Supporting Information for:

Structural and Photophysical Properties of Visible– and Near–Infrared–Emitting Tris Lanthanide(III) Complexes Formed with the Enantiomers of *N*,*N*'–bis(1–phenylethyl) –2,6–pyridinedicarboxamide

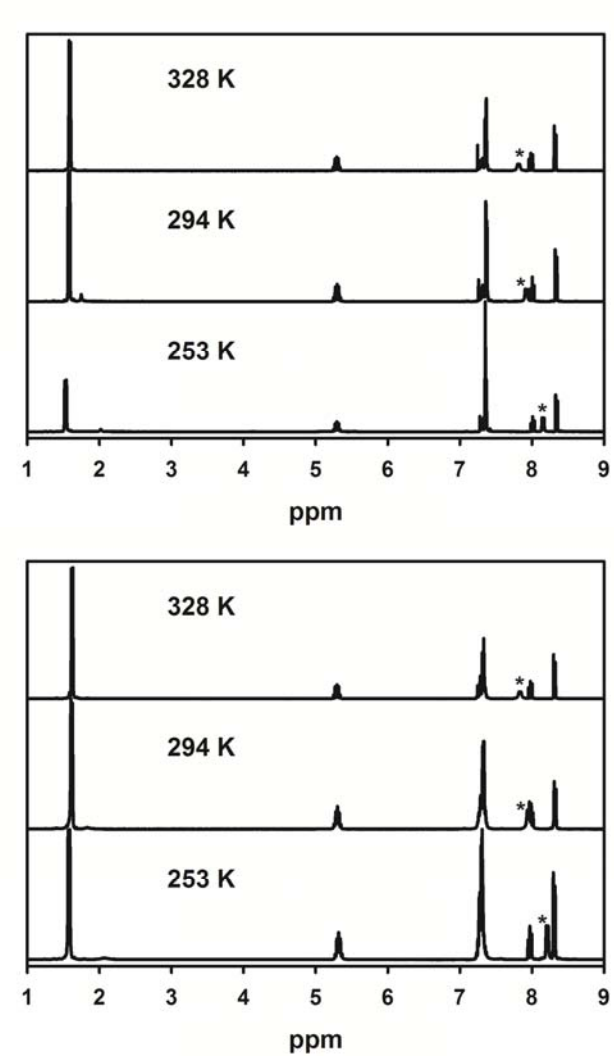
KimNgan T. Hua,[†] Jide Xu,[‡] Eliseo E. Quiroz,[†] Sabrina Lopez,[†] Andrew J. Ingram,[†] Victoria Anne Johnson,[†] Angela R. Tisch,[†] Ana de Bettencourt–Dias,[#] Daniel A. Straus,[†] and Gilles Muller*[,†]

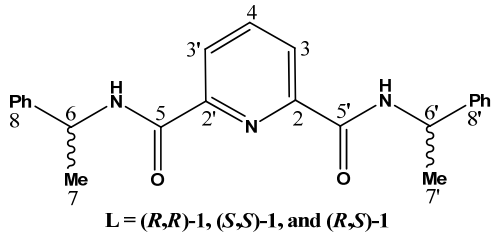
[†] San José State University, Department of Chemistry, 1 Washington Square, San José, California 95192–0101, United States

[‡] University of California, Berkeley, Department of Chemistry, Berkeley, California 94720–1460, United States

[#] University of Nevada, Reno, Department of Chemistry, 1664 N. Virginia St., Reno, Nevada 89557–0216, United States

*: gilles.muller@sjsu.edu





L = (*R*,*R*)-1, (*S*,*S*)-1, and (*R*,*S*)-1

Figure S1. Variable Temperature ^{1}H–NMR spectra of (*R*,*R*)–**1** (top) and (*R*,*S*)–**1** (bottom) in $CDCl_3$. The symbol * denotes signal arising from the proton of the NH group.

Table S1. Selected Bond Lengths (Å) and Angles (deg) in (*R*,*S*)–**1** (Standard Deviation in Parentheses).

O(1)-C(9)	1.228(3)	C(11)-C(12)	1.377(3)	C(9)-N(1)-C(7)	123.7(2)	N(2)-C(14)-C(15)	117.0(2)
O(2)-C(15)	1.237(3)	C(12)-C(13)	1.375(3)	C(10)-N(2)-C(14)	117.30(19)	C(13)-C(14)-C(15)	119.9(2)
O(3)-C(32)	1.236(3)	C(13)-C(14)	1.386(3)	C(15)-N(3)-C(16)	122.7(2)	O(2)-C(15)-N(3)	124.3(2)
O(4)-C(38)	1.236(3)	C(14)-C(15)	1.506(3)	C(32)-N(4)-C(30)	122.31(19)	O(2)-C(15)-C(14)	120.4(2)
N(1)-C(9)	1.327(3)	C(16)-C(17)	1.502(4)	C(33)-N(5)-C(37)	116.84(19)	N(3)-C(15)-C(14)	115.3(2)
N(1)-C(7)	1.467(3)	C(24)-C(25)	1.378(3)	C(38)-N(6)-C(39)	120.68(19)	N(3)-C(16)-C(18A)	115.9(8)
N(2)-C(10)	1.337(3)	C(24)-C(29)	1.380(3)	C(6)-C(1)-C(2)	121.9(3)	N(3)-C(16)-C(17)	110.0(2)
N(2)-C(14)	1.342(3)	C(25)-C(26)	1.373(4)	C(3)-C(2)-C(1)	120.0(3)	C(18A)-C(16)-C(17)	116.2(8)
N(3)-C(15)	1.333(3)	C(26)-C(27)	1.363(4)	C(2)-C(3)-C(4)	119.4(3)	N(3)-C(16)-C(18B)	105.2(8)
N(3)-C(16)	1.460(3)	C(27)-C(28)	1.372(3)	C(3)-C(4)-C(5)	120.6(3)	N(4)-C(30)-C(29)	112.32(19)
N(4)-C(32)	1.331(3)	C(28)-C(29)	1.383(3)	C(6)-C(5)-C(4)	121.6(3)	N(4)-C(30)-C(31)	111.09(19)
N(4)-C(30)	1.454(3)	C(29)-C(30)	1.515(3)	C(5)-C(6)-C(1)	116.6(2)	C(29)-C(30)-C(31)	110.60(19)
N(5)-C(33)	1.345(3)	C(30)-C(31)	1.521(3)	C(5)-C(6)-C(7)	122.2(2)	O(3)-C(32)-N(4)	123.9(2)
N(5)-C(37)	1.345(3)	C(32)-C(33)	1.497(3)	C(1)-C(6)-C(7)	121.2(2)	O(3)-C(32)-C(33)	119.3(2)
N(6)-C(38)	1.330(3)	C(33)-C(34)	1.382(3)	N(1)-C(7)-C(8)	110.65(19)	N(4)-C(32)-C(33)	116.8(2)
N(6)-C(39)	1.462(3)	C(34)-C(35)	1.366(3)	N(1)-C(7)-C(6)	110.3(2)	N(5)-C(33)-C(34)	122.6(2)
C(1)-C(6)	1.375(4)	C(36)-C(37)	1.373(3)	C(8)-C(7)-C(6)	114.8(2)	N(5)-C(33)-C(32)	117.3(2)
C(1)-C(2)	1.386(4)	C(37)-C(38)	1.505(3)	O(1)-C(9)-N(1)	124.4(2)	C(34)-C(33)-C(32)	120.1(2)
C(2)-C(3)	1.350(4)	C(39)-C(41)	1.515(3)	O(1)-C(9)-C(10)	119.6(2)	C(35)-C(34)-C(33)	119.9(2)
C(3)-C(4)	1.351(4)	C(39)-C(40)	1.516(3)	N(1)-C(9)-C(10)	116.1(2)	C(34)-C(35)-C(36)	118.2(2)
C(4)-C(5)	1.385(4)	C(41)-C(46)	1.372(3)	N(2)-C(10)-C(11)	122.8(2)	C(37)-C(36)-C(35)	119.0(2)
C(5)-C(6)	1.367(3)	C(41)-C(42)	1.374(3)	N(2)-C(10)-C(9)	118.0(2)	N(5)-C(37)-C(36)	123.5(2)
C(6)-C(7)	1.511(3)	C(42)-C(43)	1.389(4)	C(11)-C(10)-C(9)	119.1(2)	N(5)-C(37)-C(38)	116.81(19)
C(7)-C(8)	1.508(3)	C(43)-C(44)	1.372(4)	C(10)-C(11)-C(12)	119.5(2)	C(36)-C(37)-C(38)	119.7(2)
C(9)-C(10)	1.509(3)	C(44)-C(45)	1.347(5)	C(13)-C(12)-C(11)	118.6(2)	O(4)-C(38)-N(6)	123.5(2)
C(10)-C(11)	1.376(3)	C(45)-C(46)	1.374(4)	C(12)-C(13)-C(14)	118.7(2)	O(4)-C(38)-C(37)	119.8(2)

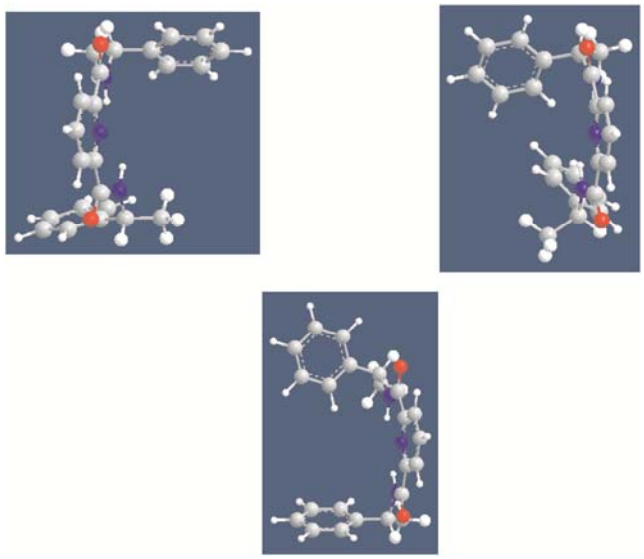


Figure S2. Geometric optimization of the three optical isomers of **L**, (*R*,*R*)–**1** (top left), (*S*,*S*)–**1** (top right), and (*R*,*S*)–**1** (bottom), as obtained by DFT B3LYP 6–31G(d) calculations.

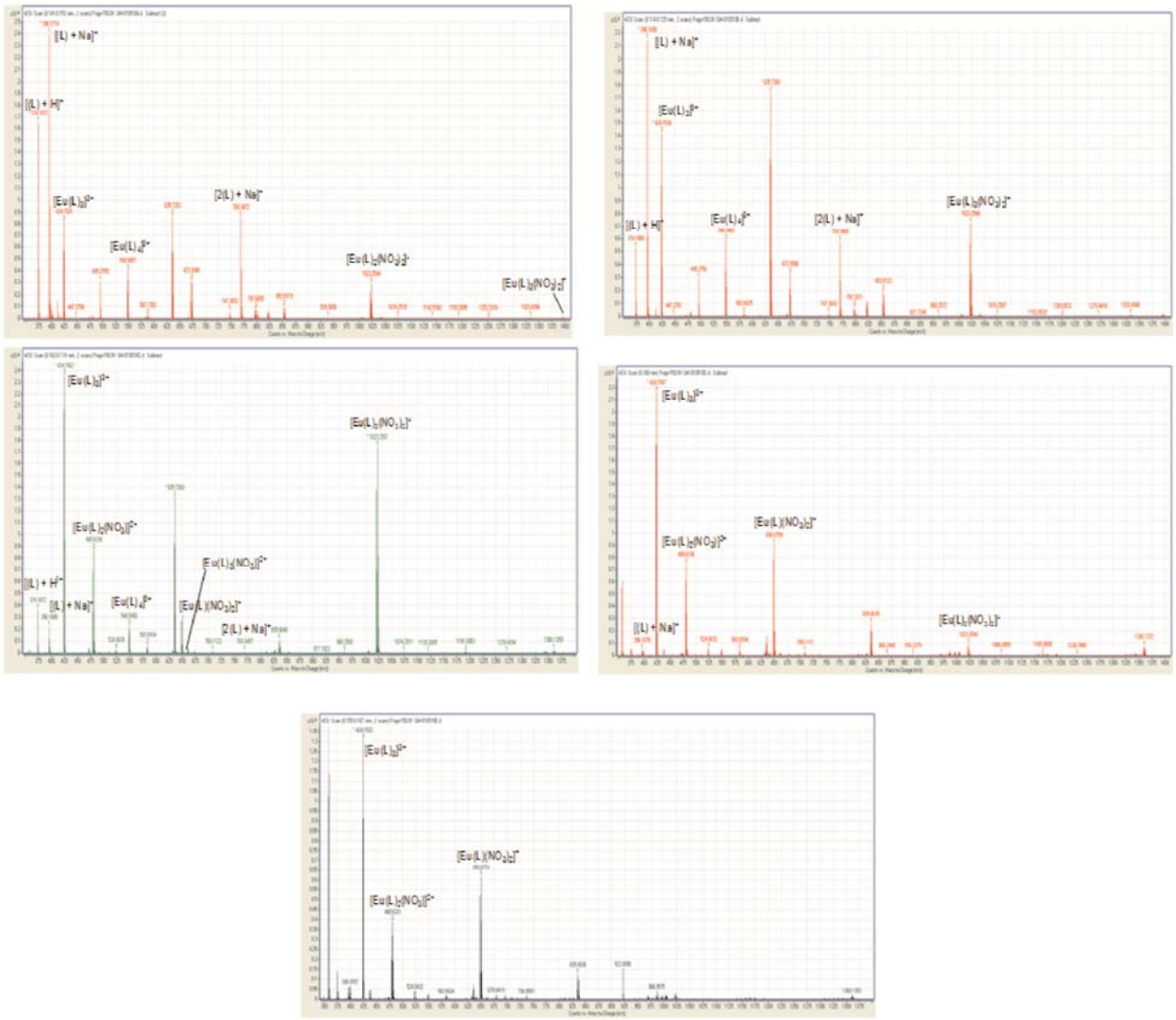


Figure S3. ES–MS spectra of Eu(III) and **L** in anhydrous MeCN at 298 K (**L** = (*R*,*R*)–**1**)).

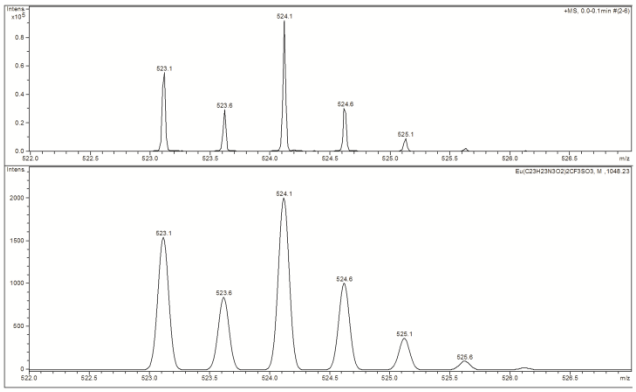


Figure S4. Detail of the ES–MS signal arising from the $[Eu\mathbf{L}_3]^{3+}$ species observed in the ES–MS Spectra of Solutions ($[\mathbf{L}]_t$ = 2 × 10^{-3} M in Anhydrous MeCN) with Ratios R = $[Eu]_t/[\mathbf{L}]_t$ = 0–4 at 298 K (**L** = (*R*,*R*)–**1**)).

Table S2. Species Observed in the ES–MS Spectra of Solutions ($[L]_t$ = 2 × 10^{-3} M in Anhydrous MeCN) with Ratios R = $[Eu]_t/[\mathbf{L}]_t$ = 0.25, 0.33, 0.5, and 1.0 at 298 K (**L** = (*R*,*R*)–**1**)).

Species	m/z^a	Species	m/z^a
$[(\mathbf{L}) + Na]^+$	396.2	$[Eu(\mathbf{L})(Otf)(CH_3CN)_{12}]^{2+}$	583.7
$[Eu(\mathbf{L})_3]^{3+}$	424.2	$[Eu(\mathbf{L})_3(Otf)]^{2+}$	710.7
$[Eu(\mathbf{L})_2(Otf)]^{2+}$	524.1	$[Eu(\mathbf{L})_2(Otf)_2]^+$	667.2
$[Eu(\mathbf{L})_4]^{3+}$	548.6	$[Eu(\mathbf{L})_3(Otf)_2]^+$	1197.2

[a] m/z values given for the maximum of the peak at unit mass resolution where Otf^- denotes $CF_3SO_3^-$.

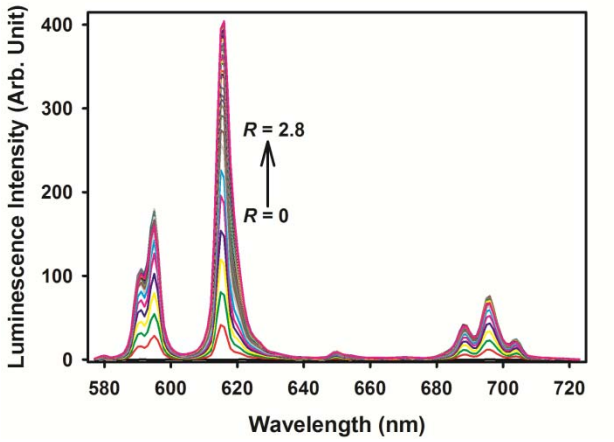


Figure S5. Time–resolved luminescence spectra obtained while titrating 5.15 × 10^{-5} M (*R*,*R*)–**1** with 1.09 × 10^{-3} M $Eu(NO_3)_3$ at 298 K in anhydrous MeCN, in the presence of 0.05 M Et_4NClO_4, and under N_2 atmosphere. R = $[Eu]_t/[(R,R)–\mathbf{1}]_t$.

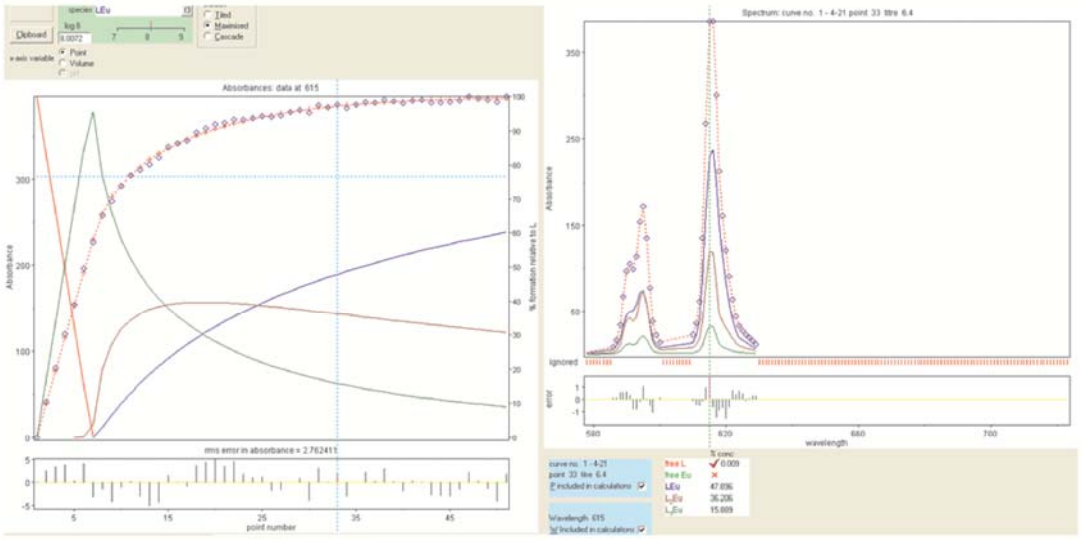


Figure S6. Example of Hyperquad2006 refinement data fits from a time–resolved luminescence titration of 5.15 × 10^{-5} M (*R*,*R*)–**1** with 1.09 × 10^{-3} M $Eu(NO_3)_3$ in anhydrous MeCN (μ = 0.05 M Et_4NClO_4) at 298 K and under N_2 atmosphere.

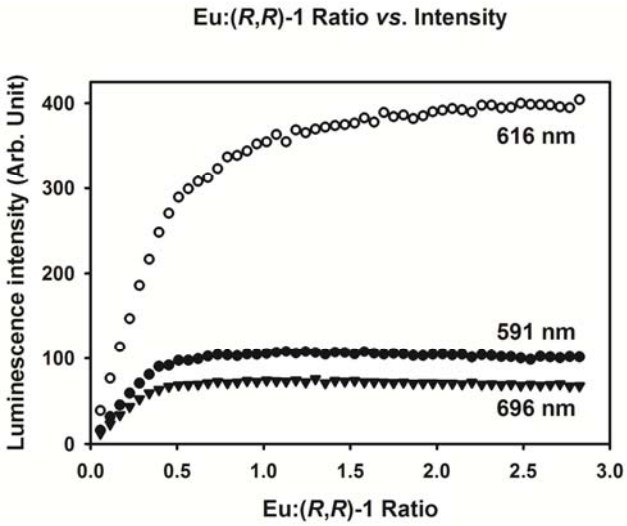


Figure S7. Luminescence intensity *vs.* R plots at various wavelengths during the time–resolved luminescence titration of 5.15×10^{-5} M (*R*,*R*)–**1** with 1.09×10^{-3} M $Eu(NO_3)_3$ in anhydrous MeCN (μ = 0.05 M Et_4NClO_4) at 298 K and under N_2 atmosphere. $R = [Eu]_t/[(R,R)\text{–}\mathbf{1}]_t$.

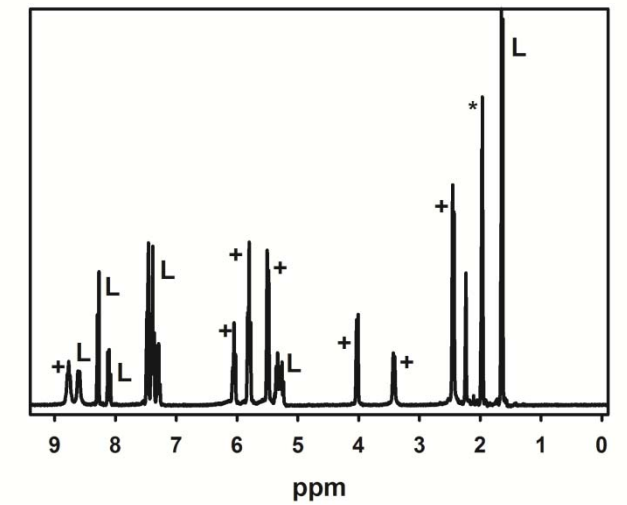


Figure S8. ^{1}H–NMR spectrum of a solution containing a ratio, $R = [Eu]_t/[\mathbf{L}]_t$ of 0.2 in CD_3CN (* symbol) at 298 K. The symbols **L** and **+** denote signals arising from the **L** and 1:3 species, respectively (**L** = (*R*,*R*)–1)).

Table S3. Details of the Crystallographic Data Collection, Structural Determination, and Refinement for $[Ln\mathbf{L}_3]^{3+}$ (Ln(III) = Eu, Gd, Tb, Yb and **L** = (*R*,*R*)–**1** and/or (*S*,*S*)–**1**).

	$[Eu\mathbf{L}_3]^{3+}$ (**L** = (*S*,*S*)–**1**))	$[Gd\mathbf{L}_3]^{3+}$ (**L** = (*R*,*R*)–**1**))	$[Gd\mathbf{L}_3]^{3+}$ (**L** = (*S*,*S*)–**1**))
empirical formula	$C_{70.88}H_{76.50}Cl_3EuN_9O_{7.88}$	$C_{70.88}H_{76.50}Cl_3GdN_9O_{7.88}$	$C_{70.88}H_{76.50}Cl_3GdN_9O_{7.88}$
fw	1438.72	1444.01	1444.01
T (K)	147(2)	151(2)	143(2)
cryst syst	cubic	cubic	cubic
space group	I23	I23	I23
a/Å	25.965(2)	25.967(2)	25.955
b/Å	25.965(2)	25.967(2)	25.955
c/Å	25.965(2)	25.967(2)	25.955
α/deg	90	90	90
β/deg	90	90	90
γ/deg	90	90	90
V/Å^3	17505.1	17509.2	17484.9
Z	8	8	8
abs coeff (mm^{-1})	0.856	0.897	0.898
D_c/mg·m^{-3}	1.092	1.096	1.097
reflns collected	40303	56168	82880
unique reflns	5358	5364	7003
R_{int}	0.0316	0.0436	0.0420
params	278	341	275
final *R* [I > 2σ(*I*)]	0.0297	0.0271	0.0310
wR2	0.0816	0.0734	0.0787

Table S4. Details of the Crystallographic Data Collection, Structural Determination, and Refinement for $[Ln\mathbf{L}_3]^{3+}$ (Ln(III) = Tb, Yb and **L** = (*R*,*R*)–**1** and/or (*S*,*S*)–**1**).

	$[Tb\mathbf{L}_3]^{3+}$ (**L** = (*R*,*R*)–**1**))	$[Tb\mathbf{L}_3]^{3+}$ (**L** = (*S*,*S*)–**1**))	$[Yb\mathbf{L}_3]^{3+}$ (**L** = (*S*,*S*)–**1**))
empirical formula	$C_{70.50}H_{76.25}Cl_3N_9O_{7.50}Tb$	$C_{71.50}H_{79}Cl_3N_9O_{8.50}Tb$	$C_{71.50}H_{79}Cl_3N_9O_{8.50}Yb$
fw	1434.93	1465.71	1479.83
T (K)	151(2)	151(2)	131(2)
cryst syst	cubic	cubic	cubic
space group	I23	I23	I23
a/Å	25.938(2)	25.942(2)	25.849
b/Å	25.938(2)	25.942(2)	25.949
c/Å	25.938(2)	25.942(2)	25.949
α/deg	90	90	90
β/deg	90	90	90
γ/deg	90	90	90
V/Å^3	17450.6	17458.6	17271.5
Z	8	8	8
abs coeff (mm^{-1})	0.950	0.951	1.226
D_c/mg·m^{-3}	1.092	1.115	1.138
reflns collected	103517	35964	56820
unique reflns	5337	5329	5277
R_{int}	0.0406	0.0308	0.0307
params	274	279	278
final *R* [I > 2σ(*I*)]	0.0219	0.0227	0.0193
wR2	0.0597	0.0637	0.0515

Table S5. Selected Bond Lengths (Å) and Angles (deg) in Δ–[Eu((*S*,*S*)–**1**)$_3$]$^{3+}$ (Standard Deviation in Parentheses).

N(2)-Eu(1)	2.555(3)
Eu(1)-O(1)#1	2.388(2)
Eu(1)-O(1)#2	2.388(2)
Eu(1)-O(1)	2.388(2)
Eu(1)-O(2)	2.404(2)
Eu(1)-O(2)#1	2.404(2)
Eu(1)-O(2)#2	2.404(2)
Eu(1)-N(2)#1	2.555(3)
Eu(1)-N(2)#2	2.555(3)
C(10)-N(2)-Eu(1)	119.6(2)
C(14)-N(2)-Eu(1)	120.1(2)
C(15)-N(3)-C(16)	122.7(3)
O(1)#1-Eu(1)-O(1)#2	81.05(9)
O(1)#1-Eu(1)-O(1)	81.05(9)
O(1)#2-Eu(1)-O(1)	81.05(9)
O(1)#1-Eu(1)-O(2)	144.99(8)
O(1)#2-Eu(1)-O(2)	82.72(8)
O(1)-Eu(1)-O(2)	126.53(8)
O(1)#1-Eu(1)-O(2)#1	126.53(8)
O(1)#2-Eu(1)-O(2)#1	144.99(8)
O(1)-Eu(1)-O(2)#1	82.72(8)
O(2)-Eu(1)-O(2)#1	82.41(9)
O(1)#1-Eu(1)-O(2)#2	82.72(8)
O(1)#2-Eu(1)-O(2)#2	126.53(8)
O(1)-Eu(1)-O(2)#2	144.99(8)
O(2)-Eu(1)-O(2)#2	82.41(9)
O(2)#1-Eu(1)-O(2)#2	82.41(9)
O(1)#1-Eu(1)-N(2)#1	63.30(8)
O(1)#2-Eu(1)-N(2)#1	139.19(9)
O(1)-Eu(1)-N(2)#1	74.66(8)
O(2)-Eu(1)-N(2)#1	138.04(9)
O(2)#1-Eu(1)-N(2)#1	63.30(8)
O(2)#2-Eu(1)-N(2)#1	70.33(8)
O(1)#1-Eu(1)-N(2)	139.19(9)
O(1)#2-Eu(1)-N(2)	74.66(8)
O(1)-Eu(1)-N(2)	63.30(8)
O(2)-Eu(1)-N(2)	63.30(8)
O(2)#1-Eu(1)-N(2)	70.33(8)
O(2)#2-Eu(1)-N(2)	138.04(9)
N(2)#1-Eu(1)-N(2)	119.953(5)
O(1)#1-Eu(1)-N(2)#2	74.66(8)
O(1)#2-Eu(1)-N(2)#2	63.30(8)
O(1)-Eu(1)-N(2)#2	139.19(9)
O(2)-Eu(1)-N(2)#2	70.33(8)
O(2)#1-Eu(1)-N(2)#2	138.04(9)
O(2)#2-Eu(1)-N(2)#2	63.30(8)
N(2)#1-Eu(1)-N(2)#2	119.953(5)
N(2)-Eu(1)-N(2)#2	119.953(5)
C(9)-O(1)-Eu(1)	125.7(2)
C(15)-O(2)-Eu(1)	125.8(2)

Symmetry transformations used to generate equivalent atoms:
#1 -z+1,-x+1,y #2 -y+1,z,-x+1 #3 -x+1,-y,z

Table S6. Selected Bond Lengths (Å) and Angles (deg) in Λ–[Gd((*R*,*R*)–**1**)$_3$]$^{3+}$ (Standard Deviation in Parentheses).

N(2)-Gd(1)	2.543(2)
O(1)-Gd(1)	2.393(2)
O(2)-Gd(1)	2.3811(18)
Gd(1)-O(2)#1	2.3811(18)
Gd(1)-O(2)#2	2.3811(18)
Gd(1)-O(1)#1	2.393(2)
Gd(1)-O(1)#2	2.393(2)
Gd(1)-N(2)#1	2.543(2)
Gd(1)-N(2)#2	2.543(2)
C(10)-N(2)-Gd(1)	119.74(19)
C(14)-N(2)-Gd(1)	120.54(18)
C(15)-O(1)-Gd(1)	125.93(18)
C(9)-O(2)-Gd(1)	125.33(19)
O(2)#1-Gd(1)-O(2)#2	80.86(8)
O(2)#1-Gd(1)-O(2)	80.86(8)
O(2)#2-Gd(1)-O(2)	80.86(8)
O(2)#1-Gd(1)-O(1)#1	127.02(7)
O(2)#2-Gd(1)-O(1)#1	144.74(7)
O(2)-Gd(1)-O(1)#1	83.03(7)
O(2)#1-Gd(1)-O(1)	144.74(7)
O(2)#2-Gd(1)-O(1)	83.03(7)
O(2)-Gd(1)-O(1)	127.02(7)
O(1)#1-Gd(1)-O(1)	82.04(8)
O(2)#1-Gd(1)-O(1)#2	83.03(7)
O(2)#2-Gd(1)-O(1)#2	127.02(7)
O(2)-Gd(1)-O(1)#2	144.74(7)
O(1)#1-Gd(1)-O(1)#2	82.04(8)
O(1)-Gd(1)-O(1)#2	82.04(8)
O(2)#1-Gd(1)-N(2)	139.18(8)
O(2)#2-Gd(1)-N(2)	74.54(7)
O(2)-Gd(1)-N(2)	63.61(7)
O(1)#1-Gd(1)-N(2)	70.20(7)
O(1)-Gd(1)-N(2)	63.49(7)
O(1)#2-Gd(1)-N(2)	137.74(8)
O(2)#1-Gd(1)-N(2)#1	63.61(7)
O(2)#2-Gd(1)-N(2)#1	139.18(8)
O(2)-Gd(1)-N(2)#1	74.54(7)
O(1)#1-Gd(1)-N(2)#1	63.49(7)
O(1)-Gd(1)-N(2)#1	137.74(8)
O(1)#2-Gd(1)-N(2)#1	70.20(7)
N(2)-Gd(1)-N(2)#1	119.948(4)
O(2)#1-Gd(1)-N(2)#2	74.54(7)
O(2)#2-Gd(1)-N(2)#2	63.61(7)
O(2)-Gd(1)-N(2)#2	139.18(8)
O(1)#1-Gd(1)-N(2)#2	137.74(8)
O(1)-Gd(1)-N(2)#2	70.20(7)
O(1)#2-Gd(1)-N(2)#2	63.49(7)
N(2)-Gd(1)-N(2)#2	119.947(4)
N(2)#1-Gd(1)-N(2)#2	119.948(4)

Symmetry transformations used to generate equivalent atoms:
#1 y,z,x #2 z,x,y #3 -x+1,-y+2,z

Table S7. Selected Bond Lengths (Å) and Angles (deg) in Δ–[Gd((*S*,*S*)–**1**)$_3$]$^{3+}$ (Standard Deviation in Parentheses).

N(2)-Gd(1)	2.541(2)
O(1)-Gd(1)	2.3751(16)
O(2)-Gd(1)	2.3962(18)
Gd(1)-O(1)#1	2.3751(16)
Gd(1)-O(1)#2	2.3751(16)
Gd(1)-O(2)#1	2.3962(18)
Gd(1)-O(2)#2	2.3962(18)
Gd(1)-N(2)#1	2.541(2)
Gd(1)-N(2)#2	2.541(2)
C(14)-N(2)-Gd(1)	120.61(16)
C(10)-N(2)-Gd(1)	119.57(16)
C(9)-O(1)-Gd(1)	125.70(16)
C(15)-O(2)-Gd(1)	125.74(16)
O(1)#1-Gd(1)-O(1)	80.68(7)
O(1)#1-Gd(1)-O(1)#2	80.68(7)
O(1)-Gd(1)-O(1)#2	80.68(7)
O(1)#1-Gd(1)-O(2)#1	127.16(6)
O(1)-Gd(1)-O(2)#1	83.14(7)
O(1)#2-Gd(1)-O(2)#1	144.68(6)
O(1)#1-Gd(1)-O(2)#2	83.14(7)
O(1)-Gd(1)-O(2)#2	144.68(6)
O(1)#2-Gd(1)-O(2)#2	127.16(6)
O(2)#1-Gd(1)-O(2)#2	82.02(8)
O(1)#1-Gd(1)-O(2)	144.68(6)
O(1)-Gd(1)-O(2)	127.16(6)
O(1)#2-Gd(1)-O(2)	83.14(7)
O(2)#1-Gd(1)-O(2)	82.02(8)
O(2)#2-Gd(1)-O(2)	82.02(8)
O(1)#1-Gd(1)-N(2)#1	63.74(7)
O(1)-Gd(1)-N(2)#1	74.44(6)
O(1)#2-Gd(1)-N(2)#1	139.06(7)
O(2)#1-Gd(1)-N(2)#1	63.50(6)
O(2)#2-Gd(1)-N(2)#1	70.25(7)
O(2)-Gd(1)-N(2)#1	137.76(7)
O(1)#1-Gd(1)-N(2)	139.06(7)
O(1)-Gd(1)-N(2)	63.74(7)
O(1)#2-Gd(1)-N(2)	74.44(6)
O(2)#1-Gd(1)-N(2)	70.25(7)
O(2)#2-Gd(1)-N(2)	137.76(7)
O(2)-Gd(1)-N(2)	63.50(6)
N(2)#1-Gd(1)-N(2)	119.950(4)
O(1)#1-Gd(1)-N(2)#2	74.44(6)
O(1)-Gd(1)-N(2)#2	139.06(7)
O(1)#2-Gd(1)-N(2)#2	63.74(7)
O(2)#1-Gd(1)-N(2)#2	137.76(7)
O(2)#2-Gd(1)-N(2)#2	63.50(6)
O(2)-Gd(1)-N(2)#2	70.25(7)
N(2)#1-Gd(1)-N(2)#2	119.950(4)
N(2)-Gd(1)-N(2)#2	119.950(4)

Symmetry transformations used to generate equivalent atoms:
#1 y,z,x #2 z,x,y #3 -x,y,-z+1

Table S8. Selected Bond Lengths (Å) and Angles (deg) in Λ–[Tb((*R*,*R*)–**1**)$_3$]$^{3+}$ (Standard Deviation in Parentheses).

N(2)-Tb(1)	2.5278(19)
O(1)-Tb(1)	2.3813(17)
O(2)-Tb(1)	2.3723(16)
Tb(1)-O(2)#1	2.3723(16)
Tb(1)-O(2)#2	2.3723(16)
Tb(1)-O(1)#2	2.3813(17)
Tb(1)-O(1)#1	2.3813(17)
Tb(1)-N(2)#2	2.5278(19)
Tb(1)-N(2)#1	2.5278(19)
C(14)-N(2)-Tb(1)	120.68(15)
C(10)-N(2)-Tb(1)	119.55(15)
C(15)-O(1)-Tb(1)	126.07(16)
C(9)-O(2)-Tb(1)	125.37(16)
O(2)#1-Tb(1)-O(2)#2	80.88(7)
O(2)#1-Tb(1)-O(2)	80.88(7)
O(2)#2-Tb(1)-O(2)	80.88(7)
O(2)#1-Tb(1)-O(1)#2	82.87(6)
O(2)#2-Tb(1)-O(1)#2	127.54(6)
O(2)-Tb(1)-O(1)#2	144.14(6)
O(2)#1-Tb(1)-O(1)	144.14(6)
O(2)#2-Tb(1)-O(1)	82.87(6)
O(2)-Tb(1)-O(1)	127.54(6)
O(1)#2-Tb(1)-O(1)	82.12(7)
O(2)#1-Tb(1)-O(1)#1	127.54(6)
O(2)#2-Tb(1)-O(1)#1	144.14(6)
O(2)-Tb(1)-O(1)#1	82.87(6)
O(1)#2-Tb(1)-O(1)#1	82.12(7)
O(1)-Tb(1)-O(1)#1	82.12(7)
O(2)#1-Tb(1)-N(2)#2	74.16(6)
O(2)#2-Tb(1)-N(2)#2	64.04(6)
O(2)-Tb(1)-N(2)#2	139.35(6)
O(1)#2-Tb(1)-N(2)#2	63.56(6)
O(1)-Tb(1)-N(2)#2	69.99(6)
O(1)#1-Tb(1)-N(2)#2	137.74(7)
O(2)#1-Tb(1)-N(2)#1	64.04(6)
O(2)#2-Tb(1)-N(2)#1	139.35(6)
O(2)-Tb(1)-N(2)#1	74.16(6)
O(1)#2-Tb(1)-N(2)#1	69.99(6)
O(1)-Tb(1)-N(2)#1	137.74(7)
O(1)#1-Tb(1)-N(2)#1	63.56(6)
N(2)#2-Tb(1)-N(2)#1	119.942(4)
O(2)#1-Tb(1)-N(2)	139.35(6)
O(2)#2-Tb(1)-N(2)	74.16(6)
O(2)-Tb(1)-N(2)	64.04(6)
O(1)#2-Tb(1)-N(2)	137.74(7)
O(1)-Tb(1)-N(2)	63.56(6)
O(1)#1-Tb(1)-N(2)	69.99(6)
N(2)#2-Tb(1)-N(2)	119.942(4)
N(2)#1-Tb(1)-N(2)	119.942(4)

Symmetry transformations used to generate equivalent atoms:
#1 y,z,x #2 z,x,y #3 -x+2,y,-z+1

Table S9. Selected Bond Lengths (Å) and Angles (deg) in Δ–[Tb((*S*,*S*)–**1**)$_3$]$^{3+}$ (Standard Deviation in Parentheses).

N(2)-Tb(1)	2.528(2)
O(1)-Tb(1)	2.3657(16)
O(2)-Tb(1)	2.3817(17)
Tb(1)-O(1)#1	2.3657(16)
Tb(1)-O(1)#2	2.3657(16)
Tb(1)-O(2)#1	2.3817(17)
Tb(1)-O(2)#2	2.3817(17)
Tb(1)-N(2)#1	2.528(2)
Tb(1)-N(2)#2	2.528(2)
C(14)-N(2)-Tb(1)	120.39(16)
C(10)-N(2)-Tb(1)	119.57(16)
C(9)-O(1)-Tb(1)	125.44(16)
C(15)-O(2)-Tb(1)	125.96(16)
O(1)-Tb(1)-O(1)#1	80.81(7)
O(1)-Tb(1)-O(1)#2	80.81(7)
O(1)#1-Tb(1)-O(1)#2	80.81(7)
O(1)-Tb(1)-O(2)#1	144.21(6)
O(1)#1-Tb(1)-O(2)#1	127.50(6)
O(1)#2-Tb(1)-O(2)#1	82.91(6)
O(1)-Tb(1)-O(2)	127.50(6)
O(1)#1-Tb(1)-O(2)	82.91(6)
O(1)#2-Tb(1)-O(2)	144.21(6)
O(2)#1-Tb(1)-O(2)	82.13(7)
O(1)-Tb(1)-O(2)#2	82.91(6)
O(1)#1-Tb(1)-O(2)#2	144.21(6)
O(1)#2-Tb(1)-O(2)#2	127.50(6)
O(2)#1-Tb(1)-O(2)#2	82.13(7)
O(2)-Tb(1)-O(2)#2	82.13(7)
O(1)-Tb(1)-N(2)	63.95(6)
O(1)#1-Tb(1)-N(2)	74.11(6)
O(1)#2-Tb(1)-N(2)	139.17(7)
O(2)#1-Tb(1)-N(2)	137.87(7)
O(2)-Tb(1)-N(2)	63.62(6)
O(2)#2-Tb(1)-N(2)	70.11(7)
O(1)-Tb(1)-N(2)#1	139.17(7)
O(1)#1-Tb(1)-N(2)#1	63.95(6)
O(1)#2-Tb(1)-N(2)#1	74.11(6)
O(2)#1-Tb(1)-N(2)#1	63.62(6)
O(2)-Tb(1)-N(2)#1	70.11(7)
O(2)#2-Tb(1)-N(2)#1	137.87(7)
N(2)-Tb(1)-N(2)#1	119.952(4)
O(1)-Tb(1)-N(2)#2	74.11(6)
O(1)#1-Tb(1)-N(2)#2	139.17(7)
O(1)#2-Tb(1)-N(2)#2	63.95(6)
O(2)#1-Tb(1)-N(2)#2	70.11(7)
O(2)-Tb(1)-N(2)#2	137.87(7)
O(2)#2-Tb(1)-N(2)#2	63.62(6)
N(2)-Tb(1)-N(2)#2	119.952(4)
N(2)#1-Tb(1)-N(2)#2	119.952(4)

Symmetry transformations used to generate equivalent atoms:
#1 -y+1,z,-x+1 #2 -z+1,-x+1,y #3 -x+1,-y,z

Table S10. Selected Bond Lengths (Å) and Angles (deg) in Δ–[Yb((*S*,*S*)–**1**)$_3$]$^{3+}$ (Standard Deviation in Parentheses).

N(2)-Yb(1)	2.469(2)
O(1)-Yb(1)	2.3205(15)
O(2)-Yb(1)	2.3310(17)
Yb(1)-O(1)#1	2.3205(15)
Yb(1)-O(1)#2	2.3205(15)
Yb(1)-O(2)#1	2.3310(17)
Yb(1)-O(2)#2	2.3310(17)
Yb(1)-N(2)#1	2.469(2)
Yb(1)-N(2)#2	2.469(2)
C(10)-N(2)-Yb(1)	120.08(16)
C(14)-N(2)-Yb(1)	120.52(15)
C(9)-O(1)-Yb(1)	124.93(15)
C(15)-O(2)-Yb(1)	125.51(16)
O(1)#1-Yb(1)-O(1)	79.98(6)
O(1)#1-Yb(1)-O(1)#2	79.98(6)
O(1)-Yb(1)-O(1)#2	79.98(6)
O(1)#1-Yb(1)-O(2)	84.05(6)
O(1)-Yb(1)-O(2)	129.98(6)
O(1)#2-Yb(1)-O(2)	142.66(5)
O(1)#1-Yb(1)-O(2)#1	129.98(6)
O(1)-Yb(1)-O(2)#1	142.66(5)
O(1)#2-Yb(1)-O(2)#1	84.05(6)
O(2)-Yb(1)-O(2)#1	80.80(7)
O(1)#1-Yb(1)-O(2)#2	142.66(5)
O(1)-Yb(1)-O(2)#2	84.05(6)
O(1)#2-Yb(1)-O(2)#2	129.98(6)
O(2)-Yb(1)-O(2)#2	80.80(7)
O(2)#1-Yb(1)-O(2)#2	80.80(7)
O(1)#1-Yb(1)-N(2)#1	65.16(6)
O(1)-Yb(1)-N(2)#1	138.53(6)
O(1)#2-Yb(1)-N(2)#1	72.71(6)
O(2)-Yb(1)-N(2)#1	69.95(6)
O(2)#1-Yb(1)-N(2)#1	64.85(6)
O(2)#2-Yb(1)-N(2)#1	137.41(7)
O(1)#1-Yb(1)-N(2)	72.71(6)
O(1)-Yb(1)-N(2)	65.16(6)
O(1)#2-Yb(1)-N(2)	138.53(6)
O(2)-Yb(1)-N(2)	64.85(6)
O(2)#1-Yb(1)-N(2)	137.41(7)
O(2)#2-Yb(1)-N(2)	69.95(6)
N(2)#1-Yb(1)-N(2)	119.975(3)
O(1)#1-Yb(1)-N(2)#2	138.53(6)
O(1)-Yb(1)-N(2)#2	72.71(6)
O(1)#2-Yb(1)-N(2)#2	65.16(6)
O(2)-Yb(1)-N(2)#2	137.41(7)
O(2)#1-Yb(1)-N(2)#2	69.95(6)
O(2)#2-Yb(1)-N(2)#2	64.85(6)
N(2)#1-Yb(1)-N(2)#2	119.975(3)
N(2)-Yb(1)-N(2)#2	119.975(3)
O(1)#1-Yb(1)-C(9)#1	18.62(6)
O(1)-Yb(1)-C(9)#1	97.83(6)
O(1)#2-Yb(1)-C(9)#1	77.91(6)
O(2)-Yb(1)-C(9)#1	76.34(6)

O(2)#1-Yb(1)-C(9)#1	111.52(6)
O(2)#2-Yb(1)-C(9)#1	151.57(6)
N(2)#1-Yb(1)-C(9)#1	46.68(6)
N(2)-Yb(1)-C(9)#1	85.03(6)
N(2)#2-Yb(1)-C(9)#1	142.85(6)
O(1)#1-Yb(1)-C(9)#2	97.83(6)
O(1)-Yb(1)-C(9)#2	77.91(6)
O(1)#2-Yb(1)-C(9)#2	18.62(6)
O(2)-Yb(1)-C(9)#2	151.57(6)
O(2)#1-Yb(1)-C(9)#2	76.34(6)
O(2)#2-Yb(1)-C(9)#2	111.52(6)
N(2)#1-Yb(1)-C(9)#2	85.03(6)
N(2)-Yb(1)-C(9)#2	142.85(6)
N(2)#2-Yb(1)-C(9)#2	46.68(6)
C(9)#1-Yb(1)-C(9)#2	96.52(6)
O(1)#1-Yb(1)-C(9)	77.91(6)
O(1)-Yb(1)-C(9)	18.62(6)
O(1)#2-Yb(1)-C(9)	97.83(6)
O(2)-Yb(1)-C(9)	111.52(6)
O(2)#1-Yb(1)-C(9)	151.57(6)
O(2)#2-Yb(1)-C(9)	76.34(6)
N(2)#1-Yb(1)-C(9)	142.85(6)
N(2)-Yb(1)-C(9)	46.68(6)
N(2)#2-Yb(1)-C(9)	85.03(6)
C(9)#1-Yb(1)-C(9)	96.52(6)
C(9)#2-Yb(1)-C(9)	96.52(6)

Symmetry transformations used to generate equivalent atoms:
#1 -y+1,z,-x+1 #2 -z+1,-x+1,y #3 x,-y,-z+1

Table S11. Selected least–squares planes data (standard deviations are indicated within parentheses) and interplanar angles (deg) in $[Ln\mathbf{L}_3]^{3+}$ (Ln(III) = Eu, Yb and **L** = (*R*,*R*)–**1** and (*S*,*S*)–**1**).

	Nr	Description	Deviation Max. (Å)	Atom	Interplanar Angles (deg) 1–2	2–3
$[Eu((R,R)–\mathbf{1})_3]^{3+}$	1	N1–O1–C9–C10	0.0093(26)	C9	5.86(0.12)	7.35(0.16)
	2	N2–C10–C11–C12–C13–C14	–0.0055(26)	C12		
	3	N3–O2–C15–C14	0.0009(29)	C15		
$[Eu((S,S)–\mathbf{1})_3]^{3+}$	1	N1–O1–C9–C10	0.0047(27)	C9	4.24(0.14)	7.79(0.16)
	2	N2–C10–C11–C12–C13–C14	–0.0116(28)	C12		
	3	N3–O2–C15–C14	–0.0033(29)	C15		
$[Yb((R,R)–\mathbf{1})_3]^{3+}$	1	N1–O1–C9–C10	0.0053(24)	C9	4.16(0.12)	6.75(0.14)
	2	N2–C10–C11–C12–C13–C14	–0.0072(20)	C14		
	3	N3–O2–C15–C14	–0.0037(24)	C15		
$[Yb((S,S)–\mathbf{1})_3]^{3+}$	1	N1–O1–C9–C10	0.0080(19)	C9	3.88(0.10)	7.31(0.12)
	2	N2–C10–C11–C12–C13–C14	0.0137(19)	C11		
	3	N3–O2–C15–C14	–0.0067(21)	C15		

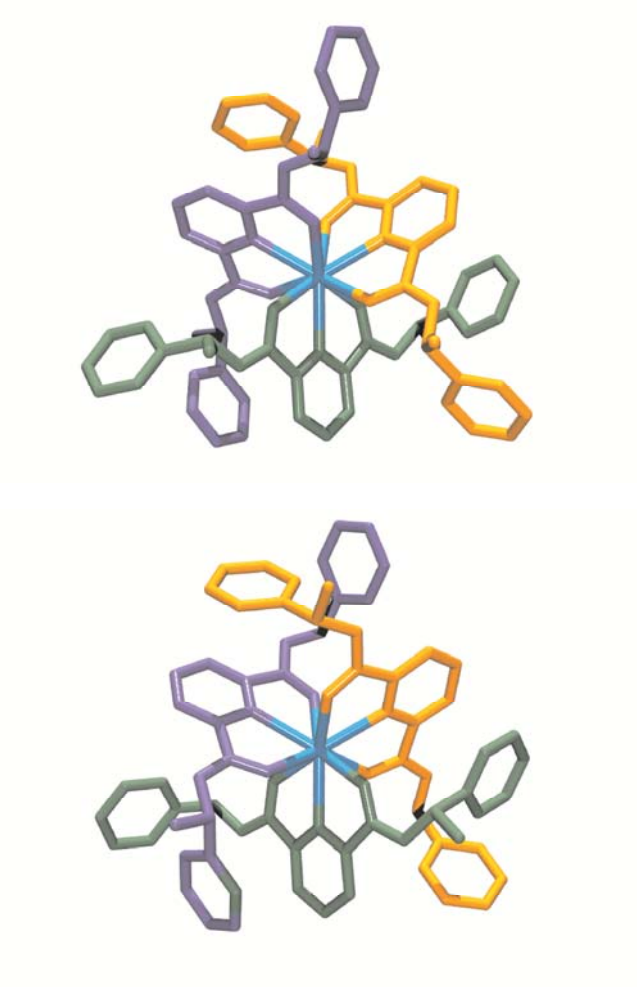


Figure S9. Structure of the Λ–[Gd((*R*,*R*)–**1**)$_3$]$^{3+}$ (top) and Δ–[Gd((*S*,*S*)–**1**)$_3$]$^{3+}$ (bottom) cations.

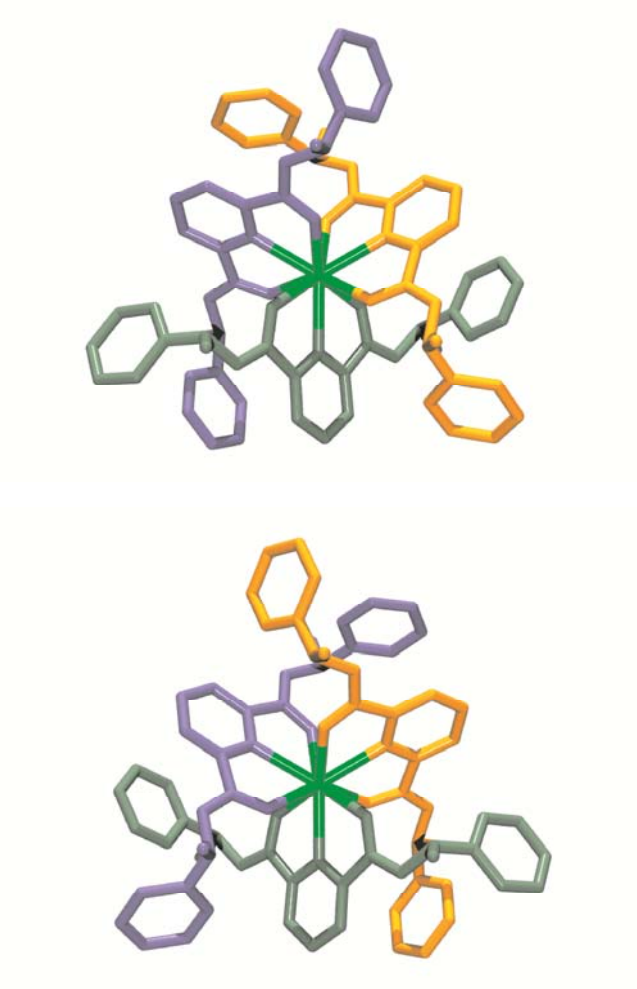


Figure S10. Structure of the Λ–[Tb((*R*,*R*)–**1**)$_3$]$^{3+}$ (top) and Δ–[Tb((*S*,*S*)–**1**)$_3$]$^{3+}$ (bottom) cations.

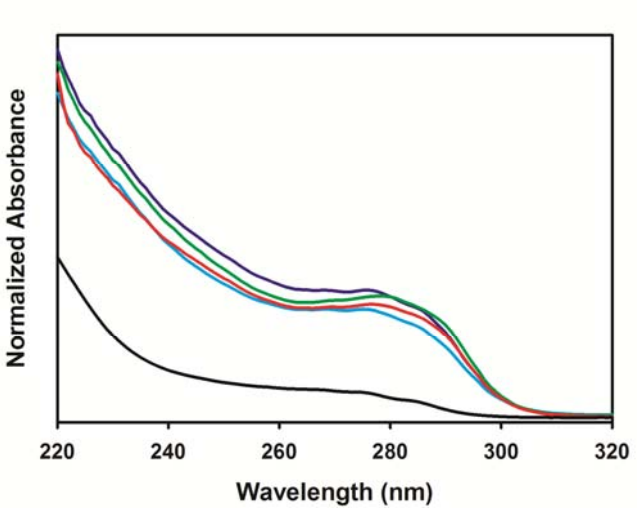


Figure S11. Normalized electronic spectra of **L** (black trace, 5.4×10^{-5} M) and $[Ln\mathbf{L}_3]^{3+}$ (Ln(III) = Eu, Gd, Tb, and Er) complexes (blue, red, cyan, and green traces, respectively, 2.8–4.5 $\times 10^{-4}$ M) in anhydrous MeCN at 298 K.

Luminescence Sensitization Determination

The luminescence sensitization (η_{sens}) value was determined for the Eu(III) complex using the following equation[1]:

$$Q_{tot}^{Eu} = \eta_{ISC} \cdot \eta_{ET} \cdot Q^{Eu} = \eta_{sens} \cdot Q^{Eu}$$

where Q^{Eu}_{tot} is the europium–centered luminescence quantum yield obtained upon ligand excitation (1.0%), Q^{Eu} the intrinsic luminescence quantum yield of the Eu(III) ion, η_{sens} the efficiency of the luminescence sensitization by the ligand, η_{ISC} the efficiency of the intersystem crossing process from the ligand singlet to triplet state, and η_{ET} the efficiency of the ligand–to–metal energy transfer. The intrinsic quantum yield Q^{Eu} is defined as the ratio between the observed and radiative lifetimes of the Eu($^5D_0$) level:

$$Q^{Eu} = \tau_{obs}/\tau_R$$

where the radiative lifetime τ_R can be estimated from:

$$\tau_R = \frac{1}{A_{MD,0} \cdot n^3} \cdot \left(\frac{I_{MD}}{I_{tot}} \right)$$

$A_{MD,0}$ is the spontaneous emission probability of the Eu($^5D_0 \rightarrow {}^7F_1$) transition (14.65 s^{-1}), n is the refractive index (1.354 for the MeCN solution) and I_{MD}/I_{tot} is the intensity ratio of the Eu($^5D_0 \rightarrow {}^7F_1$) transition to the total emission of the $^5D_0$ level. For $[Eu\mathbf{L}_3]^{3+}$ with **L** = (*R*,*R*)–**1** or (*S*,*S*)–**1**, I_{MD}/I_{tot} = 0.24, leading to τ_R = 6.6 × 10^{-3} ms, Q^{Eu} = 265.2 (τ_{obs} = 1.75 ms) and η_{sens} = 4.0 × 10^{-5}. As a comparison, η_{sens} values of 0.03 (Q^{Eu}_L = 1.4%), 7.0 × 10^{-4} (Q^{Eu}_L = 0.01%), and in the range of 0.01–0.02 (Q^{Eu}_L ~1%) have been obtained for Eu(III) 1:1 and 1:2 complexes with the chiral ligand 2,6–bis(1–*S*–neopentylbenzimidazol–2–yl)pyridine,[2] and for Eu(III) 1:1 complexes with nitrobenzoic acid ligand derivatives,[3] respectively.

References

(1) Wertz, M. H. V.; Jukes, R. T. F.; Verhoeven, J. W. *Phys. Chem.* **1985**, *89*, 5649–5654

(2) Muller, G.; Maupin, C. L.; Riehl, J. P.; Birkedal, H.; Piguet, C.; Bünzli, J.–C. G. *Eur. J. Inorg. Chem.* **2003**, 4065–4072

(3) de Bettencourt–Dias, A.; Viswanathan, S *Dalton Trans.*, **2006**, 4093–4103