w), 668.13 (m), 653.33(m), 628.51(m), 607.4(m), 585.47(s), 576.77(s), 564.77(s), 552.01(s). Anal. Calcd. for $C_{30}H_{39}N_9O_{29}S_3Eu_2$: C, 25.96; H, 2.69; N, 9.08. Found: C, 26.10; H, 2.69; N, 9.02. CCDC reference number: 2092898.

$[Tb_2(L^{SR})_3(H_2O)_5]\cdot 3H_2O$ (Complex 6·3H_2O)

To a solution of $TbCl_3$•6H_2O (0.125 mmol) in EtOH (15 mL) was added to a solution of 3,5-dinitrosalicylaldehyde (0.125 mmol) and L-cysteine (0.125 mmol) in EtOH/H_2O (15 ml/5 ml) was treated with 1 equivalents of pyridine. The resulting yellow solution yielded rectangular, yellow crystals of the helical chain complex after one night. (yield: 22.8%) The structure of the helical chain complex, Λ-Form $[Tb_2(L^{SR})_3(H_2O)_5]_\infty\cdot 3H_2O$, crystallized in the Orthorhombic $P2_12_12_1$ space group. This complex also can be synthesized by added L^{SR}/L^{RR} (0.125 mmol) as a ligand. To a solution of $TbCl_3$•6H_2O (0.125 mmol) in EtOH (15 mL) was added a solution of L^{SR}/L^{RR} (0.125 mmol) and 1 equivalents of pyridine in EtOH/H_2O (15 ml/5 ml). The resulting yellow solution gave well-formed rectangular, yellow crystals of the helical chain complex after one night. (yield: 15.6%) Select IR data (cm^{-1}): 1595.45(m), 1574.52(s), 1522.14(w), 1491.65(m), 1470.79(s), 1432.01(s), 1403.50(s), 1360.33(s), 1317.83(w), 1277.09(m), 1249.31(m), 1170.67(m), 1150.33(s), 1075.14(m), 1004.44(s), 957.56(s), 935.92(s), 924.63(s), 910.19(m), 895.13(m), 868.02(s), 842.80(m), 807.51(s), 790.88(m), 747.93(m), 732.33(m), 707.36(w), 626.42(m). Anal. Calcd. for $C_{30}H_{39}N_9O_{29}S_3Tb_2$: C, 25.71; H, 2.66; N, 8.99. Found: C, 25.85; H, 2.68; N, 8.95. CCDC reference number: 2116475.

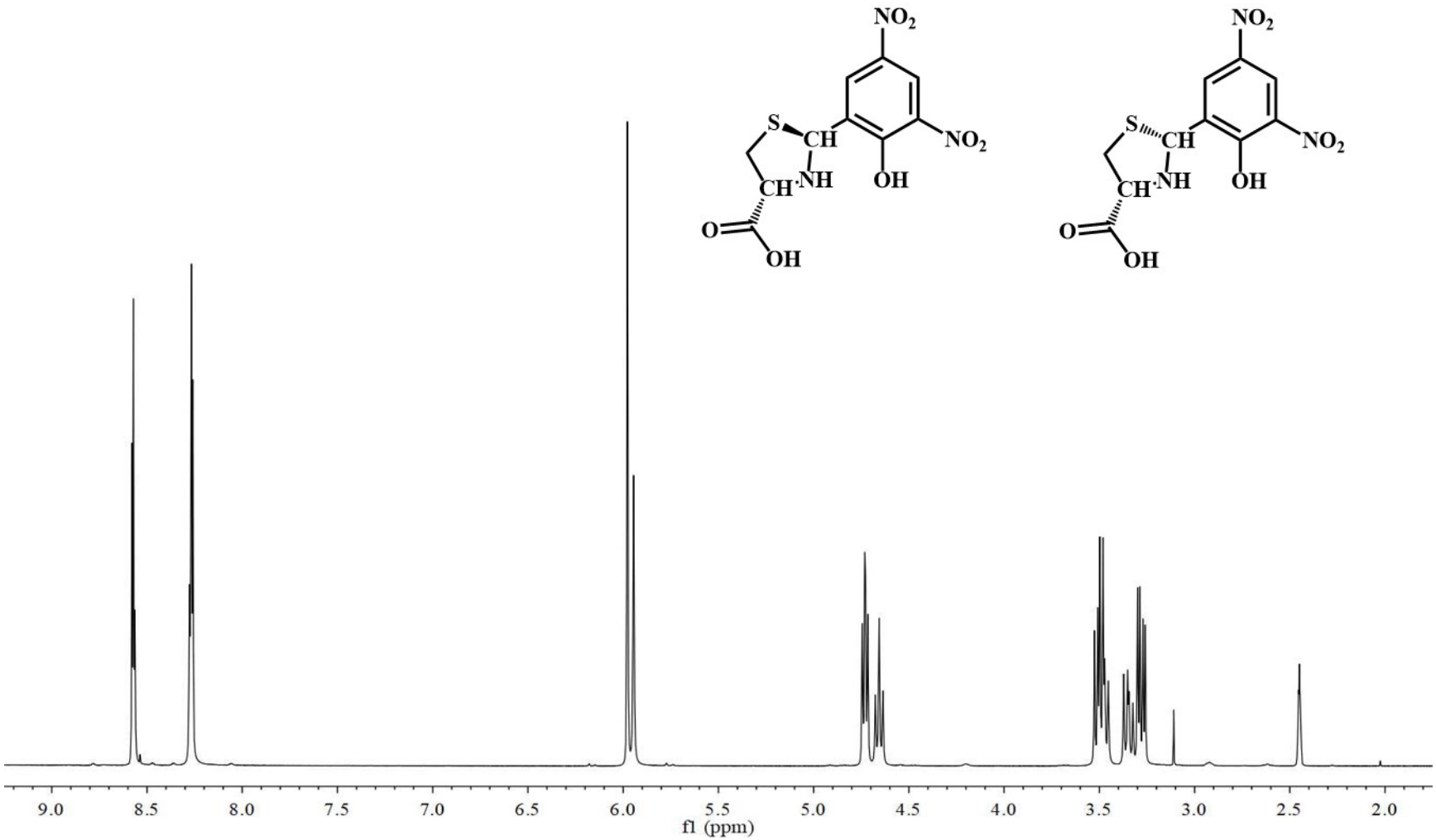


Figure S1. 1H NMR spectra of 2-(2-hydroxy-3,5-dinitrophenyl)thiazolidine-4-carboxylic acid of L^{SR} and L^{RR}.

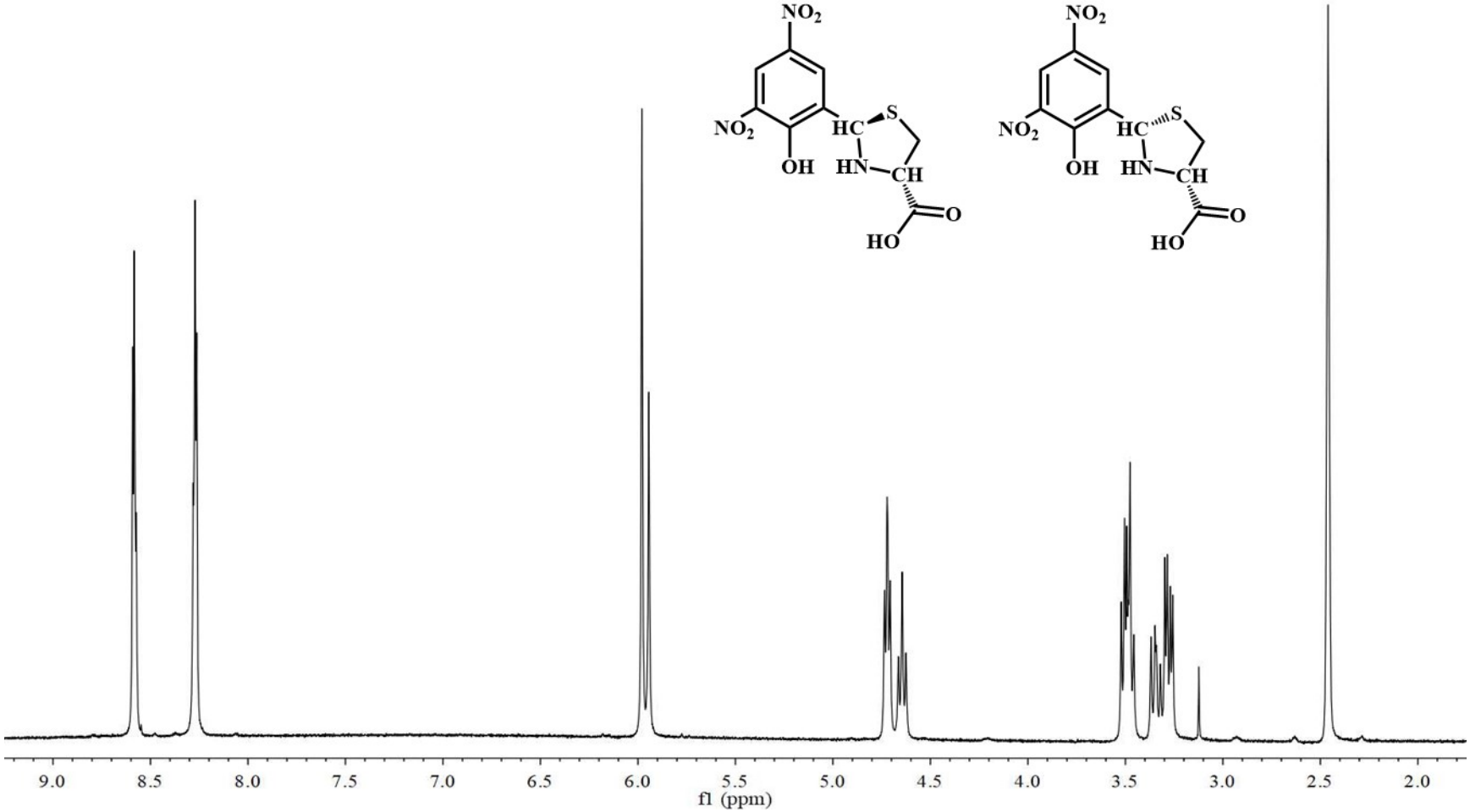
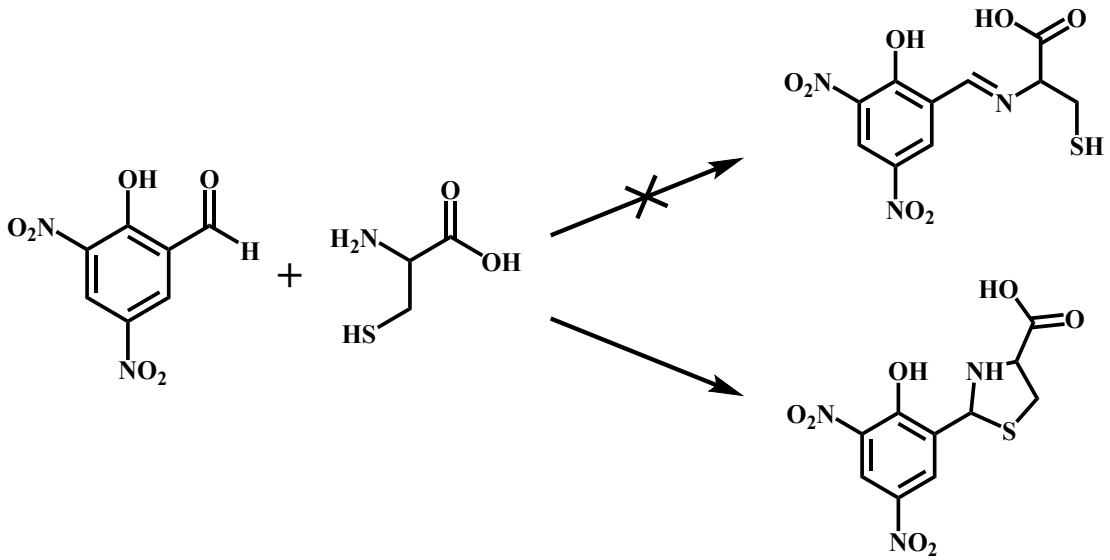


Figure S2. ^{1}H NMR spectrum of 2-(2-hydroxy-3,5-dinitrophenyl)thiazolidine-4-carboxylic acid of L^{RS} and L^{SS}



Scheme S1. Synthetic route for Cysteine reacted with 3,5-dinitrosalicylaldehyde to form heterocyclic thiazolidine.

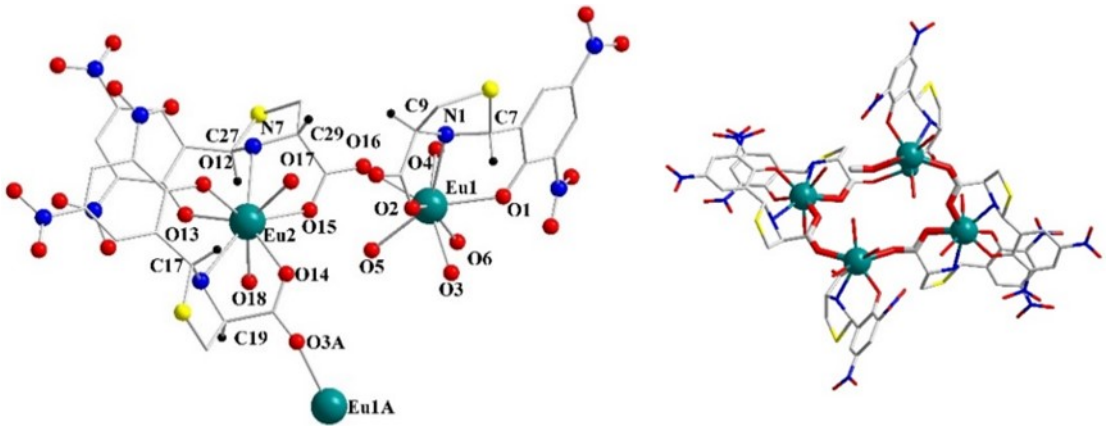


Figure S3. The molecular structure of complex **2** (right). Symmetry equivalent positions denoted by an "A" in the label. Color code: Nile blue (Eu), Red (O), Blue (N) and Yellow (S). Perspective view of the single-stranded helix along the 4_1 screw axis of complex **2** (right).

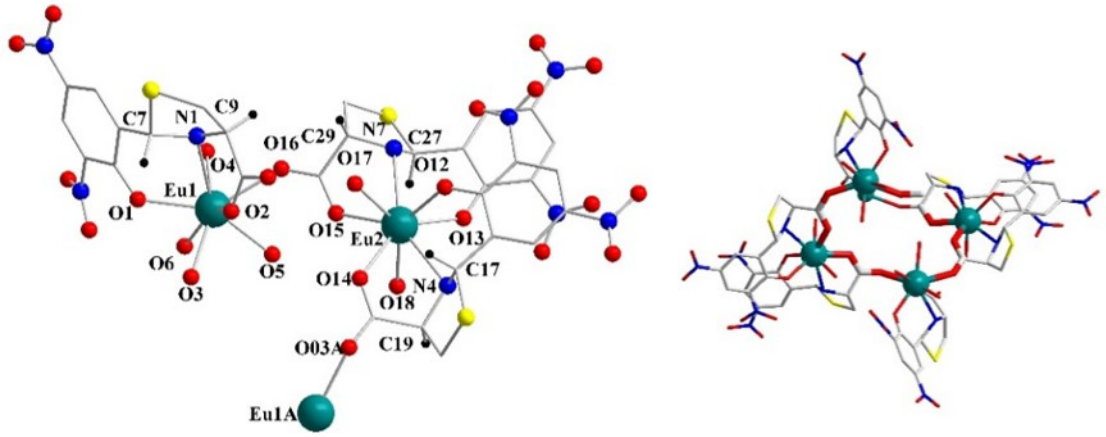


Figure S4. The molecular structure of complex **4** (left). Symmetry equivalent positions denoted by an "A" in the label. Color code: Nile blue (Eu), Red (O), Blue (N) and Yellow (S). Perspective view of the single-stranded helix along the 4_3 screw axis of complex **4** (left).

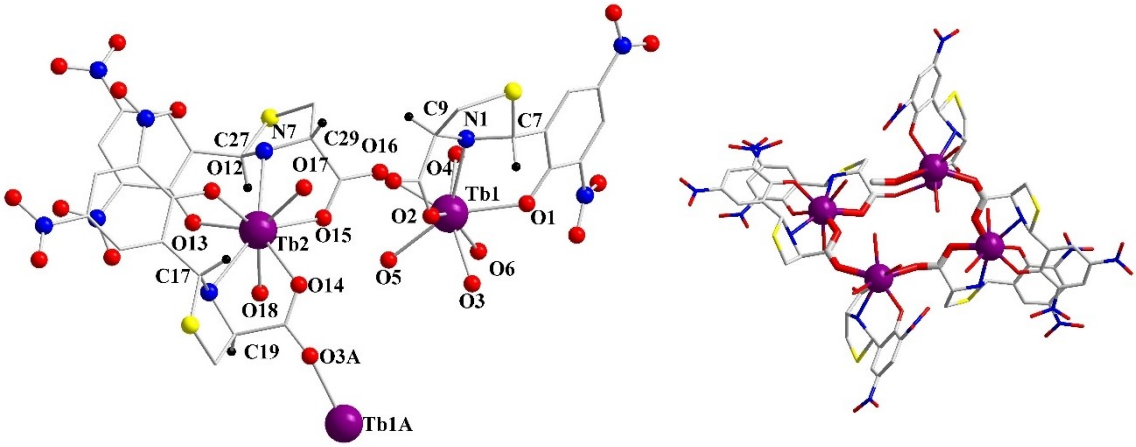


Figure S5. The molecular structure of complex **3** (left). Symmetry equivalent positions denoted by an "A" in the label. Color code: Purple (Tb), Red (O), Blue (N) and Yellow (S). Perspective view of the single-stranded helix along the 4_3 screw axis of complex **3**(left).

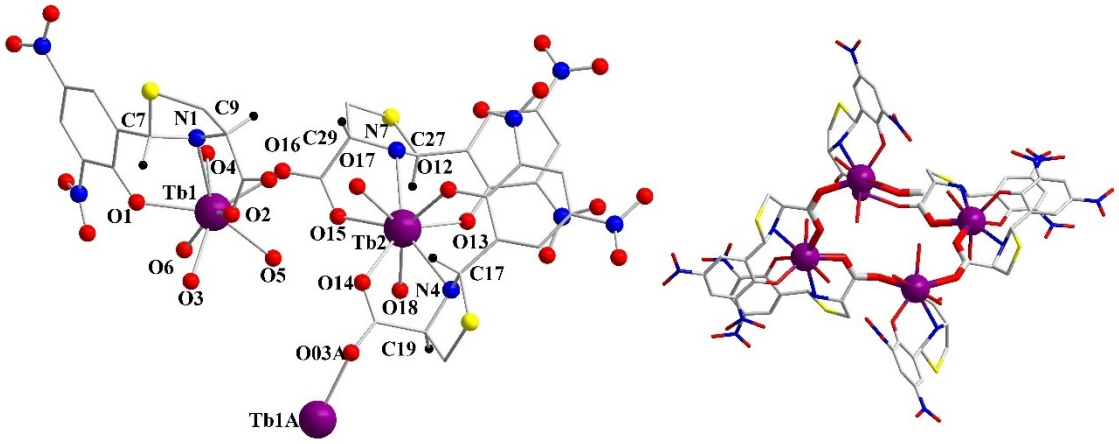


Figure S6. The molecular structure of complex **6** (left). Symmetry equivalent positions denoted by an "A" in the label. Color code: Purple (Tb), Red (O), Blue (N) and Yellow (S). Perspective view of the single-stranded helix along the 4_3 screw axis of complex **6**(left).

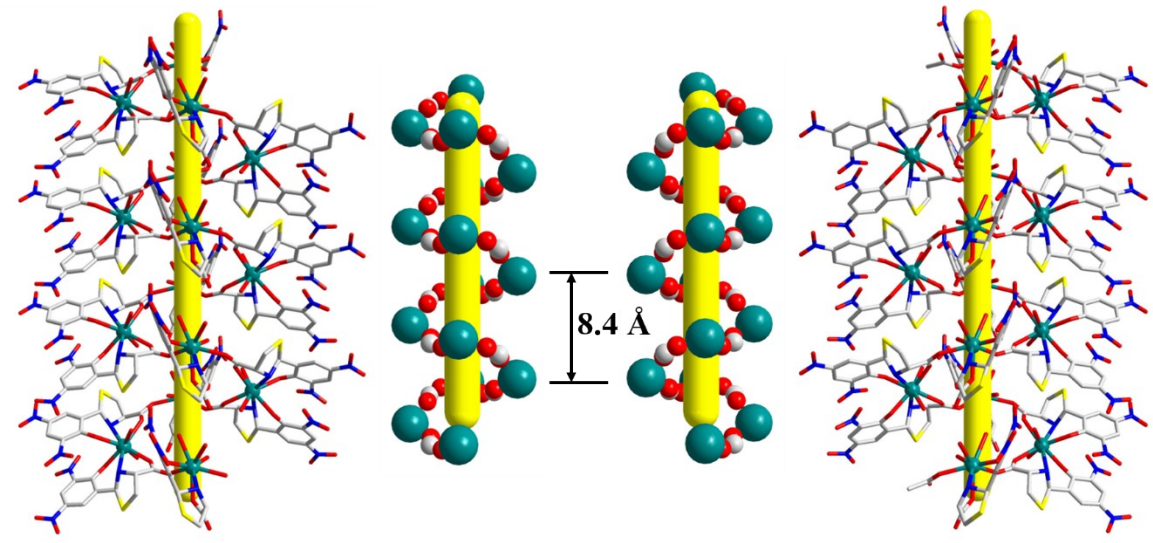


Figure S7. Perspective and space-filling views of the helical structures of complexes **2** (right) and **5** (left).

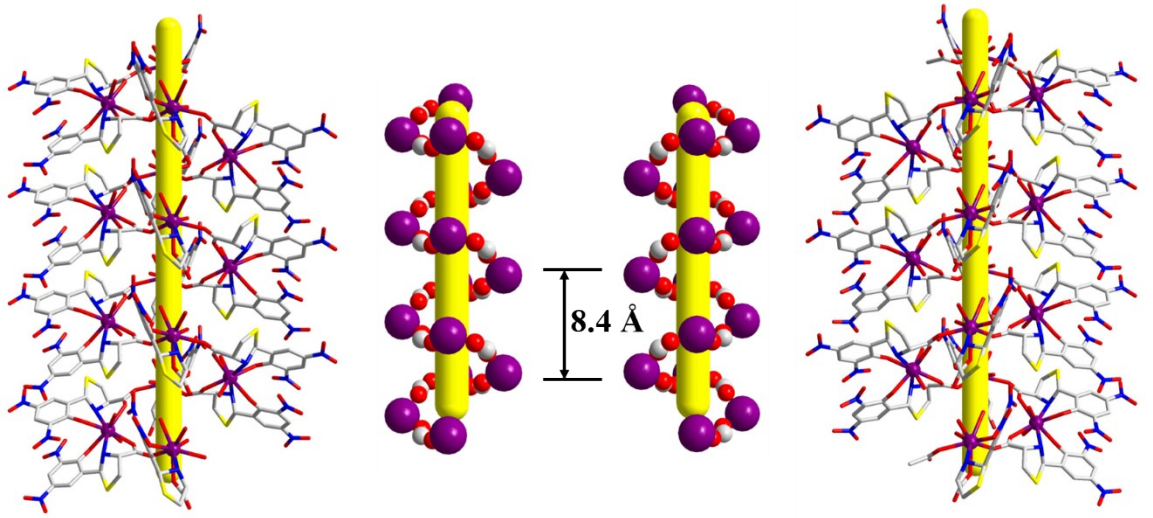


Figure S8. Perspective and space-filling views of the helical structures of complexes **3** (right) and **6** (left).

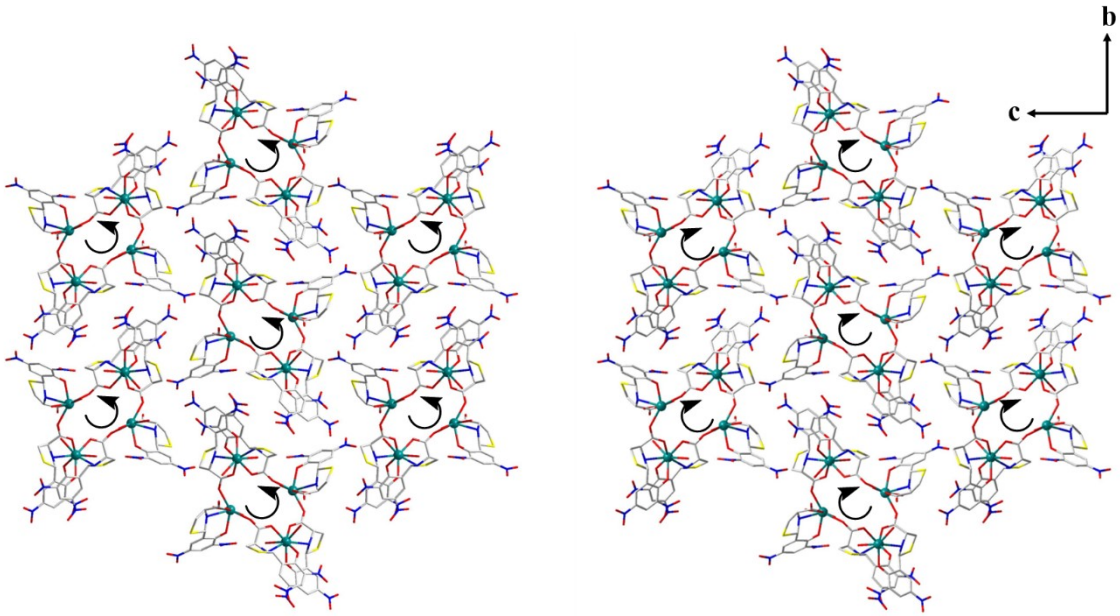


Figure S9. The packing arrangements of **1** (right) and **4** (left) viewed along the **a** axis. The hydrogen atoms and solvent molecules are omitted for clarity.

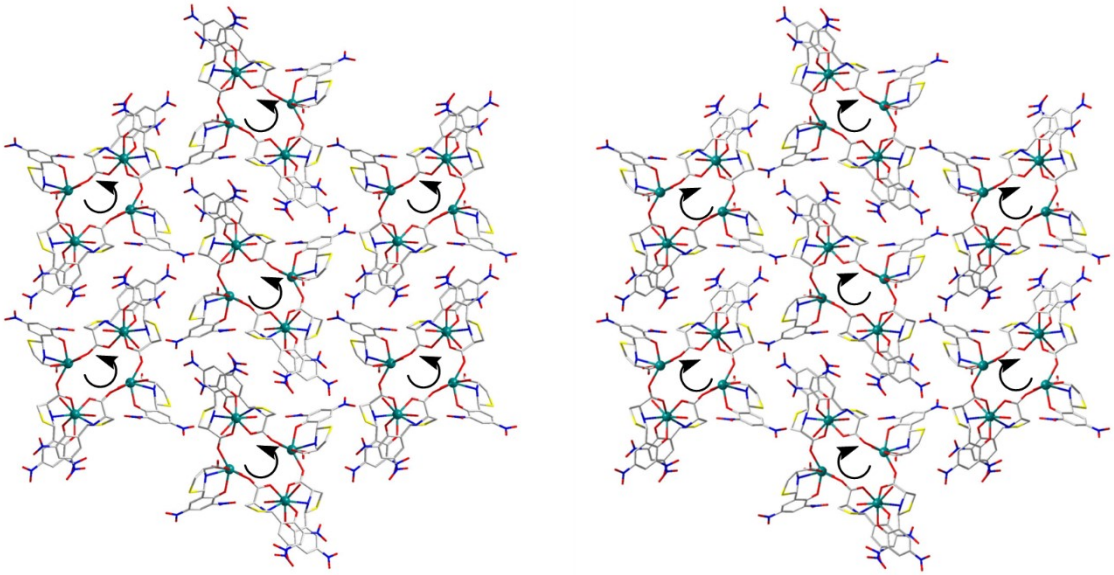


Figure S10. The packing arrangements of **2** (right) and **5** (left) viewed along the **a** axis. The hydrogen atoms and solvent molecules are omitted for clarity.

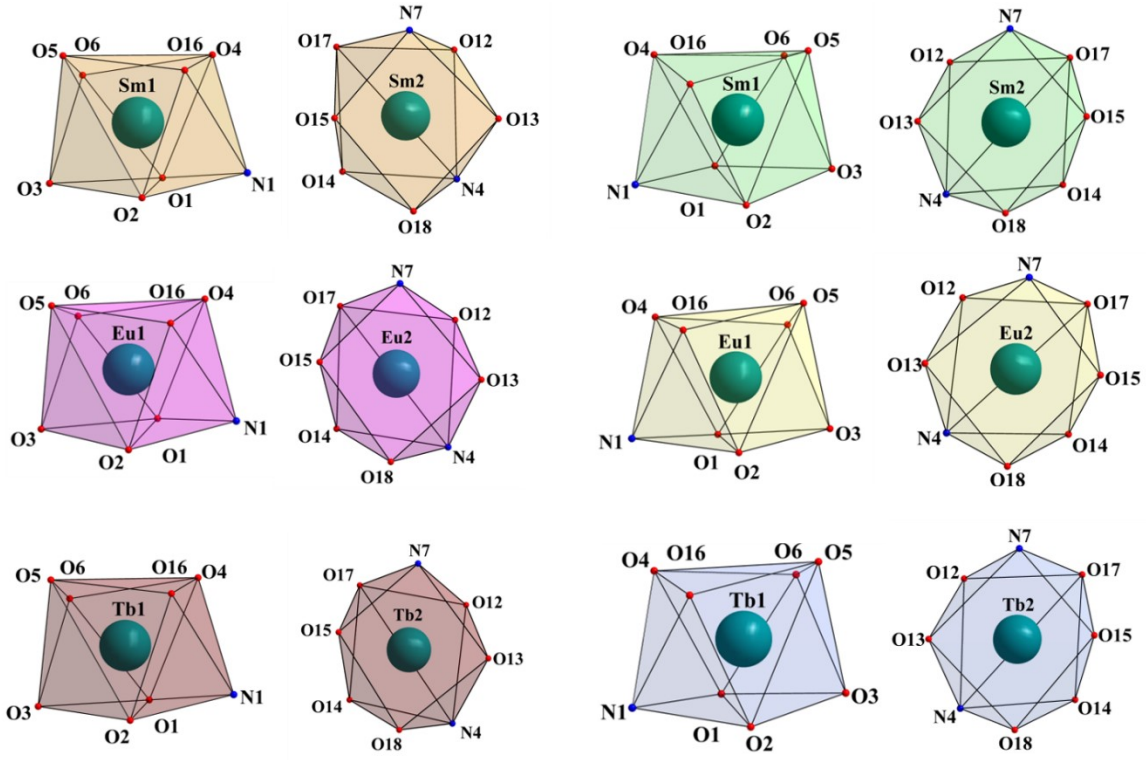


Figure S11. (Top) The coordination geometry of Sm^{III} centers in complexes **1** and **4**; (mid) The coordination geometry of Eu^{III} in complexes **2** and **5**; (Bottom) The coordination geometry of Tb^{III} in complexes **3** and **6**.

Table S1. Summary of SHAPE analysis for complexes **1, 2, 3, 4, 5 and 6.**

Vertices	Code	Label	Shape	Symmetry
8	1	OP-8	Octagon	D8h
	2	HPY-8	Heptagonal pyramid	C7v
	3	HBPY-8	Hexagonal bipyramid	D6h
	4	CU-8	Cube	Oh
	5	SAPR-8	Square antiprism	D4d
	6	TDD-8	Triangular dodecahedron	D2d
	7	JGBF-8	Johnson - Gyrobifastigium (J26)	D2d
	8	JETBPY-8	Johnson - Elongated triangular bipyramid (J14)	D3h
	9	JBTP-8	Johnson - Biaugmented trigonal prism (J50)	C2v
	10	BTPR-8	Biaugmented trigonal prism	C2v
	11	JSD-8	Snub disphenoid (J84)	D2d
	12	TT-8	Triakis tetrahedron	Td
	13	ETBPY-8	Elongated trigonal bipyramid (see 8)	D3h

Complex 1 Eight coordinate Sm^{III} center

	OP -8	HPY -8	HBPY -8	CU -8	SAPR -8	TDD -8	JGBF -8	JETBPY -8	JBTPR -8	BTPR -8	JSD -8	TT -8	ETBPY -8
Sm1	30.285	23.209	14.614	8.979	1.541	0.995	14.856	25.094	2.585	2.307	3.307	9.652	21.320
Sm2	31.694	21.685	16.602	10.310	0.883	2.638	15.671	25.207	2.742	2.645	4.450	11.023	22.447

Complex 2 Eight coordinate Eu^{III} center

	OP -8	HPY -8	HBPY -8	CU -8	SAPR -8	TDD -8	JGBF -8	JETBPY -8	JBTPR -8	BTPR -8	JSD -8	TT -8	ETBPY -8
Eu1	30.345	23.300	14.702	9.002	1.524	0.939	14.753	25.268	2.542	2.296	3.185	9.640	21.506
Eu2	31.495	21.865	16.757	10.297	0.830	2.706	15.873	25.189	2.750	2.625	4.545	11.030	22.432

Complex 3 Eight coordinate Tb^{III} center

	OP -8	HPY -8	HBPY -8	CU -8	SAPR -8	TDD -8	JGBF -8	JETBPY -8	JBTPR -8	BTPR -8	JSD -8	TT -8	ETBPY -8
Tb1	30.255	23.464	14.824	9.085	1.467	0.904	14.570	25.393	2.533	2.221	3.119	9.726	21.716
Tb2	31.229	22.025	17.003	10.297	0.741	2.882	16.241	25.253	2.737	2.631	4.777	11.009	22.446

Complex 4 Eight coordinate Sm^{III} center

	OP -8	HPY -8	HBPY -8	CU -8	SAPR -8	TDD -8	JGBF -8	JETBPY -8	JBTPR -8	BTPR -8	JSD -8	TT -8	ETBPY -8
Sm1	30.232	23.181	14.571	8.987	1.526	0.993	14.905	25.075	2.585	2.307	3.295	9.662	21.252
Sm2	31.761	21.717	16.655	10.351	0.891	2.627	15.762	25.167	2.742	2.624	4.456	11.082	22.394

Complex 5 Eight coordinate Eu^{III} center

	OP -8	HPY -8	HBPY -8	CU -8	SAPR -8	TDD -8	JGBF -8	JETBPY -8	JBTPR -8	BTPR -8	JSD -8	TT -8	ETBPY -8
Eu1	30.342	23.297	14.666	9.029	1.541	0.940	14.722	25.148	2.583	2.326	3.163	9.668	21.436
Eu2	31.526	21.753	16.825	10.411	0.831	2.691	15.948	25.157	2.738	2.624	4.570	11.130	22.375

Complex 6 Eight coordinate Tb^{III} center

	OP -8	HPY -8	HBPY -8	CU -8	SAPR -8	TDD -8	JGBF -8	JETBPY -8	JBTPR -8	BTPR -8	JSD -8	TT -8	ETBPY -8
Tb1	30.302	23.358	14.758	9.023	1.527	0.882	14.569	25.362	2.575	2.233	3.102	9.661	21.69
Tb2	31.347	21.983	16.968	10.355	0.754	2.815	16.249	25.246	2.739	2.622	4.749	11.065	22.427

Table S2. Crystallographic Data of Complexes **1**, **2**, **3, 4, 5** and **6**.

Complex	**1**	**2**	**3**
formula	$C_{60}H_{72}N_{18}O_{58}S_6Sm_4$	$C_{60}H_{68}Eu_4N_{18}O_{58}S_6$	$C_{60}H_{72}N_{18}O_{58}S_6Tb_4$
Formula weight	2767.11	2769.52	2773.38
Temp (K)	150.15 K	150.15 K	150.15 K
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	8.4352(4)	8.4163(4)	8.3933(7)
b (Å)	17.0889(8)	17.0714(9)	17.0645(12)
c (Å)	31.8495(16)	31.8351(15)	31.759(2)
α (deg)	90°	90°	90°
β (deg)	90°	90°	90°
γ (deg)	90°	90°	90°
V(Å^3)	4591.1(4)	4574.0(4)	4548.8(6)
Z	2	2	2
D_{calc}(Mg/m^3)	2.002	2.011	2.020
Absorption coefficient	2.778 mm^{-1}	2.963 mm^{-1}	3.328 mm^{-1}
F(000)	2732	2732	2720
Crystal size / mm	0.845 x 0.693 x 0.589	0.568 x 0.454 x 0.356	0.423 x 0.566 x 0.455
Reflections collected	70808	72487	71490
Indep. reflns (R_{int})	0.0563	0.0537	0.0608
R1[I > 2σ(I)]	0.0350	0.0277	0.0308
wR2 [I > 2σ(I)]	0.0929	0.0753	0.0839

Complex	**4**	**5**	**6**
formula	$C_{60}H_{72}N_{18}O_{58}S_6Sm_4$	$C_{60}H_{68}Eu_4N_{18}O_{58}S_6$	$C_{60}H_{72}N_{18}O_{58}S_6Tb_4$
Formula weight	2769.13	2775.57	2803.40
Temp (K)	150.15 K	150.15 K	150.15 K
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	8.4336(5)	8.4307(4)	8.4028(7)
b (Å)	17.0920(10)	17.0678(9)	17.0704(15)
c (Å)	31.8609(19)	31.7941(15)	31.728(3)
α (deg)	90°	90°	90°
β (deg)	90°	90°	90°
γ (deg)	90°	90°	90°
V(Å^3)	4592.7(5)	4575.0(4)	4551.0(7)
Z	2	2	2
D_{calc}(Mg/m^3)	2.002	2.015	2.046
Absorption coefficient	2.777 mm^{-1}	2.962 mm^{-1}	3.330 mm^{-1}
F(000)	2736	2744	2760
Crystal size / mm	0.837 x 0.697 x 0.689	0.678 x 0.563 x 0.366	0.825 x 0.793 x 0.459
Reflections collected	71402	73144	70190
Indep. reflns (R_{int})	0.0441	0.0596	0.0470
R1[I > 2σ(I)]	0.0274	0.0321	0.0283
wR2 [I > 2σ(I)]	0.0767	0.0815	0.0865

Table S3. Selected angle and bond lengths (Å) for complexes **1, 2, 3, 4, 5 and 6.**

Complex	1	4
∠O(1)-Sm(1)-O(2)	103.4(3)	103.5(2)
∠O(1)-Sm(1)-N(1)	73.1(2)	72.76(19)
∠O(2)-Sm(1)-N(1)	64.2(2)	64.4(2)
∠O(4)-Sm(1)-N(1)	73.2(3)	73.2(2)
∠O(16)-Sm(1)-O(4)	75.7(3)	75.3(2)
∠O(16)-Sm(1)-N(1)	72.6(2)	72.7(2)
∠O(12)-Sm(2)-O(14)	108.9(3)	108.6(2)
∠O(12)-Sm(2)-N(7)	81.8(2)	81.9(2)
∠O(13)-Sm(2)-O(14)	140.7(2)	140.67(19)
∠O(14)-Sm(2)-O(15)	89.9(2)	90.1(2)
∠O(14)-Sm(2)-N(4)	64.7(2)	64.66(19)
∠O(15)-Sm(2)-N(4)	143.7(2)	143.71(18)
∠O(15)-Sm(2)-N(7)	63.9(2)	63.87(19)
∠N(4)-Sm(2)-N(7)	149.5(2)	149.42(19)
Sm(1)-Sm(2)	6.0925(7)	6.0944(6)
Sm(1)-O(1)	2.333(7)	2.330(6)
Sm(1)-O(2)	2.383(6)	2.389(5)
Sm(1)-O(3)	2.339(7)	2.346(5)
Sm(1)-O(4)	2.422(7)	2.421(6)
Sm(1)-O(5)	2.429(7)	2.430(6)
Sm(1)-O(6)	2.443(7)	2.443(6)
Sm(1)-O(16)	2.412(7)	2.417(5)
Sm(1)-N(1)	2.654(8)	2.653(7)

Sm(2)-O(12)	2.305(7)	2.308(6)
Sm(2)-O(13)	2.343(6)	2.342(5)
Sm(2)-O(14)	2.378(6)	2.380(5)
Sm(2)-O(15)	2.410(7)	2.414(6)
Sm(2)-O(17)	2.454(7)	2.446(6)
Sm(2)-O(18)	2.421(7)	2.429(6)
Sm(2)-N(4)	2.614(8)	2.620(6)
Sm(2)-N(7)	2.616(8)	2.614(6)

Complex	2	5
∠O(1)-Eu(1)-O(2)	103.4(2)	103.6(2)
∠O(1)-Eu(1)-N(1)	72.83(19)	73.0(2)
∠O(2)-Eu(1)-N(1)	64.80(19)	64.7(2)
∠O(4)-Eu(1)-N(1)	73.2(2)	73.5(2)
∠O(16)-Eu(1)-O(4)	75.4(2)	75.5(2)
∠O(16)-Eu(1)-N(1)	72.62(19)	72.6(2)
∠O(12)-Eu(2)-O(14)	109.4(2)	109.4(2)
∠O(12)-Eu(2)-N(7)	81.65(19)	81.7(2)
∠O(13)-Eu(2)-O(14)	140.75(18)	140.4(2)
∠O(14)-Eu(2)-O(15)	89.14(19)	89.2(2)
∠O(14)-Eu(2)-N(4)	65.04(19)	65.0(2)
∠O(15)-Eu(2)-N(4)	143.53(18)	143.5(2)
∠O(15)-Eu(2)-N(7)	64.11(18)	64.1(2)
∠N(4)-Eu(2)-N(7)	149.46(19)	149.4(2)
Eu(1)-Eu(2)	6.3865(8)	6.3797(8)

Eu(1)-O(1)	2.318(5)	2.323(6)
Eu(1)-O(2)	2.366(5)	2.369(6)
Eu(1)-O(3)	2.335(5)	2.332(6)
Eu(1)-O(4)	2.399(6)	2.400(7)
Eu(1)-O(5)	2.406(6)	2.407(7)
Eu(1)-O(6)	2.434(6)	2.438(7)
Eu(1)-O(16)	2.405(5)	2.415(6)
Eu(1)-N(1)	2.637(6)	2.641(7)
Eu(2)-O(12)	2.298(5)	2.298(6)
Eu(2)-O(13)	2.328(5)	2.330(6)
Eu(2)-O(14)	2.365(5)	2.363(6)
Eu(2)-O(15)	2.404(5)	2.404(6)
Eu(2)-O(17)	2.429(6)	2.426(7)
Eu(2)-O(18)	2.410(5)	2.407(6)
Eu(2)-N(4)	2.602(6)	2.605(7)
Eu(2)-N(7)	2.603(6)	2.599(7)

Complex	3	6
∠O(1)-Tb(1)-O(2)	104.1(2)	104.0(2)
∠O(1)-Tb(1)-N(1)	73.3(2)	73.1(2)
∠O(2)-Tb(1)-N(1)	65.1(2)	65.3(2)
∠O(4)-Tb(1)-N(1)	74.1(2)	73.9(3)
∠O(16)-Tb(1)-O(4)	75.3(2)	75.2(2)
∠O(16)-Tb(1)-N(1)	72.7(2)	72.7(2)
∠O(12)-Tb(2)-O(14)	110.4(2)	110.1(3)
∠O(12)-Tb(2)-N(7)	81.3(2)	81.2(2)

∠O(13)-Tb(2)-O(14)	140.4(2)	140.6(2)
∠O(14)-Tb(2)-O(15)	87.4(2)	87.7(2)
∠O(14)-Tb(2)-N(4)	65.5(2)	65.5(2)
∠O(15)-Tb(2)-N(4)	143.0(2)	143.1(2)
∠O(15)-Tb(2)-N(7)	64.7(2)	64.6(2)
∠N(4)-Tb(2)-N(7)	149.5(2)	149.4(2)
Tb(1)-O(1)	2.301(6)	2.301(6)
Tb(1)-O(2)	2.343(6)	2.351(6)
Tb(1)-O(3)	2.310(6)	2.310(7)
Tb(1)-O(4)	2.374(7)	2.373(7)
Tb(1)-O(5)	2.376(7)	2.384(7)
Tb(1)-O(6)	2.411(7)	2.416(8)
Tb(1)-O(16)	2.387(6)	2.386(6)
Tb(1)-N(1)	2.613(8)	2.616(8)
Tb(2)-O(12)	2.275(6)	2.279(7)
Tb(2)-O(13)	2.310(6)	2.312(6)
Tb(2)-O(14)	2.337(6)	2.341(6)
Tb(2)-O(15)	2.373(6)	2.378(7)
Tb(2)-O(17)	2.404(7)	2.405(7)
Tb(2)-O(18)	2.379(6)	2.376(7)
Tb(2)-N(4)	2.580(7)	2.578(7)
Tb(2)-N(7)	2.566(7)	2.567(8)

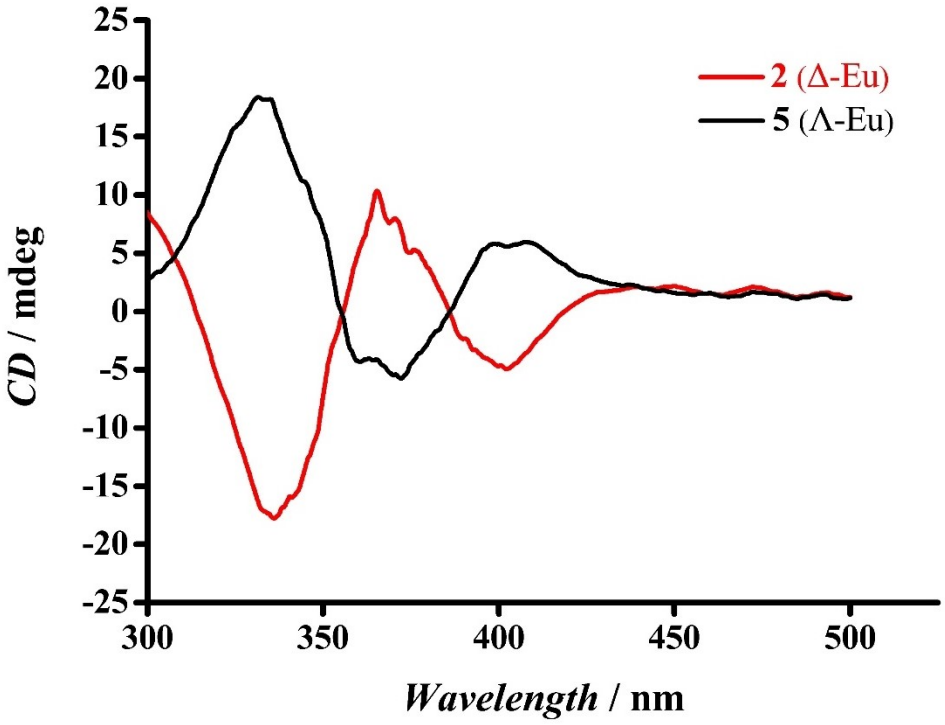


Figure S12. Circular dichroism (CD) spectra of complexes **2** (red) and **5** (black)

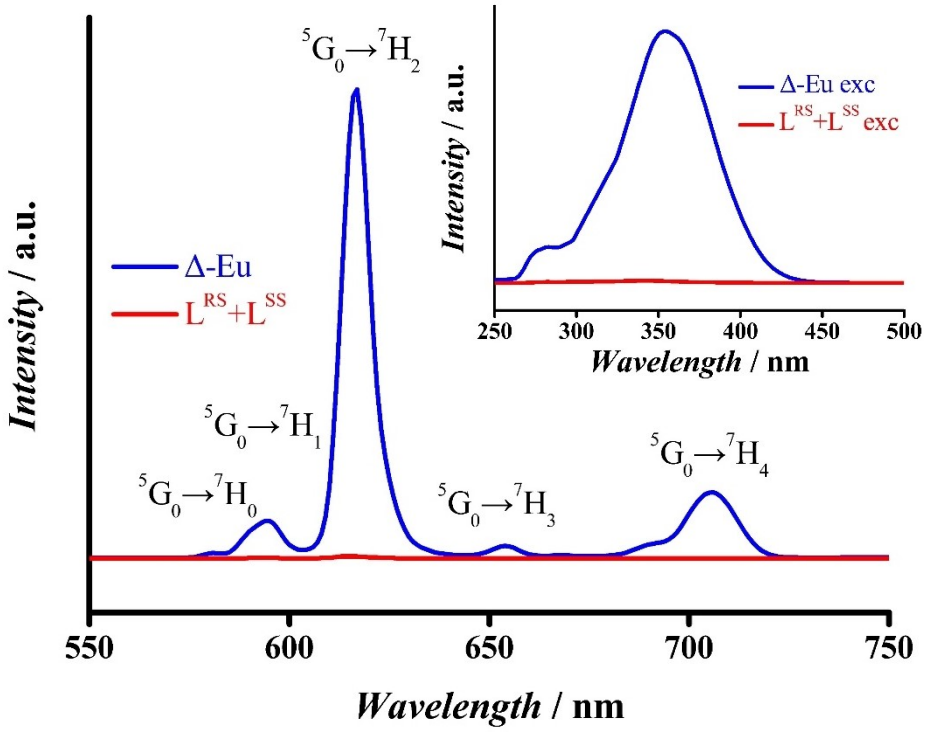


Figure S13. Solution emission spectrum (DMF) and excitation spectrum (inset) of **Ligand** and **2.**

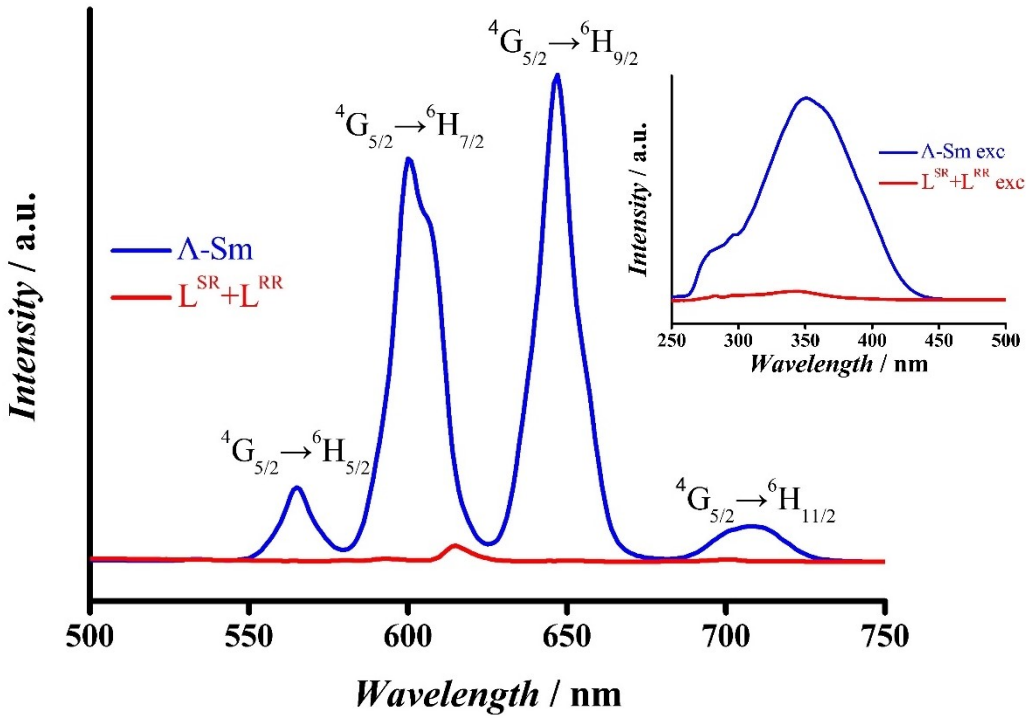


Figure S14. Solution emission spectrum (DMF) and excitation spectrum (inset) of **Ligand** and **4.**

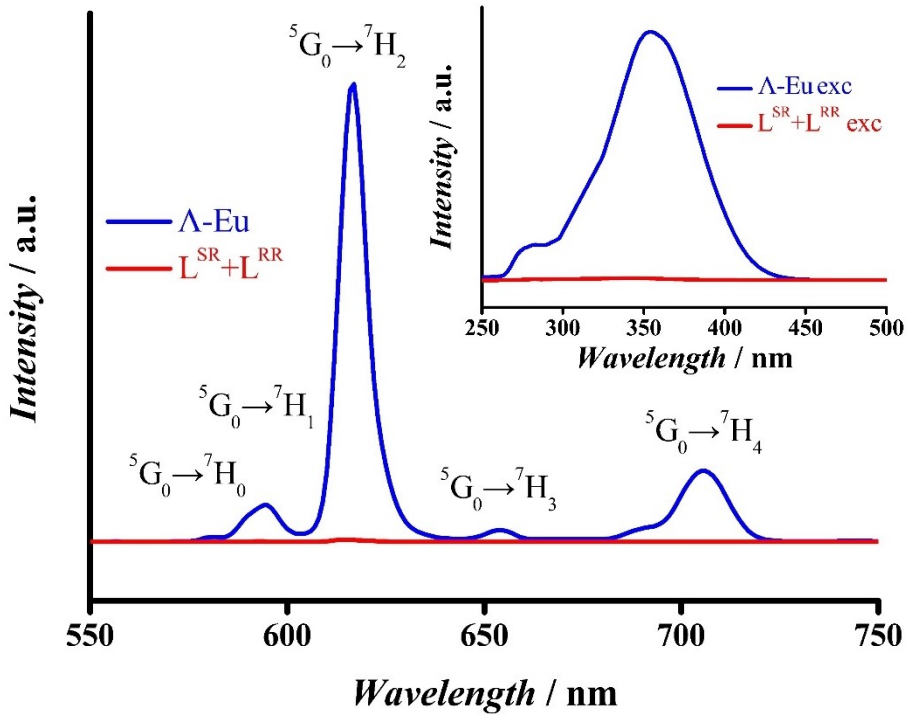


Figure 15. Solution emission spectrum (DMF) and excitation spectrum (inset) of **Ligand** and **5.**

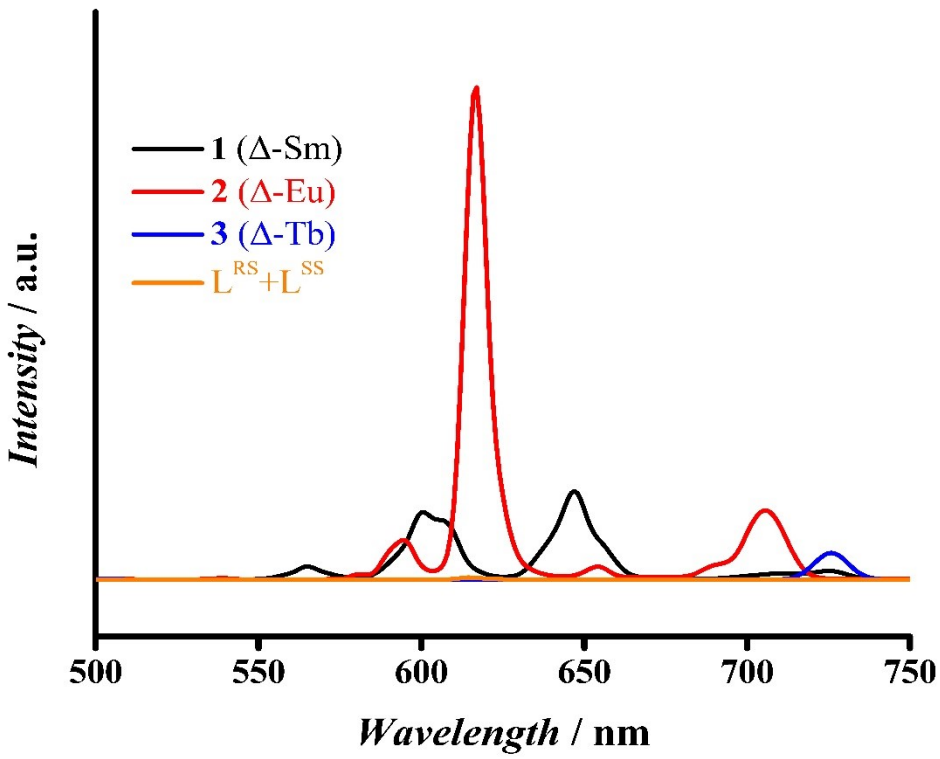


Figure S16. Solution emission spectrum (DMF) of complexes **1**, **2, 3** and Ligand

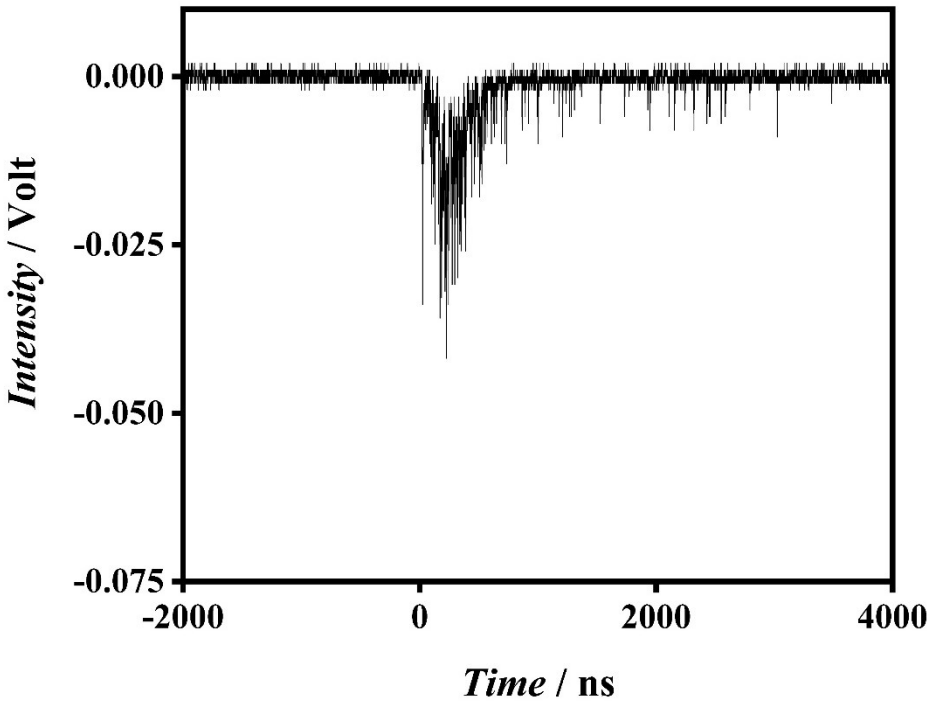


Figure 17. Time-dependent luminescence profiles of complex **1** at room temperature. The luminescence lifetime was monitored by a photomultiplier supplying at -1.7 kV.

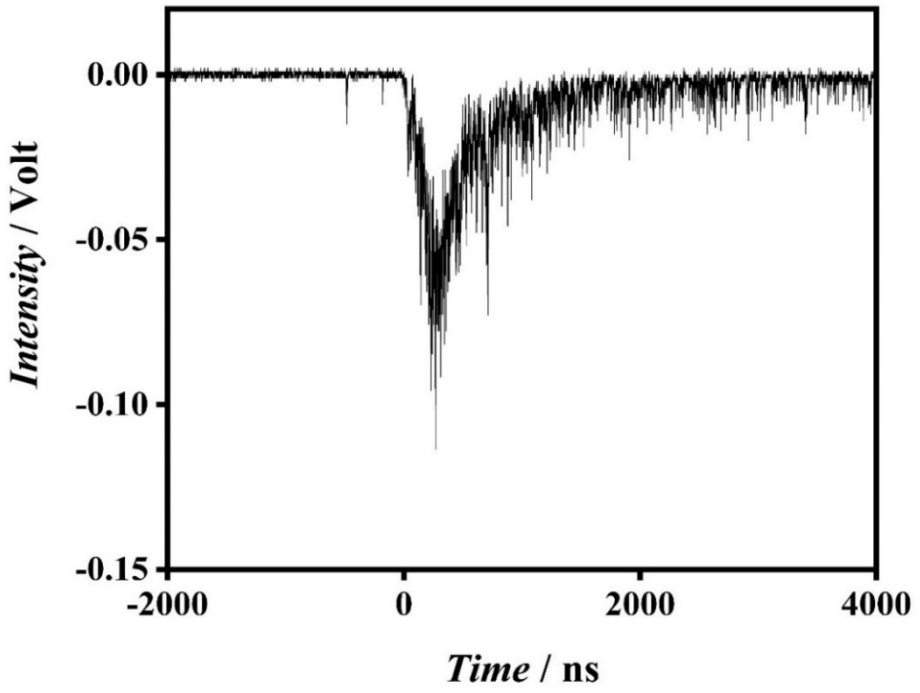


Figure S18. Time-dependent luminescence profiles of complex **2** at room temperature. The luminescence lifetime was monitored by a photomultiplier supplying at -1.7 kV.

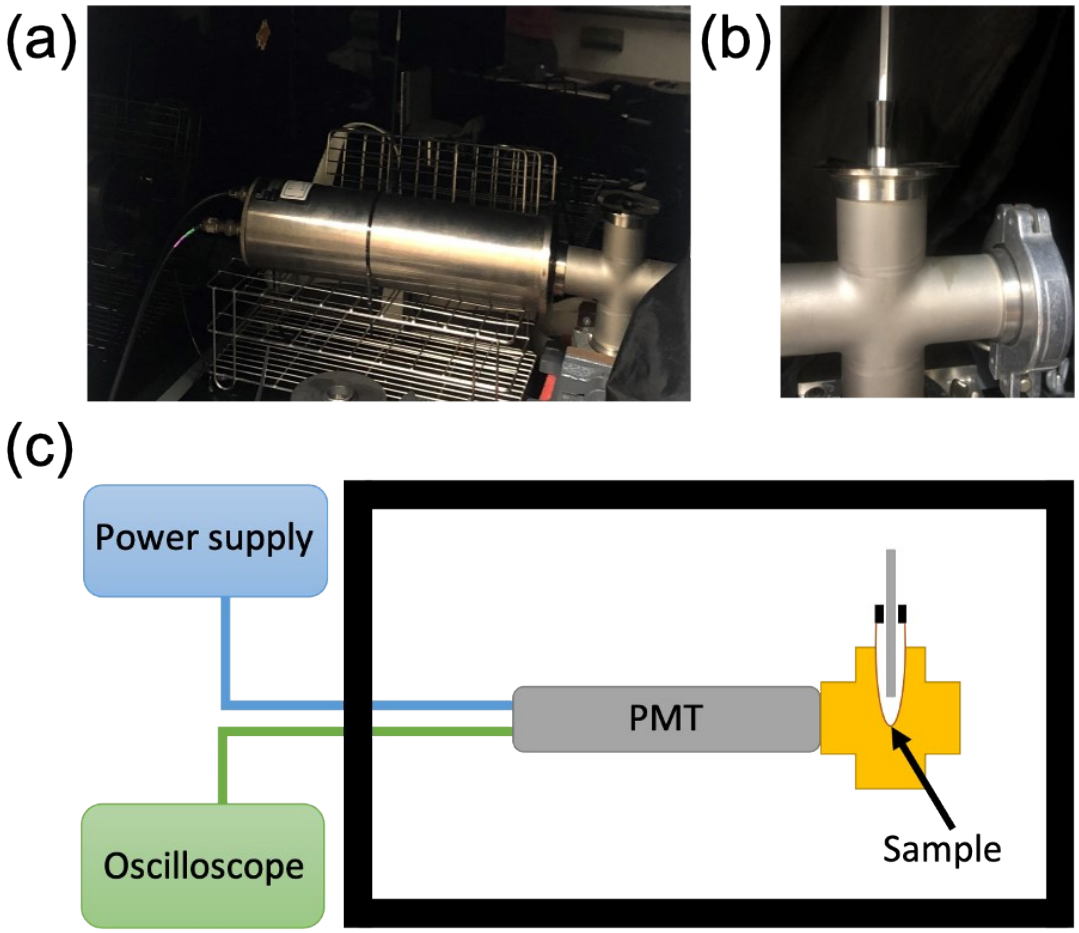


Figure S19. The experimental setup for TL measurement in a darkroom (a) photomultiplier, (b) glass sample holder and stainless-steel rod and (c) Structure diagram of the instrument.

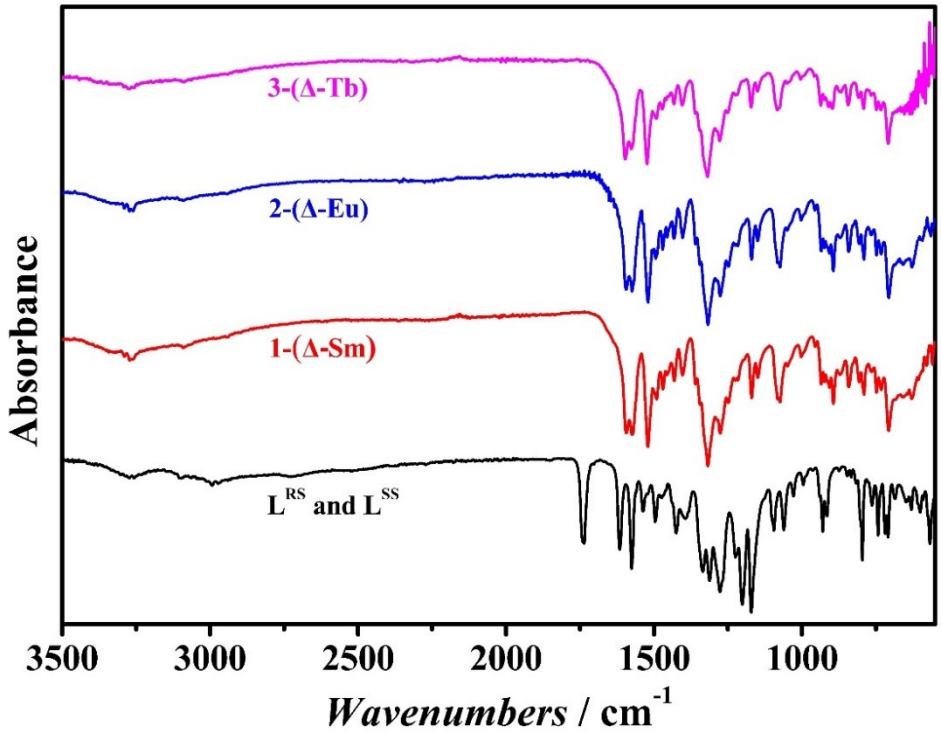


Figure S20. FTIR spectra of complexes **1-3** and ligand from 3500 to 550 cm^{-1}.

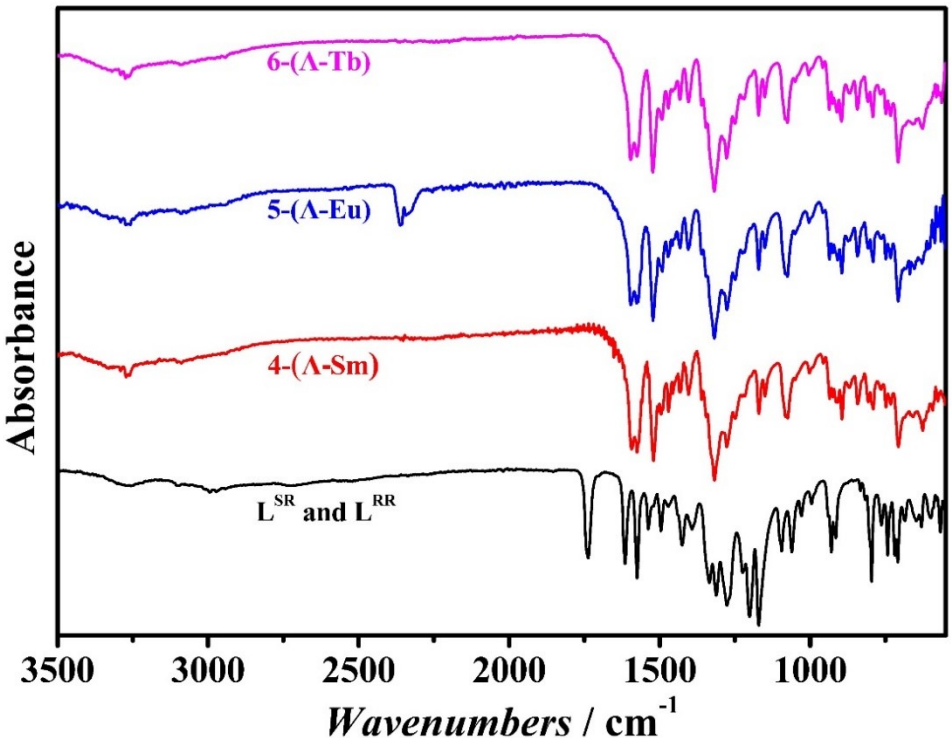


Figure S21. FTIR spectra of complexes **4-6** and ligand from 3500 to 550 cm-[1].

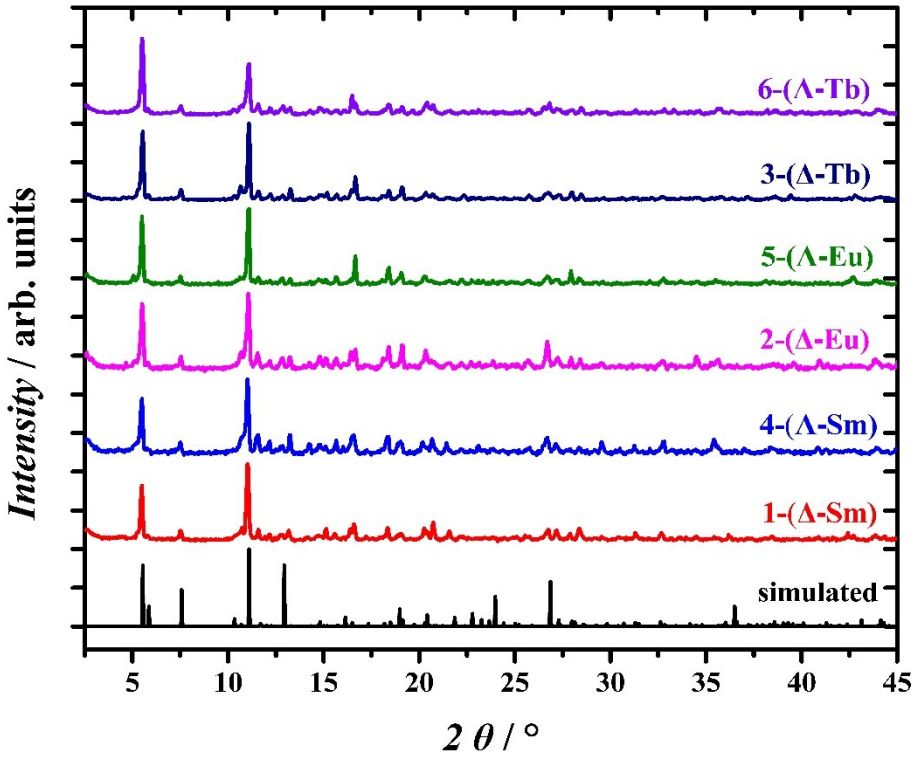


Figure S22. PXRD patterns for **1-6** and comparison with the simulated ones generated from single-crystal data.

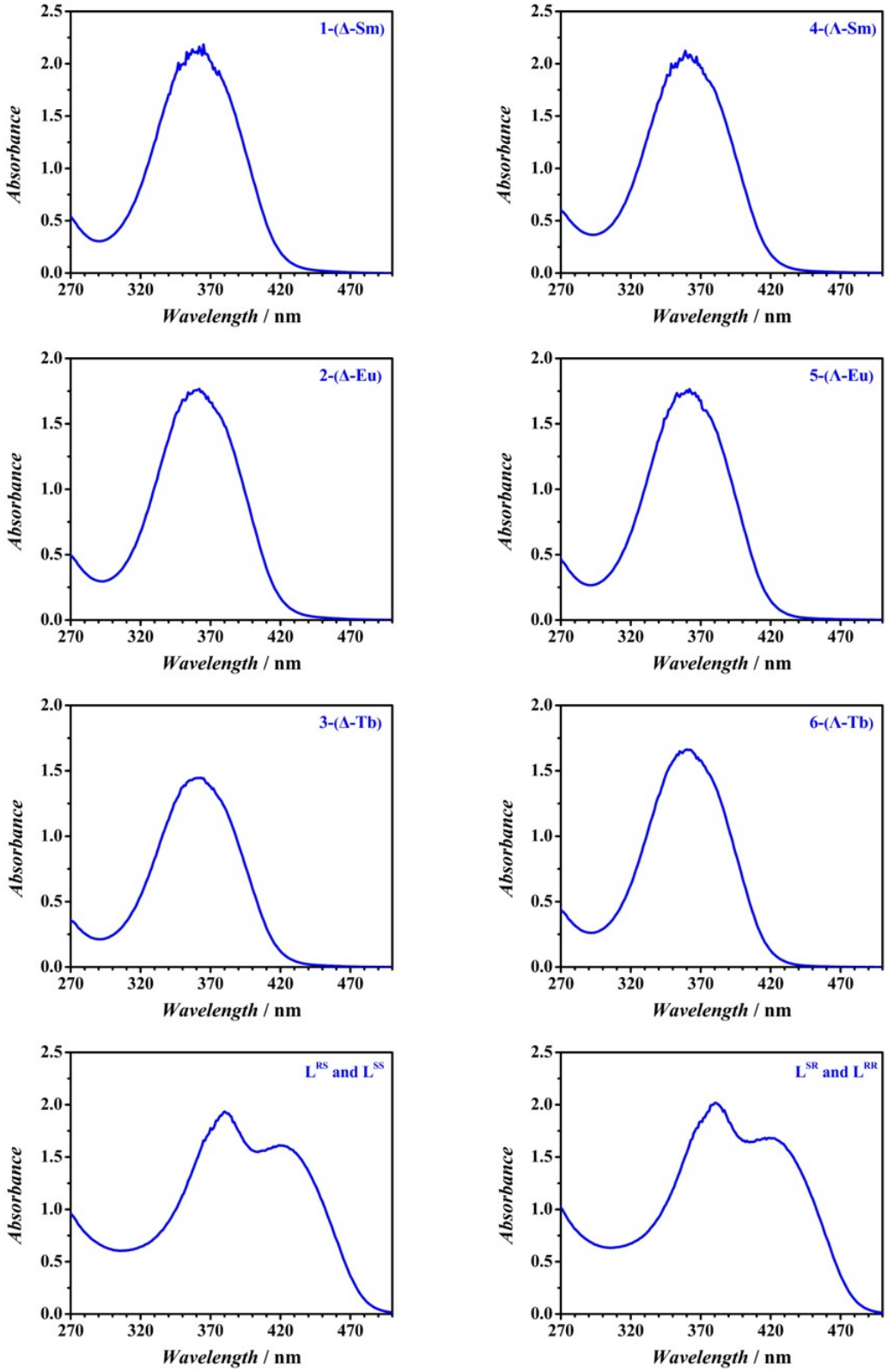


Figure S23 UV-Vis spectra of complexes **1**-**6** and ligands.