Dinuclear enantiopure Ln^{3+} complexes with (S-) and (R-) 2-Phenylbutirate Ligands. Luminescence, CPL and magnetic properties.

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SUPPLEMENTARY INFORMATION

1. <u>Structural characterization.</u>

 $[Nd_2(\mu$ -*R/S*-2PhBu)₄(*R/S*-2PhBu)₄(Bphen)₂]: (*R/S*-Nd-a) Selected IR bands (ATR-IR, cm⁻¹ for **R-Nd-a**): 3056.8(w), 3020.3(w), 2960.5(w), 2927.3(w), 2867.5(w), 1595.6(s), 1555.7(m), 1539.1(s), 1519.2(m), 1492.6(m), 1449.4(m), 1402.9(s), 1296.7(w), 1230.3(w), 1084.1(w), 854.9(w), 831.7(w), 801.8(w), 692.3(s), 625.8(w), 569.4(w), 542.80(w). Anal. Calc. For C₁₀₈H₉₈N₄Nd₂O₁₂ (1932.5 g/mol): C, 67.1; N, 2.9; H, 5.1 %. Found: C, 67; N, 2.9; H, 5.2 % for *R*-Nd-a and found: C, 67.1; N, 2.9; H, 5.2 % for *S*-Nd-a.

 $[Sm_2(\mu-R/S-2PhBu)_4(R/S-2PhBu)_4(Bphen)_2]$: (R/S-Sm-a) Selected IR bands (ATR-IR, cm⁻¹ for R-Sm-a): 3053.5(w), 3026.9(w), 2957.2(w), 2927.3(w), 2870.9(w), 1595.6(s), 1578.9(m), 1545.8(s), 1519.2(m), 1489.3(w), 1452.8(w), 1409.6(s), 1300.0(w), 1230.2(w), 1087.4(w), 851.7(w), 835.1(w), 805.2(w), 742.1(m), 695.6(s), 625.8(m), 576.0(m), 542.8(m). Anal. Calc. For C₁₀₈H₉₈N₄O₁₂Sm₂ (1944.7 g/mol): C, 66.7; N, 2.9; H, 5.1 %. Found: C, 66.6; N, 2.9; H, 5.2 % for **R**-Sm-a and found: C, 66.7; N, 2.9; H, 5.1 % for **S-Sm-a**.

 $[Eu_2(\mu-R/S-2PhBu)_4(R/S-2PhBu)_4(Bphen)_2]$: (R/S-Eu-a) Selected IR bands (ATR-IR, cm⁻¹ for R-Eu-a): 3053.5(w), 3020(w), 2957.2(w), 2930.6(w), 2870.8(w), 1598.9(s), 1575.7(m), 1549.1(s), 1518.2(m), 1489.3(m), 1449.4(m), 1406.2(s), 1296.7(w), 1230.2(w), 1087.4(w), 851.7(w), 831.7(w), 801.9(w), 738.7(m), 692.3(s), 629.2(m), 572.7(m), 542.8(m) Anal. Calc. For C₁₀₈H₉₈N₄O₁₂Sm₂ (1944.7 g/mol): C, 66.7; N, 2.9; H, 5.1 %. Found: C, 66.6; N, 2.9; H, 5.2 % for **R-Sm-a** and found: C, 66.7; N, 2.9; H, 5.1 % for **S-Sm-a**.

[Tb₂(μ-R/S-2PhBu)₄(R/S-2PhBu)₄(Bphen)₂]: (R/S-Tb-a) Selected IR bands (ATR-IR, cm⁻¹ **R-Tb-a**): 3053.5(w), 3021.0(w), 2960.2(w), 2931.9(w), 2872.5(w), 1601.4(s), 1579.2(m), 1553.8(s), 1522,3(m), 1493.4(m), 1453.6(m), 1409.7(s), 1299.5(w), 1235.2(w), 1094.3(w), 864.3(w), 835.3(w), 804.2(w), 740.7(m), 694.1(s),

635.8(m), 572.7(m), 541.8(m) Anal. Calc. For C₁₀₈H₉₈N₄O₁₂Tb₂ (1961.8 g/mol): C, 66.1; N, 2.8; H, 5.0 %. Found: C, 65.9; N, 2.8; H, 5.1 % for **R-Tb-a** and found: C, 66.1; N, 2.8; H, 5.0 % for **S-Tb-a**.

[**Tb**₂(μ -**R/S-2PhBu**)₄(**R/S-2PhBu**)₄(**Bphen**)₂]: (**R/S-Tb-b**) Selected IR bands (ATR-IR, cm⁻¹ **R-Tb-a**): 3098.4(w), 3057.3(w), 3021.7(w), 2962.6(w), 2929.3(w), 2875.3(w), 1650.7(s), 1587.9(m), 1545.8(s), 1525.4(w), 1500.4(w), 1447.7(m), 1421.8(s), 1379.3(w), 1237.3(w), 1096.9(w), 860.5(w), 837.3(w), 805.3(w), 776.4(m), 747.7(m), 700.7(s), 630.7(w), 590.8(w), 554.6(w). Anal. Calc. For C₁₀₈H₉₈N₄O₁₂Tb₂ (1961.8 g/mol): C, 66.1; N, 2.8; H, 5.0 %. Found: C, 66.0; N, 2.8; H, 5.0 % for **R-Tb-b** and found: C, 65.9; N, 2.8; H, 5.1 % for **S-Tb-b**.

 $[Dy_2(\mu-R/S-2PhBu)_4(R/S-2PhBu)_4(Bphen)_2]$: (R/S-Dy-a) Selected IR bands (ATR-IR, cm⁻¹ R-Dy-a): 3051.4(w), 3019.4(w), 2955.6(w), 2925.3(w), 2865.3(w), 1595.6(s), 1573.1(m), 1543.5(s), 1515.3(m), 1482.5(m), 1441.1(m), 1401.9(s), 1293.4(w), 1226.0(w), 1083.7(w), 848.7(w), 825.9(w), 799.3(w), 730.1(m), 691.4(s), 619.5(m), 571.3(m), 540.6(m) Anal. Calc. For C₁₀₈H₉₈Dy₂N₄O₁₂ (1968.9 g/mol): C, 65.9; N, 2.8; H, 5.0 %. Found: C, 65.5; N, 2.8; H, 5.1 % for **R-Dy-a** and found: C, 65.0; N, 2.8; H, 5.0 % for **S-Dy-a**.

[**D** $y_2(\mu$ -**R**/**S**-2**P**h**B**u)₄(**R**/**S**-2**P**h**B**u)₄(**B**phen)₂]: (**R**/**S**-**D**y-**b**) Selected IR bands (ATR-IR, cm⁻¹ **R**-**D**y-**b**): 3086.3(w), 3056.5(w), 3022.6(w), 2962.3(w), 2928.6(w), 2873.1(w), 1648.6(s), 1579.3(m), 1542.7(s), 1522.6(w), 1498.5(w), 1440.3(m), 1415.6(s), 1301.8(w), 1234.8(w), 1093.6(w), 855.3(w), 833.6(w), 802.3(w), 769.4(m), 743.6(m), 699.4(s), 627.2(w), 576.1(w), 547.5(w). Anal. Calc. For C₁₀₈H₉₈Dy₂N₄O₁₂ (1968.9 g/mol): C, 65.9; N, 2.8; H, 5.0 %. Found: C, 66.0; N, 2.8; H, 5.2 % for **R-Dy-b** and found: C, 65.8; N, 2.8; H, 5.0 % for **S-Dy-b**.

 $[Tm_2(\mu-R/S-2PhBu)_4(R/S-2PhBu)_4(Bphen)_2]$: (R/S-Tm-b) Selected IR bands (ATR-IR, cm⁻¹ R-Tm-b): 3086.7(w), 3053.5(w), 3023.6(w), 2960.5(w), 2924.0(w), 2870.1(w), 1645.4(s), 1575.7(m), 1545.8(s), 1519.2(w), 1489.3(w), 1439.48(m), 1412.9(s), 1300(w), 1230.3(w), 1090.8(w), 851.7(w), 831.7(w), 801.9(w), 768.6(m), 742.1(m), 695.6(s), 625.8(w), 576.0(w), 546.1(w). Anal. Calc. For C₁₀₈H₉₈N₄O₁₂Tm₂ (1981.8 g/mol): C, 65.5; N, 2.8; H, 5.0 %. Found: C, 65.4; N, 2.8; H, 4.9 % for **R**-**Tm-b** and found: C, 65.4; N, 2.8; H, 4.9 % for **S-Tm-b**.

[Yb₂(μ-R/S-2PhBu)₄(R/S-2PhBu)₄(Bphen)₂]: (R/S-Yb-b) Selected IR bands (ATR-IR, cm⁻¹ **R-Yb-b**): 3083.4(w), 3060.2(w), 3023.6(w), 2957.2(w), 2924.0(w), 2870.9(w), 1645.4(s), 1598.9(w), 1578.9(m), 1545.8(s), 1519.2(w), 1489.3(w),

1409.6(s), 1296.7(w), 1233.6(w), 1087.5(w), 851.7(w), 835.1(w), 808.5(w), 771.9(s), 742.1(s), 692.3(s), 625.8(w), 572.7(w), 542.8(w). Anal. Calc. For C₁₀₈H₉₈N₄O₁₂Yb₂ (1990.0 g/mol): C, 65.2; N, 2.8; H, 5.0 %. Found: C, 65.2; N, 2.8; H, 5.0 % for **R-Yb-b** and found: C, 65.2; N, 2.8; H, 5.0 % for **S-Yb-b**.

Table S1. Selected bond distances (Å) for S-Eu-a and S-Tm-b.								
S-Eu-a				S-Tm-b				
Eu1-O1	2.481(4)	Eu2-O4	2.413(4)	Tm1-01	2.356(8)	Tm2-O4	2.258(7)	
Eu1-O2	2.434(5)	Eu2-O6	2.397(5)	Tm1-O2	2.382(8)	Tm2-O6	2.266(7)	
Eu1-O3	2.356(5)	Eu2-08	2.326(4)	Tm1-O3	2.268(9)	Tm2-08	2.289(9)	
Eu1-05	2.366(4)	Eu2-09	2.773(4)	Tm1-05	2.290(9)	Tm2-O10	2.249(9)	
Eu1-07	2.518(5)	Eu2-	2.401(5)	Tm1-07	2.234(9)	Tm2-O11	2.342(9)	
		O10						
Eu1-08	2.594(4)	Eu2-	2.404(5)	Tm1-09	2.291(7)	Tm2-O12	2.412(8)	
		011						
Eu1-09	2.439(4)	Eu2-	2.543(4)	Tm1-N1	2.516(10)	Tm2-N3	2.585(7)	
		012						
Eu1-N1	2.583(4)	Eu2-N3	2.648(4)	Tm1-N2	2.579(7)	Tm2-N4	2.526(10)	
Eu1-N2	2.649(4)	Eu2-N4	2.567(4)					
Eu1Eu2		4.000(5)		Tm1Tm2		4.287(7)		



Figure S1. Powder X-Ray Diffraction (PDRX) spectra of S-Eu-a (top, green line) andS-Tm-b (bottom, yellow line) powder samples compared to the calculated PDRX spectra obtained from the calculated Single Crystal Structure (black lines).



Fig. S2. Powder X-Ray Diffraction of al the enantiomeric pairs showing *structure a* type. First spectra, in black, corresponds to the calculated spectra from the single crystal structure of **S-Eu-a**.



Fig. S3. Powder X-Ray Diffraction of al the enantiomeric pairs showing *structure b* type. First spectra, in black, corresponds to the calculated spectra from the single crystal structure of S-Tm-a.

1. Luminescence properties.



Fig S4. Excitation spectra of polycrystalline samples monitored at the emission wavelength (λ_{em}) of of 1062 nm (${}^{4}F_{3/2} \rightarrow {}^{4}I_{11/2}$) for S-Nd-a, 597 nm (${}^{4}G_{5/2} \rightarrow {}^{6}H_{9/2}$) for S-Sm-a, 615 nm (${}^{5}D_{0} \rightarrow {}^{7}F_{2}$) for S-Eu-a, at 546 nm (${}^{5}D_{4} \rightarrow {}^{7}F_{5}$) for S-Tb-a and S-Tb-b, at 574 nm for S-Dy-a and 576 nm (${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$) for S-Dy-b and at 975 nm (${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$) for S-Yb-b.



Fig. S5. Absorption spectra of a) the Ln³⁺ compounds in chloroform solutions c = 10⁻⁶ M; and b) their ligand precursors in chloroform (4,4'-dinonyl-2,2'-bipy) or 1mM NaOH (Btfa) superimposed to 1-Sm Absorption spectrum

emission spectra of	f the presented lanthanide coo	rdination compounds.
	S-Sm-a	
	Polycrystalline	1 mM DCM solution
⁴ G _{5/2} → ⁶ H _{5/2}	563 nm	564 nm
⁴ G _{5/2} → ⁶ H _{7/2}	597 nm	599 nm
⁴ G _{5/2} → ⁶ H _{9/2}	644 nm	646 nm
⁴ G _{5/2} → ⁶ H _{11/2}	707 nm	707 nm
	S-Eu-a	
	Polycrystalline	1 mM DCM solution
${}^{5}D_{0} \rightarrow {}^{7}F_{0}$	581 nm	581 nm
${}^{5}D_{0} \rightarrow {}^{7}F_{1}$	594 nm	595 nm
${}^{5}D_{0} \rightarrow {}^{7}F_{2}$	615 nm	616 nm
${}^{5}D_{0} \rightarrow {}^{7}F_{3}$	652 nm	657 nm
${}^{5}D_{0} \rightarrow {}^{7}F_{4}$	701 nm	701 nm
	S-Tb-a and S-Tb-b	
	Polycrystalline	1 mM DCM solution
${}^{5}\mathrm{D}_{4} \rightarrow {}^{7}\mathrm{F}_{6}$	491 nm	491 nm
${}^{5}\mathrm{D}_{4} \rightarrow {}^{7}\mathrm{F}_{5}$	546 nm	546 nm
${}^{5}D_{4} \rightarrow {}^{7}F_{4}$	585 nm	588 nm
${}^{5}D_{4} \rightarrow {}^{7}F_{3}$	623 nm	622 nm
	S-Dy-a	
	Polycrystalline	1 mM DCM solution
⁷ F _{9/2} → ⁶ H _{15/2}	481 nm	-
$^{7}\mathrm{F}_{9/2} \rightarrow ^{6}\mathrm{H}_{13/2}$	574 nm	-
	S-Dy-b	
	Polycrystalline	1 mM DCM solution
$^{7}\mathrm{F}_{9/2} \rightarrow ^{6}\mathrm{H}_{15/2}$	481 nm	_
$^{7}\mathrm{F}_{9/2} \rightarrow ^{6}\mathrm{H}_{13/2}$	574 nm	-
	S-Yb-b	
	Polycrystalline	1 mM DCM solution
$^{7}\mathrm{F}_{5/2} \rightarrow ^{2}\mathrm{F}_{7/2}$	976 nm	976 nm
	S-Nd-a	
	Polycrystalline	1 mM DCM solution
${}^{4}\mathrm{F}_{3/2} \rightarrow {}^{4}\mathrm{I}_{9/2}$	886 nm	886 nm
${}^{4}\mathrm{F}_{3/2} \rightarrow {}^{4}\mathrm{I}_{11/2}$	1061 nm	1064 nm
${}^{4}F_{3/2} \rightarrow {}^{4}I_{13/2}$	1339 nm	1339 nm



and in 1mM DCM solution (left).



Figure S7. ¹H-NMR spectra of compounds *S*-Eu-a (top) and *S*-Tb-b (bottom).

Photoluminescence quantum yield (ϕ_{Ln}^{L}) and luminescence decay time (τ_{obs}):

The amount of energy absorbed by the chromophore ligands that is transferred to the excited state of the lanthanide ion is known as the sensitization efficiency (η_{sens}), and it plays a significant role in the overall quantum yield, which is defined as: $\phi_{Ln}^L = \eta_{sens} \cdot \phi_{Ln}^{Ln}$

The other factor that determines the ϕ_{Ln}^L value is the intrinsic quantum yield (ϕ_{Ln}^{Ln}) that alludes to the quantum yield once the emitting level of the lanthanide ion has been populated. The ϕ_{Ln}^{Ln} is supposed to be higher than the total quantum yield because although it considers deactivation mechanisms such as back-transfer energy and other quenching effects, it does not depend on ligand-Ln³⁺ energy transfer efficiency. The intrinsic quantum yield is related to the ratio between the measured time decay and the radiative lifetime τ_{rad} as shown in Eq. S1

$$\phi_{Ln}^{Ln} = \frac{k_r}{k_r + k_{nr}} = \frac{\tau_{obs}}{\tau_{rad}} \qquad \text{Eq. S1}$$

The radiative lifetime (τ_{rad}) is the luminescence lifetime in absence of non-radiative deactivations. Because of the pure magnetic dipole character that europium(III)'s ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition, τ_{rad} from the ${}^{5}D_{0}$ emissive level can be calculated from the corrected emission spectrum and a simplified equation presented in Eq. S2 [1]:

$$\frac{1}{t_{rad}} = A_{MD,0} \times n^3 \left(\frac{I_{TOT}}{I_{MD}} \right)$$
Eq. S2

 $A_{MD,0}$ is a constant (14.65 cm⁻¹), *n* is the refractive index (1.517 for microcrystalline

sample and 1.4125 for DCM solution, 20°C) and I_{MD} is the ratio between the total integrated area measured from the corrected Eu(III) emission spectrum (I_{TOT}) to the integrated area of the pure magnetic dipole transition ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ (I_{MD}).





Fig. S8. Circular Dichroism spectra of *R/S*-Tb-b pair measured in the solid state.



Fig. S9. Circular Dichroism spectra of compounds *R/S*-Dy-a and *R/S*-Dy-b measured in 1 mM DCM solution.





Fig.S10 Up left, Solid State CPL spectra of R/S-Eu-a complexes on a quartz plate deposition. Up right and bottom, spectra measured at the different positions. The final CPL spectrum consists of the average of these CPL spectra.



Fig.S11. *Up left*, dissymmetry factor (g_{lum}) with wavelength plot for **R/S-Tb-b** enantiomeric pair extracted from the CPL measurement of the polycrystalline samples. *Up right and bottom*, spectra measured at the different positions. The final CPL spectrum consists of the average of these CPL spectra



Fig.S12. Dissymmetry factor (g_{lum}) with wavelength plot for R/S-Eu-a enantiomeric pair extracted from the CPL measurement of the 1mM DCM solutions.



Fig.S13. Dissymmetry factor (g_{lum}) with wavelength plot for **R/S-Tb-b** enantiomeric pair extracted from the CPL measurement of the 1mM DCM solutions obtained for each Tb³⁺ ⁵D₄ \rightarrow ⁷F_J transitions. For transition ⁵D₄ \rightarrow ⁷F₆, CPL bands were very poor therefore consistent g_{lum} values could not be extracted.

6. Magnetic properties:



a. Static measurements:

Fig. S14. M vs the magnetic field plot measured at 2K for all compounds.



Fig.S15 Temperature dependence of χ_M " for **S-Dy-a** (left) and **S-Dy-b** (right). Continuous lines serve as an eye guide. The AC data was recorded under an oscillating magnetic field of $4 \cdot 10^{-4}$ T and a direct current magnetic field (H_{dc}) of 0 G.

$$\chi_{AC}(\omega) = \chi_S + \frac{\chi_T - \chi_S}{1 + (i\omega\tau)^{(1-\alpha)}}$$

Eq. S3. Generalized Debye model that describes a system with a distribution of the magnetization relaxation time. Where χ_S and χ_T are the adiabatic and thermal susceptibilities, τ is the relaxation of the magnetization time and ω is the angular frequency of the ac field (ω = 1/2 π f). χ_T is the susceptibility in the limit of the lowest field frequencies where the thermal equilibrium of the system is observed. χ_S (lower than the χ_T) is observed when the oscillations of the ac field are fast compared to the time constant, τ , and the magnetic system remains isolated from its environment. The α parameter quantifies the width of the τ distribution and it ranges from 0 to 1. The wider the time distribution, α acquires a larger value.



Fig.S16 ac measurements of **R-Dy-b** monitored at a constant temperature (3.5 K) and at different H_{dc} in the range of 0 to 5000 G were carried out. The representation of τ with H_{dc} show two maximum peaks. The first and more intense one appears at 600 G while

the second maximum value of τ is found around 3000 G indicating two different relaxation processes taking place at those two applied magnetic fields.



Fig. S17. ac measurements of **R-Nd-a** (left) and **R-Yb-b** (right) monitored at a constant temperature (2 K for **R-Nd-a** and 2.5 K for **R-Yb-b**) and at different Hdc in the range of 0 to 1 T for **R-Nd-a** and of 0 to 0.8 T for **R-Yb-b** were carried out. The field dependence of relaxation of the magnetization times (τ) is different in both compounds. The sudden increase of τ on increasing the magnetic field till the optimal field is reached is more pronounced for R-Yb-b accounting to a higher reduction of the QTM. After the maximum value of τ is accomplished, the curve increases on applying higher H accounting to the prevail of the Direct process.

7. References:

[1] M. H. V. Werts, R. T. F. Jukes, J. W. Verhoeven, *Phys. Chem. Chem. Phys.*, 2002, 4, 1542.