Electronic Supplementary Information (ESI)

Chiral lanthanide hexaazamacrocycles for circularly polarized luminescence, high relaxivity and magnetic resonance imaging

Yuxin Tang,[a] Minghong Jian,[c] Baobing Tang,[b] Zhenhua Zhu,[d] Zhenxin Wang,[c] and Yunling Liu*[b]

Abstract: Multifunctional lanthanide complexes have been extensively studied in recent years owing to their widespread applications in physics, chemistry and biology, including quantum information processing, molecular spintronics and theranostics. The multifunctionality includes chirality, luminescence, magnetism, ferroelectricity and fluorescence/magnetic resonance imaging etc. Although various of N- and O-donor ligands have shown the ability to synthesize these complexes, Schiff bases are still the mostly widely used in constructing the air stable species. Herein, we report the facile gram-level synthesis of three pairs of lanthanide macrocycle enantiomers via a in situ [2+2] imine condensation with trivalent lanthanide ion as template. Eu(III)-based compounds, **R/S-Eu** and **R/S-Eu-Ph$_3$PO**, both shown efficient circularly polarized luminescence (CPL) with maximum dissymmetry factors (g_{lum}) of 0.098 and 0.110, respectively. The latter exhibited stronger emission intensity and longer luminescence lifetime than the former due to the lower vibrational coordination structures around Eu(III) ion. Gd(III)-based species, **R/S-Gd**, possess a relatively high relaxivity up to 35.04 and 34.09 mM^{-1} S^{-1} for R- and S-enantiomer, benefitting from the presence of one coordinated water molecule and abundant intermolecular H-bonds. In addition, the results of MTT assay and in vitro experiments demonstrated the low toxicity and efficient MRI of Gd(III)-chelates to A549 cells.

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Table S1. Crystal Data and Structure Refinement for R-Gd and S-Gd.

Compound reference	R-Gd	S-Gd
Chemical formula	$C_{92}H_{104}O_{10}N_{12}Cl_6Gd_2$	$C_{92}H_{104}O_{10}N_{12}Cl_6Gd_2$
Formula Mass	2065.07	2065.07
Temperature (K)	180.0	180.0
Crystal system	monoclinic	monoclinic
Space group	$P2_1$	$P2_1$
a (Å)	18.1664(4)	18.1673(4)
b (Å)	10.6762(2)	10.6796(2)
c (Å)	25.5474(6)	25.5480(5)
α (°)	90	90
β (°)	101.5720(10)	101.6180(10)
γ (°)	90	90
Unit cell volume (Å^3)	4854.15(18)	4855.25(17)
Z	2	2
ρ_{calc} (g/cm^3)	1.413	1.413
μ / mm^{-1}	1.580	1.580
F (000)	2100.0	2100.0
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
Reflections collected	58921	47035
Independent reflections	16980	16953
R_{int}	0.0411	0.0319
GOF on F^2	1.059	1.052
R_1 ($I \geq 2\sigma$ (I))	0.0350	0.0340
wR_2 (all data)	0.0950	0.0934
Flack parameter	0.000(4)	0.002(4)
CCDC number	2313860	2313872

Table S2. Crystal Data and Structure Refinement for R-Eu and S-Eu.

Compound reference	R-Eu	S-Eu
Chemical formula	$C_{93}H_{106}O_{10}N_{12}Cl_6Eu_2$	$C_{93}H_{108}O_{11}N_{12}Cl_6Eu_2$
Formula Mass	2068.51	2086.53
Temperature (K)	180.0	180.0
Crystal system	monoclinic	monoclinic
Space group	$P2_1$	$P2_1$
a (Å)	18.1911(5)	18.1836(4)
b (Å)	10.6843(2)	10.6889(3)
c (Å)	25.5720(7)	25.5445(7)
α (°)	90	90
β (°)	101.6420(10)	101.5940(10)
γ (°)	90	90
Unit cell volume (Å^3)	4867.9(2)	4863(6)
Z	2	2
ρ_{calc} (g/cm^3)	1.411	1.425
μ / mm^{-1}	1.502	1.505
F (000)	2112.0	2132.0
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
Reflections collected	54896	48433
Independent reflections	17147	17076
R_{int}	0.0464	0.0593
GOF on F^2	1.049	1.059
R_1 ($I \geq 2\sigma$ (I))	0.0388	0.0432
wR_2 (all data)	0.1065	0.1072
Flack parameter	0.005(5)	0.001(6)
CCDC number	2313859	2313857

Table S3. Crystal data and structure refinement for R-Eu-Ph_3PO and S-Eu-Ph_3PO.

Compound reference	R-Eu-Ph_3PO	S-Eu-Ph_3PO
Chemical formula	$C_{82}H_{80}Cl_3EuN_6O_{18}P_2$	$C_{82}H_{80}Cl_3EuN_6O_{18}P_2$
Formula Mass	1757.77	1757.77
Temperature (K)	180.0	180.0
Crystal system	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
a (Å)	13.3179(4)	13.3140(3)
b (Å)	21.3425(6)	21.3334(6)
c (Å)	27.7275(8)	27.7364(7)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
Unit cell volume (Å^3)	7881.2(4)	7878.1(3)
Z	4	4
ρ_{calc} (g/cm^3)	1.481	1.482
μ / mm^{-1}	1.013	1.013
F (000)	3608.0	3608.0
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
Reflections collected	57344	54203
Independent reflections	13906	13912
R_{int}	0.0637	0.0828
GOF on F^2	1.061	1.068
R_1 (I ≥2 σ (*I*))	0.0362	0.0434
wR_2 (all data)	0.0870	0.0935
Flack parameter	-0.006(5)	-0.011(6)
CCDC number	2326932	2326934

Table S4. Crystal data and structure refinement for R-Y.

Compound reference	R-Y
Chemical formula	$C_{94}C_{l6}H_{112}N_{12}O_{12}Y_2$
Formula Mass	1992.47
Temperature (K)	180.0
Crystal system	monoclinic
Space group	$P2_1$
a (Å)	18.1007(6)
b (Å)	10.6935(4)
c (Å)	25.4908(9)
α (°)	90
β (°)	101.5390(10)
γ (°)	90
Unit cell volume (Å^3)	4834.3(3)
Z	2
ρ_{calc} (g/cm^3)	1.369
μ / mm^{-1}	1.425
F (000)	2072.0
Radiation	MoKα (λ = 0.71073)
Reflections collected	64570
Independent reflections	16956
R_{int}	0.0761
GOF on F^2	1.036
R_1 (I ≥2 σ (*I*))	0.0496
wR_2 (all data)	0.1361
Flack parameter	0.012(3)
CCDC number	2328816

Table S5. Selected bond distances (Å) for complexes R-Gd and S-Gd.

R-Gd		S-Gd	
Gd1−Cl3	2.715(2)	Gd1−Cl3	2.7179(19)
Gd1−Cl4	2.662(2)	Gd1−Cl4	2.663(2)
Gd1−O2	2.424(5)	Gd1−O2	2.416(5)
Gd2−Cl1	2.671(2)	Gd2−Cl1	2.676(2)
Gd2−Cl2	2.705(2)	Gd2−Cl2	2.705(2)
Gd2−O1	2.503(6)	Gd2−O1	2.501(6)
Gd1−N7	2.608(6)	Gd1−N7	2.604(6)
Gd1−N8	2.571(6)	Gd1−N8	2.578(6)
Gd1−N9	2.678(6)	Gd1−N9	2.667(6)
Gd1−N10	2.641(6)	Gd1−N10	2.637(6)
Gd1−N11	2.582(6)	Gd1−N11	2.595(6)
Gd1−N12	2.681(6)	Gd1−N12	2.679(6)
Gd2−N1	2.602(6)	Gd2−N1	2.596(6)
Gd2−N2	2.568(7)	Gd2−N2	2.571(7)
Gd2−N3	2.650(7)	Gd2−N3	2.652(6)
Gd2−N4	2.593(7)	Gd2−N4	2.597(6)
Gd2−N5	2.590(6)	Gd2−N5	2.590(6)
Gd2−N6	2.675(6)	Gd2−N6	2.688(6)

Table S6. Selected bond angles (°) for complexes R-Gd and S-Gd.

R-Gd		S-Gd	
Cl3−Gd1−Cl4	148.43(7)	Cl3−Gd1−Cl4	148.44(6)
O2−Gd1−Cl3	71.84(15)	O2−Gd1−Cl3	71.72(14)
O2−Gd1−Cl4	139.53(15)	O2−Gd1−Cl4	139.63(14)
Cl1−Gd2−Cl2	146.18(7)	Cl1−Gd2−Cl2	146.12(6)
O1−Gd2−Cl1	75.22(14)	O1−Gd2−Cl1	75.24(13)
O1−Gd2−Cl2	138.58(14)	O1−Gd2−Cl2	138.62(14)
N1−Gd2−N2	61.6(2)	N1−Gd2−N2	61.3(2)
N2−Gd2−N3	61.0(2)	N2−Gd2−N3	60.7(2)
N3−Gd2−N4	61.0(2)	N3−Gd2−N4	61.3(2)
N4−Gd2−N5	62.1(2)	N4−Gd2−N5	62.1(2)
N5−Gd2−N6	59.74(19)	N5−Gd2−N6	59.61(18)
N6−Gd2−N1	60.66(19)	N6−Gd2−N1	61.01(18)
N7−Gd1−N8	62.32(19)	N7−Gd1−N8	62.2(2)
N8−Gd1−N9	60.55(18)	N8−Gd1−N9	60.65(18)
N9−Gd1−N10	60.14(18)	N9−Gd1−N10	60.41(18)
N10−Gd1−N11	61.2(2)	N10−Gd1−N11	60.94(19)
N11−Gd1−N12	60.27(19)	N11−Gd1−N12	60.12(19)
N12−Gd1−N7	60.73(19)	N12−Gd1−N7	60.80(19)

Table S7. Selected bond distances (Å) for complexes R-Eu and S-Eu.

R-Eu		S-Eu	
Eu1−Cl3	2.726(2)	Eu1−Cl3	2.725(3)
Eu1−Cl4	2.673(2)	Eu1−Cl4	2.678(3)
Eu1−O2	2.429(6)	Eu1−O2	2.434(6)
Eu2−Cl1	2.684(2)	Eu2−Cl1	2.686(3)
Eu2−Cl2	2.718(2)	Eu2−Cl2	2.716(3)
Eu2−O1	2.522(6)	Eu2−O1	2.518(7)
Eu1−N7	2.612(7)	Eu1−N7	2.608(8)
Eu1−N8	2.573(7)	Eu1−N8	2.588(8)
Eu1−N9	2.668(7)	Eu1−N9	2.657(8)
Eu1−N10	2.641(6)	Eu1−N10	2.642(7)
Eu1−N11	2.592(7)	Eu1−N11	2.588(8)
Eu1−N12	2.685(7)	Eu1−N12	2.679(8)
Eu2−N1	2.603(6)	Eu2−N1	2.606(7)
Eu2−N2	2.569(8)	Eu2−N2	2.585(9)
Eu2−N3	2.660(7)	Eu2−N3	2.646(8)
Eu2−N4	2.609(7)	Eu2−N4	2.605(8)
Eu2−N5	2.595(7)	Eu2−N5	2.592(8)
Eu2−N6	2.671(7)	Eu2−N6	2.668(7)

Table S8. Selected bond angles (°) for complexes R-Eu and S-Eu.

R-Eu		S-Eu	
Cl3−Eu1−Cl4	148.54(7)	Cl3−Eu1−Cl4	148.63(8)
O2−Eu1−Cl3	72.69(16)	O2−Eu1−Cl3	70.45(18)
O2−Eu1−Cl4	139.51(16)	O2−Eu1−Cl4	139.69(18)
Cl1−Eu2−Cl2	146.07(7)	Cl1−Eu2−Cl2	146.19(18)
O1−Eu2−Cl1	75.41(15)	O1−Eu2−Cl1	75.44(16)
O1−Eu2−Cl2	138.50(15)	O1−Eu2−Cl2	138.36(18)
N1−Eu2−N2	61.3(2)	N1−Eu2−N2	61.1(2)
N2−Eu2−N3	60.8(2)	N2−Eu2−N3	60.4(3)
N3−Eu2−N4	61.4(2)	N3−Eu2−N4	61.7(3)
N4−Eu2−N5	61.8(2)	N4−Eu2−N5	62.1(3)
N5−Eu2−N6	59.9(2)	N5−Eu2−N6	59.5(2)
N6−Eu2−N1	60.7(2)	N6−Eu2−N1	60.9(2)
N7−Eu1−N8	61.9(2)	N7−Eu1−N8	62.1(2)
N8−Eu1−N9	60.7(2)	N8−Eu1−N9	60.7(2)
N9−Eu1−N10	60.4(2)	N9−Eu1−N10	60.3(2)
N10−Eu1−N11	61.2(2)	N10−Eu1−N11	60.8(2)
N11−Eu1−N12	60.1(2)	N11−Eu1−N12	60.1(2)
N12−Eu1−N7	60.7(2)	N12−Eu1−N7	60.8(2)

Table S9. Selected bond distances (Å) for complexes R-Eu-Ph_3PO and S-Eu-Ph_3PO.

R-Eu-Ph_3PO		S-Eu-Ph_3PO	
Eu1−O1	2.293(4)	Eu1 −O1	2.292(4)
Eu1−O2	2.325(4)	Eu1−O2	2.325(5)
Eu1−O3	2.467(4)	Eu1−O3	2.468(5)
Eu1−N1	2.629(5)	Eu1 −N1	2.630(6)
Eu1−N2	2.658(5)	Eu1 −N2	2.660(6)
Eu1−N3	2.585(5)	Eu1−N3	2.573(6)
Eu1−N4	2.623(4)	Eu1−N4	2.623(6)
Eu1−N5	2.686(5)	Eu1−N5	2.686(6)
Eu1−N6	2.606(4)	Eu1−N6	2.610(6)

Table S10. Selected bond angles (°) for complexes R-Eu-Ph_3PO and S-Eu-Ph_3PO.

R-Eu-Ph_3PO		S-Eu-Ph_3PO	
O1−Eu1−O2	145.36(16)	O1−Eu1−O2	145.24(19)
O1−Eu1−O3	142.89(15)	O1−Eu1−O3	142.77(18)
O1−Eu1−N1	97.11(15)	O1−Eu1−N1	96.96(18)
O1−Eu1−N2	75.35(16)	O1−Eu1−N2	75.40(18)
O1−Eu1−N3	77.84(15)	O1−Eu1−N3	77.98(19)
O1−Eu1−N4	95.93(16)	O1−Eu1−N4	96.0(2)
O1−Eu1−N5	74.19(15)	O1−Eu1−N5	74.07(18)
O1−Eu1−N6	78.23(14)	O1−Eu1−N6	78.19(17)
O2−Eu1−O3	71.68(15)	O2−Eu1−O3	71.90(18)
O2−Eu1−N1	85.25(15)	O2−Eu1−N1	85.30(18)
O2−Eu1−N2	132.73(16)	O2−Eu1−N2	132.70(18)
O2−Eu1−N3	129.68(15)	O2−Eu1−N3	129.77(18)
O2−Eu1−N4	83.44(16)	O2−Eu1−N4	83.5(2)
O2−Eu1−N5	75.72(15)	O2−Eu1−N5	75.81(17)
O2−Eu1−N6	72.51(15)	O2−Eu1−N6	72.43(17)
O3−Eu1−N1	80.24(15)	O3−Eu1−N1	80.24(19)
O3−Eu1−N2	71.25(16)	O3−Eu1−N2	71.06(18)
O3−Eu1−N3	72.75(15)	O3−Eu1−N3	72.53(18)
O3−Eu1−N4	89.95(16)	O3−Eu1−N4	89.91(19)
O3−Eu1−N5	137.77(15)	O3−Eu1−N5	137.98(18)
O3−Eu1−N6	129.13(15)	O3−Eu1−N6	129.10(18)
N1−Eu1−N2	60.42(15)	N1−Eu1−N2	60.33(19)
N1−Eu1−N5	123.14(14)	N1−Eu1−N5	123.24(18)
N2−Eu1−N5	149.53(15)	N2−Eu1−N5	149.46(18)
N3−Eu1−N1	121.94(16)	N3−Eu1−N1	121.74(19)
N3−Eu1−N2	62.46(16)	N3−Eu1−N2	62.3(2)

N3−Eu1−N4	62.13(15)	N3−Eu1−N4	62.14(19)
N3−Eu1−N5	111.03(15)	N3−Eu1−N5	111.07(18)
N3−Eu1−N6	156.06(15)	N3−Eu1−N6	156.17(17)
N4−Eu1−N1	166.92(16)	N4−Eu1−N1	166.98(18)
N4−Eu1−N2	124.51(15)	N4−Eu1−N2	124.41(19)
N4−Eu1−N5	59.98(14)	N4−Eu1−N5	60.06(17)
N6−Eu1−N1	61.87(15)	N6−Eu1−N1	61.74(19)
N6−Eu1−N2	111.42(15)	N6−Eu1−N2	111.30(19)
N6−Eu1−N4	120.26(15)	N6−Eu1−N4	120.54(18)
N6−Eu1−N5	61.34(14)	N6−Eu1−N5	61.56(18)

Table S11. The CShM values calculated by SHAPE 2.1 for R-Gd and S-Gd.
The lowest CShM value is highlighted.[1, 2]

Coordination Geometry	R-Gd		S-Gd	
	Gd1	**Gd2**	**Gd1**	**Gd2**
Enneagon (D_{9h})	32.892	32.671	32.916	32.708
Octagonal pyramid (C_{8v})	22.048	21.799	22.102	21.693
Heptagonal bipyramid (D_{7h})	13.265	13.922	13.324	13.827
Johnson triangular cupola J3 (C_{3v})	14.858	15.272	14.889	15.349
Capped cube J8 (C_{4v})	5.616	6.205	5.633	6.257
Spherical-relaxed capped cube (C_{4v})	4.326	4.418	4.335	4.459
Capped square antiprism J10 (C_{4v})	7.693	7.543	7.648	7.470
Spherical capped square antiprism (C_{4v})	6.320	6.187	6.289	6.125
Tricapped trigonal prism J51 (D_{3h})	7.668	7.737	7.663	7.678
Spherical tricapped trigonal prism (D_{3h})	7.464	7.207	7.446	7.159
Tridiminished icosahedron J63 (C_{3v})	11.949	12.305	11.899	12.298
Hula-hoop (C_{2v})	**2.663**	**2.743**	**2.681**	**2.734**
Muffin (C_s)	4.686	4.627	4.646	4.576

Table S12. The CShM values calculated by SHAPE 2.1 for R-Eu and S-Eu. The lowest CShM value is highlighted.[1, 2]

Coordination Geometry	R-Eu		S-Eu	
	Eu1	**Eu2**	**Eu1**	**Eu2**
Enneagon (D_{9h})	32.921	32.622	32.858	32.664
Octagonal pyramid (C_{8v})	22.139	21.734	22.249	21.620
Heptagonal bipyramid (D_{7h})	13.364	13.839	13.305	13.801
Johnson triangular cupola J3 (C_{3v})	14.925	15.395	14.987	15.486
Capped cube J8 (C_{4v})	5.587	6.224	5.532	6.215
Spherical-relaxed capped cube (C_{4v})	4.295	4.437	4.200	4.423
Capped square antiprism J10 (C_{4v})	7.766	7.559	7.803	7.549
Spherical capped square antiprism (C_{4v})	6.384	6.179	6.412	6.199
Tricapped trigonal prism J51 (D_{3h})	7.757	7.743	7.799	7.718
Spherical tricapped trigonal prism (D_{3h})	7.535	7.217	7.508	7.257
Tridiminished icosahedron J63 (C_{3v})	11.835	12.312	11.798	12.300
Hula-hoop (C_{2v})	**2.610**	**2.724**	**2.590**	**2.681**
Muffin (C_s)	4.753	4.622	4.755	4.635

Table S13. The CShM values calculated by SHAPE 2.1 for R-Eu-Ph_3PO and S-Eu-Ph_3PO.

Coordination Geometry	**R-Eu-Ph_3PO**	**S-Eu-Ph_3PO**
Enneagon(D_{9h})	31.760	31.803
Octagonal pyramid(C_{8v})	20.951	20.891
Heptagonal bipyramid(D_{7h})	14.305	14.294
Johnson triangular cupola J3(C_{3v})	15.254	15.280
Capped cube J8(C_{4v})	7.414	7.399
Spherical-relaxed capped cube(C_{4v})	6.371	6.373
Capped square antiprism J10(C_{4v})	6.170	6.179
Spherical capped square antiprism(C_{4v})	5.143	5.133
Tricapped trigonal prism J51(D_{3h})	6.273	6.303
Spherical tricapped trigonal prism(D_{3h})	5.972	5.960
Tridiminished icosahedron J63(C_{3v})	12.303	12.308
Hula-hoop(C_{2v})	3.828	3.838
Muffin(C_s)	3.684	3.683

Table S14. The CShM values calculated by SHAPE 2.1 for R-Y.

Coordination Geometry	Y1	Y2
Enneagon(D_{9h})	32.946	32.829
Octagonal pyramid(C_{8v})	21.942	21.668
Heptagonal bipyramid(D_{7h})	13.308	13.995
Johnson triangular cupola J3(C_{3v})	14.833	15.260
Capped cube J8(C_{4v})	5.676	6.182
Spherical-relaxed capped cube(C_{4v})	4.416	4.428
Capped square antiprism J10(C_{4v})	7.477	7.282
Spherical capped square antiprism(C_{4v})	6.145	5.953
Tricapped trigonal prism J51(D_{3h})	7.487	7.474
Spherical tricapped trigonal prism(D_{3h})	7.286	6.966
Tridiminished icosahedron J63(C_{3v})	12.064	12.466
Hula-hoop(C_{2v})	2.790	2.845
Muffin(C_s)	4.559	4.432

Table S15. CPL brightness for R/S-Eu and R/S-Eu-Ph_3PO.

Compound	ε/$M^{-1}cm^{-1}$ (λ_{abs}/nm)	φ	Transition	$\lvert g_{lum}\rvert$ (λ/nm)	β	B_{CPL}/M^{-1} cm^{-1}
R/S-Eu	46558 (312)	0.18	$^5D_0\rightarrow{}^7F_0$	0.042 (582)	0.007	1.27
			$^5D_0\rightarrow{}^7F_1$	0.098 (597)	0.174	71.45
			$^5D_0\rightarrow{}^7F_2$	0.024 (616)	0.395	39.72
			$^5D_0\rightarrow{}^7F_3$	0.055 (651)	0.044	10.14
R/S-Eu-Ph_3PO	21864 (312)	0.17	$^5D_0\rightarrow{}^7F_0$	0.032 (582)	0.004	0.24
			$^5D_0\rightarrow{}^7F_1$	0.110 (597)	0.151	30.89
			$^5D_0\rightarrow{}^7F_2$	0.029 (616)	0.266	14.35
			$^5D_0\rightarrow{}^7F_3$	0.060 (651)	0.021	2.34

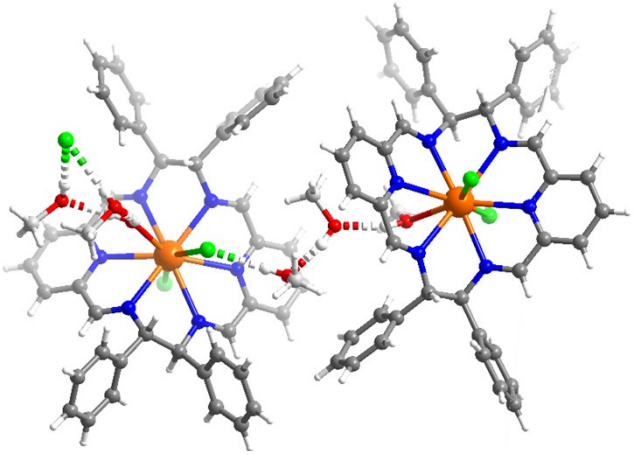

Fig. S1 The intermolecular H-bonds in S-Gd.

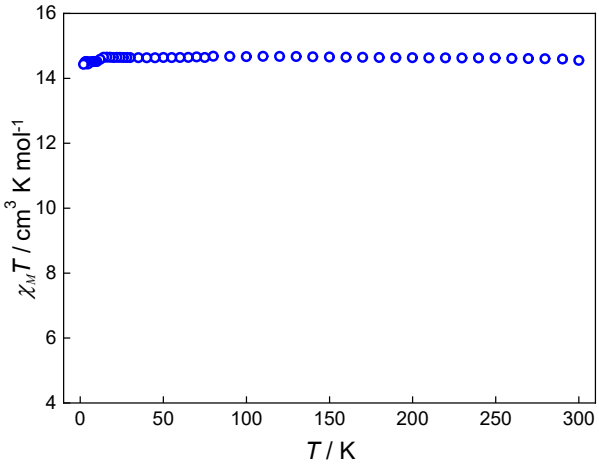

Fig. S2 The variable-temperature magnetic susceptibilities of S-Gd.

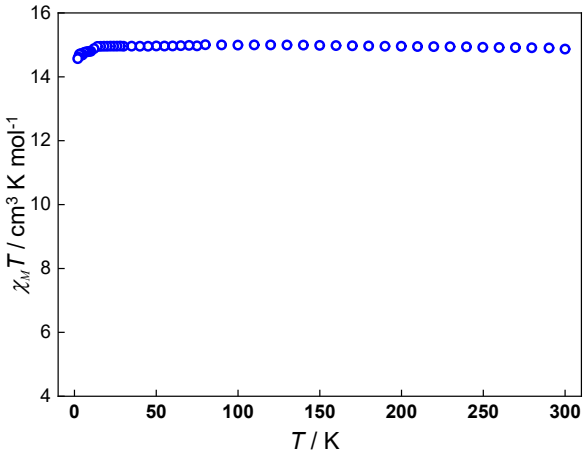

Fig. S3 The variable-temperature magnetic susceptibilities of R-Gd.

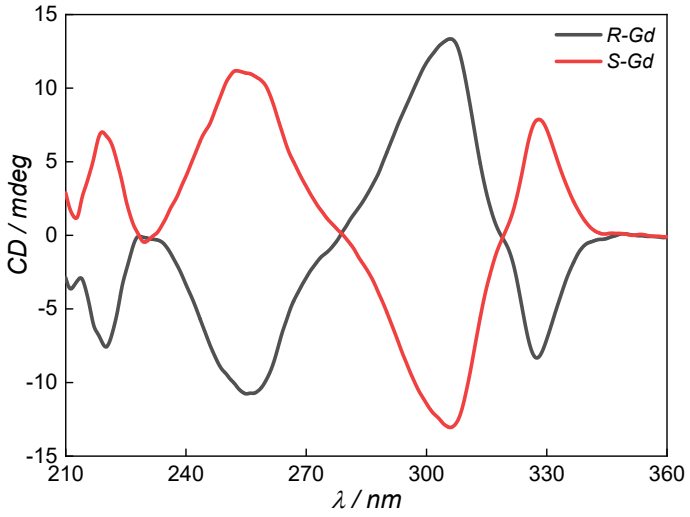

Fig. S4 CD spectra of R/S-Eu in CH_3OH (c = 1 × 10^{-5} mol L^{-1}).

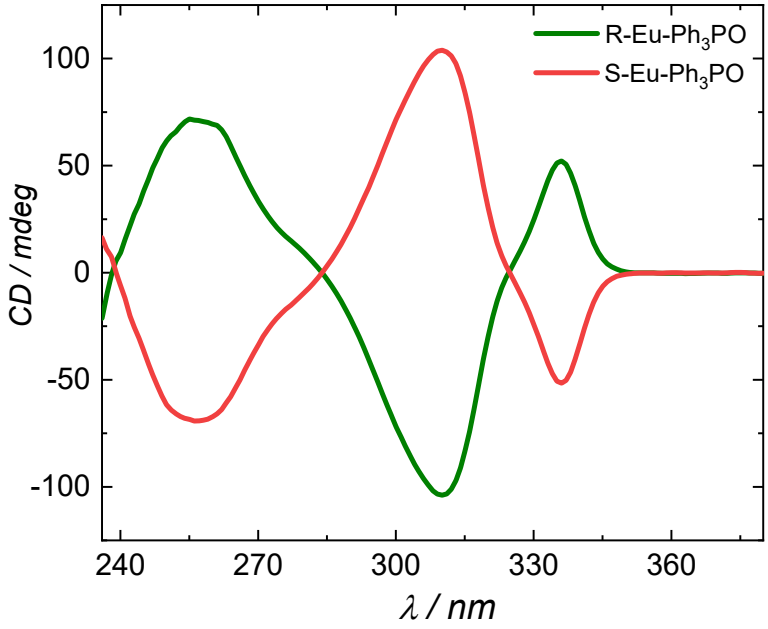

Fig. S5 CD spectra of R/S-Eu-Ph_3PO in CH_3OH (c = 1 × 10^{-5} mol L^{-1}).

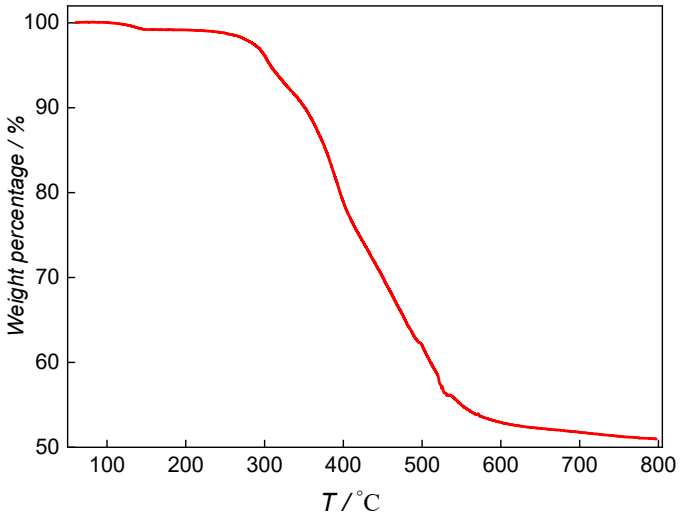

Fig. S6 Thermogravimetric analysis of S-Eu.

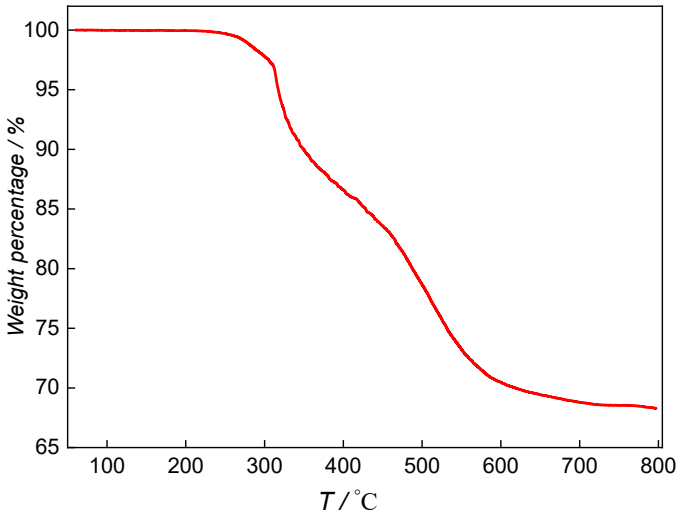

Fig. S7 Thermogravimetric analysis of S-Gd.

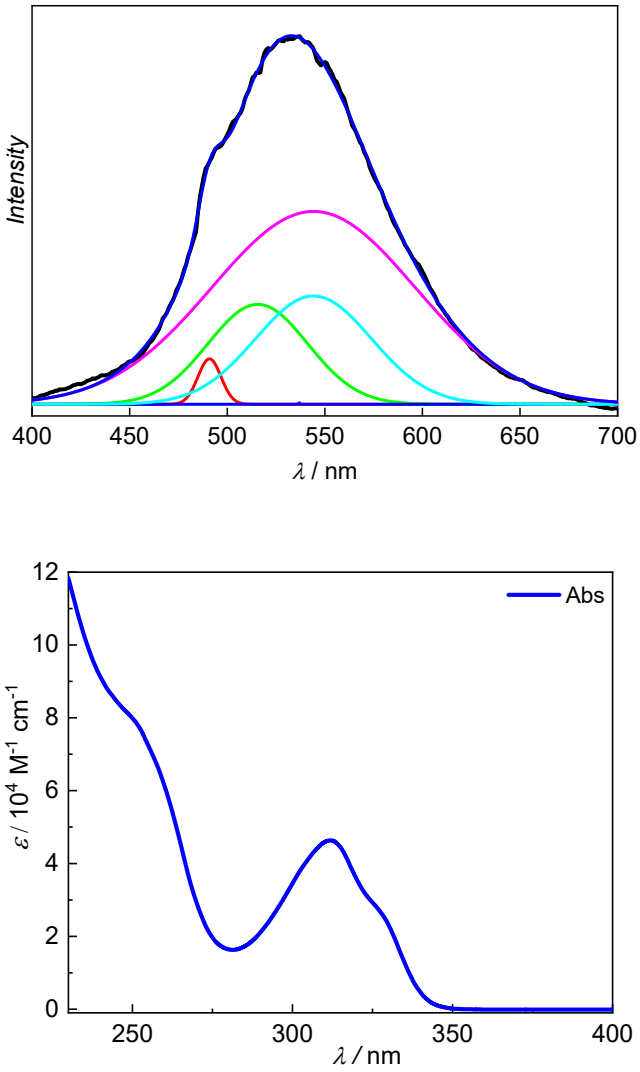

Fig. S8 (Top) Phosphorescence spectrum of **S-Gd** collected in the solid state under excitation at 306 nm (black line, 77 K) and its Gaussian decomposition (colored traces); (Bottom) Absorption spectra of S-Eu in molar absorptivity **in CH_3OH ($c = 1 \times 10^{-5}$ mol L^{-1}).**

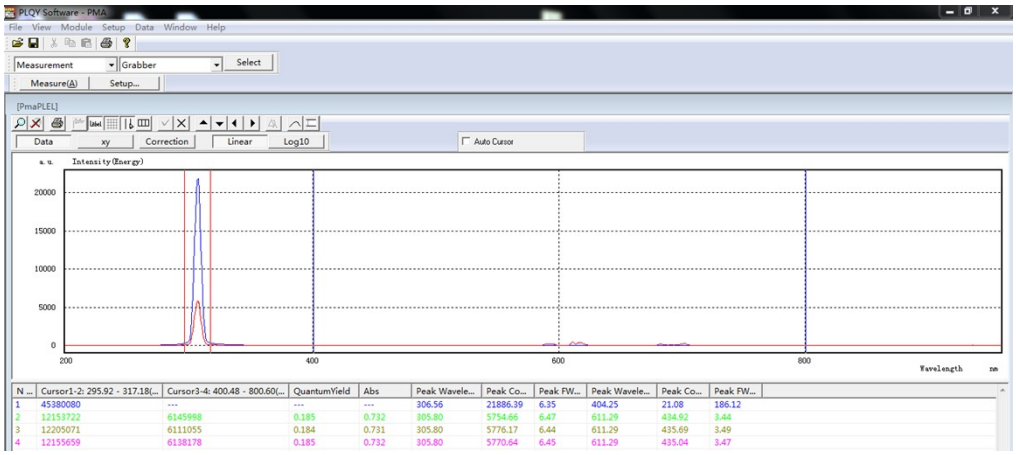

Fig. S9 Quantum yield of **S-Eu** in CH_3OH (1.0×10^{-5} M) at room temperature.

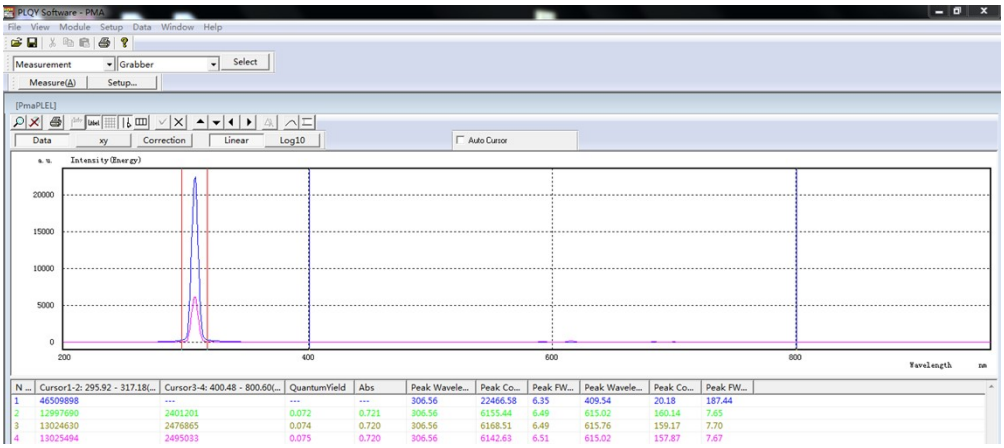

Fig. S10 Quantum yield of **S-Eu** in H_2O (1.0×10^{-5} M) at room temperature.

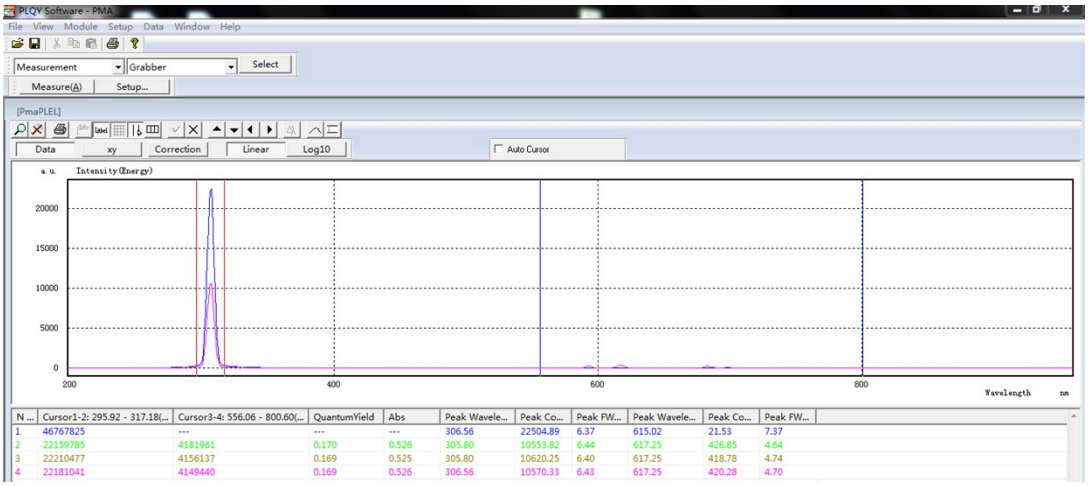

Fig. S11 Quantum yield of **S-Eu-Ph$_3$PO** in CH_3OH (1.0×10^{-5} M) at room temperature.

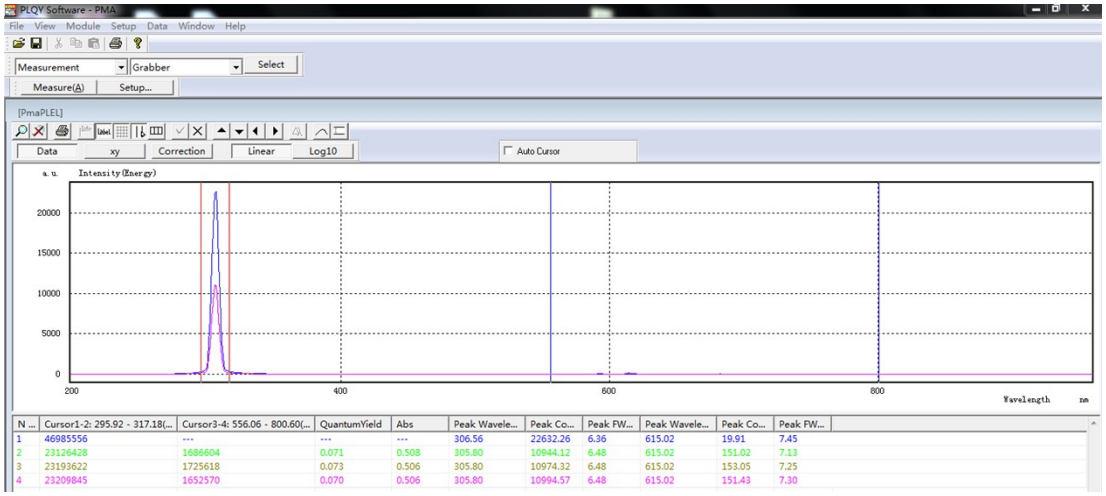

Fig. S12 Quantum yield of **S-Eu-Ph$_3$PO** in H_2O (1.0×10^{-5} M) at room temperature.

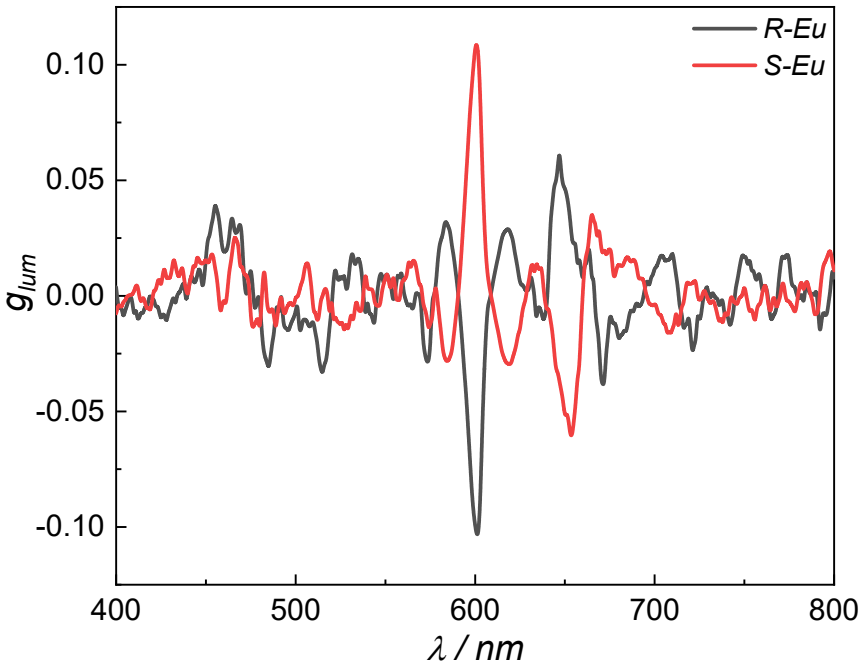

Fig. S13 Circularly polarized luminescence (g_{lum}) spectra of **R/S-Eu** collected from 1.2 × 10^{-5} M solutions in CH_3OH at room temperature upon excitation at 329 nm.

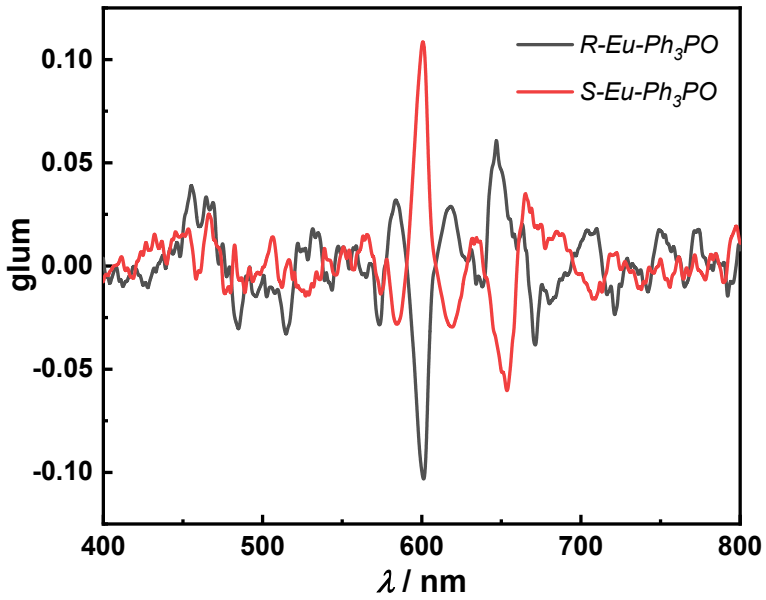

Fig. S14 Circularly polarized luminescence (g_{lum}) spectra of **R/S-Eu-Ph$_3$PO** collected from 1.2 × 10^{-5} M solutions in CH_3OH at room temperature upon excitation at 329 nm.

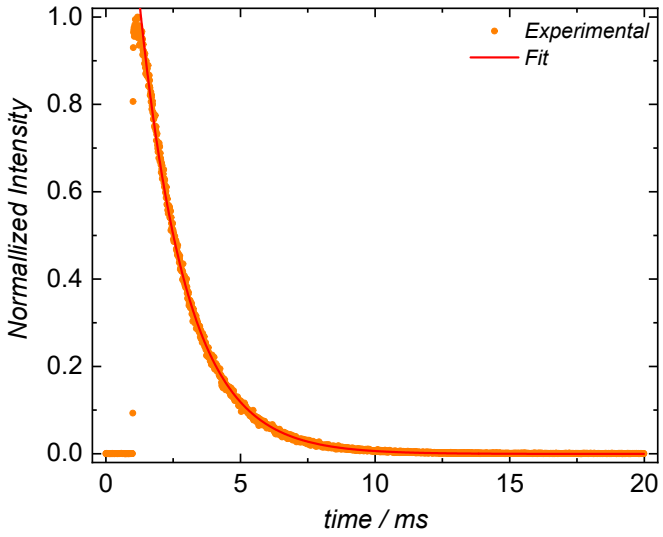

Fig. S15 Decay curve of **S-Eu** in D_2O at room temperature, c = 1.0 × 10^{-5} M, gives the luminescence lifetime of 1.734 ms.

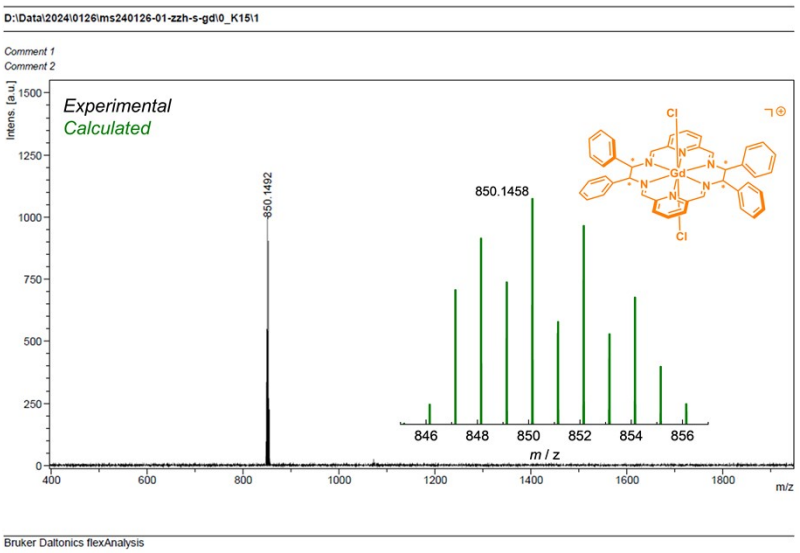

Fig. S16 HR-MALDI-TOF spectrum of **S-Gd** in CH_3OH at room temperature.

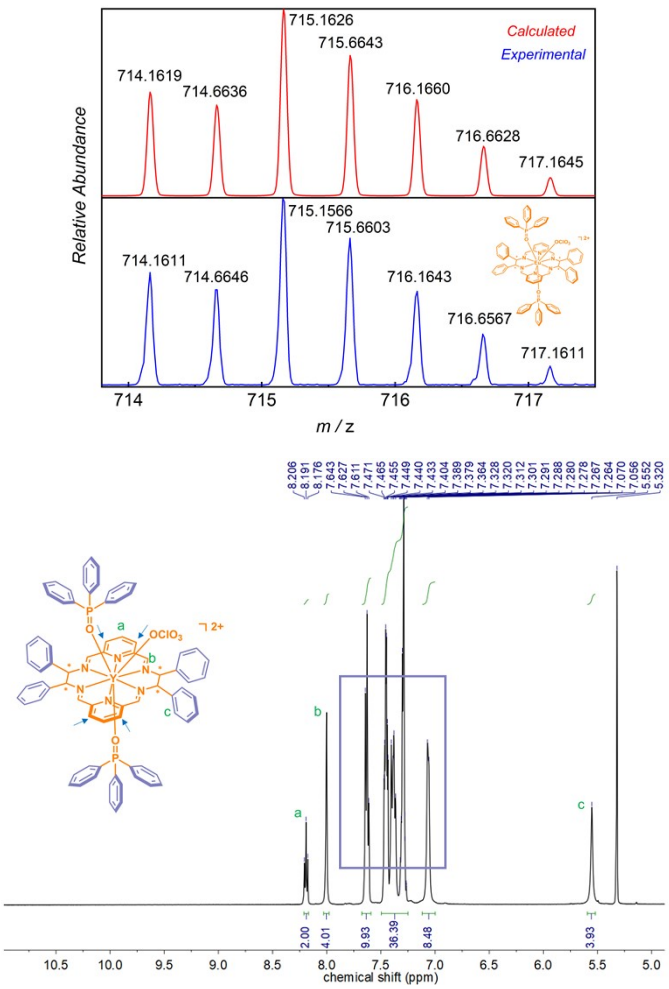

Fig. S17 HR-ESI-MS and simulated spectra of **S-Eu-Ph$_3$PO** in CH_3OH (top) and ^1H spectrum of isostructural Y(III) compound in CD_3OD (bottom).

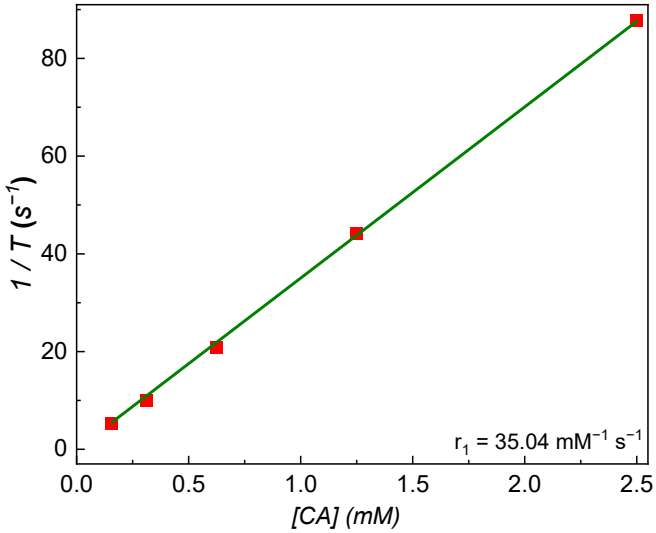

Fig. S18 Relaxivity determined from concentration-dependent T_1-weighted MR measurements at 1.2 T of **R-Gd** at room temperature.

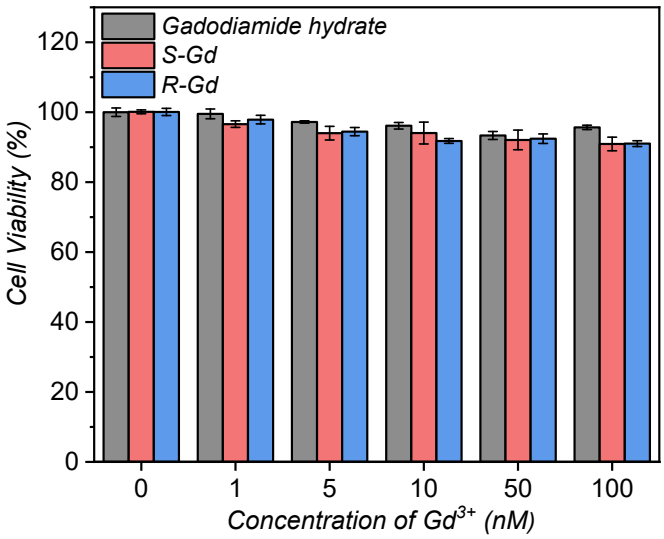

Fig. S19 Cell viabilities of A549 cells after incubated with various concentrations of Gd(III)-based compounds for 24 h.

References

1. D. Casanova, J. Cirera, M. Llunell, P. Alemany, D. Avnir and S. Alvarez, *J. Am. Chem. Soc.*, 2004, **126**, 1755-1763.
2. M. Pinsky and D. Avnir, *Inorg. Chem.*, 1998, **37**, 5575-5582.