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Nonlinear Optical Activity in Dipolar Organic-Lanthanide Complexes

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Supporting Information for publication

Synthesis of Complexes and Characterization by FT-IR and ESI-MS.

Figure S1 Selected SHG of lanthanide complexes (Ln = Dy, Er, Gd and Tb, λ_{ex} = 1.15 μm).

Figure S2. Powder XRD of the series of lanthanide complexes (Type **I**, Ln = Y, Ce, Pr, Nd, Eu and Gd; Type **II**, Ln = Lu, Yb, Tm and Er) in the solid state. (Full powder pattern of Figure 9).

Figure S3. UV-vis absorption spectrum of cinnamic acid and its lanthanide complexes (1.0 x 10^{-5} M, MeOH).

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Table S3. Selected bond angles (°) of Ln = Eu **6** (Type **I**) and Ln = Er **12** (Type **II**) complexes.

Synthesis of lanthanide complexes. [(*trans*-cinnamate)$_3$Ln]$_n$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er, Ho, Yb, Tm, Lu and Y): *Trans*-cinnamic acid (300 mg) was used as the chelating ligand with various lanthanide nitrate salts (Aldrich, 99.99%) in the mole ratio 3.5 to 1. The mixtures were stirred for 12 hours in methanol at room temperature and the pale colored precipitates were filtered out and were re-crystallized with acetonitrile. The purified products were isolated as pale-colored crystals.

Ln = La, **1**: white powder; yield: 519 mg (44%). MS (ESI): m/z 581 (M^+ + 2), 580 (M^+ + 1), 579 (M^+). Ln = Ce, **2**: pale yellow powder; yield: 632 mg (51%). MS (ESI): m/z 582 (M^+ + 2), 581 (M^+ + 1), 580 (M^+). Ln = Pr, **3**: pale green powder; yield: 706 mg (58%). MS (ESI): m/z 583 (M^+ + 2), 582 (M^+ + 1), 581 (M^+). Ln = Nd, **4**: pale purple powder; yield: 711 mg (60%). MS (ESI): m/z 588 (M^+ + 3), 587 (M^+ + 2), 586 (M^+ + 1), 585 (M^+), 584 (M^+ - 1), 583 (M^+ - 2), 582 (M^+ - 3). Ln = Sm, **5**: white powder; yield: 603 mg (48%). MS (ESI): m/z 596 (M^+ + 5), 595 (M^+ + 4), 594 (M^+ + 3), 593 (M^+ + 2), 592 (M^+ + 1), 591 (M^+), 590 (M^+ - 1), 589 (M^+ - 2), 588 (M^+ - 3), 587 (M^+ - 4). Ln = Eu, **6**: pale yellow powder; yield: 680 mg (57%). MS (ESI): m/z 594 (M^+ + 1), 593 (M^+), 592 (M^+ - 1), 591 (M^+ - 2). IR (KBr): 1533, 1504 cm^{-1} asym ν(COO^-), 1448, 1402 cm^{-1} sym ν(COO^-). Ln = Gd, **7**: white powder; yield: 358 mg (30%). MS (ESI): m/z 602 (M^+ + 3), 601 (M^+ + 2), 600 (M^+ + 1), 599 (M^+), 598 (M^+ - 1), 597 (M^+ - 2), 596 (M^+ - 3). IR (KBr): 1533, 1504 cm^{-1} asym ν(COO^-), 1449, 1402 cm^{-1} sym ν(COO^-). Ln = Tb, **8**: white powder; yield: 530 mg (44%). MS (ESI): m/z 600 (M^+), 599 (M^+ - 1), 598 (M^+ - 2). IR (KBr): 1533, 1504 cm^{-1} asym ν(COO^-), 1448, 1404 cm^{-1} sym ν(COO^-). Ln = Dy, **9**: white powder; yield: 579 mg (47%). MS (ESI): m/z 605 (M^+ + 2), 604 (M^+ + 1), 603 (M^+), 602 (M^+ - 1), 601 (M^+ - 2), 600 (M^+ - 3). Ln = Y, **10**: white powder; yield: 501 mg (46%). MS (ESI): m/z 532 (M^+ + 2), 531 (M^+ + 1), 530 (M^+). Ln = Ho, **11**: pale pink powder; yield: 599 mg (48%). MS (ESI): m/z 606 (M^+), 605 (M^+ - 1), 604 (M^+ - 2). Ln = Er, **12**: pale pink powder; yield: 582 mg (47%). MS (ESI): m/z 609 (M^+ + 1), 608 (M^+), 607 (M^+ - 1), 606 (M^+ - 2), 605 (M^+ - 3). Ln = Tm, **13**: white powder; yield: 609 mg (49%). MS (ESI): m/z 611 (M^+ + 2), 610 (M^+ + 1), 609 (M^+). Ln = Yb, **14**: white powder; yield: 689 mg (55%). MS (ESI): m/z 617 (M^+ + 3), 616 (M^+ + 2), 615 (M^+ + 1), 614 (M^+), 613 (M^+ - 1), 612 (M^+ - 2), 611 (M^+ - 3), 610 (M^+ - 4); IR (KBr): 1533, 1504 cm^{-1} asymν(COO^-), 1448, 1402 cm^{-1} sym ν(COO^-). Ln = Lu, **15**: white powder; yield: 689 mg (55%). MS (ESI): m/z 616 (M^+ + 2), 615 (M^+ + 1) IR (KBr): 1534, 1504 cm^{-1} asym ν(COO^-), 1448, 1402 cm^{-1} sym ν(COO^-). The crystal data of the 14 lanthanide complexes are listed in Table S1.

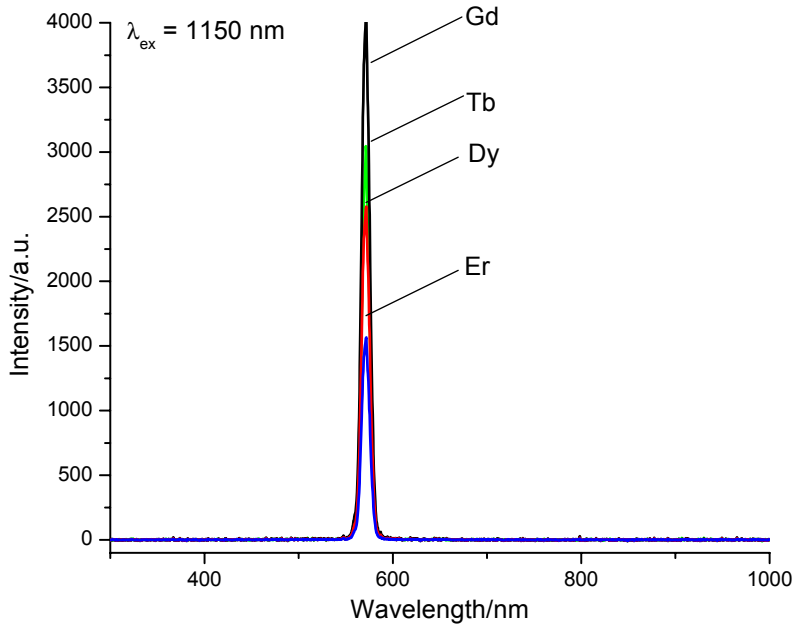


Figure S1 Selected SHG of lanthanide complexes (Ln = Dy, Er, Gd and Tb, λ_{ex} = 1.15 μm).

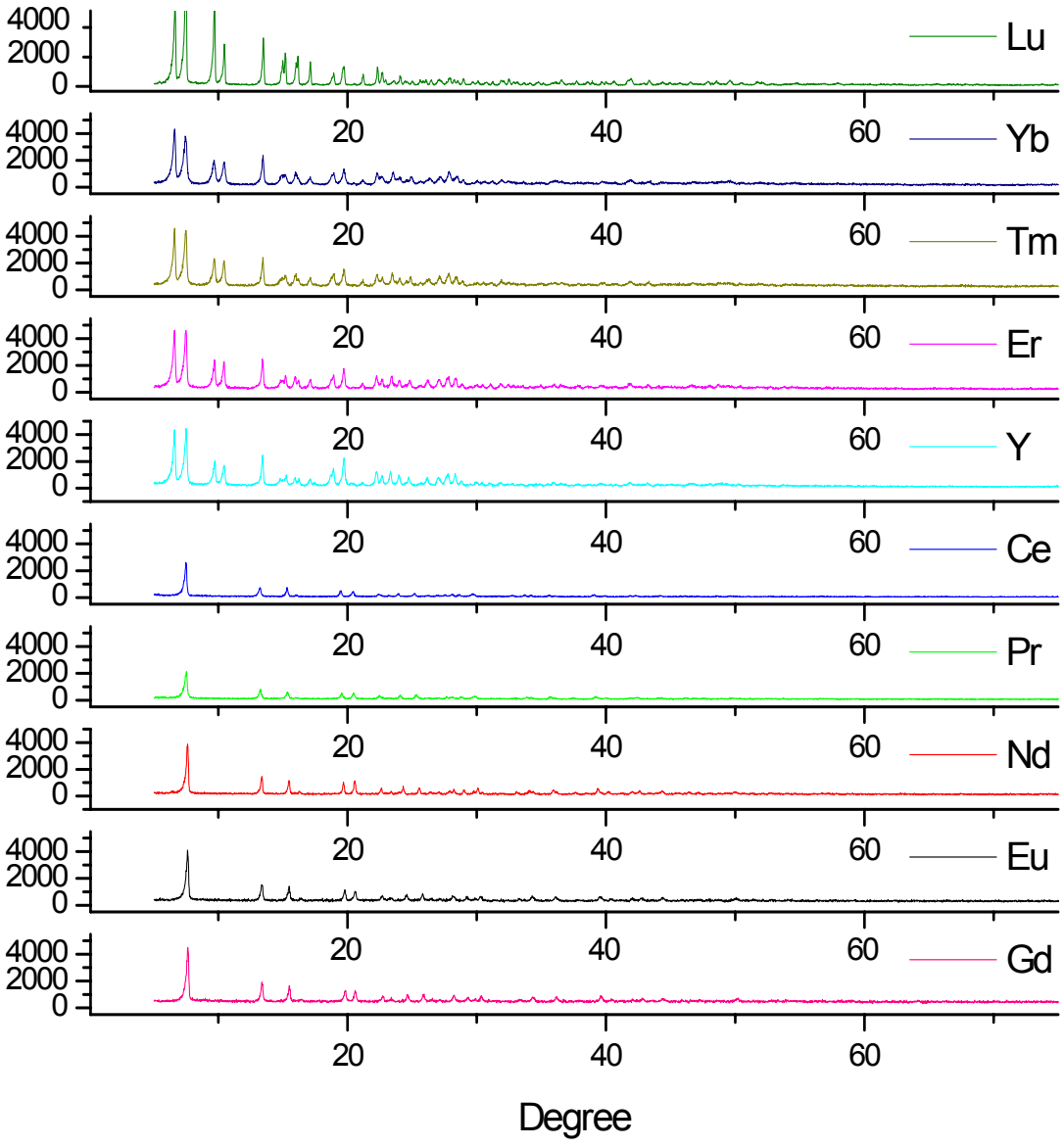


Figure S2. Powder XRD of the series of lanthanide complexes (Type **I**, Ln = Y, Ce, Pr, Nd, Eu and Gd; Type **II**, Ln = Lu, Yb, Tm and Er) in the solid state. (Full powder pattern of Figure 10).

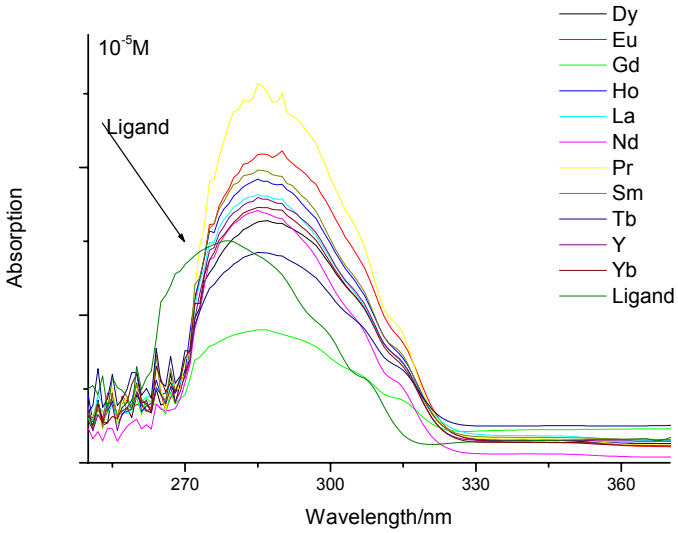
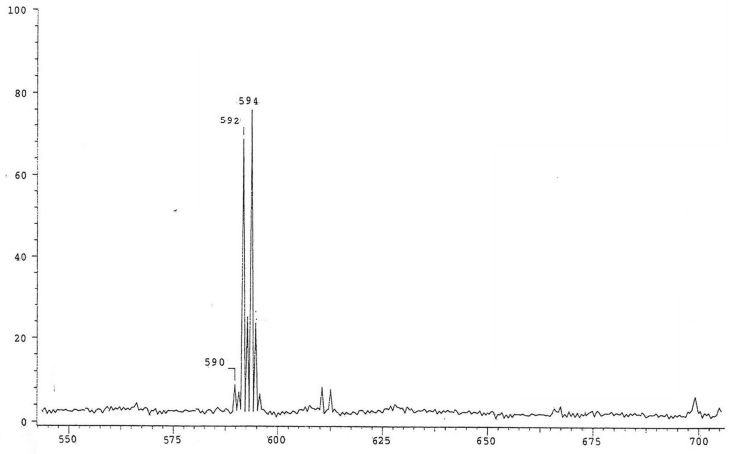


Figure S3. UV-vis absorption spectrum of cinnamic acid and its lanthanide complexes (1.0×10^{-5} M, MeOH).

Eu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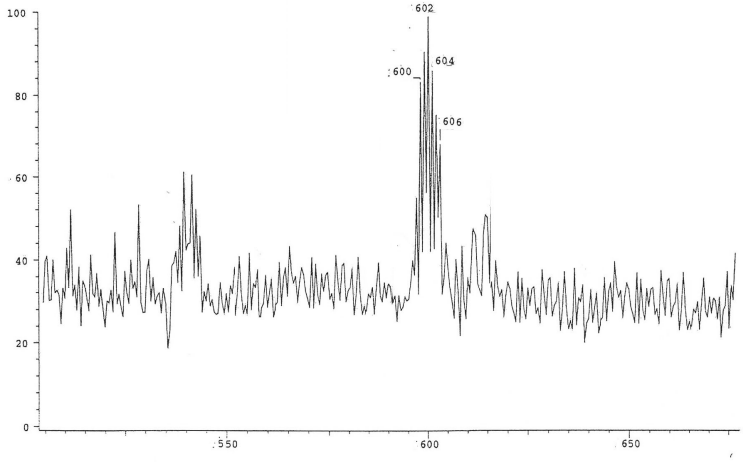
60
40
20
0
594
592
590
550
575
600
625
650
675
700

Gd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80
60
40
20
0
602
600
604
606
550
600
650

Tb

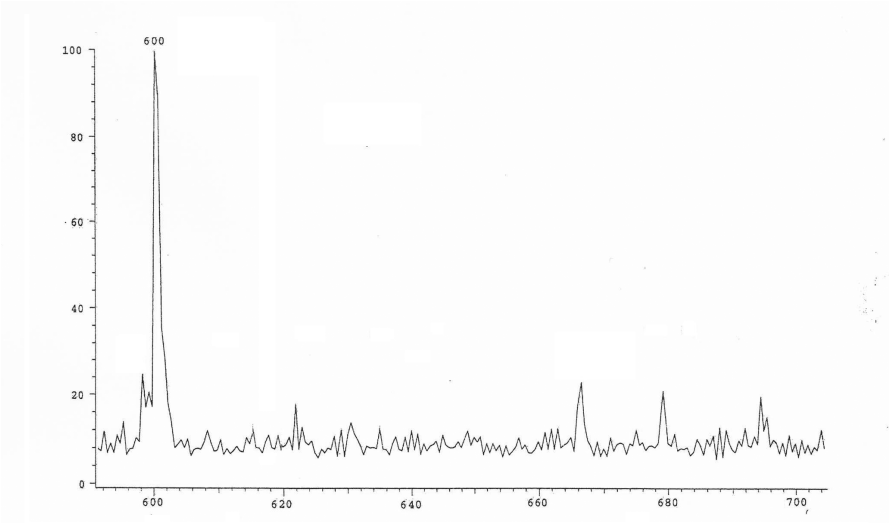
100
80
60
40
20
0
600
600
620
640
660
680
700

Table S1. Crystallographic data collection, intensity measurements and structure refinement and geometric parameters for $Ln[C_9H_7O_2)_3]_n$.

	La	Ce	Nd	Sm	Eu	Gd	Tb	Y	Dy	Ho	Er	Tm	Yb	Lu
F. W.	580.36	581.58	585.7	591.86	593.42	598.71	600.38	530.37	603.96	606.39	608.72	610.39	614.50	616.43
T/°C	301	301	301	301	303	301	303	301	301	301	301	301	301	301
Crystal system	Trigonal	Trigonal	Trigonal	Trigonal	Trigonal	Trigonal	Trigonal	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space Group	R3c (#161)	R3c (#161)	R3c (#161)	R3c (#161)	R3c (#161)	R3c (#161)	R3c (#161)	$P2_1$ (#4)	$P2_1$ (#4)	$P2_1$ (#4)	$P2_1$ (#4)	$P2_1$ (#4)	$P2_1$ (#4)	$P2_1$ (#4)
a **/Å**	22.636(2)	22.646(2)	22.657(3)	22.646(2)	22.649(4)	22.654(6)	22.647(4)	11.543(10)	11.520(11)	11.544(1)	11.548(1)	11.564(1)	11.574(2)	11.598(2)
b **/Å**	22.636(2)	22.646(2)	22.657(3)	22.646(2)	22.649(4)	22.654(6)	22.647(4)	7.918(7)	7.936(7)	7.917(9)	7.886(1)	7.870 (9)	7.848(2)	7.817(2)
c **/Å**	7.7554(10)	7.9212(7)	7.830(1)	7.7670(11)	7.744(1)	7.722(2)	7.703(1)	13.062(11)	13.078(12)	13.071(2)	13.048(1)	13.042(2)	13.043(3)	13.021(3)
α / °	90	90	90	90	90	90	90	90	90	90	90	90	90	90
β / °	90	90	90	90	90	90	90	94.139(2)	94.049(2)	94.136(2)	94.15(1)	94.280(2)	94.384(3)	94.354(3)
γ / °	120	120	120	120	120	120	120	90	90	90	90	90	90	90
V / Å^3	3441.4(6)	3518.2(5)	3481.3(9)	3449.5(7)	3440.3(10)	3432.0(16)	3421.5(10)	1190.8(2)	1192.7(2)	1191.5(3)	1185.1(2)	1183.6(2)	1181.3(4)	1176.1(4)
Z	6	6	6	6	6	6	6	2	2	2	2	2	2	2
d_{calc} / g cm^{-3}	1.680	1.647	1.676	1.709	1.718	1.738	1.748	1.479	1.682	1.690	1.706	1.713	1.727	1.740
μ / mm^{-1}	1.896	1.981	2.277	2.601	2.770	2.948	3.136	2.492	3.117	3.364	3.572	3.780	3.999	4.2378
$F_{(000)}$	1728	1734	1746	1758	1764	1770	1776	540	594	596	598	600	602	604
Crystal size / mm	0.01X0.02X 0.48	0.06X0.07X0 .41	0.02X0.04X0.4 1	0.05X0.07X0.3 6	0.08X0.18X 0.42	0.05X0.06X 0.48	0.04X0.05X 0.48	0.08X0.17X 0.38	0.15X0.21X 0.41	0.13X0.14X 0.30	0.12X0.16X 0.44	0.06X0.17X 0.35	0.08X0.17X 0.38	0.02x0.03x 0.48
No. of unique reflns. (Total)	6925	7227	7574	6304	6841	6917	7000	7456	6882	7328	6989	7338	7370	7162
No. of obsd reflns. (I>2σ(I))	1435	1493	1236	1081	1605	1701	1703	2450	2719	2708	2681	2628	2644	3761
R_1 (I>2σ(I))	0.031	0.018	0.015	0.015	0.019	0.018	0.035	0.029	0.019	0.21	0.022	0.020	0.030	0.033
wR (all data)	0.034	0.021	0.017	0.018	0.024	0.022	0.038	0.028	0.023	0.26	0.027	0.021	0.037	0.041
Goodness of fit/S	1.034	1.006	1.067	1.054	1.054	1.043	1.081	1.024	1.014	1.038	1.024	1.046	1.029	1.001
Max. shift/error	0.043	<0.001	0.013	0.028	0.031	0.021	0.003	<0.0001	0.015	0.028	0.034	0.00	0.023	0.012

Table S1. (cont)

	La	Ce	Nd	Sm	Eu	Gd	Tb	Y	Dy	Ho	Er	Tm	Yb	Lu
Coordination	8	9	9	9	9	9	9	7	7	7	7	7	7	7
M…M / Å	3.878(4)	3.961	3.915(1)	3.884(1)	3.872(2)	3.861(1)	3.852(3)	4.124(1)	4.135(1)	4.122(2)	4.107(2)	4.096(1)	4.083(3)	4.067(2)
M—O / Å	2.397(5) - 2.625(4)	2.466(2) - 2.678(2)	2.429(3) – 2.644(3)	2.397(7) – 2.633(3)	2.389(3) - 2.633(3)	2.377(4) - 2.624(3)	2.359(8) – 2.628(6)	2.236(3) - 2.478(3)	2.254(3) - 2.489(3)	2.247(4)- 2.474(4)	2.228(4)- 2.465(4)	2.221(4)- 2.453(4)	2.209(7)- 2.443(7)	2.190(6)- 2.445(7)
Dihedral angle / ° (COOM) *vs* C=C	9.3(7)	10.2(3)	10.4(3)	10.4(4)	10.0(5)	9.8(4)	10.0(9)	2.2(6) 11.7(2), 13.0(4)	1.6(8), 11.5(3), 12.6(5)	2.7(7), 12.3(3), 13.1(6)	24.9(8), 105.2(5), 148.1(3)	4.0(8), 12.0(2), 13.7(5)	2.8(18), 13.6(4), 14.5(9)	4.2(16), 11.6(5), 31.6(5)
Dihedral angle / ° (COOM) *vs* —Ph	25.4(2)	24.9(1)	25.4(1)	25.8(1)	25.8(2)	26.1(2)	26.3(4)	8.7(1), 15.6(1), 30.3(2)	7.9(2), 9.3(2), 28.9(2)	8.2(2), 14.9(2), 30.2(2)	30.6(2), 94.5(5),145 .9(2)	8.1(2), 16.1(2), 30.4(2)	8.6(3), 17.6(3), 31.0(4)	8.5(3), 16.0(3), 34.2(3)

Table S2. Selected bond lengths (Å) of Ln = Eu **6** (Type **I**) and Ln = Er **12** (Type **II**) complexes.

Eu		Er	
Eu(1)-O(1)	2.633(3)	Er(1)-O(1)	2.265(5)
Eu(1)-O(1)[a]	2.633(3)	Er(1)-O(2)	2.242(5)
Eu(1)-O(1)[b]	2.633(3)	Er(1)-O(3)	2.302(4)
Eu(1)-O(1)[c]	2.443(3)	Er(1)-O(3)[a]	2.465(4)
Eu(1)-O(1)[e]	2.443(3)	Er(1)-O(4)	2.360(5)
Eu(1)-O(2)	2.389(3)	Er(1)-O(5)	2.228(4)
Eu(1)-O(2)[a]	2.389(4)	Er(1)-O(6)	2.250(5)
Eu(1)...Eu(1)[d]	3.872(2)	Er(1) ... Er(1)[a]	4.107(2)

Symmetry code of **6**: a = -Y,+X-Y,+Z; b = -X+Y,-X,+Z; c = -X+Y,+Y,1/2+Z; d = +X,+X-Y,1/2+Z; e= -Y,-X,1/2+Z. Symmetry code of **12**: a = -X,1/2+Y,-Z.

Table S3. Selected bond angles (°) of Ln = Eu **6** (Type **I**) and Ln = Er **12** (Type **II**) complexes.

Eu		Er	
O(1)[a]-Eu(1)-O(1)	65.26(9)	O(2)-Er(1)-O(1)	154.1(2)
O(1)[b]-Eu(1)-O(1)	65.26(8)	O(3)-Er(1)-O(1)	77.2(2)
O(1)[c]-Eu(1)-O(1)	124.75(9)	O(3)[a]-Er(1)-O(1)	131.7(2)
O(1)[d]-Eu(1)-O(1)	102.92(9)	O(4)-Er(1)-O(1)	77.8(2)
O(1)[e]-Eu(1)-O(1)	161.3(1)	O(5)-Er(1)-O(1)	92.6(2)
O(1)[d]-Eu(1)-O(1)[c]	71.1(1)	O(6)-Er(1)-O(1)	93.1(2)
O(2)-Eu(1)-O(1)	51.4(1)	O(3)-Er(1)-O(2)	76.8(2)
O(2)-Eu(1)-O(1)[c]	73.9(1)	O(3)[a]-Er(1)-O(2)	74.2(2)
O(2)[a]-Eu(1)-O(1)	116.1(1)	O(4)-Er(1)-O(2)	128.0(2)
O(2)[b]-Eu(1)-O(1)	80.7(1)	O(5)-Er(1)-O(2)	87.5(2)
O(2)-Eu(1)-O(1)[e]	140.3(1)	O(6)-Er(1)-O(2)	89.0(2)
Eu(1)-O(1)-Eu(1)[c]	99.34(8)	Er(1)-O(3)-Er(1)[a]	118.9(2)

Symmetry code of **6**: a = -Y,+X-Y,+Z; b = -X+Y,-X,+Z; c = -X+Y,+Y,1/2+Z; d = +X,+X-Y,1/2+Z; e= -Y,-X,1/2+Z. Symmetry code of **12**: a = -X,1/2+Y,-Z.