Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.
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Supporting information

Circularly Polarized activity from two photon excitable Europium and Samarium chiral bioprobes

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S1. LIGANDS CHARACTERIZATION

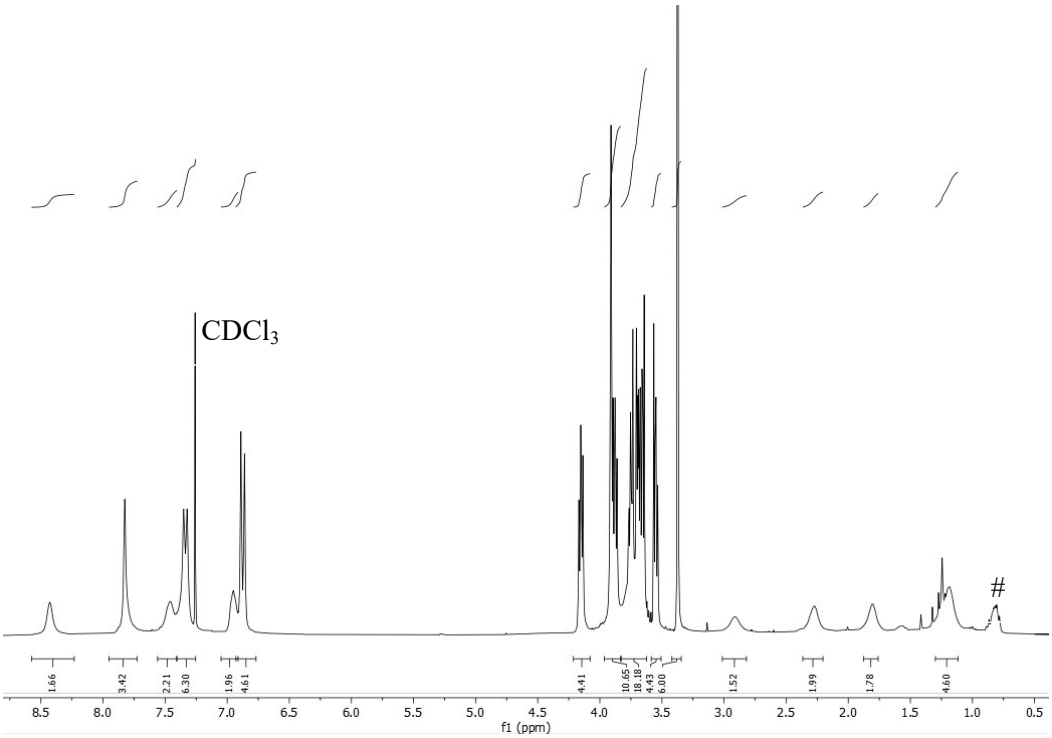


Figure S1: ^{1}H-NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of ligand (S,S)-**3**. # is related to "grease"[1]

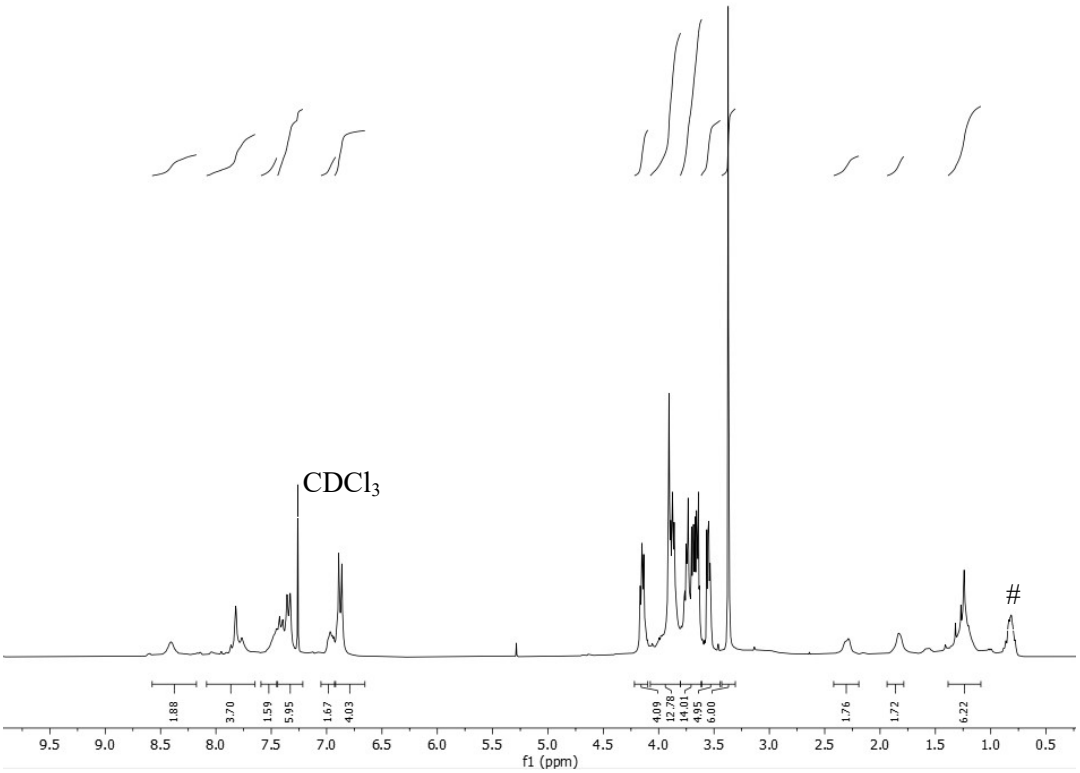
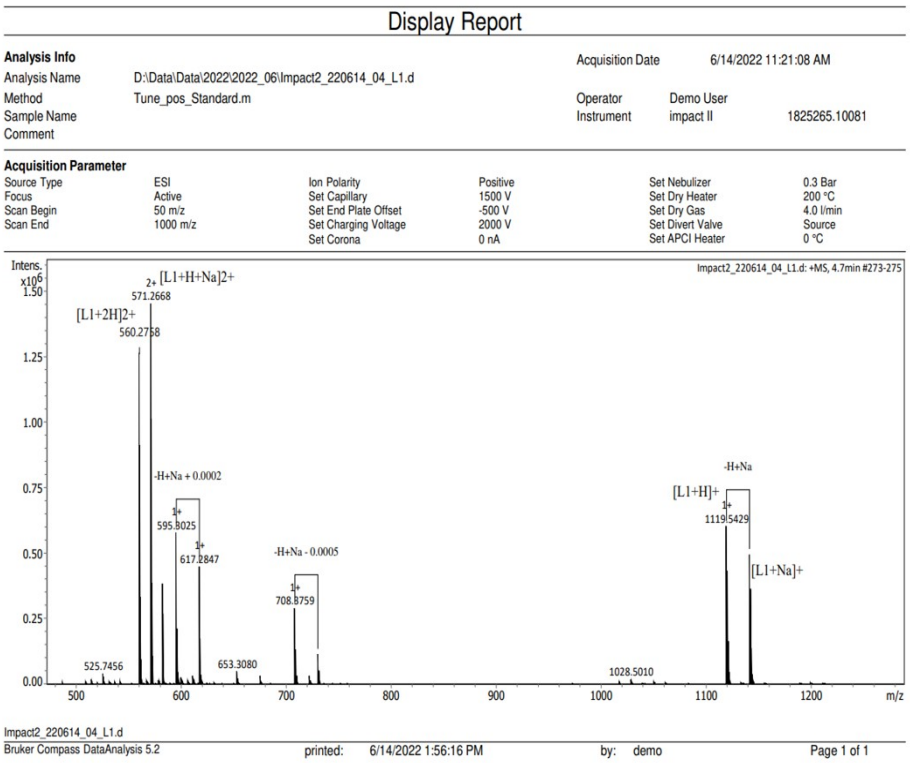


Figure S2: ^{1}H-NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of ligand (R,R)-**3**. # is related to "grease"[1]



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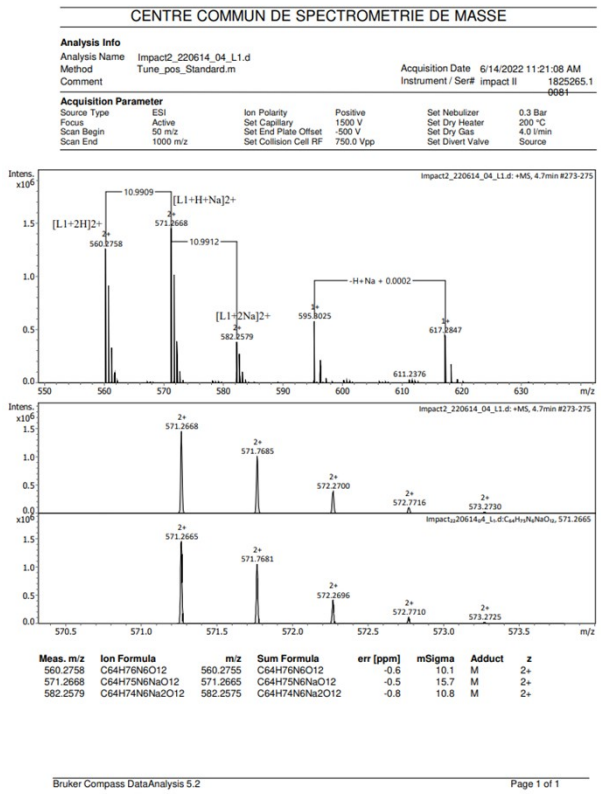

CENTRE COMMUN DE SPECTROMETRIE DE MASSE

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Meas. m/z	Ion Formula	m/z	Sum Formula	err [ppm]	mSigma	Adduct	z
560.2758	C64H76N6O12	560.2755	C64H76N6O12	-0.6	10.1	M	2+
571.2668	C64H75N6NaO12	571.2665	C64H75N6NaO12	-0.5	15.7	M	2+
582.2579	C64H74N6Na2O12	582.2575	C64H74N6Na2O12	-0.8	10.8	M	2+

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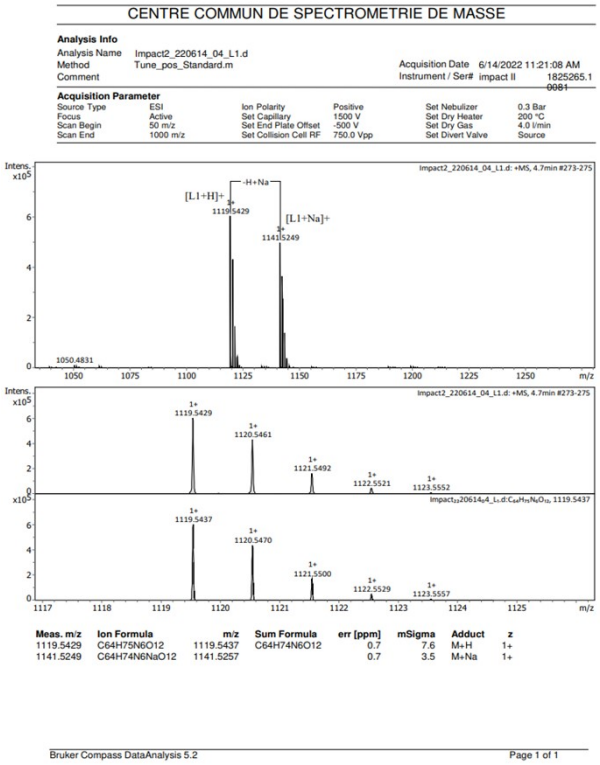

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Scan End	1000 m/z	Set Collision Cell RF	750.0 Vpp	Set Divert Valve	Source

Meas. m/z	Ion Formula	m/z	Sum Formula	err [ppm]	mSigma	Adduct	z
1119.5429	C64H75N6O12	1119.5437	C64H74N6O12	0.7	7.6	M+H	1+
1141.5249	C64H74N6NaO12	1141.5257		0.7	3.5	M+Na	1+

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Figure S3. HR–MS spectrum of (*S,S*)–**3**.

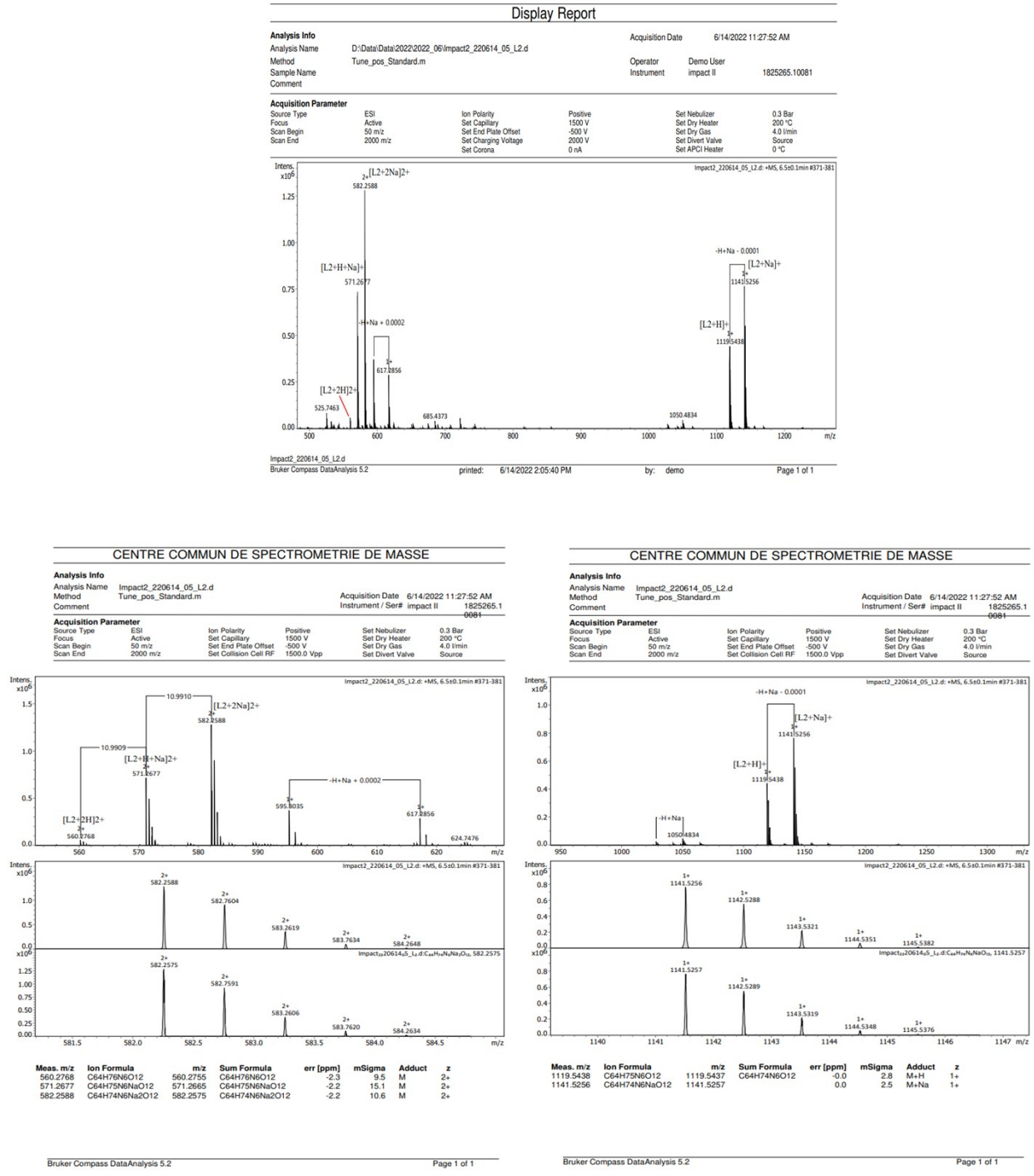


Figure S4. HR–MS spectrum of (*R*,*R*)–**3**.

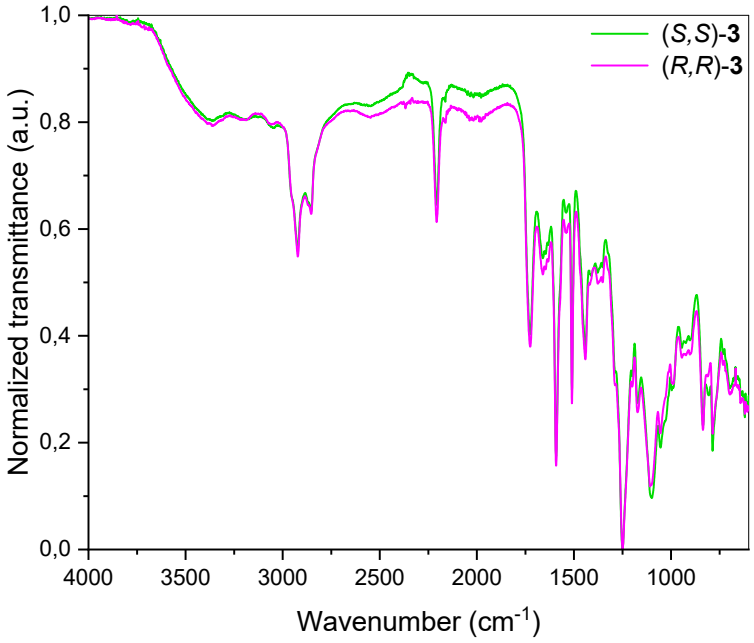
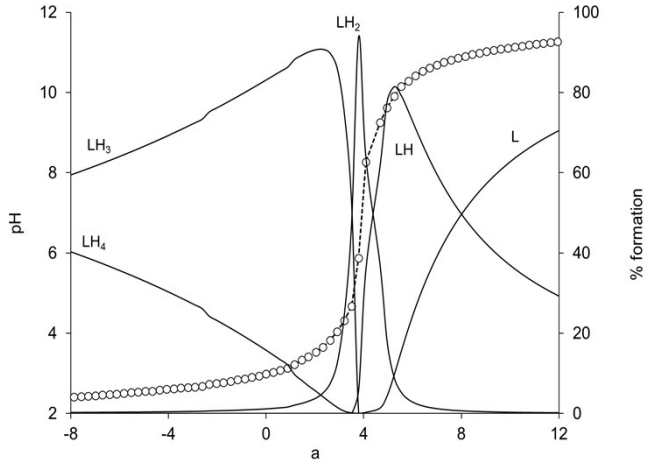


Figure S5. FT–IR spectra of both the enantiomer of (S,S) and the (R,R) enantiomer of **3**.

a)



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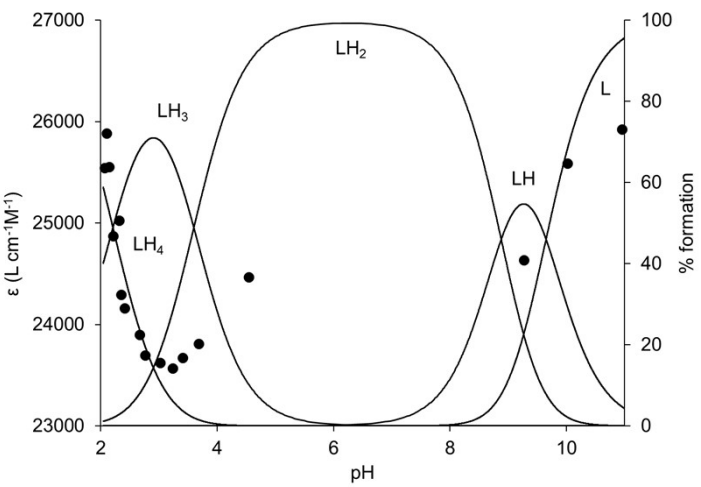

Figure S6. a) Experimental (○) and calculated (dashed line) pH values in the potentiometric titration of the ligand L (25 °C, μ = 0.1 M NaCl); total ligand 0.43 mM). a = (added mol OH^-) / (mol/L). b) Species distribution of the ligand L with molar absorbance values at λ= 320 nm (ε) obtained by acid–base spectrophotometric titration (25 °C, μ = 0.1 M NaCl). The speciation was calculated using the reported protonation constants (Table 1). Charges omitted for clarity.

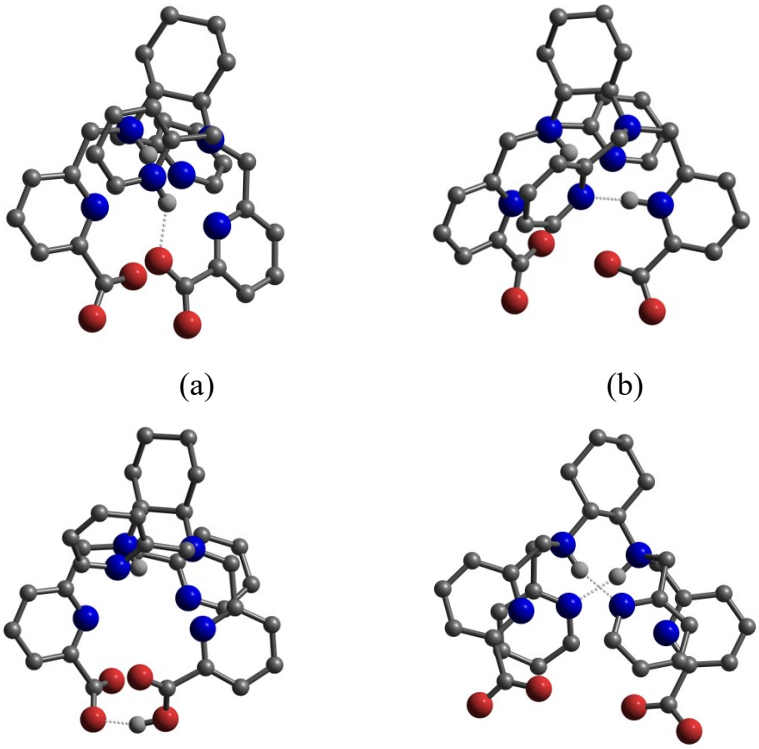

Figure S7. Minimum energy structures of the LH_2 protonated species of the analogue of L (L'') where the antennas were reduced to decrease the number of degrees of freedom. In these structures, one proton is attached to one aliphatic amine group and the second occupies different protonation sites. The calculations were carried out at DFT/ωB97X-D/6-31+G(d) level. Hydrogen atoms attached to carbons have been hidden for clarity.

S2. COMPLEXES CHARACTERIZATION

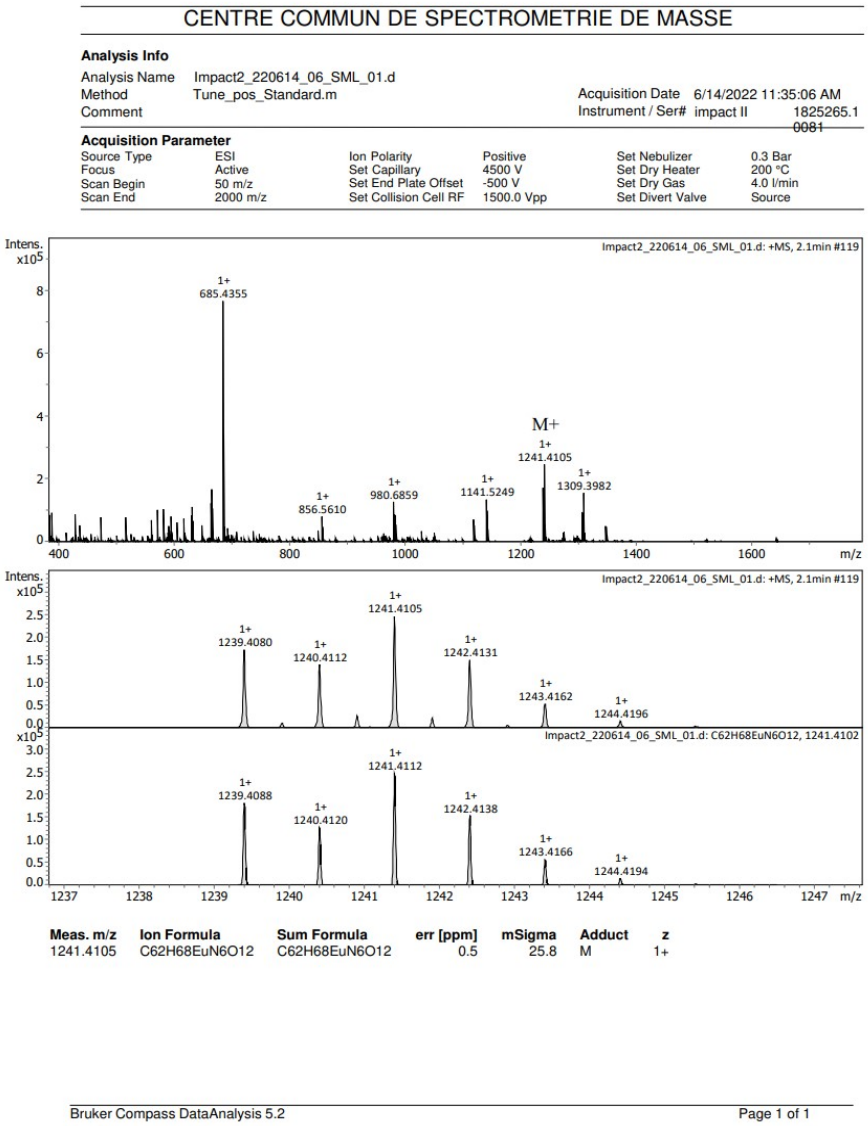

Figure S8. HR–MS spectrum of (*S,S*)–[Eu**L**]Cl.

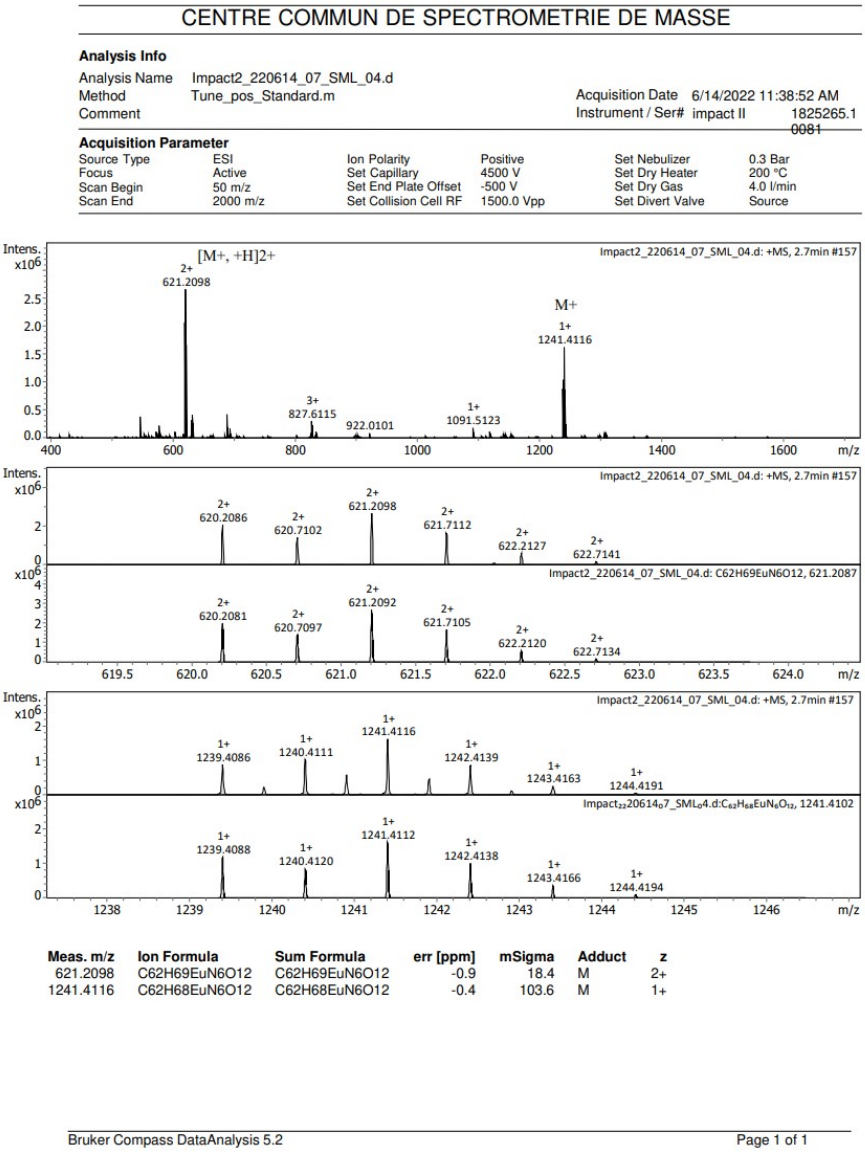

Figure S9. HR–MS spectrum of (*R*,*R*)–[Eu**L**]Cl.

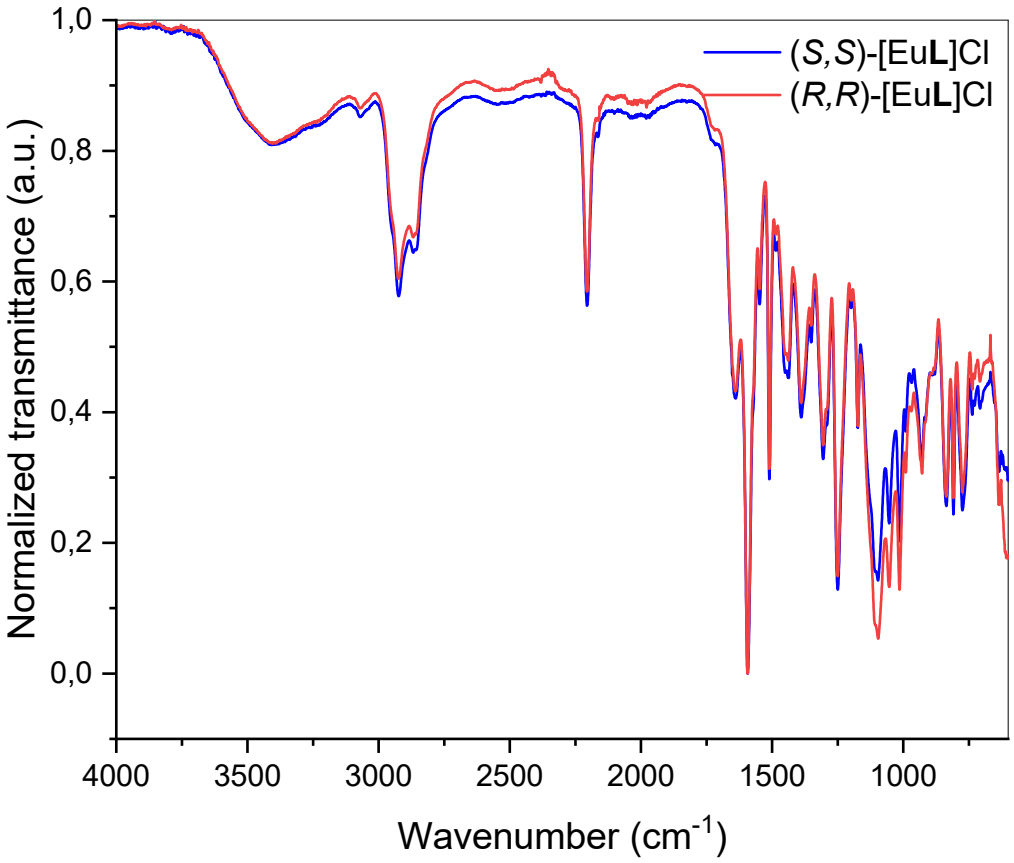

Figure S10. FT–IR spectra of both the enantiomer of [Eu**L**]Cl complex.

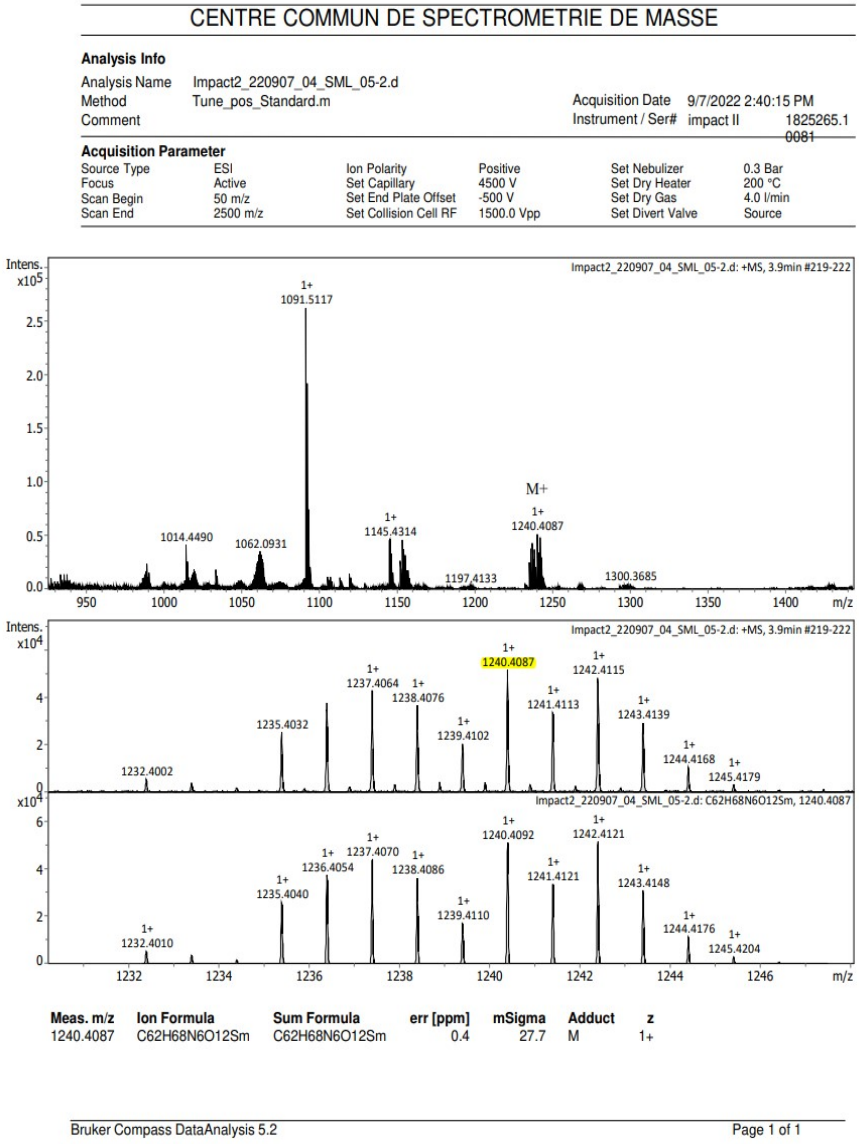

Figure S11. HR–MS spectrum of (*S,S*)–[Sm**L**]Cl.

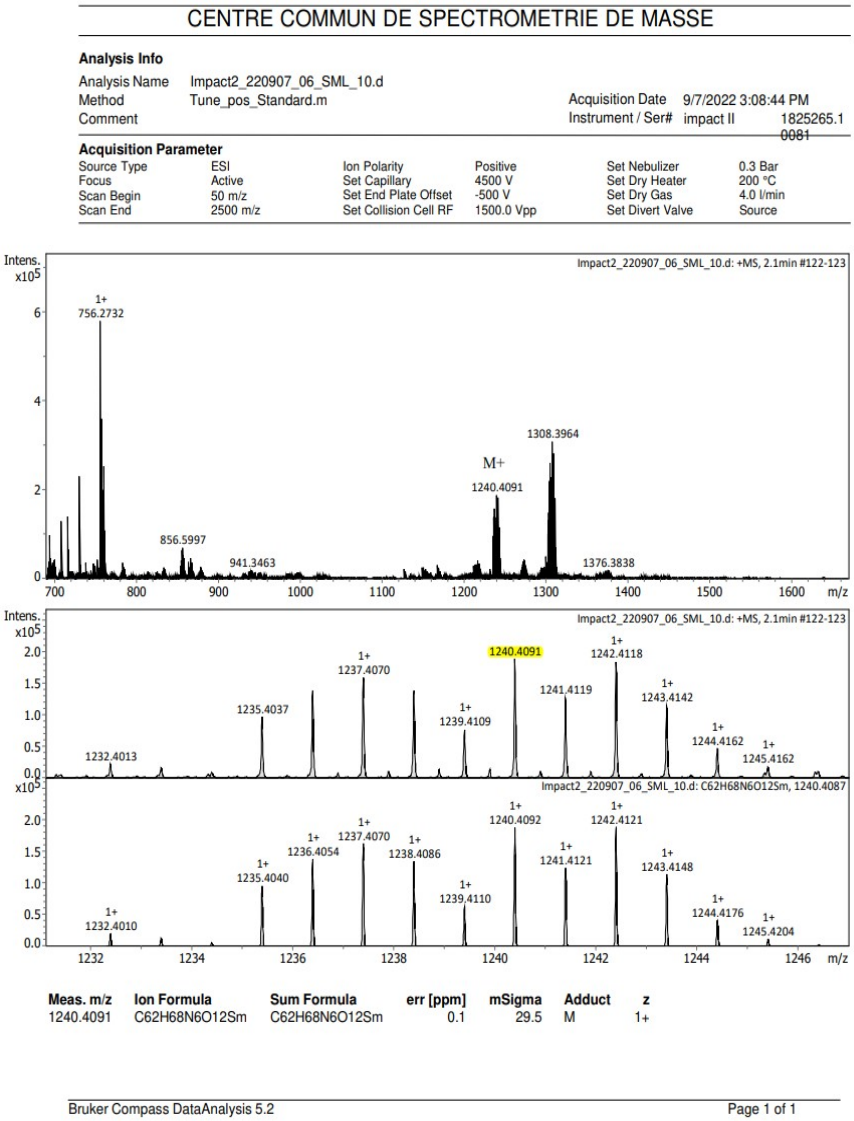

Figure S12. HR–MS spectrum of (*R,R*)–[Sm**L**]Cl.

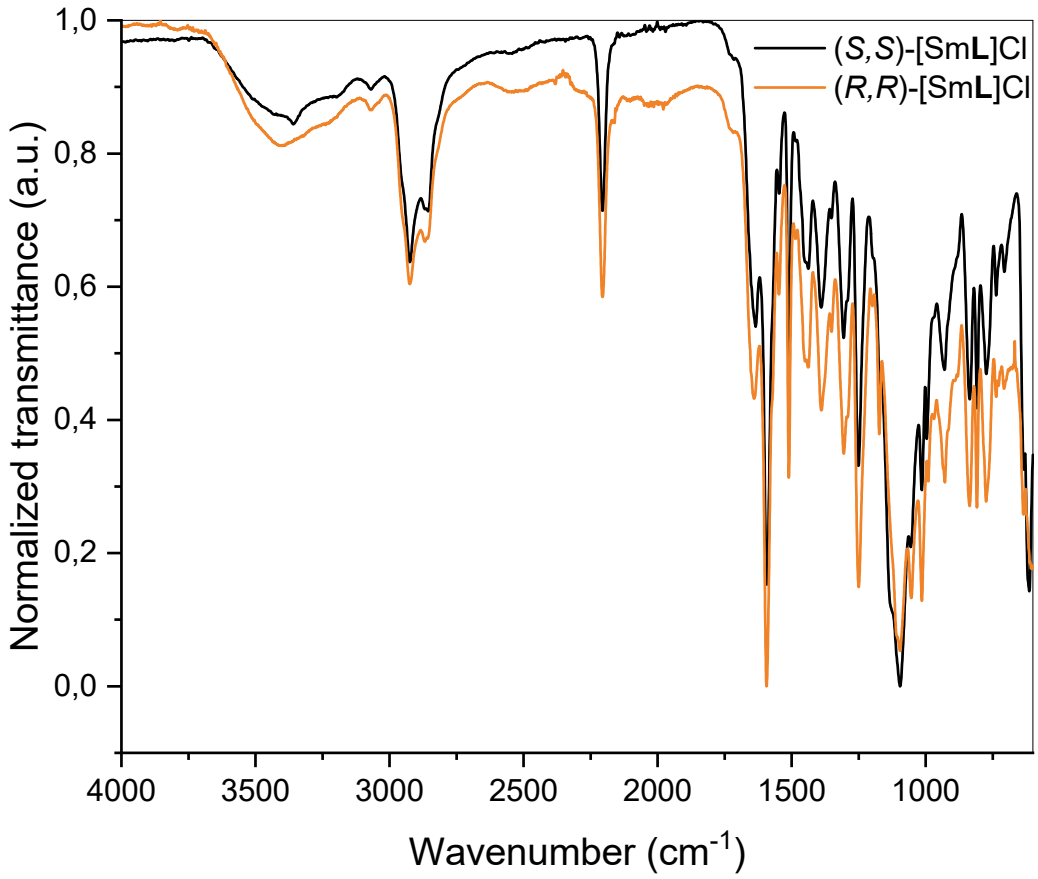

Figure S13. FT–IR spectra of both the enantiomer of [Sm**L**]Cl complex.

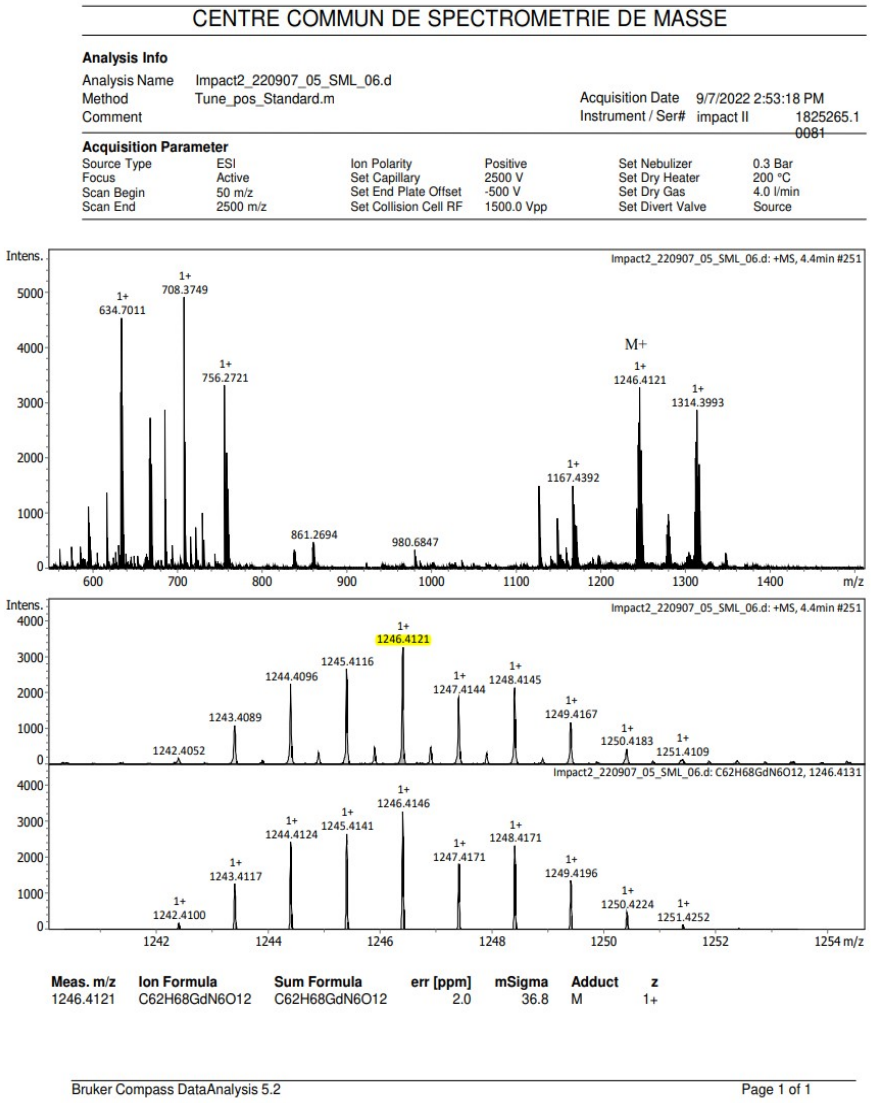

Figure S14. HR–MS spectrum of (*S,S*)–[Gd**L**]Cl.

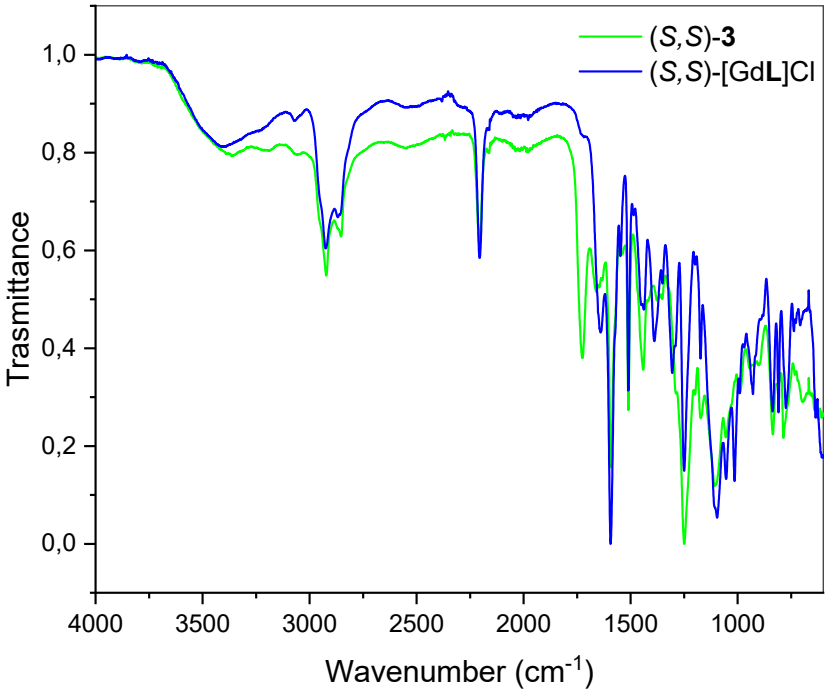

Figure S15. FT–IR spectra of (S,S) enantiomer of **3** and its related [Gd**L**]Cl complex.

S3. PHOTOPHYSICAL COMPLEXES CHARACTERIZATION

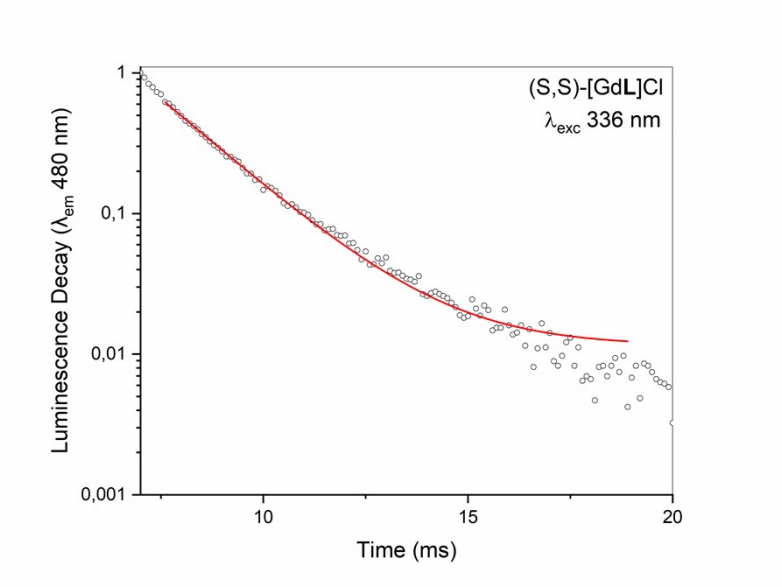

Figure S16. Luminescence (phosphorescence) decay of the triplet state of the ligand **L** in (S,S)–[Gd**L**]Cl embedded in ethanol:methanol 4:1 matrix at 77 K. λ_{exc} = 336 nm, λ_{em} = 485 nm. τ = 1.62 ms.

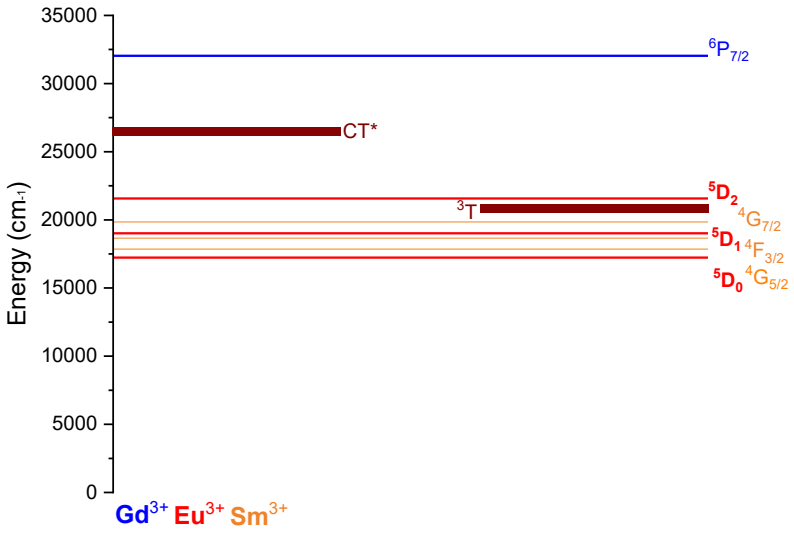

Figure S17. Energy level position of the lower excited states of Eu(III) (red lines/labels), Sm(III) (orange/labels), Gd(III) (blue line/label) and of the ligand (charge transfer and triplet levels at 26100 cm^{-1} and 20833 cm^{-1}, respectively).[2]

Table S1. Photophysical data of europium and samarium complexes in methanol at room temperature.

	(S,S)–[Eu**L**]Cl	(S,S)–[Eu**L**]Cl	(S,S)–[Sm**L**]Cl	(R,R)–[Sm**L**]Cl
ε ($L \cdot mol^{-1} \cdot cm^{-1}$)	47581 (337 nm) 36273 (254 nm)	47 546 (337 nm) 37801 (254 nm)	47461 (337 nm) 36195 (254 nm)	47462 (337 nm) 34525 (254 nm)
τ (ms)	890 (1520 CH_3OD)	860 (1500 CH_3OD)	23 (124 CH_3OD)	23 (123 CH_3OD)
m	0.97 [a]	1.03 [a]	1 [b]	1 [b]
ϕ [c]	0.21	0.24	0.021	0.025
σ [d] (GM)	112	86	–	–
g_{Abs}	1.55 (259 nm) 1.67 (286 nm)	–1.41 (259 nm) –1.42(286 nm)	1.69 (259 nm) 2.50 (284 nm)	–1.46 (259 nm) –1.61 (284 nm)
g_{lum} [e]	-0.125 (594 nm) +0.128 (596 nm) +0.065 (615 nm)	+0.129 (594 nm) -0.134 (596 nm) -0.066 (615 nm)	+0.204 (564 nm) -0.098 (598 nm)	–0.184 (564 nm) +0.091 (598 nm)
$B^{337\ nm}$ ($L \cdot mol^{-1} \cdot cm^{-1}$)	9992	11411	997	1186

[a] $m = 2{,}1\ (\tau_{CH3OH}^{-1} - \tau_{CD3OD}^{-1})$.[3] [b] $q_{methanol}$ factor = 0.028[4] [c] Using quinine sulfate in H_2SO_4 1N as standard (Φ = 54.6%, λ_{ex} = 340 nm). [d] Determined in methanol. [e] g_{lum} values are referred to the most intense component of the $^5D_0 \rightarrow {}^7F_1$ (593 nm) and $^5D_0 \rightarrow {}^7F_2$ (615 nm) transitions for Eu^{3+} and $^4G_{5/2} \rightarrow {}^6H_{5/2}$ (564 nm) $^4G_{5/2} \rightarrow {}^6H_{7/2}$ (598 nm) transitions for Sm^{3+}.

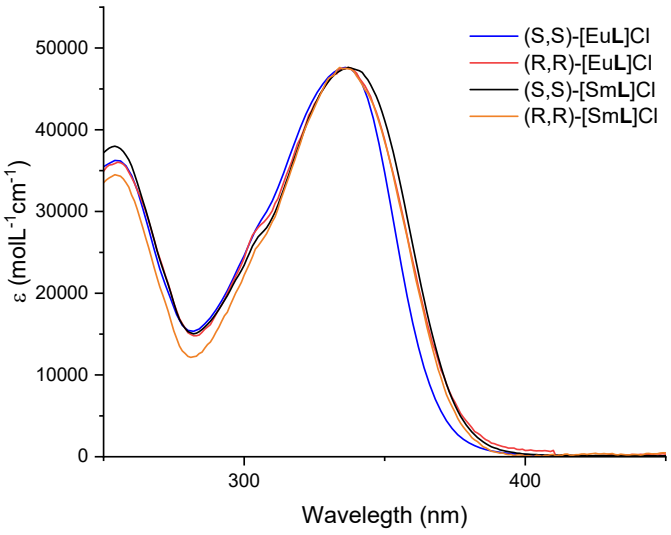

Figure S18. Electronic absorption of both the enantiomers of [Eu**L**]Cl and [Sm**L**]Cl in methanol solution at room temperature.

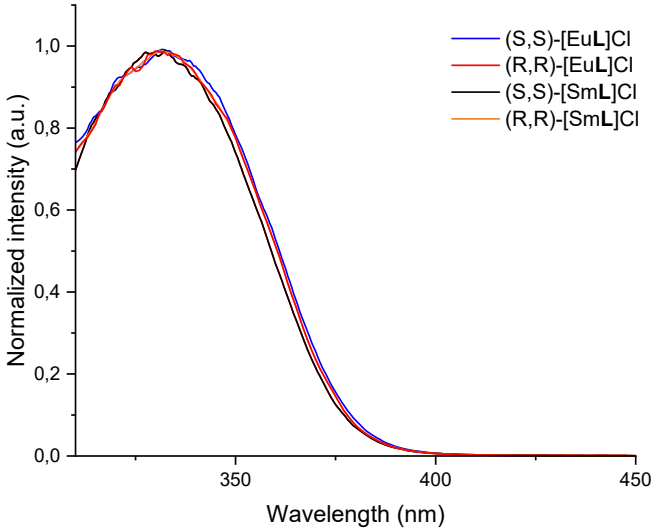

Figure S19. Normalized excitation spectra of both the enantiomers of [Eu**L**]Cl and [Sm**L**]Cl in water (10^{-6} M) at room temperature (λ_{em} 614 nm and 645 nm, respectively).

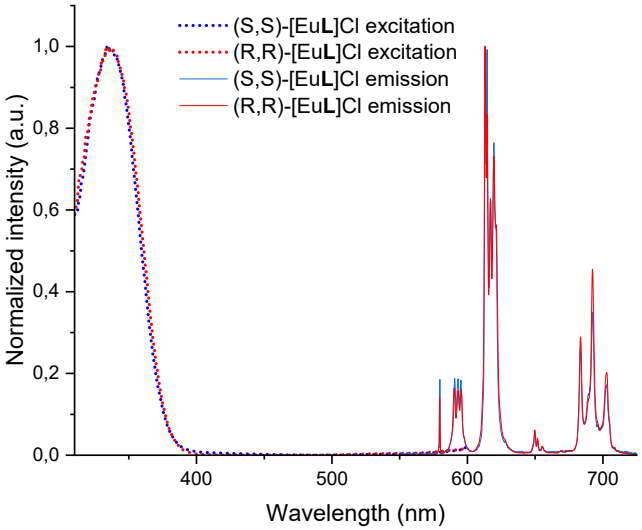

Figure S20. Normalized excitation and luminescence emission spectra of both the enantiomers of [Eu**L**]Cl in methanol solution (10^{-6} M) at room temperature. λ_{exc} 337 nm, λ_{em} 614 nm.

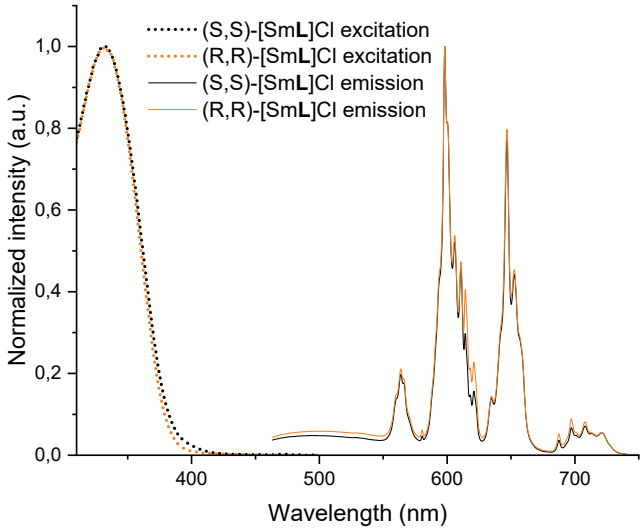

Figure S21. Normalized excitation and luminescence emission spectra of both the enantiomers of [Sm**L**]Cl in methanol solution (10^{-6} M) at room temperature. λ_{exc} 337 nm, λ_{em} 645 nm.

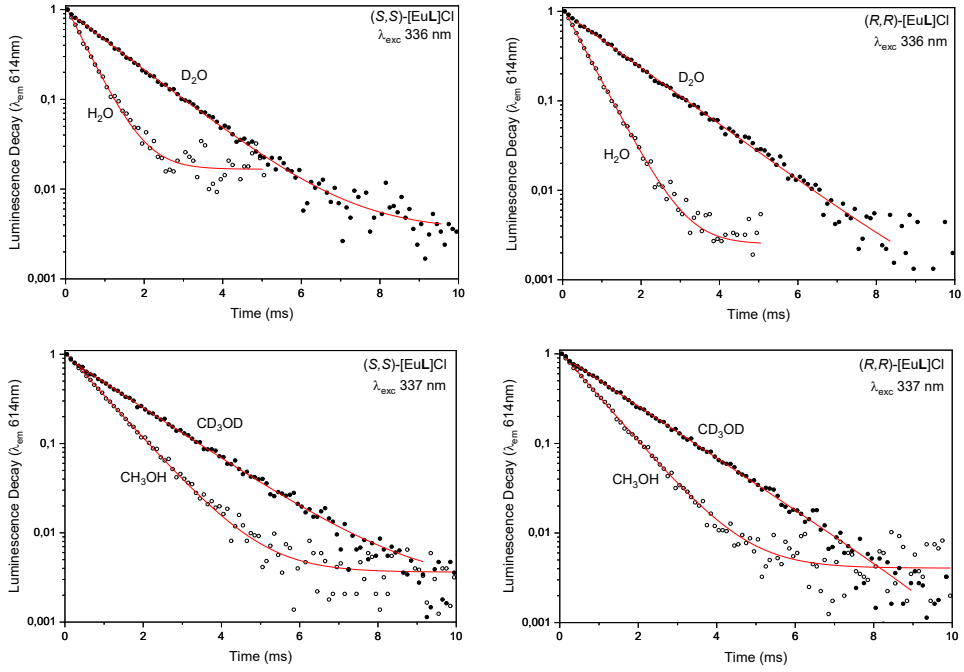

Figure S22. Luminescence decay curve of the emitting $^5D_0$ level of Eu(III) for (*S,S*)–[Eu**L**]Cl enantiomer dissolved in H_2O/D_2O (up left); CH_3OH/CD_3OD (bottom left) and for (*R,R*)–[Eu**L**]Cl enantiomer dissolved in H_2O/D_2O (up right); CH_3OH/CD_3OD (bottom right). All the curves are collected at room temperature. For (*S,S*)–[Eu**L**]Cl τ_{H2O} = 0.48(1) ms, τ_{D2O} = 1.30(1) ms; τ_{CH3OH} = 0.89(1) ms, τ_{CD3OD}= 1.52(1) ms. For (*R,R*)–[Eu**L**]Cl τ_{H2O} = 0.52(1) ms, τ_{D2O} = 1.38(1) ms; τ_{CH3OH} = 0.86(1) ms, τ_{CD3OD}= 1.50(1) ms.

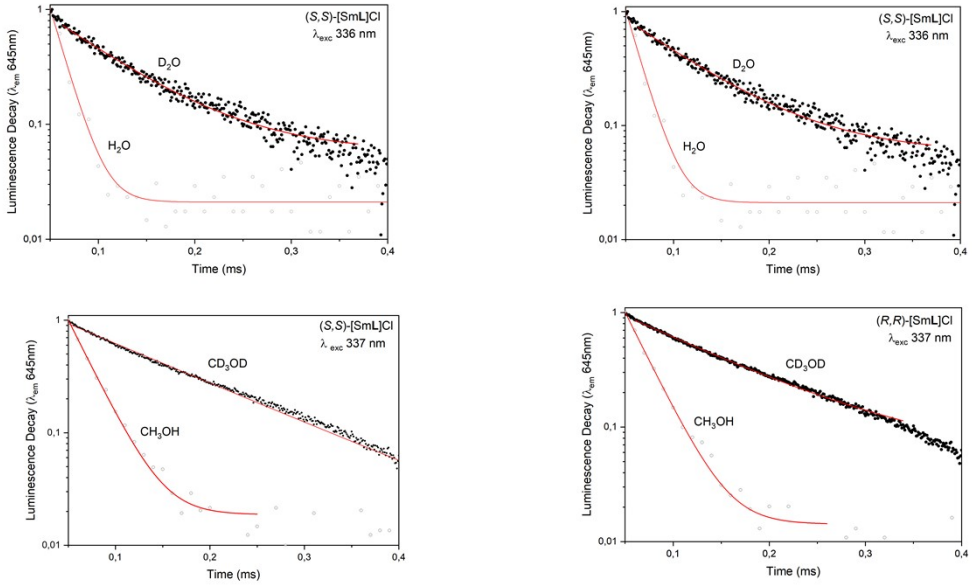

Figure S23. Luminescence decay curve of the emitting $^4G_{5/2}$ level of Sm(III) for (*S,S*)–[Sm**L**]Cl enantiomer dissolved in H_2O/D_2O (up left); CH_3OH/CD_3OD (bottom left) and for (*R,R*)–[Sm**L**]Cl enantiomer dissolved in H_2O/D_2O (up right); CH_3OH/CD_3OD (bottom rigth). All the curves are collected at room temperature. For (*S,S*)–[Sm**L**]Cl τ_{H2O} = 14.8(6) µs, τ_{D2O} = 72.4(9) µs; τ_{CH3OH} = 23.2(3) µs, τ_{CD3OD}= 123.6(9) µs. For (*R,R*)–[Sm**L**]Cl τ_{H2O} = 13.9(3) µs, τ_{D2O} = 66.4(9) µs; τ_{CH3OH} = 22.9(4) µs, τ_{CD3OD}= 122.9(9) µs.

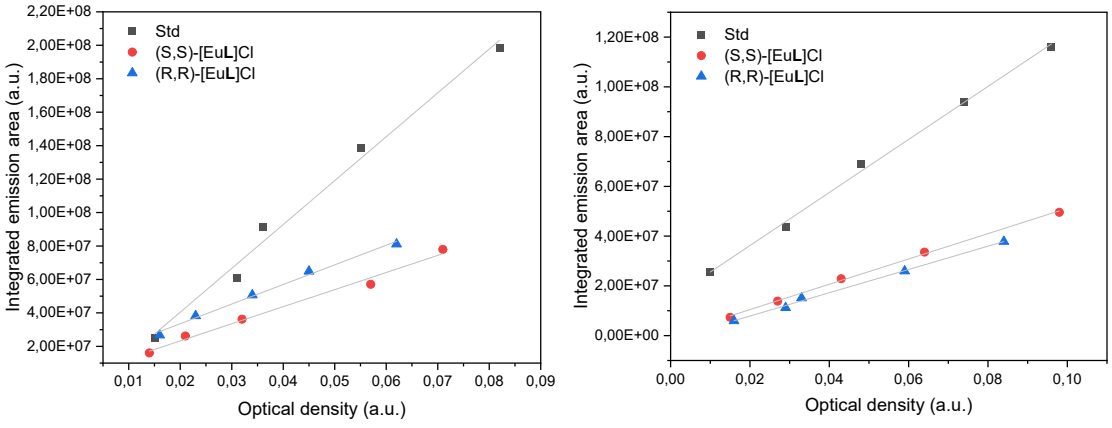

Figure S24. Linear relationship between the integrated emission area of Eu(III) and the optical density of the excitation source for both the enantiomers of [Eu**L**]Cl complexes in methanol (left) and in water solution (right). The same relationship is reported for the reference quinine sulfate (Std; 1N aqueous solution of sulfuric acid). λ_{exc} 340 nm.

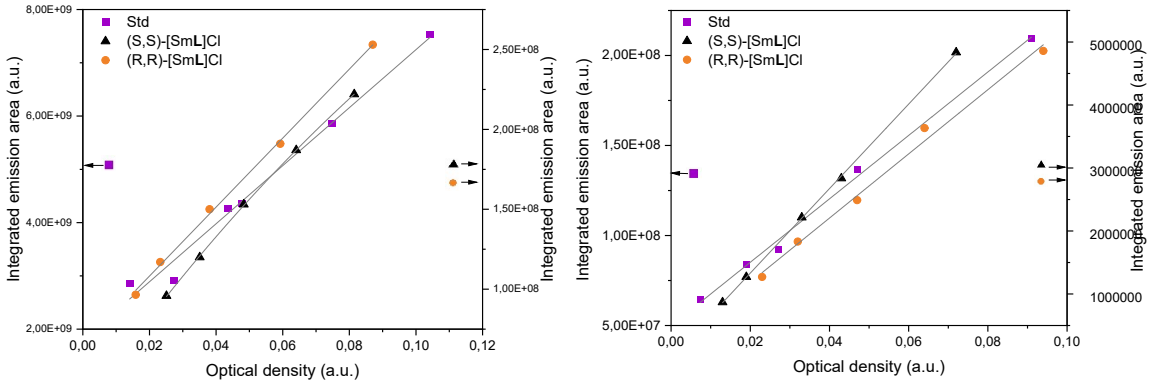

Figure S25. Linear relationship between the integrated emission area of Sm(III) and the optical density of the excitation source for both the enantiomers of [SmL]Cl complexes in methanol solution (left) and in aqueous solution (right). The same relationship is reported for the reference quinine sulfate (Std; 1N aqueous solution of sulfuric acid). λ_{exc} 340 nm.

The photostability measurement was conducted with compound (S,S)-[Eu**L**]Cl dissoved in methanol (optical density ca 0.15) and in a 10 mm quartz cuvette under continuous stirring in the fluorimeter. Calibration of the fluorimeter irradiation was measured with a ThorLab power-meter. The slits were fixed at 14 nm and we checked that detector saturation was avoided. In this condition, the incident power at 324 nm was measured at P_{inc} = 3.5 mW.

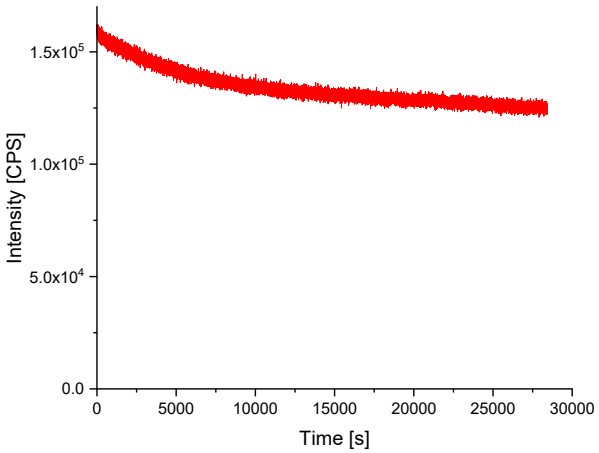

Figure S26. Variation of the emission intensity of (S,S)-[Eu**L**]Cl in methanol (at 615 nm) under 324 nm irradiation (P_{inc} = 3.5 mW).

S4. CHIROPTIC MEASUREMENTS

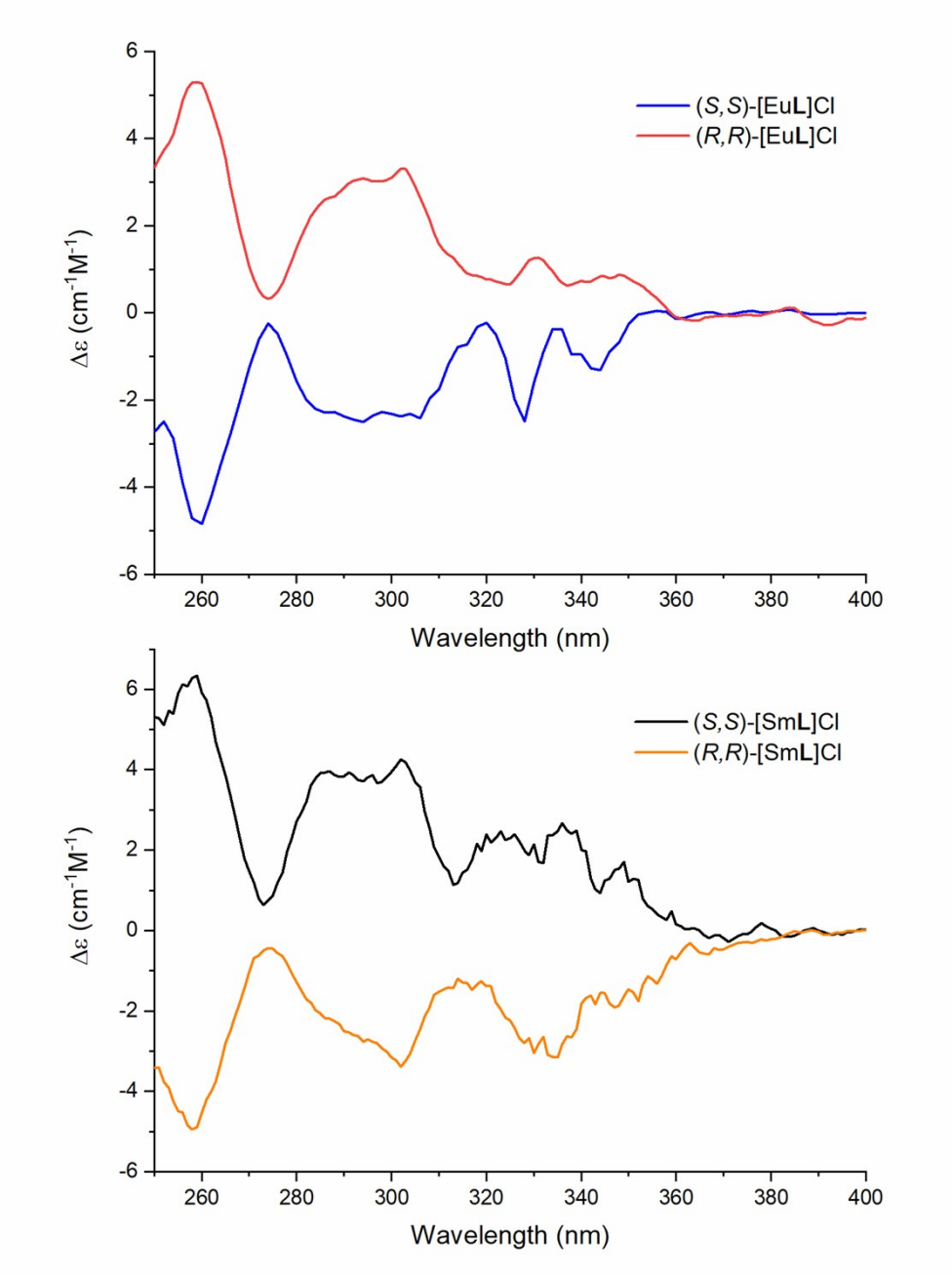

Figure S27. ECD spectra of both the enantiomers of the [Eu**L**]Cl (up) and [Sm**L**]Cl (bottom) complexes in methanol solution (10^{-6} M) at room temperature.

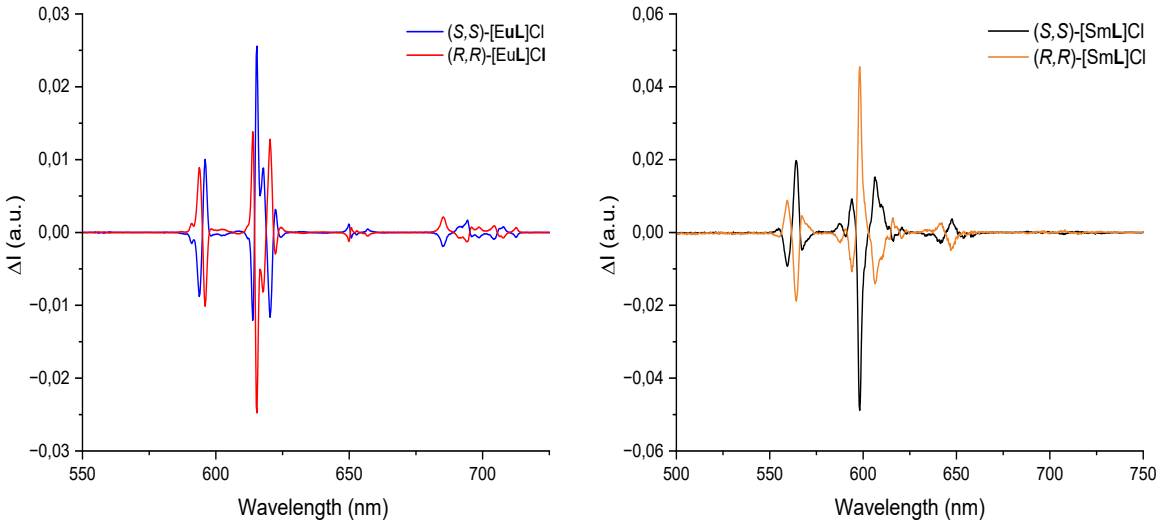

Figure S28. CPL spectra of both the enantiomers of the [Eu**L**]Cl (left) and [Sm**L**]Cl (right) complexes in methanol solution (10^{-4} M) at room temperature.

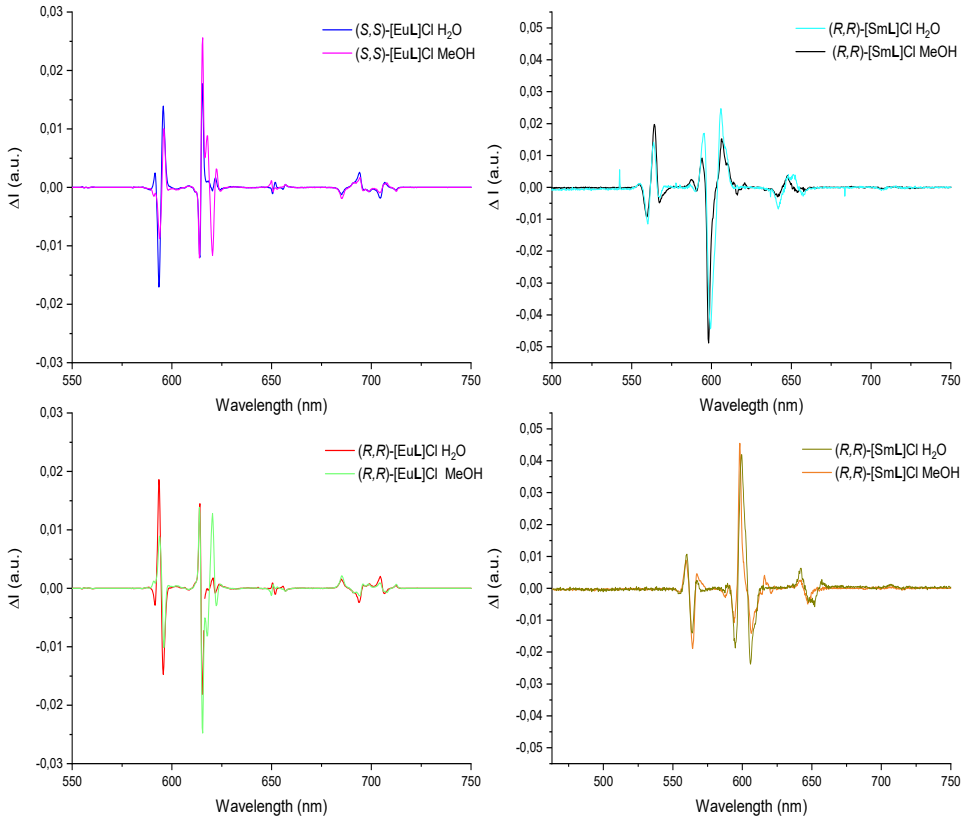

Figure S29. Overlap of CPL spectra in water and methanol (10^{-4} M) at room temperature of (S,S)–[Eu**L**]Cl (up left), (R,R)–[Eu**L**]Cl (bottom left), (S,S)–[Sm**L**]Cl) (up right), (R,R)–[Sm**L**]Cl (bottom right) complexes.

S5. TWO PHOTONS ABSORPTION

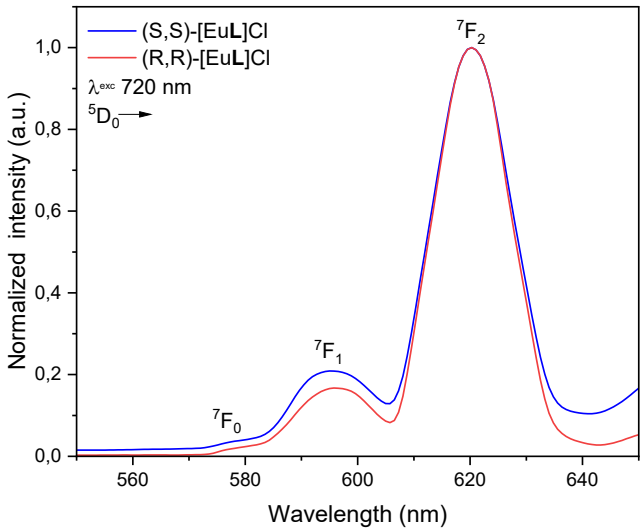

Figure S30. Luminescence spectra of both the enantiomers of [Eu**L**]Cl in methanol solution (10^{-5} M) upon two–photon excitation in the NIR spectral region (λ_{exc} =720 nm).

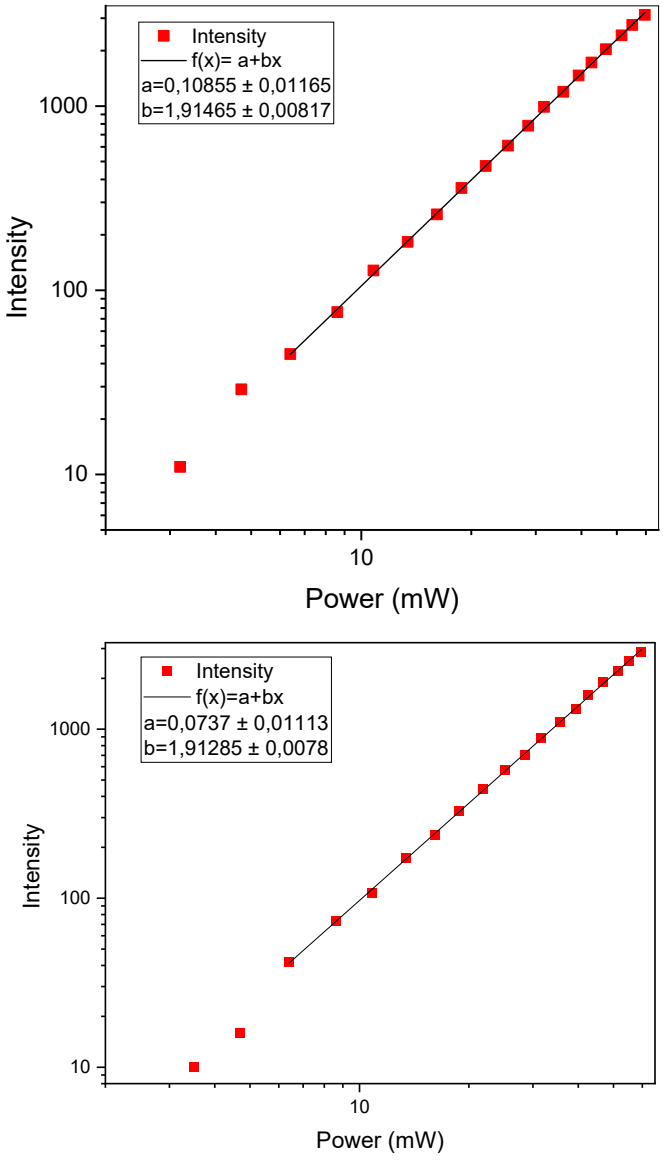

Figure S31. Variation of the luminescence intensity of Eu(III) with the laser excitation power (λ_{ex} =720 nm) for (*S,S*)–[Eu**L**]Cl (upper) and (*R,R*)–[Eu**L**]Cl (bottom) both dissolved in methanol (10^{-5} M).

S6. REFERENCES

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