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SUPPORTING INFORMATION

Towards opto-structural parameters to enhance the circularly polarized luminescence brightness of Eu^{III} β-diketone complexes with chiral auxiliary ligands

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Supplementary note S1 – State-of-the-art of Eu^{III} complexes presenting CPL

Table S1. State-of-the-art of Eu^{III} complexes displaying CPL, comparing molar absorptivity ($\mathcal{E} / M^{-1} \text{ cm}^{-1}$), overall emission quantum yield (ϕ_{Ln}^L), dissymmetry factor (g_{lum}), branching ration (β_i) and CPL brightness (B_{CPL}).¹ The structure of the ligands is represented in Figure S1.

Complex	^ε / M ⁻¹ cm ⁻¹ ^{(λ} abs/ nm)	$\phi_{Ln}^{\ L}$	g _{lum} (λ/nm)	β_i	В _{СРL} / М ⁻¹ ст ⁻¹
Cs[Eu(bfbc)] ²	35,000 (310)	0 03	1.38 (595)	0.07	50.7
	55 000 (510)	0.05	0.25 (614)	0.45	59.1
$[Fu(tta)_{a}(Ph-nyhox)]^{3}$	35 000 (345)	05	0.11 (595)	0.09	86.6
	55 000 (545)	0.5	0.01 (614)	0.74	64.7
[Fu ₂ (11) ₂] ^{2+ 4}	80 000 (303)	0.13	0.088 (590)	0.22	100.7
	80 000 (303)		0.058 (615)	0.57	171.9
[Fu(1 2) ₂] ^{2+ 5}	55 000 (365)	0.11	0.26 (595)	0.13	102
[[]([]27]3]			0.11 (616)	0.64	213
$[Fu(tta)_{3}(Pr-pyhox)]^{3}$	27 000 (245)	0.4	0.24 (595)	0.08	103.7
	27 000 (343)		0.02 (614)	0.78	84.2
[Eu(L3)] ⁶	65 000 (342)	0.54	0.11 (599)	0.06	116
[Eu(L4)] ⁶	65 000 (356)	0.5	0.12 (599)	0.06	117
[Eu(L5)] ⁷	55 000 (360)	0.55	0.11 (598)	0.08	133.1
[Eu(L6)] ⁶	65 000 (343)	0.46	0.15 (599)	0.06	134.5
(ΔΔΔΔ-1) ⁸	60 0000 (380)	0.68	0.11 (592)	0.05	1122
(ΔΔΔΔ-2) ⁸	80 0000 (380)	0.81	0.2 (592)	0.05	3240



Figure S1. Structure of the ligands represented in Table S1.¹

Supplementary note S2 - Experimental section

Materials

Eu₂O₃ and Gd₂O₃ (99.9%), 1,1,1,5,5,5-Hexafluoro-2,4-pentanedione (98%), 2,6-Pyridinedicarboxylic acid (99%), Pyrazine-2,3-dicarboxylic acid (97%), Pyridine-2-carboxylic acid (99%), (S)-2-Amino-3-phenylpropionic acid (99%, optical purity ee: 98%), (S)-(–)-2-Amino-3-phenyl-1propanol (98%, optical purity ee: 99%), N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC.HCI-99%), 1-Hydroxybenzotriazole hydrate (HOBt-99%) were purchased from Merck and used without any further purification. The chiral ligands were synthesized from enantiomerically pure aminoalcohols, whose chirality is maintained during the reaction steps.

Synthesis of the chiral S-Bn-pybox pro-ligand

The chiral ligand S-Bn-pybox (pyridine bis-oxazoline) was synthesized according to the scheme shown in Figure S2. First, the amino acid (I) has been reduced to amino alcohol (II). Second, the formation of the diamide (IV) through the reaction of the 2,6-Pyridinedicarboxylic acid (III) with L-phenylalaninol (structure II) and EDC·HCI + HOBt was done.⁹ The third step is the formation of alkyl chloride with the addition of thionyl chloride to the amido-alcohol (IV). Lastly, the intramolecular cyclization in a basic medium was performed for the formation of the oxazoline ring and consequently the chiral ligand (V).



Figure S2. Scheme of the S-Bn-pybox chiral ligand synthesis.

S-Bn-pybox :¹H NMR (250 MHz, Chloroform-*d*, Figure S3) = δ 8.23 ppm (d, *J* = 7.8 Hz, 2H), 7.91 ppm (dd, *J* = 8.2, 7.4 Hz, 1H), 7.39 – 7.20 ppm (m, 11H), 4.67 ppm (tdd, *J* = 9.0, 6.3, 3.4 Hz, 2H), 4.48 ppm (dd, *J* = 9.4, 8.6 Hz, 2H), 4.28 ppm (dd, *J* = 8.6, 7.6 Hz, 2H), 3.29 ppm (dd, *J* = 13.7, 5.2 Hz, 2H), 2.77 ppm (dd, *J* = 13.7, 8.9 Hz, 2H). ¹³C NMR (63 MHz, CDCl₃, Figure S4) = δ 163.75, 146.34, 144.50, 137.88, 128.84, 128.25, 126.90, 53.92, 47.44 ppm. ESI-MS (Figure S5) = *m/z* calculated for S-Bn-pybox + H⁺ (C₂₅H₂₃N₃O₂H⁺) 398.18622, found 398.18630. [α]_D = -62°. FTIR (cm⁻¹), Figure S6 = 3056 (w), 3029 (w),

2957 (w), 2088 (w), 1657 (m), 1638 (m), 1602 (w), 1575 (m), 1540 (m), 1525 (m), 1496 (m), 1474 (m), 1454 (m), 1425 (m), 1359 (m), 1339 (m), 1319 (m), 1288 (w), 1272 (w), 1242 (m), 1219 (m), 1180 (m), 1162 (m), 1133 (s), 113 (w), 1093 (w), 1071 (m), 1029 (m), 992 (w), 978 (s), 962 (s), 933 (w), 899 (w), 859 (w), 837 (m), 764 (m), 755 (m), 743 (s), 702 (s), 664 (s), 647 (s), 621 (w), 587 (w), 556 (w), 518 (w), 504 (m), 485 (m), 450 (m), 434 (m), 413 (m).



Figure S3. ¹H-NMR spectrum of the S-Bn-pybox pro-ligand in CDCl₃.



Figure S4. ¹³C-NMR spectrum of the S-Bn-pybox pro-ligand in CDCl₃.



Figure S5. (a) Experimental mass spectrum of the S-Bn-pybox ($C_{25}H_{23}N_3O_2$) pro-ligand compared with the (b) simulated one using the protonated ligand ($C_{25}H_{23}N_3O_2 + H^+$).



Figure S6. FTIR spectrum of the S-Bn-pybox pro-ligand.

Synthesis of the (R)-Cl-(S)-Ph-pzox pro-ligand

The chiral ligand (R)-Cl-(S)-Ph-pzox (pyrazine oxazoline) was synthesized from the L-phenylglicinol (VI) and the pyrazine-2,3-dicarboxilic acid (V) (Figure S3) following the synthesis procedure for the chiral ligand S-Bn-pybox.



Figure S7. Scheme of the (R)-Cl-(S)-Ph-pzox chiral ligand synthesis.

(R)-Cl-(S)-Ph-pzox = ¹H NMR (250 MHz, Chloroform-*d*, Figure S8) = δ 8.79 – 8.66 ppm (m, 2H), 7.71 ppm (d, *J* = 8.5 Hz, 1H), 7.50 – 7.25 ppm (m, 10H), 5.62 ppm (dd, *J* = 8.5, 4.7 Hz, 1H), 4.86 ppm (d, *J* = 45.2 Hz, 1H), 4.05 ppm (d, *J* = 5.4 Hz, 2H), 2.01 ppm (d, *J* = 6.3 Hz, 2H). ¹³C NMR (63 MHz, CDCl₃, Figure S9) = δ 163.75, 146.34, 144.50, 137.88, 128.84, 128.25, 126.90, 77.59, 77.08, 76.57, 53.92, 47.44 ppm. ESI-MS (Figure S10) = *m*/*z* calculated for (R)-Cl-(S)-Ph-pzox + H⁺ (C₂₂H₁₉ClN₄O₂H⁺) 398.18622, found 398.18630. [α]_D = +114°. FTIR (cm⁻¹), Figure S11 = 3062 (w), 3034 (w), 2965 (w), 2930 (w), 1736 (w), 1640 (s), 1558 (m), 1541 (m), 1516 (s), 1495 (s), 1475 (w), 1456 (m), 1435 (m), 1400 (m), 1375 (w), 1355 (w), 1337 (w), 1308 (w), 1287 (m), 1278 (m), 1253 (m), 1218 (m), 1190 (m), 1163 (m), 1111 (s), 1062 (m), 1027 (m), 1002 (w), 982 (m), 949 (m), 906 (m), 876 (m), 857 (m), 830 (m), 800 (w), 769 (s), 749 (m), 731 (m), 693 (s).



Figure S8. ¹H-NMR spectrum of the (R)-Cl-(S)-Ph-pzox pro-ligand in CDCl₃.



Figure S9. ¹³C-NMR spectrum of the (R)-Cl-(S)-Ph-pzox pro-ligand in CDCl₃.



Figure S10. (a) Experimental mass spectrum of (R)-Cl-(S)-Ph-pzox ($C_{22}H_{19}ClN_4O_2$) compared with the (b) simulated one for the protonated pro-ligand with a water molecule ($C_{22}H_{19}ClN_4O_2 + H^+ + H_2O$).



Figure S11. FTIR spectrum of the (R)-Cl-(S)-Ph-pzox pro-ligand.

Synthesis of the S-Ph-pyox pro-ligand

The chiral pro-ligand S-Ph-pyox (pyridine oxazoline) was synthesized according to the scheme shown in Figure S7. First, pyridine-2-carboxylic acid (IX) was esterified in the presence of methanol and thionyl chloride, leading to the ester methyl (X). Subsequently, the ester was heated in a sealed tube

in the presence of the amino alcohol L-phenylglicinol. The last two steps are according to those described above for alkyl chloride formation and cyclization (S-Bn-pybox).¹⁰



Figure S12. Scheme of the S-Ph-pyox chiral ligand synthesis.

S-Ph-pyox = ¹H NMR (250 MHz, Chloroform-*d*, Figure S13) = δ 8.73 ppm (d, *J* = 7.7 Hz, 1H), 8.53 ppm (d, *J* = 4.8 Hz, 1H), 8.17 ppm (d, *J* = 7.8 Hz, 1H), 7.83 ppm (td, *J* = 7.7, 1.8 Hz, 1H), 7.42 – 7.25 ppm (m, 6H), 5.28 ppm (dt, *J* = 7.7, 5.4 Hz, 1H), 4.00 ppm (d, *J* = 5.3 Hz, 2H). ¹³C NMR (63 MHz, CDCl₃, Figure S14) = δ 164.73, 149.53, 148.14, 139.01, 137.48, 128.86, 128.56, 127.86, 126.88, 126.40, 122.45, 66.54, 56.13 ppm. ESI-MS (Figure S15): *m/z* calculated for S-Ph-pyox + H⁺ (C₁₄H₁₂N₂OH⁺) 225.10237, found 225.10224. [α]_D = -10°. FTIR (cm⁻¹, Figure S16) = 3086 (w), 3058 (w), 3028 (w), 2929 (w), 2875 (w), 1654 (s), 1591 (m), 1568 (m), 1515 (s), 1495 (m), 1465 (s), 1431 (s), 1354 (w), 1287 (m), 1242 (m), 1190 (w), 1154 (m), 1066 (m), 1040 (m), 1027 (m), 996 (m), 905 (w), 837 (w), 819 (m), 746 (s), 696 (s).



Figure S13. ¹H-NMR spectrum of the S-Ph-pyox pro-ligand in $CDCl_3$. The extra proton observed within the 7.25 – 7.5 ppm is associated with $CHCl_3$ formed by proton exchange in $CDCl_3$.



Figure S14. ¹³C-NMR spectrum of S-Ph-pyox pro-ligand in CDCl₃.



Figure S15. (a) Experimental mass spectrum of S-Ph-pyox ($C_{14}H_{12}N_2O$) compared with the (b) simulated one for the protonated pro-ligand ($C_{14}H_{12}N_2O + H^+$).



Figure S16. FTIR spectrum of the S-Ph-pyox pro-ligand.

Synthesis of the complexes

Lanthanide(III) acetates and $[Ln(hfa)_3(H_2O)_2]$ (hfa = hexafluoroacetylacetonate) precursor complex were prepared as reported elsewhere.^{11,12}

The chiral lanthanide complexes were synthesized by dissolving 50-100 mg of the chiral ligand and a stoichiometric amount (1:1) of the precursor complex in 10 mL of methanol. The chiral ligand was added dropwise into the solution of the precursor complex. The reaction solution was refluxed and stirring for 24 h. The solvents were evaporated, and the solids were dried at 40 °C for 24 h. The powder complexes were obtained after solvent evaporation and despite several attempts to crystalize the product, no good-quality crystals for single-crystal X-ray (SC-XRD) analysis were obtained.

 $[Gd(hfa)_{3}(S-Bn-pybox)] = ESI-MS: m/z \text{ calculated for } ([Gd(hfa)_{3}(S-Bn-pybox)] + 3H^{+} + CH_{3}OH)$ 1211,1165 found 1211.1855 (Figure S18 – S20). FTIR (cm⁻¹, Figure S36) = 1653 (s), 1585 (m), 1553 (m), 1523 (m), 1498 (s), 1453 (m), 1382 (m), 1345 (w), 1253 (s), 1194 (s), 1135 (s), 1098 (m), 1041 (w), 1016 (m), 971 (m), 946 (m), 850 (w), 831 (w), 793 (m), 746 (m), 700 (m), 660 (m), 583 (m), 547 (w), 525 (w), 506 (w), 462 (w). Anal. Calcd (%) for C₄₀H₂₆O₈F₁₂N₃Gd (1176.1 g mol⁻¹): C, 40.8; H, 2.23; N, 3.57. Found: C, 39.15; H, 2.86; N, 3.47.

 $[Gd(hfa)_3((R)-Cl-(S)-Ph-pzox)] = ESI-MS: m/z$ calculated for $([Gd(hfa)_3((R)-Cl-(S)-Ph-pzox)] + H^+ + H_2O + CH_3OH)$ 1236.0520, found 1236.0528 (Figure S24-27). FTIR (cm⁻¹, Figure S36) = 1649 (s), 1557 (m), 1530 (m), 1494 (m), 1473 (m), 1454 (m), 1416 (m), 1373 (w), 1350 (w), 1318 (w), 1254 (s), 1198 (s), 1135 (s), 1097 (s), 1079 (m), 1056 (m), 1027 (m), 950 (w), 874 (w), 840 (w), 795 (m), 764 (m), 738 (m), 723 (m), 697 (m), 659 (m), 581 (m), 525 (m).

 $[Gd(hfa)_{3}(S-Ph-pyox)] = ESI-MS: m/z calculated for ([Gd(hfa)_{3}(S-Ph-pyox)] + 2H^{+} + Na^{+}) 1027.9882,$ found 1027.9966 (Figure S21-23). FTIR (cm⁻¹, Figure S36) = 1651 (s), 1634 (s), 1594 (m), 1572 (m), 1554 (m), 1528 (m), 1496 (m), 1475 (m), 1400 (w), 1345 (w), 1309 (w), 1252 (s), 1194 (s), 1137 (s), 1097 (m), 1069 (m), 1054 (m), 1032 (m), 1012 (m), 950 (w), 842 (w), 798 (m), 753 (m), 740 (m), 725 (m), 699 (m), 659 (s), 634 (w), 583 (m), 528 (m). Anal. Calcd (%) for C₂₉H₁₅N₂O₇F₁₈Gd (1002.67 g mol⁻¹): C, 34.74; H, 1.51; N, 2.79. Found: C, 31.82; H, 2.10; N, 2.96.

 $[Eu(hfa)_3(S-Bn-pybox)] = ESI-MS: m/z calculated for ([Eu(hfa)_3(S-Bn-pybox)] + Na^+) 1192.05 found 1192.06 (Figure S28 – S30). FTIR (cm⁻¹, Figure S36) = 1653 (s), 1585 (m), 1553 (m), 1523 (m), 1498 (s), 1453 (m), 1382 (m), 1345 (w), 1253 (s), 1194 (s), 1135 (s), 1098 (m), 1041 (w), 1016 (m), 971 (m), 946 (m), 850 (w), 831 (w), 793 (m), 746 (m), 700 (m), 660 (m), 583 (m), 547 (w), 525 (w), 506 (w), 462 (w).$

 $[Eu(hfa)_3((R)-Cl-(S)-Ph-pzox)] = ESI-MS: m/z calculated for ([Eu(hfa)_3((R)-Cl-(S)-Ph-pzox)] + Na⁺ + H₂O) 1219.00351, found 1219.00275 (Figure S33 and S34). FTIR (cm⁻¹, Figure S36) = 1649 (s), 1557 (m), 1530 (m), 1494 (m), 1473 (m), 1454 (m), 1416 (m), 1373 (w), 1350 (w), 1318 (w), 1254 (s), 1198 (s), 1135 (s), 1097 (s), 1079 (m), 1056 (m), 1027 (m), 950 (w), 874 (w), 840 (w), 795 (m), 764 (m), 738 (m), 723 (m), 697 (m), 659 (m), 581 (m), 525 (m).$

 $[Eu(hfa)_3(S-Ph-pyox)] = ESI-MS: m/z calculated for ([Eu(hfa)_3(S-Ph-pyox)] + H_2O + Na^+) 1036.97882,$ found 1036.97968 (Figure S31 and 32). FTIR (cm⁻¹, Figure S36) = 1651 (s), 1634 (s), 1594 (m), 1572 (m), 1554 (m), 1528 (m), 1496 (m), 1475 (m), 1400 (w), 1345 (w), 1309 (w), 1252 (s), 1194 (s), 1137 (s), 1097 (m), 1069 (m), 1054 (m), 1032 (m), 1012 (m), 950 (w), 842 (w), 798 (m), 753 (m), 740 (m), 725 (m), 699 (m), 659 (s), 634 (w), 583 (m), 528 (m).

Characterization

¹³C and ¹H NMR. Proton and carbon nuclear magnetic resonance (¹H NMR and ¹³C NMR) measurements were performed in a Bruker spectrometer, model Avance III 250 MHz by dissolving the samples (~30 mg) in deuterated chloroform.

Mass spectrometry. Mass spectra of ligands and Eu^{III} and Gd^{III} chiral complexes were obtained in a 1:1 (volume) solution of methanol and water, using electron spray, positive or negative mode, in the range of 150 to 2000 m/z in the Thermo Q Mass Spectrometer -Exactive (Q-Obritrap).

TG and DTA. Thermogravimetric (TG) and differential thermal analysis (DTA) were performed in a TA Instruments SDT Q600 equipment. The measurement was carried out under a dynamic atmosphere of synthetic air (100 mL min⁻¹) and a heating rate of 10 °C min⁻¹.

SROT. Specific rotation (SROT) values were collected by a Perkin Elmer-341 Polarimeter, using a 10 mm optical path and a sodium lamp at a wavelength of 589 nm, at 20 °C.

UV-VIS absorption. Ultraviolet and visible (UV-Vis) absorption spectra were collected using an Agilent HP 8453 spectrophotometer at 300 K, step of 1 nm.

CD. Circular dichroism (CD) spectra were collected using a Jasco J-720 Spectropolarimeter with an Xe lamp (450 W). Parameters: standard sensitivity of 100 mdeg, 1 nm date pitch, 2.0 nm bandwidth, continuous scan mode, 1 s response, scan speed of 100 nm min⁻¹ and 8 accumulations.

DRS. Diffuse reflectance spectra (DRS) in the absorbance mode were obtained for the unmixed powder complexes using a SHIMADZU UV-2450 equipment with integrating sphere, increment of 1 nm, and BaSO₄ as reflectance standard.

PL. Photoluminescence spectra (PL) of powder complexes were obtained at 293 K in a Horiba Jobin-Yvon FL3-22-iHR-320 spectrofluorometer in front-face mode using a Xe lamp (450 W) as excitation source. All spectra were corrected according to the response of the photomultiplier (Hamamatsu PMT) and Xe lamp emission. Emission lifetime was recorded by using a time correlated single-photon counting (TCSPC) system (FluoroHub-B) linked with a pulsed 150 W Xenon lamp.

Absolute emission quantum yield. Emission quantum yield (${}^{\Phi_L^{ln}}$) was measured in a Quanta - ϕ F-3029 integrating sphere coupled by optic fibers to the previously mentioned fluorimeter. For reference, the empty sphere coated with Spectralon^{*} (reflectance > 95%) was used. The emission quantum yield is given by Equation S1, where N_{Em} and N_{Abs} are the number of photons emitted and absorbed by the sample, respectively, I_{em} is the emission spectrum of the sample, and I_{ex}^{st} stand for the excitation spectra of the light used to excite the sample and the integrating sphere empty, respectively.

$$\Phi_{L}^{Ln} = \frac{N_{Emi}}{N_{Abs}} = \frac{\int_{\lambda_{1}}^{\lambda_{2}} I_{em}(\lambda) d\lambda}{\int_{\lambda_{3}}^{\lambda_{4}} I_{ex}^{st}(\lambda) d\lambda - \int_{\lambda_{3}}^{\lambda_{4}} I_{ex}(\lambda) d\lambda} (S1)$$

CPL. The circularly polarized luminescence (CPL) spectra of the chiral Eu^{III} complexes in solutions were obtained at 298 K using the same previously mentioned spectrofluorometer in the right angle (RA) mode. In the CPL measurement, a depolarizer at the excitation output was used, while a quarter wave plate was located after the chiral sample followed by a linear emission polarizer as shown in Figure S17. The linear polarizer is positioned by the software of the equipment itself. For the calibration of the CPL measurements, a solution of the standard complex [Eu(D-facam)₃] (0.005 mol L⁻¹) in dried dimethyl sulfoxide (DMSO) was used. Under excitation at 363 nm, the complex shows g_{lum} value of ~0.78 relative to the most intense Stark component of the emission band attributed to the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition (~585 nm) of Eu^{III}.¹³

$$\Delta I = \left(I_L(\lambda) - I_R(\lambda)\right)(S2)$$

CPL measurements are standardized by the luminescent dissymmetry factor (g_{lum}), as defined in Eqn S3. A g_{lum} value equal to ±2 indicates complete polarization of the light emitted, while a value of zero corresponds to unpolarized emission.

$$g_{lum}(\lambda) = \frac{\left(I_L(\lambda) - I_R(\lambda)\right)}{\frac{1}{2}I_L(\lambda) + I_R(\lambda)} (S3)$$

Recently, researchers in the area proposed that the measurements be reported in terms of CPL brightness (Eqn S4), which facilitates the comparison of CPL performance, as it also relates absolute quantum yield and molar absorptivity of the compound.¹⁷

$$B_{CPL} = \varepsilon_{\lambda} \cdot \phi_{Ln}^{L} \cdot \beta_{i} \cdot \frac{|g_{lum}|}{2} (S4)$$

Where ε_{λ} is the molar absorptivity at the wavelength used, ϕ_{Ln}^{L} is the absolute quantum yield of emission and β_{i} is the branching ratio (Eqn S5): ⁶

$$\beta_i = \frac{I_i}{\Sigma_I I_I} (S5)$$



Figure S17. Set up of the CPL measurements, where IN means positioned and OUT not activated. The depolarizer ensures that all the detected polarized light comes from the sample. The quarter-wave plate has the function of setting in phase the components of the electric field, hence, converting circular polarized light into linear polarized light. The linear polarizer is used as a filter to select left and right circularly polarized light. The difference in angle between the quarter-wave plate and the linear polarizer must be 45° to observe circular

polarized light. In this case, we chose to set the manual quarter-wave plate at 90° and vary the linear polarizer in 45° and 315°, to minimize errors arising from the angle precision.

Supplementary note S3 – Computational procedure

All electronic structure calculations were conducted using the ORCA 5.0.3 software package¹⁸. The methodology encompassed an initial optimization of the ground state geometry within the framework of density functional theory (DFT) employing PBE0 functional¹⁹. During the optimization, all atoms except Eu^{III} were treated with the Def2-TZVP basis set²⁰, while the adapted Stuttgart-Cologne MWB52 effective core potential^{21,22} was applied for Eu^{III}. Subsequent to the ground-state geometry optimization, energies and wavefunctions were computed using a multireference approach, specifically the CASSCF/NEVPT2+QDPT approach^{23,24}. This method involved two sequential steps: (i) establishment of an active space consisting of the seven 4*f* orbitals; (ii) complete active space self-consistent field (CASSCF) calculation to derive eigenvalues and eigenvectors of excited states²⁵. The energies of these excited states were corrected by adding the *n*-electron valence perturbation theory at second-order (NEVPT2)²⁶ wherein the inclusion of spin-orbit coupling (SOC) was realized through *quasi*-degenerate perturbation theory (QDPT) in which the Eu^{III} multiplets were mixed via the spin-orbit mean field (SOMF) operator²⁷. The multireference calculations integrated the scalar relativistic Douglas-Kroll-Hess approximation²⁸ at the second order (DKH2) with the scalar relativistic recontracted (SARC2-QZVP) basis set²⁹ specifically tailored for Eu^{III}.

Following the computation of excitation energies for the complexes, the total transition momentum was decomposed into magnetic (μ_{MD}) and electric dipole (μ_{ED}) component contributions using MultiWFN software³⁰. The dissymmetry factor was calculated according to reference [³¹], detailed in Eqn S6, where D_{if} is the total dipole momentum of the excited state and R_{if} is the rotatory strength, defined in Eqn S7, where $g_e \approx 2$ is the free-electron *g*-factor, L_n and S_n are the components of the one-electron operators for the orbital and spin angular momentum, respectively, while Ψ_{gs} represents the ground-state wavefunction and Ψ_{es} the excited state wavefunction. Subsequently, the normalized magnetic and electric pair component vectors' coordinates (*x*, *y*, *z*) were acquired through a custom *python* script. This script commences with the eigenvectors extracted from each transition as obtained from CASSCF calculation³¹. The angles between the electric and magnetic dipole were calculated by adapting the Eqn 2 of the main text, yielding Eqn S8, where the module of the electric and magnetic dipole components was taken directly by the output file of the CASSCF/NEVPT2+QDPT calculation and transformed to esu² cm² using a conversion factor for $\alpha = 471.44 \times 10^{40}$ as explained in reference³².

$$g_{if} = \frac{4R_{if}}{D_{if}}, D_{if} = |\mu_{ED}|^{2} + |\mu_{MD}|^{2} (S6)$$

$$R_{if} = Im[\mu_{if} \cdot m_{if}] = Im\left[\sum_{n} \langle \Psi_{gs} | er_{n} | \Psi_{es} \rangle \left(\Psi_{gs} \left| \frac{e}{2m_{e}c} L_{n} + g_{e}S_{n} \right| \Psi_{es} \right) \right] (S7)$$

$$\arccos \theta = \frac{1g_{lum}(|\mu_{ED}|^{2} + |\mu_{MD}|^{2})}{|\mu_{ED}| \cdot |\mu_{MD}|} (S8)$$

The solvent was included in the multireference excited state calculations as a static medium by considering the dielectric constant and refractive index of acetonitrile (36.6 and 1.344, respectively) and dichloromethane (9.08 and 1.424, respectively) using the universal solvation model (SMD)³³.

Supplementary note S4 –Judd-Ofelt parameters and photophysical properties Experimental Judd-Ofelt parameters and experimental photophysical properties

For Eu^{III} complexes, experimental Ω_2 and Ω_4 (Eqn S9) Judd-Ofelt intensity parameters, radiative (Eqn S10) and non-radiative decay probabilities (*A*), and intrinsic emission quantum yield (Φ_{Eu}^{Eu} , Eqn S11) were obtained from the emission spectrum through the LUMPAC^{*} software. ³⁴ In these equations, ω is the angular frequency of incident radiation, $\chi = n(n+2)^2/9$ is the Lorentz local-field correction, *n* is the refractive index of the medium (1.500), $|\langle^7 F_J||U^{(\lambda)}||^5 D_0\rangle|^2$ is 0.0032 or 0.0023 for J = 2 and 4, respectively, $A_{0\lambda}$ is the spontaneous emission probability, $A_{01}=14,6\cdot n^3$, τ is the emitting state lifetime, and S_{0J} is the area under the band assigned to the ${}^5D_0 \rightarrow {}^7F_J$ transition. In this approach, the Ω_6 parameter is not calculated because the ${}^5D_0 \rightarrow {}^7F_6$ transition is not observed in the monitored emission range. ³⁵

$$\Omega_{\lambda} = \frac{3hc^{3}A_{0\lambda}}{8\pi e^{2}\omega^{3}\chi |\langle {}^{7}F_{J}||U^{(\lambda)}||^{5}D_{0}\rangle|^{2}} (S9)$$
$$A_{0J} = A_{01} \left(\frac{v_{01}}{v_{0J}}\right) \left(\frac{S_{0J}}{S_{01}}\right) (S10)$$
$$\Phi_{Eu}^{Eu} = \frac{A_{rad}}{A_{Total}} = \frac{\tau_{total}}{\tau_{rad}} (S11)$$

Theoretical intensity parameters.

The theoretical intensity parameters $\begin{pmatrix} \Omega^{theo}_{\lambda} \end{pmatrix}$ play a crucial role in providing valuable insights into the chemical environment surrounding Eu^{III} ion.³⁵ These parameters were determined using Eqn S12 – S14.

$$\Omega_{\lambda tp}^{theo} = (2\lambda + 1) \sum_{t,p} \frac{|B_{\lambda tp}|^2}{2t + 1}, B_{\lambda tp} = B_{\lambda tp}^{FED} + B_{\lambda tp}^{DC} (S12)$$

$$B_{\lambda tp}^{FED} = \frac{2}{\Delta E} \langle r^{t+1} \rangle \Theta(t,\lambda) \Big(\frac{4\pi}{2t+1} \Big)^{1/2} \Big(\sum_{j} e^2 \rho_j g_j (2\beta_j)^{t+1} \frac{Y_{p,j}^{t*}}{R^{t+1}} \Big) (S13)$$

$$B_{\lambda tp}^{DC} = \Big[-\frac{(\lambda + 1)(2\lambda + 3)}{(2\lambda + 1)} \Big]^{1/2} \langle r^{\lambda} \rangle \langle f \Big| |C^{(\lambda)}| \Big| f \rangle \Big(\frac{4\pi}{2t+1} \Big)^{1/2} \times \Big(\sum_{j} [(2\beta_j)^{t+1} \alpha_{OP,j} + \alpha_j] \frac{Y_{p,j}^{t*}}{R^{t+1}} \Big) \delta_{t,\lambda+1} (S14)$$

In these equations, the forced electric dipole (FED) derived from the original Judd-Ofelt theory^{36,} ³⁷ is represented by using Eqn S13 in the framework of the simple overlap model (SOM)³⁸. The numerical factors $(\Theta(t,\lambda))$ establish the relationship between the *f-g* and *f-d* interconfigurational transitions and 4*f* radial integrals, with specific values as follows: $\Theta(1,2) = -0.17$, $\Theta(3,2) = 0.34$, $\Theta(3,4) = 0.18$, $\Theta(5,4) = -0.24$, $\Theta(5,6) = -0.24$, and $\Theta(7,6)$

= 0.24 V. Trannoy, A. N. C. Neto, C. D. S. Brites, L. D. Carlos, H. Serier - Brault, *Adv.*, 2021, **9**, 200193.

³⁹. Additionally, ΔE represents the average energy denominator method⁴⁰. The overlap charge associated with the coordinating atom and Ln^{III} is described by the charge factor (g_j , Eqn S15) and overlap integral (ρ_j), while $\beta_j = (1 \pm \rho_j)^{-1}_{35}$. The site environment symmetry is considered by summing over j with the conjugated spherical harmonics ($Y_{p,j}^{t*}$). On the other hand, Eqn S14 expresses the contribution of dynamic coupling (DC)⁴¹ within the framework of the bond overlap model (BOM)³⁵. This model characterises the polarizability of the ligand through $\alpha_{OP,j}$, and α'_j . The former represents the bond overlap polarizability (Eqn S16) while the latter denotes the effective polarizability of the ligand³⁵.

$$g_{j} = R_{j} \sqrt{\frac{k_{j}}{2\Delta\varepsilon_{j}}} (S15)$$
$$\alpha_{OP,j} = \frac{e^{2}\rho_{j}^{2}R_{j}^{2}}{2\Delta\varepsilon_{j}} (S16)$$

In these equations, R_j is the bond length, $\Delta \varepsilon_j$ is the first excitation energy associated with the Ln–L ligating atom species, and k_j is the force constant of the Ln – L bond. The electron charge is represented by e while ρ_j is the overlap integral. The values of $\Delta \varepsilon_j$ and ρ_j were extracted from reference [⁴²] using an exponential fit.

Intramolecular energy transfer.

The rates of intramolecular energy transfer (IET) from the antenna ligand to Eu^{III} were computed by considering three mechanisms: dipole–dipole (W_{d-d}), dipole–multipole (W_{d-m}), and exchange (W_{ex}). These calculations were performed according to Eqn S17–S19^{43,44,45,46}. In all equations R_{l} is the donor-acceptor distance and Ω^{FED}_{λ} denotes the intensity parameters regarding only the FED contribution. The squared reduced matrix elements $\langle \Psi'J' | |U^{(\lambda)}| | \Psi J \rangle^2$ were obtained from ref [⁴⁷], and the matrix elements $\langle \Psi'J' | |S| | \Psi J \rangle^2$ were calculated using wave functions of the free ions within the intermediate coupling scheme^{48,49}. The S_l relates to the dipole strength of the ligand transition involved in the IET process. For singlet (S₁) and triplet (T₁) states, S_L has values of 10⁻³⁶ and 10⁻⁴⁰ esu² cm², respectively⁴³. The multiplicity of the excited states is considered in the degeneracy factor (G = 1 or 3 for S₁ and T₁, respectively), while $\langle r^{\lambda} \rangle$ is the 4*f* radial integrals and $\langle f | | C^{(\lambda)} | | f \rangle$ corresponds to the reduced matrix elements of Racah's tensor operators⁵⁰. Additionally, the effect of shielding is considered through the term $(1 - \sigma_k)$ (for k = 1 and 2) related to the overlap integrals between the valence ligand orbitals and the lanthanide⁵¹. The spin operator in the ligand is given by s_m , and μ_z represents the dipole operator component along the *z*-axis⁴³.

$$W_{d-d} = \frac{S_{L}(1-\sigma_{1})^{2}4\pi e^{2}}{(2J+1)G \ \hbar R_{L}^{6}} \sum_{\lambda} \Omega^{FED}_{\lambda} \langle \psi' J' \ \left| \ |U^{(\lambda)}| \ \left| \ \psi J \right\rangle^{2} F \ (S17)$$

$$W_{d-m} = \frac{S_{L}}{(2J+1)G \ \hbar} \sum_{\lambda} (\lambda+1) \frac{\langle r^{\lambda} \rangle^{2}}{(R^{\lambda+2})^{2}} \times \langle f \ \left| \ |C^{(\lambda)}| \ \right| f \rangle^{2} (1-\sigma_{\lambda})^{2} \langle \psi' J' \ \left| \ |U^{(\lambda)}| \ \left| \ \psi J \right\rangle^{2} F \ (S18)$$

$$W_{ex} = \frac{(1-\sigma_{\lambda})^{2} 8\pi e^{2}}{(2J+1)G \ \hbar R_{L}^{4}} \langle \psi' J' \ \left| \ |S| \ \left| \ \psi J \right\rangle^{2} \sum_{m} \left| \left| \langle \varphi \ \right| \sum_{j} \mu_{z}(j) s_{m}(j) \ \left| \ \varphi \ \ast \right| \right|^{2} F \ (S19)$$

In the context of lanthanide-based systems, the IET process is a non-resonant energy transfer mechanism⁴⁶. Consequently, the energy mismatch condition between the donor (ligands) and acceptor (Eu^{III}) is essential, as shown in Eqn S19. In this equation, the quantitative difference between the barycentre of the donor and the acceptor state of the lanthanide ion is denoted by δ . Furthermore, the parameter γ_D represents the bandwidth at half-height of the donor states (S₁ and T₁) and is assumed to have a value of 3000 cm⁻¹ for both singlet and triplet states⁴³.

$$F = \frac{1}{\hbar \gamma_D} \sqrt{\frac{\ln(2)}{\pi}} e^{-\left(\frac{\delta}{\hbar \gamma_D}\right)^2 \ln(2)}$$
(S20)

Rate equations and overall emission quantum yield.

After determining the rates of IET, the next step involves solving a system of rate equations, which consists of coupled ordinary differential equations (ODEs). This system can be solved numerically through time propagation⁴³, enabling the obtention of the population dynamics of each energy level. The set of ODEs is presented in Eqn S21, where both summations encompass all levels within the system^{43,52}. The populations of the levels $|i\rangle$ and $|j\rangle$ are denoted as P_i and P_j , respectively, while $W_{j\rightarrow i}$ and $W_{i\rightarrow j}$ represent the rates of energy transfer between these states. Thus, a rate equation model with *N*-levels can be described by a set of *N*-coupled ODEs.

$$\frac{dP_i(t)}{dt} = \sum_{j=1}^{N} W_{j \to i} P_j(t) - \sum_{j=1}^{N} W_{i \to j} P_i(t), i \neq j \quad (S21)$$

In this study, a set of coupled ODEs was solved using Radau methods. These methods have been successfully employed in previous investigations, delivering reliable results at a feasible computational cost^{53,54,55}. Each simulation was conducted over a time interval ranging from 0 – 50 ms with a step size of 1 ns. By solving the rate equations model, it is possible to estimate the population of the emitting level (⁵D₀, P_E) of Eu^{III} and consequently the emission intensity $I = A_{rad}P_E$. Here A_{rad} is the spontaneous emission coefficient calculated from the Judd-Ofelt intensity parameters^{36,37,43}.



Supplementary note S5 – Mass spectrometry of the Gd^{III} chiral complexes

Figure S18. Mass spectrum of [Gd(hfa)₃(S-Bn-pybox)].



Figure S19. Experimental mass spectrum of $[Gd(hfa)_3(S-Bn-pybox)]$ with emphasis on the 969 m/z region compared with the simulated one for the complex lacking one of the β -diketones.



Figure S20. Experimental mass spectrum of $[Gd(hfa)_3(S-Bn-pybox)]$ with emphasis on the 1211 m/z region compared with the simulated one for the complex with three protons (3H⁺) and one molecule of methanol.



re S21. Mass spectrum [Gd(hfa)₃(S-Ph-pyox)].



Figure S22. Experimental mass spectrum of $[Gd(hfa)_3(S-Ph-pyox)]$ with emphasis on the 1056 m/z region compared with the simulated one for the complex without one of the β -diketones and with two water molecules.



Figure S23. Experimental mass spectrum of $[Gd(hfa)_3(S-Ph-pyox)]$ with emphasis on the 1027 m/z region compared to the simulated one for the protonated complex (2 H⁺) with one sodium ion (Na⁺). Gdhfa3sphpzbox#234-2121 RT: 2.63-3.87 AV: 279 NL: 5.98E7



Figure S24. Mass spectrum of [Gd(hfa)₃((R)-Cl-(S)-Ph-pzox)].



Figure S25. Experimental mass spectrum of $[Gd(hfa)_3((R)-Cl-(S)-pzox)]$ with emphasis on the 1232 m/z region compared with the simulated one for the protonated complex (H⁺) with two (R)-Cl-(S)-Ph-pzox ligands and one β -diketone and three water molecules.



Figure S26. Experimental mass spectrum of $[Gd(hfa)_3((R)-Cl-(S)-pzox)]$ with emphasis on the 996 m/z region compared with the simulated one for the complex lacking one of the β -diketones and with one water molecule.



Figure S27. Experimental mass spectrum of $[Gd(hfa)_3((R)-CI-(S)-pzox)]$ with emphasis on the 1236 m/z region compared with the simulated one for the protonated complex (H⁺) with one water molecule and one of methanol.



Figure S28. Mass spectrum of [Eu(hfa)₃(S-Bn-pybox)].



Figure S29. Experimental mass spectrum of $[Eu(hfa)_3(S-Bn-pybox)]$ with emphasis on the 1194 m/z region compared with the simulated one for the complex associated with one Na⁺. The fragment at 1194.05 m/z (with some contribution of the other at 1194.15 m/z) was studied by MS2 fragmentation, Figure S30.





Figure S30. MS2 experimental mass spectrum of $[Eu(hfa)_3(S-Bn-pybox)]$ with emphasis on the 1195 m/z region compared with the simulated one for the $([Eu(hfa)_3(S-Bn-pybox)] + Na^+)$ and $([Eu(hfa)_2(S-Bn-pybox)]^+)$ fragments.



Figure S32. Experimental mass spectrum of $[Eu(hfa)_3(S-Ph-pyox)]$ with emphasis on the 1039 m/z region compared to the simulated one for the complex associated with one sodium ion (Na⁺) and one H₂O.



Figure S33. Mass spectrum of [Eu(hfa)₃((R)-Cl-(S)-Ph-pzox)].



Figure S34. Experimental mass spectrum of $[Eu(hfa)_3((R)-Cl-(S)-Ph-pzox)]$ with emphasis on the 1221 m/z region compared to the simulated one for the complex associated with one sodium ion (Na⁺) and one H₂O.



Supplementary note S6 – Thermogravimetry of the complexes

Figure S35. TG (in blue) and DTA (in red) curves of the chiral Ln^{III} complexes (a) $[Eu(hfa)_3(S-Bn-pybox)]$, (b) $[Gd(hfa)_3(S-Bn-pybox)]$, (c) $[Eu(hfa)_3((R)-CI-(S)-Ph-pzox)]$ (d) $[Gd(tta)_3((R)-CI-(S)-Ph-pzox)]$, (e) $[Eu(hfa)_3(S-Ph-pyox)]$, and (f) $[Gd(hfa)_3(S-Ph-pyox)]$.

Table S2. Residual mass calculated from TG compared to the expected value from the thermal decomposition of								
the chiral complexes, leading to the formation of the respective Ln_2O_3 .								
	Residual	Residual		Residual	Residual			
Complex	mass	mass (%)	Complex	mass (%)	mass (%)			
	(%) cal	exn		cal	eyn			

Complex	mass mass (%) (%) cal. exp.		Complex	mass (%) cal.	mass (%) exp.
[Eu(hfa)₃(S-Bn-pybox)]	15	15	[Gd(hfa)₃(S-Bn-pybox)]	15	15
[Eu(hfa)₃(S-Ph-pyox)]	17	14	[Gd(hfa)₃(S-Ph-pyox)]	20*	23
[Eu(hfa)₃((R)-Cl-(S)-Ph-pzox)]	15	15	[Gd(hfa)₃((R)-Cl-(S)-Ph- pzox)]	15	17

* The calculation of the theoretical residual mass used Ln₂O₂CO₃ as the final residue.



Figure S36. FTIR spectra of (a) $[Ln(hfa)_3(S-Bn-pybox)]$, (b) $[Ln(hfa)_3((R)-Cl-(S)-Ph-pzox)]$, and (c) $[Ln(hfa)_3(S-Ph-pyox)]$ (Ln – Eu or Gd). The FTIR spectra of chiral Gd^{III} and Eu^{III} complexes (Fig. S29) present C=C and C=O coupled vibrational modes at 1520 cm⁻¹ as well as a bending mode coupled to C–H + C=C vibrations at about 1500 cm⁻¹. The bands between 1150 and 1050 cm⁻¹ are assigned to coupled vibrations of C–F₃ + C–H bonds, while the vibrational modes assigned to the C=O stretch are found at about 1650 cm⁻¹ for all the complexes.

Supplementary note S8 – Additional photoluminescence data

The excitation spectra of the powder complexes, Fig. 3, are characterized by a broad excitation band within the 250 – 420 nm assigned to ligand-centered $S_n \leftarrow S_0$ transitions ($\pi^* \leftarrow \pi$ processes) as well as a sharp band at 464 nm coming from the Eu^{III 5}D₂ \leftarrow ⁷F₀ transition. Upon ligand excitation at about 350 nm, Fig. 3, the typical Eu^{III} emission within the orange-red spectral window is observed due to the Eu^{III 5}D₀ \rightarrow ⁷F₁ (J = 0-4) electronic transitions whose higher intensity of the band assigned to the ⁵D₀ \rightarrow ⁷F₂ transition suggests that the Ln^{III} is inserted in low-symmetry sites. By comparing the excitation and emission spectral of the chiral complexes with the [Eu(hfa)₃(H₂O)₂] precursor, some important differences are observed, which confirm that the chiral ligand is indeed coordinated to Eu^{III}, changing the local symmetry of the Eu^{III} first coordination environment compared to the precursor complex. These differences are better seen by comparing the relative intensity of the ligand-centered excitation bands at about 275 nm and 350 nm compared to the Eu^{IIII} *f*-*f* band at 464 nm, the number of *J* components observed per each ⁵D₀ \rightarrow ⁷F_J transition in the emission spectra, and also in the relative intensities of these bands, ensuring that the local Eu^{IIII} microsymmetry is changing after the coordination of the chiral ligand.

Eu^{III} is a special case within the Ln^{III} series because it can be used as a spectroscopic probe to get further insights into its local microssimetry. This feature arises from the fact that for Eu^{III}, the ⁵D₀ emitting state is non-degenerate, thus, the number of Stark components of each emission band depends only on the receptor level of the transition. As a consequence, since Eu^{III} is a non-Kramers ions, the maximum crystal field (CF) splitting of a level into M_J Stark sublevels should be 2J + 1 (J = total angular momentum quantum number), hence, the number of components per each ${}^5D_0 \rightarrow {}^7F_J$ transition is given by 2J + 1.

Figure S37. High-resolution photoluminescence spectra (13 K) of (a) [$Eu(hfa)_3(S-Bn-pybox)$], (b) [$Eu(hfa)_3((R)-Cl-(S)-Ph-pzox)$], and (c) [$Eu(hfa)_3(S-Ph-pyox)$] upon 370 nm excitation.

Point group	⁷ F ₀	⁷ F ₁	⁷ F ₂	⁷ F ₃	⁷ F ₄
C ₁ , C _s e C ₂	1	3	5	7	9
C _{2v}	1	3	4	5	7
C _i and C _{2h}	0	3	0	0	0
D ₂	0	3	0	6	6
D _{2h}	0	3	3	0	0
D _{2d}	0	2	0	3	3
D ₃	0	2	2	4	4
C ₃	1	2	2	5	6
C _{3v}	1	2	3	3	5
C _{3h}	0	2	1	3	4
C_{3i} , D_{3d} , D_{6h} , C_{4h} , D_{4h} and T	0	2	0	0	0
D _{3h}	0	2	1	2	3
C ₄	1	2	2	3	5
C _{4v}	1	2	2	2	4
D _{4d}	0	2	0	1	2
S ₄	0	2	3	4	4
D_4	0	2	1	3	3
C ₆ and C _{6v}	1	2	2	2	2
D ₆	0	2	1	2	1
T _d	0	1	1	1	1
T _h , O _h and I _h	0	1	0	0	0
0	0	1	0	1	1

Table S3. Number of J components observed for the $Eu^{III 5}D_0 \rightarrow {}^7F_J$ transitions depending on the Eu^{III} point group.⁵⁶

Supplementary note S9 – Triplet state determination and absorption properties

The Gd^{III} complexes were considered to determine the triple state energy since the energy of Gd^{III} excited levels is considerably higher than the typical energy of triplet states, inhibiting any ET process. As a consequence, the emission of Gd^{III} systems arises mainly from triplet states. The triplet excited-state energy of the analogous Gd^{III} complex was determined by the measurement of the time-resolved low-temperature (77 K) phosphorescence spectra (Fig. S31).

Figure S38. Time-resolved (delay of 0.5 ms) emission spectra (77 K) of (a) $[Gd(hfa)_3(S-Bn-pybox)]$, (b) $[Gd(hfa)_3((R)-Cl-(S)-Ph-pzox)]$, and (c) $[Gd(hfa)_3(S-Ph-pyox)]$ compared with the steady-state emission. The deconvolution of each spectrum was carried out by applying a gaussian function. To avoid any emission coming from short-lived singlet excited states or vibronic components, time-resolved emission spectra measured at 77 K were recorded while the zero-phonon transition energy obtained by the band energy inset was considered for the assignment. The peak at 16200 cm⁻¹ is assigned to the Eu^{III} emission, usually found as contaminants in Gd₂O₃ (purity of 99.9%) yet, the band position of such contaminant does not match the region where emission bands are important for triplet state determination, so, the analyses are not compromised.

By taking advantage of the electronic nature of Gd^{III}, the ligand-to-metal charge transfer (LMCT) states can be elucidated by diffuse reflectance spectroscopy, since no LMCT states should be observed for the Gd^{III} complexes. The arithmetic subtraction of the diffuse reflectance spectra of complexes containing Eu^{III} by their Gd^{III} analogous clearly shows the presence of LMCT states (Fig. S32) for the Eu^{III} complexes. The complex [Eu(hfa)₃((R)-Cl-(S)-Ph-pzox)], for instance, showed a LMCT band in the region of 20883 cm⁻¹ (Fig. S32b).

Figure S39. Diffuse reflectance spectra (DRS) of (a) $[Ln(hfa)_3(S-Bn-pybox)]$, (b) $[Ln(hfa)_3((R)-Cl-(S)-Ph-pzox)]$, and (c) $[Ln(hfa)_3(S-Ph-pyox)]$ (Ln = Eu or Gd). The difference between the DRS spectra of Eu^{III} and Gd^{III} analogous complexes is shown in the bottom of the figure.

Figure S40. Emission decay curves monitoring the excitation at about 345 nm and the Eu^{III} emission at 613 nm for (a) [Eu(hfa)₃(H₂O)₂], (b) [Eu(hfa)₃(S-Bn-pybox)], (c) [Eu(hfa)₃(S-Ph-pyox)] e (d) [Eu(hfa)₃((R)-Cl-(S)-Ph-pzox)]. The continuous red line represents the best fitting to a monoexponential function ($R^2 > 0.95$).

Supplementary note S11 – Theoretical photophysical parameters of Eu^{III} complexes

Table S4. Theoretical Judd-Ofelt intensity parameters ($\Omega_{2,4,6}$) at 293 K, theoretical overall quantum yield (${}^{\Phi}{}^{L}_{Ln}$), and first singlet (S_1) and triplet (T_1) excited state energies calculated at the CASSCF/NEVPT2+QDPT level.

Complexes	Ω2	Ω_4	Ω ₆	Φ_{L}^{L}	S ₁ / cm ⁻¹	T ₁ / cm ⁻¹
	/ 10 ⁻²⁰ cm ²	/ 10 ⁻²⁰ cm ²	/ 10 ⁻²⁰ cm ²	- Ln / %		
[Eu(hfa)₃(S-Bn-pybox)]	19.3	5.80	0.56	42	35595	22845
[Eu(hfa)₃((R)-Cl-(S)-Ph-pzox)]	20.7	6.60	1.65	25	35691	22956
[Eu(hfa)₃(S-Ph-pyox)]	23.0	7.15	1.63	36	30885	22730

Table S5. Calculated donor-acceptor distance (R_l) related with Figure S34 – S36 for both singlet (S) and triplet (T) excited states and total rates of forward and backward intramolecular energy transfer (W and W^b , respectively).

Complexes	Singlet					
	R _L / Å	^W _S / s ⁻¹	W_{S}^{b} / s ⁻¹	R _L / Å	W_{T} / s ⁻¹	W_{T}^{b} / s ⁻¹
[Eu(hfa)₃(S-Bn-pybox)]	4.413	4.502×10 ⁴	6.058×10 ⁻¹⁵	4.823	6.687×10 ⁷	9.796×10 ⁶
[Eu(hfa)₃((R)-Cl-(S)-Ph-pzox)]	3.285	9.847×10 ⁵	1.038×10 ⁻¹³	4.629	9.859×10 ⁷	1.629×10 ⁷
[Eu(hfa)₃(S-Ph-pyox)]	4.269	1.172×10 ⁷	5.727×10 ⁻³	4.783	7.611×10 ⁷	9.837×10 ⁶

Figure S41. Monoelectronic states involved in the absorption spectrum singlet-singlet and singlet-triplet excitations for [Eu(hfa)₃(S-Bn-pybox)] complex calculated using CASSCF/NEVPT2+QDPT.

Figure S42. Monoelectronic states involved in the absorption spectrum singlet-singlet and singlet-triplet excitations for [Eu(hfa)₃((R)-Cl-(S)-Ph-pzox)] complex calculated using CASSCF/NEVPT2+QDPT.

Figure S43. Monoelectronic states involved in the absorption spectrum singlet-singlet and singlet-triplet excitations for [Eu(hfa)₃(S-Ph-pyox)] complex calculated using CASSCF/NEVPT2+QDPT.

Table S6. Energy transfer rates (in s⁻¹) for $[Eu(hfa)_3(S-Bn-pybox)]$ complex considering only the states that contribute more than 0.001% for S₁ and T₁. δ is the donor-acceptor (singlet/triplet-Eu³⁺) energy difference (in cm⁻¹). W_{d-d} , W_{m-d} , W_{ex} are the dipole-dipole, dipole-multipole, and exchange rates (in cm⁻¹), respectively. W and W^b are the forward and backward energy transfer rates, respectively at 298.15 K.

Pathway	Donor	Accept	δ	W_{d-d}	W_{m-d}	W _{ex}	W	W^{b}
10	S ₁	$^{7}F_{0}\rightarrow^{5}L_{6}$	10270	1.396×10 ²	9.275	0	1.488×10 ²	4.119×10 ⁻²¹
15	S_1	$^{7}F_{0}\rightarrow ^{5}G_{6}$	8843	2.757×10 ²	1.833×10 ¹	0	2.941×10 ²	7.965×10 ⁻¹⁵
18	S_1	$^{7}F_{0}\rightarrow^{5}D_{4}$	8009	1.439×10 ²	1.987×0 ³	0	2.131×10 ³	4.664×10 ⁻¹⁵
29	S1	$^{7}F_{0}\rightarrow^{5}D_{4}$	11612	5.938×10 ⁻²	1.003×10 ²	0	1.003×10 ²	1.196×10 ⁻²²
31	S_1	$^{7}F_{1}\rightarrow$ $^{5}L_{7}$	9610	3.011×10 ¹	2.001	0	3.211×10 ¹	2.803×10 ⁻¹⁹
32	S_1	$^{7}F_{1}\rightarrow ^{5}G_{2}$	9575	0	0	4.029×10 ⁴	4.029×10 ⁴	1.249×10 ⁻¹⁵
33	S_1	$^{7}F_{1}\rightarrow ^{5}G_{3}$	9345	2.027	1.959×10 ³	0	1.961×10 ³	1.318×10 ⁻¹⁶
35	S_1	$^{7}F_{1}\rightarrow ^{5}G_{6}$	9215	1.445×10 ¹	9.607×10 ⁻¹	0	1.541×10 ¹	1.044×10 ⁻¹⁸
36	S_1	$^{7}F_{1}\rightarrow ^{5}G_{5}$	9204	2.978×10 ¹	1.177×10 ¹	0	4.155×10 ¹	3.508×10 ⁻¹⁸
Total	S_1						4.502×10 ⁴	6.058×10 ⁻¹⁵
7	T ₁	$^{7}F_{0}\rightarrow ^{5}D_{1}$	3818	0	0	6.158×10 ⁷	6.158×10 ⁷	2.454×10 ⁻¹
26	T_1	$^{7}F_{1}\rightarrow ^{5}D_{0}$	5924	0	0	3.609×10 ⁶	3.609×10 ⁶	2.507×10 ⁻⁵
28	T ₁	$^{7}F_{1}\rightarrow ^{5}D_{2}$	1734	0	0	1.672×10 ⁶	1.672×10 ⁶	1.403×10 ³
32	T ₁	$^{7}F_{1}\rightarrow ^{5}G_{2}$	-3175	0	0	6.015×10 ⁻¹	6.015×10 ⁻¹	9.791×10 ⁶
Total	T ₁						6.687×10 ⁷	9.792×10 ⁶

Table S7. Energy transfer rates (in s⁻¹) for [Eu(hfa)₃((R)-Cl-(S)-Ph-pzox)] complex considering only the states that contribute more than 0.001% for S₁ and T₁. δ is the donor-acceptor (singlet/triplet-Eu³⁺) energy difference (in cm⁻¹). W_{d-d} , W_{m-d} , W_{ex} are the dipole-dipole, dipole-multipole, and exchange rates (in cm⁻¹), respectively. W and W^b are the forward and backward energy transfer rates, respectively at 298.15 K.

Pathway	Donor	Accept	δ	W _{d-d}	W _{m-d}	W _{ex}	W	W^b
10	S ₁	$^{7}F_{0}\rightarrow^{5}L_{6}$	10366	1.314×10 ³	8.986×10 ²	0	2.212×10 ³	3.856×10 ⁻²⁰
15	S_1	$^{7}F_{0}\rightarrow ^{5}G_{6}$	8939	2.651×10 ³	1.813×10 ³	0	4.465×10 ³	7.608×10 ⁻¹⁷
18	S_1	$^{7}F_{0}\rightarrow^{5}D_{4}$	8105	1.094×10 ³	6.107×10 ⁴	0	6.216×10 ⁴	8.561×10 ⁻¹⁴
29	S_1	$^{7}F_{0}\rightarrow^{5}D_{4}$	11708	3.575×10 ⁻¹	5.669×10 ²	0	5.669×10 ²	4.256×10 ⁻²²
31	S_1	${}^{7}F_{1} \rightarrow {}^{5}L_{7}$	9706	2.862×10 ²	1.958×10 ²	0	4.821×10 ²	2.648×10 ⁻¹⁸
32	S_1	${}^{7}F_{1} \rightarrow {}^{5}G_{2}$	9671	0	0	9.019×10 ⁵	9.019×10 ⁵	1.760×10 ⁻¹⁴
33	S_1	${}^{7}F_{1} \rightarrow {}^{5}G_{3}$	9441	1.369×10 ¹	1.174×10 ⁴	0	1.174×10 ⁴	4.971×10 ⁻¹⁶
35	S_1	$^{7}F_{1}\rightarrow ^{5}G_{6}$	9311	1.382×10 ²	9.453×10 ¹	0	2.327×10 ²	9.922×10 ⁻¹⁸
36	S1	${}^{7}F_{1} \rightarrow {}^{5}G_{5}$	9300	2.833×10 ²	4.873×10 ²	0	7.705×10 ²	4.094×10 ⁻¹⁷
Total	S_1						9.847×10 ⁵	1.038×10 ⁻¹³
7	T ₁	$^{7}F_{0}\rightarrow^{5}D_{1}$	3929	0	0	9.089×10 ⁷	9.089×10 ⁷	2.120×10 ⁻¹
26	T_1	$^{7}F_{1}\rightarrow^{5}D_{0}$	6035	0	0	5.138×10 ⁶	5.138×10 ⁶	2.089×10 ⁻⁵
28	T ₁	$^{7}F_{1}\rightarrow^{5}D_{2}$	1845	0	0	2.558×10 ⁶	2.558×10 ⁶	1.256×10 ³
32	T_1	$^{7}F_{1}\rightarrow ^{5}G_{2}$	-3064	0	0	1.709	1.709	1.628×10 ⁷

 T_1

9.859×10⁷ 1.629×10⁷

Table S8. Energy transfer rates (in s⁻¹) for [Eu(hfa)₃(S-Ph-pyox)] complex considering only the states that contribute more than 0.001% for S₁ and T₁. δ is the donor-acceptor (singlet/triplet-Eu³⁺) energy difference (in cm⁻¹). W_{d-d} , W_{m-d} , W_{ex} are the dipole-dipole, dipole-multipole, and exchange rates (in cm⁻¹), respectively. W and W^b are the forward and backward energy transfer rates, respectively at 298.15 K.

Pathway	Donor	Accept	δ	W _{d-d}	W _{m-d}	W _{ex}	W	W^b
10	S1	$^{7}F_{0}\rightarrow^{5}L_{6}$	5560	1.331×10 ⁴	4.920×10 ³	0	1.823×10 ⁴	3.749×10 ⁻⁹
15	S ₁	$^{7}F_{0}\rightarrow ^{5}G_{6}$	4133	9.337×10 ³	3.453×10 ³	0	1.279×104	2.572×10 ⁻⁶
18	S ₁	$^{7}F_{0}\rightarrow ^{5}D_{4}$	3299	2.536×10 ³	1.789×10 ⁵	0	1.815×10 ⁵	2.950×10 ⁻³
29	S_1	$^{7}F_{1}\rightarrow ^{5}D_{4}$	6902	2.251×10 ¹	1.758×10 ⁵	0	1.759×10 ⁵	1.557×10 ⁻⁹
31	S_1	${}^{7}F_{1} \rightarrow {}^{5}L_{7}$	4900	1.779×10 ³	6.577×10 ²	0	2.436×10 ³	1.579×10 ⁻⁷
32	S_1	${}^{7}F_{1} \rightarrow {}^{5}G_{2}$	4865	0	0	1.060×10 ⁷	1.060×10 ⁷	2.441×10 ⁻³
33	S_1	$^{7}F_{1}\rightarrow ^{5}G_{3}$	5650	1.249×10 ²	6.619×10 ⁵	0	6.620×10 ⁵	3.303×10 ⁻⁴
35	S_1	${}^{7}F_{1} \rightarrow {}^{5}G_{6}$	4505	6.410×10 ²	2.370×10 ²	0	8.781×10 ²	4.418×10 ⁻⁷
36	S_1	${}^{7}F_{1} \rightarrow {}^{5}G_{5}$	4494	1.309×10 ³	2.582×10 ³	0	3.890×10 ³	2.439×10 ⁻⁶
Total	S_1						1.172×10 ⁷	5.727×10 ⁻³
7	T ₁	$^{7}F_{0}\rightarrow^{5}D_{1}$	3703	0	0	7.001×10 ⁷	7.001×10 ⁷	4.859×10 ⁻¹
26	T ₁	$^{7}F_{1}\rightarrow ^{5}D_{0}$	5809	0	0	4.259×10 ⁶	4.259×10 ⁶	5.154×10 ⁻⁵
28	T ₁	$^{7}F_{1}\rightarrow ^{5}D_{2}$	1845	0	0	1.832×10 ⁶	1.832×10 ⁶	2.678×10 ³
32	T_1	$^{7}F_{1}\rightarrow ^{5}G_{2}$	-3064	0	0	3.469×10 ⁻¹	3.469×10 ⁻¹	9.834×10 ⁶
Total	T ₁						7.611×10 ⁷	9.837×10 ⁶

From the determined energy transfer rates, a set of coupled ordinary differential equations (ODEs), capturing the population kinetics can be generated (Eqn S22).⁵⁷ In this equation, $|0\rangle$ is the ground state (at t = 0, the S₀ and t \neq 0, ⁷F_J), $|1\rangle$ is T_{I} , $|2\rangle$ relates to S_{I} , $|3\rangle$ represents any Eu^{III} manifold other than ⁵D₀, and $|4\rangle$ represents the ⁵D₀ level. Additionally, ^{T_S}, ^{T_T}, and ^{τ} are the decay lifetimes of the S₁, T_1 , and ⁵D₀ levels. In Eu^{III}-based systems, these lifetimes typically range from 10⁻⁹ to 10⁻⁶ s for ^{T_S}, 10⁻⁶ to 10⁻³ s for ^{T_T}, and 10⁻³ s for ^{τ}. The rate of S₁ \rightarrow T₁ intersystem crossing (ISC), denoted as W_{ISC} , is on the order of 10⁷ s⁻¹ for energy gaps between S₁ and T₁ of 10000 – 15000 cm⁻¹, which is the case for the studied complex. When simulating population dynamics using Eqn 1, it is essential to consider the boundary conditions to ensure the conservation of the total population across all energy levels at any given time *t*, meaning that the sum of the population of all states, denoted as $P_N(t)$, remains constant within the time interval $0 \le t \le t_f$.

$$|0\rangle: \frac{d}{dt}P_{0} = -\phi P_{0} + \frac{1}{\tau_{T}}P_{1} + \frac{1}{\tau_{S}}P_{2} + \frac{1}{\tau}P_{4} (S22a)$$

$$|1\rangle: \frac{d}{dt}P_{1} = -\left(\frac{1}{\tau_{T}} + W^{T} + W^{T}\right)P_{1} + W_{ISC}P_{2} + W_{b}^{T}P_{3} (S22b)$$

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Supplementary note S12 – Time-resolved spectroscopy of the complexes in solution

Figure S44. Emission decay curves monitoring the excitation at about 303 nm and the Eu^{III} emission at 613 nm for the Eu^{III} complexes in ACN or DCM. The continuous red line represents the best fitting to a monoexponential or biexponential function ($R^2 > 0.95$).

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