

Supporting Information for

High Circularly Polarized Luminescence Brightness from Analogues of Shibasaki's Lanthanide Complexes

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General Methods and Material:

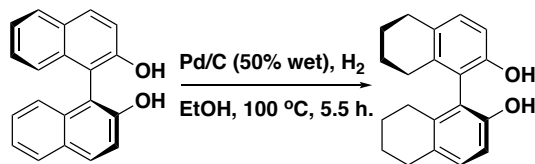
All operations were carried out using standard Schlenk techniques or in a Vigor glove box filled with N₂. The Sm(OTf)₃ was purchased from Oakwood Chemicals. The Tb(OTf)₃ was purchased from StremChemicals. The NaHMDS and Dy(OTf)₃ were purchased from Alfa Aesar. All solvents were dried using a solvent purification system from Pure Process Technology. The (R/S)-H₈-Binol were synthesized according to the literature.

NMR Spectroscopy. All NMR spectra were recorded on a Bruker AVANCE III 400 MHz spectrometer. The spectra were processed using the MestReNova software. Chemical shifts are reported in parts per million and were determined relative to the residual solvent signal (2.50 ppm for DMSO)

Photophysical Studies. All photophysical studies are performed in sealed cuvettes under dry N₂ atmosphere using anhydrous THF. Absorption, excitation, and emission spectra were recorded on a HORIBA Duetta Spectrophotometer using HORIBA EzSpec Software. Absorption spectra, excitation, and emission spectra were measured at 1.3 x 10⁻⁵ M. Circularly polarized luminescence was measured on an OLIS CPL Solo with 1.3 x 10⁻³ M solutions. Quantum yields were determined by absolute method using an integrating sphere on a HORIBA FLUOROMAX spectrofluorometer, all samples were measured at 4.3 x 10⁻⁶ M. Lifetimes were recorded from 1.3 x 10⁻⁴ M solutions using an OLIS CPL Solo spectrofluorometer. Spectra were collected using pulsed excitation at 340 nm and time-resolved emission measurements fixed at the peak of strongest emission. A first order exponential decay curve was fit to the collected data to estimate the fluorescence lifetime (τ_{obs}). Values are reported as measured lifetimes (observation wavelength).

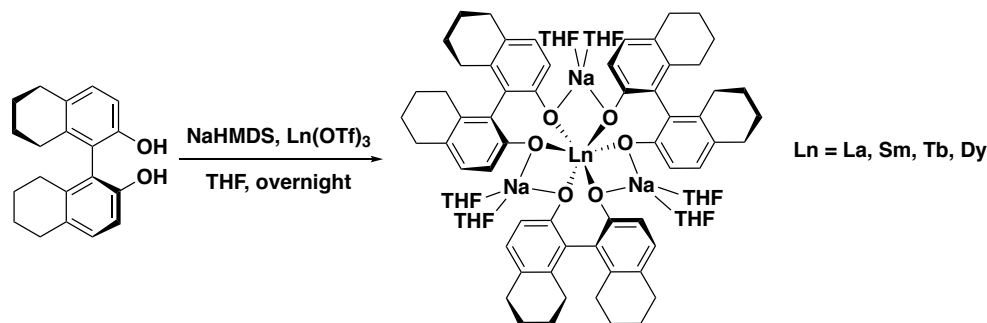
XRD Studies. Single-crystal X-ray diffraction studies were performed at Vanderbilt University. A suitable crystal of each sample was selected for analysis and mounted in a polyimide loop. All measurements were made on a Rigaku Oxford Diffraction Supernova Eos CCD with filtered Mo K α radiation at a temperature of 100 K. Using Olex2 the structure was determined with the ShelXL structure solution program using direct methods and refined with the ShelXL refinement package using least-squares minimization.

Synthesis of S-H₈-Binol Ligand



The synthesis of the S-H₈-Binol ligand followed the reported method by using Pd/C reduction.¹ The synthesis of the R-H₈-Binol ligand is similar.

General Procedure for the Synthesis of (S-H₈-Binol)₃LnNa₃ Complexes



To a mixture of (S)-H₈-Binol (3.0 equiv., 0.68 mmol) and Ln(OTf)₃ (1 equiv., 0.23 mmol) in THF (4 mL) after stirring at room temperature for 10 minutes, a solution of NaHMDS (6 equiv., 1.36 mmol) in THF (6 mL) was added dropwise. The reaction was stirred at room temperature overnight before pumping down. The obtained solid was triturated in ACN and then centrifuged to remove the supernatant for three times. The solid residue was dissolved in THF and filtered. The filtrate was pumped down to get a solid product. The synthesis of (R-H₈-Binol)₃LnNa₃ Complexes are similar.

Synthesis of (S/R-H₈-Binol)₃LaNa₃ Complexes

(S-H₈-Binol)₃LaNa₃ was produced according to the general procedure using 133 mg of La(OTf)₃ (0.23 mmol) and 200 mg of S-H₈-Binol (0.68 mmol, 3.0 equiv.). Yield: 205 mg (60%) of an off-white solid. ¹H NMR (400 MHz, DMSO-*d*₆) δ 6.54 (d, J = 8.2 Hz, 6H), 6.35 (d, J = 8.1 Hz, 6H), 2.60 – 2.56 (m, 12H), 2.19 – 2.12 (m, 6H), 1.97 – 1.90 (m, 6H), 1.65 – 1.60 (m, 6H), 1.56 – 1.43 (m, 18H) ppm; ¹³C NMR (101 MHz, DMSO-*d*₆) δ 161.9, 133.6, 127.7, 126.7, 119.7, 118.4, 29.1, 27.5, 23.5 (d, 2C) ppm. Elemental Analysis calc'd (%): C₈₄H₁₀₈LaNa₃O₁₂: C, 66.48; H, 7.17; found (%): C, 66.40; H, 7.12.

(R-H₈-Binol)₃LaNa₃ was produced according to the general procedure using 133 mg of La(OTf)₃ (0.23 mmol) and 200 mg of R-H₈-Binol (0.68 mmol, 3.0 equiv.). Yield: 204 mg (60%) of an off-white solid. ¹H NMR (400 MHz, DMSO-*d*₆) δ 6.53 (d, J = 8.2 Hz, 6H), 6.34 (d, J = 8.1 Hz, 6H), 2.59 – 2.58 (m, 12H), 2.19–2.12 (m, 6H), 1.97–1.90 (m, 6H), 1.64–1.60 (m, 6H), 1.56–1.43 (m, 18H) ppm; ¹³C NMR (101 MHz, DMSO-*d*₆) δ 161.8, 133.6, 127.7, 126.7, 119.7, 118.4, 29.1, 27.5, 23.5 (d, 2C) ppm. Elemental Analysis calc'd (%): C₈₄H₁₀₈LaNa₃O₁₂: C, 66.48; H, 7.17; found (%): C, 66.42; H, 7.18.

Synthesis of (S/R-H₈-Binol)₃SmNa₃ Complexes

(S-H₈-Binol)₃SmNa₃ was produced according to the general procedure using 135 mg of Sm(OTf)₃ (0.23 mmol) and 200 mg of S-H₈-Binol (0.68 mmol, 3.0 equiv.). Yield: 205 mg (76%) of a white solid. ¹H NMR (400 MHz, DMSO-*d*₆) δ 5.70 (d, J = 8.0 Hz, 6H), 3.21 – 3.03 (m, 12H), 2.56 – 2.53 (m, 12H), 2.45 (s, 6H), 2.02 – 1.89 (m, 18H), 1.86 – 1.80 (m, 6H) ppm; ¹³C NMR (101 MHz, DMSO-*d*₆) δ 168.56, 136.50, 131.45, 127.41, 120.33, 116.03, 30.23, 29.19, 24.72, 24.42 ppm. Elemental Analysis calc'd (%): C₈₄H₁₀₈SmNa₃O₁₂: C, 65.98; H, 7.12; found (%): C, 65.89; H, 7.10.

(R-H₈-Binol)₃SmNa₃ was produced according to the general procedure using 135 mg of Sm(OTf)₃ (0.23 mmol) and 200 mg of R-H₈-Binol (0.68 mmol, 3.0 equiv.). Yield: 205 mg (74%) of a white solid. ¹H NMR (400 MHz, DMSO-*d*₆) δ 5.70 (d, J = 7.9 Hz, 6H), 3.15 – 2.99 (m, 12H), 2.58 – 2.52 (m, 12H), 2.40 (s, 6H), 1.97 – 1.87 (m, 18H), 1.84 – 1.77 (m, 6H) ppm; ¹³C NMR (101 MHz, DMSO-*d*₆) δ 167.8, 135.8, 130.8, 126.7, 119.6, 115.3, 29.5, 28.5, 24.0, 23.7 ppm. Elemental Analysis calc'd (%): C₈₄H₁₀₈SmNa₃O₁₂: C, 65.98; H, 7.12; found (%): C, 65.94; H, 7.08.

(Note: In proton NMR, the peak at 2.4 ppm may shift as the concentration of the sample varies.)

Synthesis of (S/R-H₈-Binol)₃TbNa₃ Complexes

(S-H₈-Binol)₃TbNa₃ was produced according to the general procedure using 137 mg of Tb(OTf)₃ (0.23 mmol) and 200 mg of S-H₈-Binol (0.68 mmol, 3.0 equiv.). Yield: 280 mg (81%) of a white solid. ¹H NMR (400 MHz, DMSO-*d*₆) δ 15.00 ppm, broad peaks were observed. Because of paramagnetic effects and possible dynamic processes, all peaks appear to be broad and cannot be accurately integrated. A ¹³C NMR spectrum could not be obtained due to the paramagnetic nature of the complex. Elemental Analysis calc'd (%): C₈₄H₁₀₈TbNa₃O₁₂: C, 65.61; H, 7.08; found (%): C, 65.55; H, 7.11.

(R-H₈-Binol)₃TbNa₃ was produced according to the general procedure using 137 mg of Tb(OTf)₃ (0.23 mmol) and 200 mg of R-H₈-Binol (0.68 mmol, 3.0 equiv.). Yield: 260 mg (75%) of a white solid. ¹H NMR (400 MHz, DMSO-*d*₆) δ 15.00 ppm, broad peaks were observed. Because of paramagnetic effects and possible dynamic processes, all peaks appear to be broad and cannot be accurately integrated. A ¹³C NMR spectrum could not be obtained due to the paramagnetic nature of the complex. Elemental Analysis calc'd (%): C₈₄H₁₀₈TbNa₃O₁₂: C, 65.61; H, 7.08; found (%): C, 65.56; H, 7.11.

Synthesis of (S/R-H₈-Binol)₃DyNa₃ Complexes

(S-H₈-Binol)₃DyNa₃ was produced according to the general procedure using 138 mg of Dy(OTf)₃ (0.23 mmol) and 200 mg of S-H₈-Binol (0.68 mmol, 3.0 equiv.). Yield: 217 mg (62%) of a white solid. ¹H NMR (400 MHz, DMSO-*d*₆) δ 21.69, 14.04, 8.09 ppm, broad peaks were observed. Because of paramagnetic effects and possible dynamic processes, all peaks appear to be broad and cannot be accurately integrated. A ¹³C NMR spectrum could not be obtained due to the paramagnetic nature of the complex. Elemental Analysis calc'd (%): C₈₄H₁₀₈DyNa₃O₁₂-C₄H₈O: C, 65.51; H, 7.25; found (%): C, 65.51; H, 7.26.

(R-H₈-Binol)₃DyNa₃ was produced according to the general procedure using 138 mg of Dy(OTf)₃ (0.23 mmol) and 200 mg of R-H₈-Binol (0.68 mmol, 3.0 equiv.). Yield: 210 mg (60%) of a white solid. ¹H NMR (400 MHz, DMSO-*d*₆) δ 20.81, 14.14, 8.72 ppm, broad peaks were observed. Because of paramagnetic effects and possible dynamic processes, all peaks appear to be broad and cannot be accurately integrated. A ¹³C NMR spectrum could not be obtained due to the paramagnetic nature of the complex. Elemental Analysis calc'd (%): C₈₄H₁₀₈DyNa₃O₁₂: C, 65.46; H, 7.06; found (%): C, 65.40; H, 7.04.

NMR Spectra of (S-H₈-Binol)₃LaNa₃

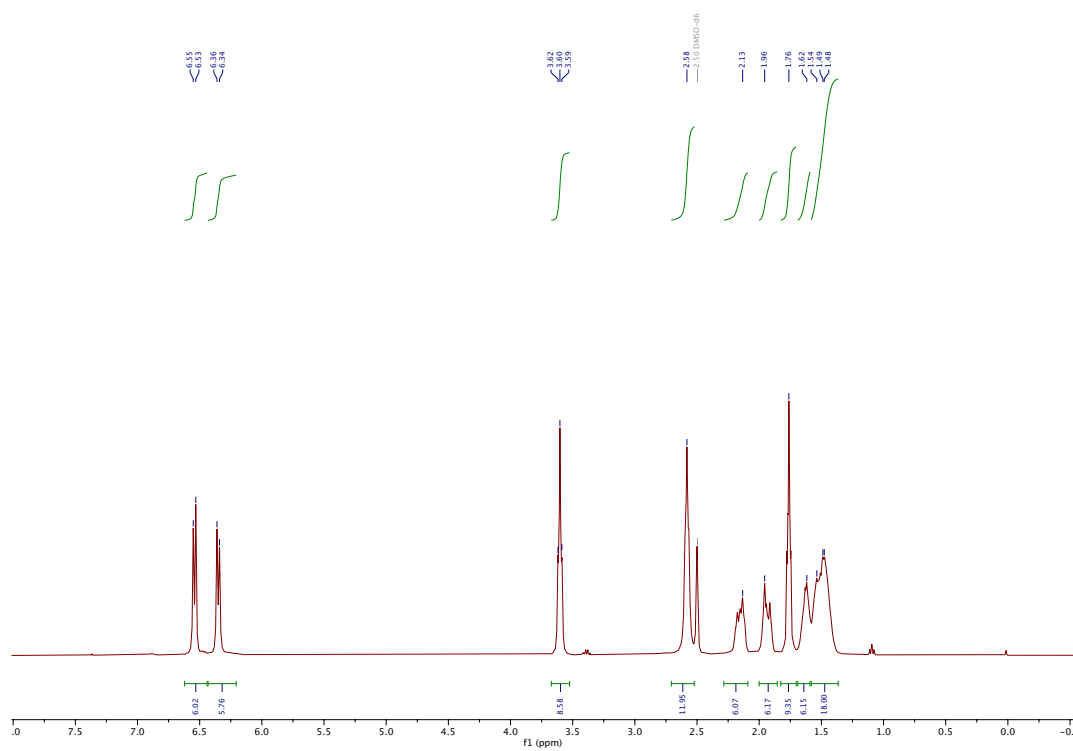


Figure S1. ¹H NMR of (S-H₈-Binol)₃LaNa₃ in DMSO-*d*₆.

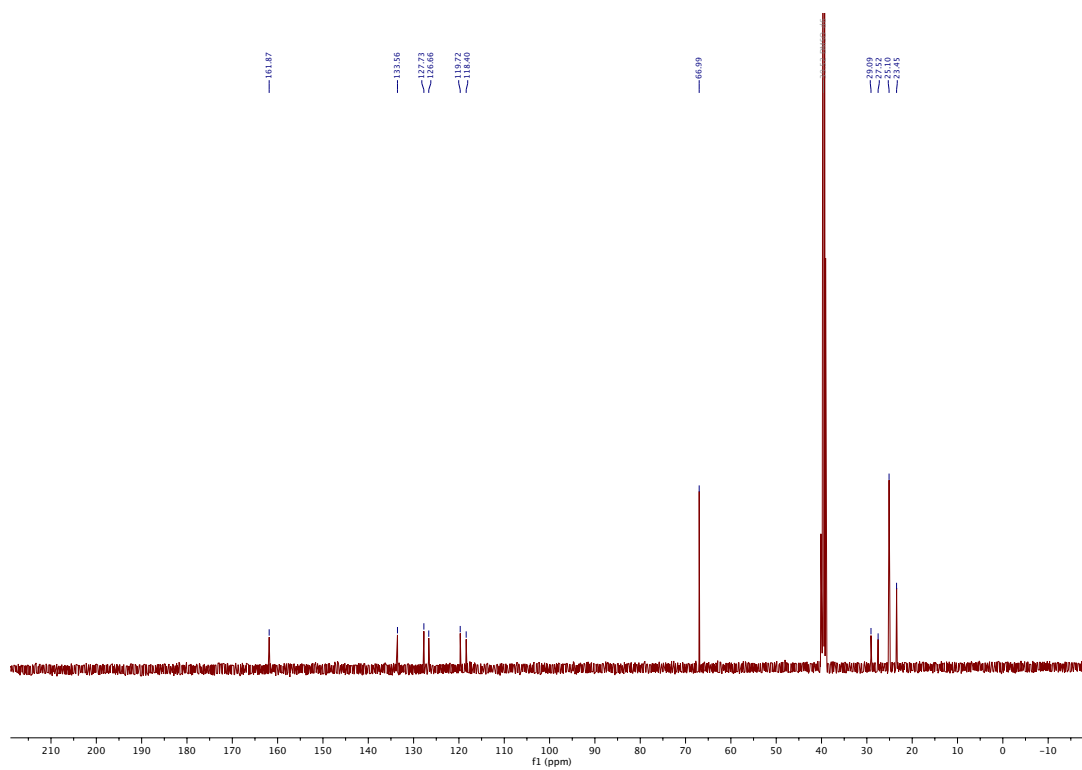


Figure S2. ¹³C NMR of (S-H₈-Binol)₃LaNa₃ in DMSO-*d*₆.

NMR Spectra of (R-H₈-Binol)₃LaNa₃

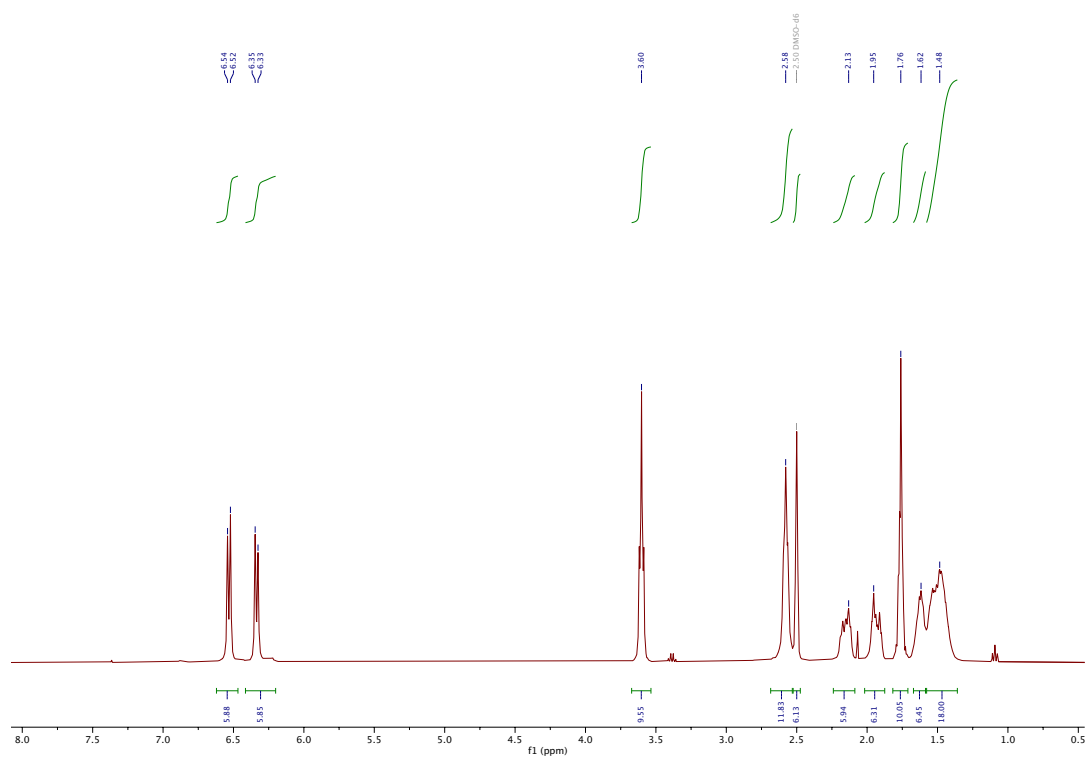


Figure S3. ¹H NMR of (R-H₈-Binol)₃LaNa₃ in DMSO-*d*₆.

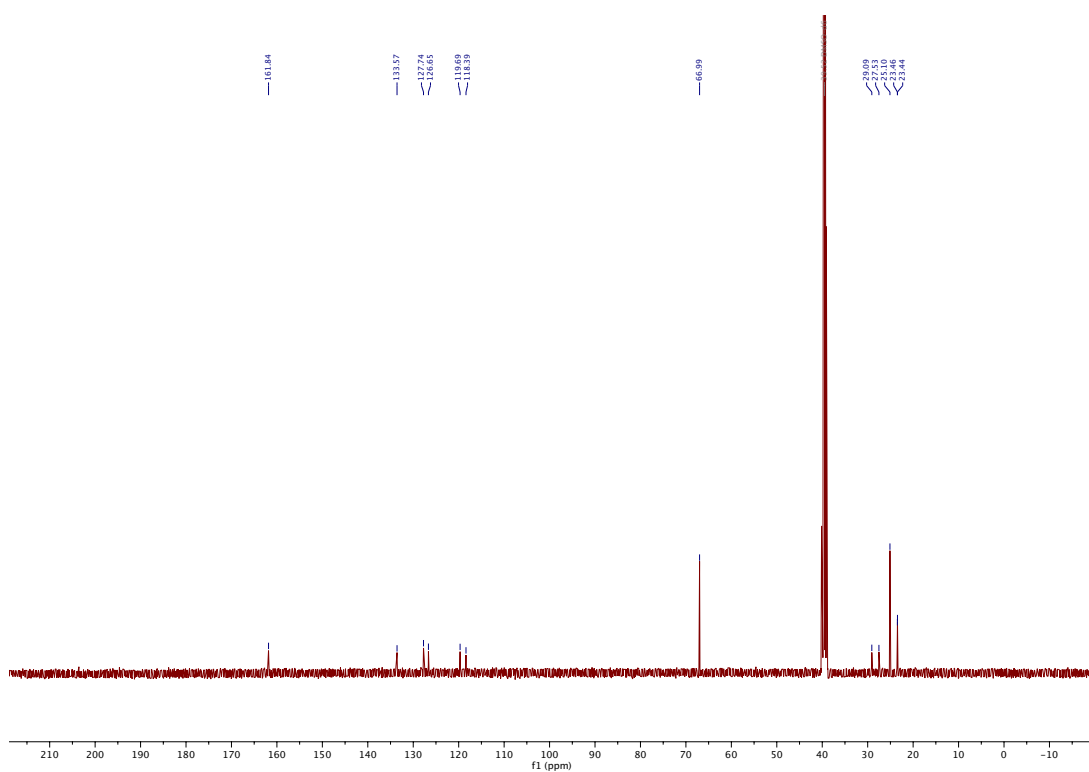


Figure S4. ¹³C NMR of (R-H₈-Binol)₃LaNa₃ in DMSO-*d*₆.

NMR Spectra of (S-H₈-Binol)₃SmNa₃

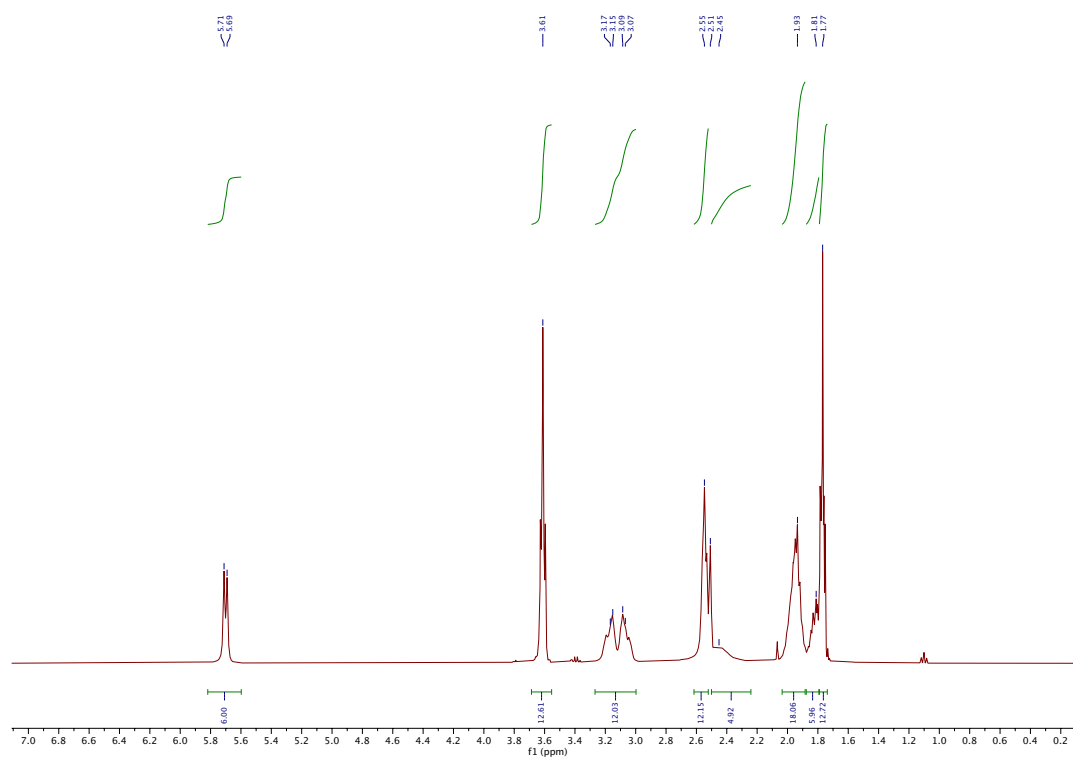


Figure S5. ¹H NMR of (S-H₈-Binol)₃SmNa₃ in DMSO-*d*₆.

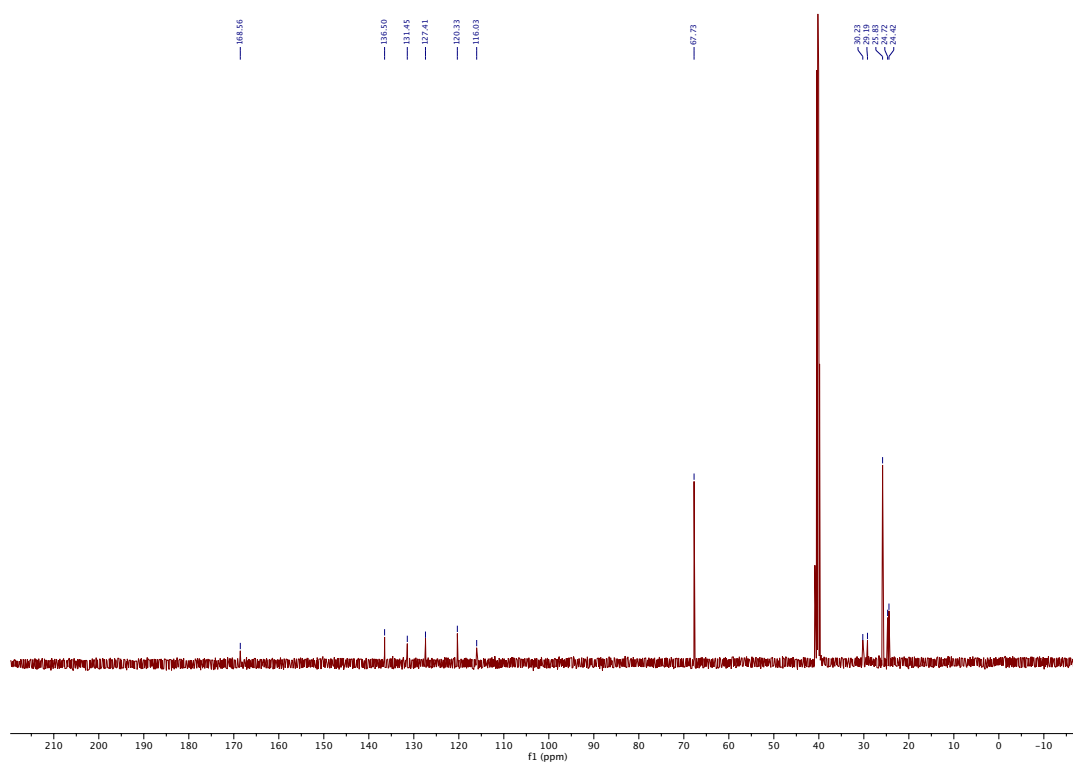


Figure S6. ¹³C NMR of (S-H₈-Binol)₃SmNa₃ in DMSO-*d*₆.

NMR Spectra of (R-H₈-Binol)₃SmNa₃

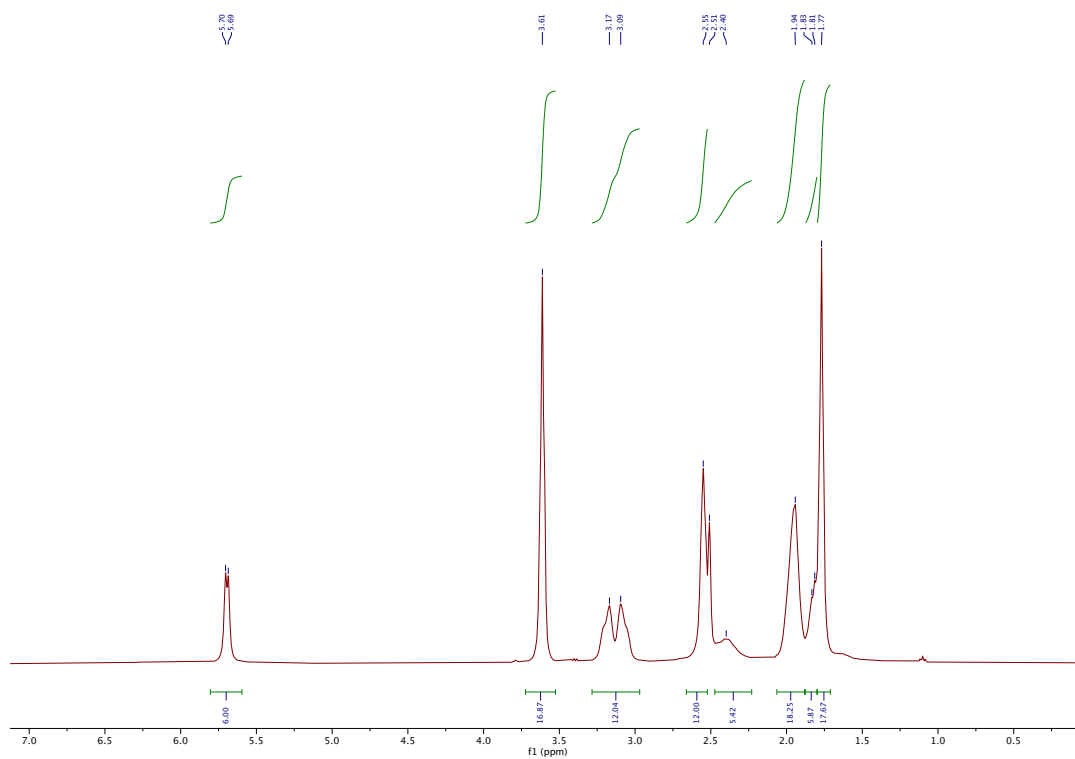


Figure S7. ¹H NMR of (R-H₈-Binol)₃SmNa₃ in DMSO-*d*₆.

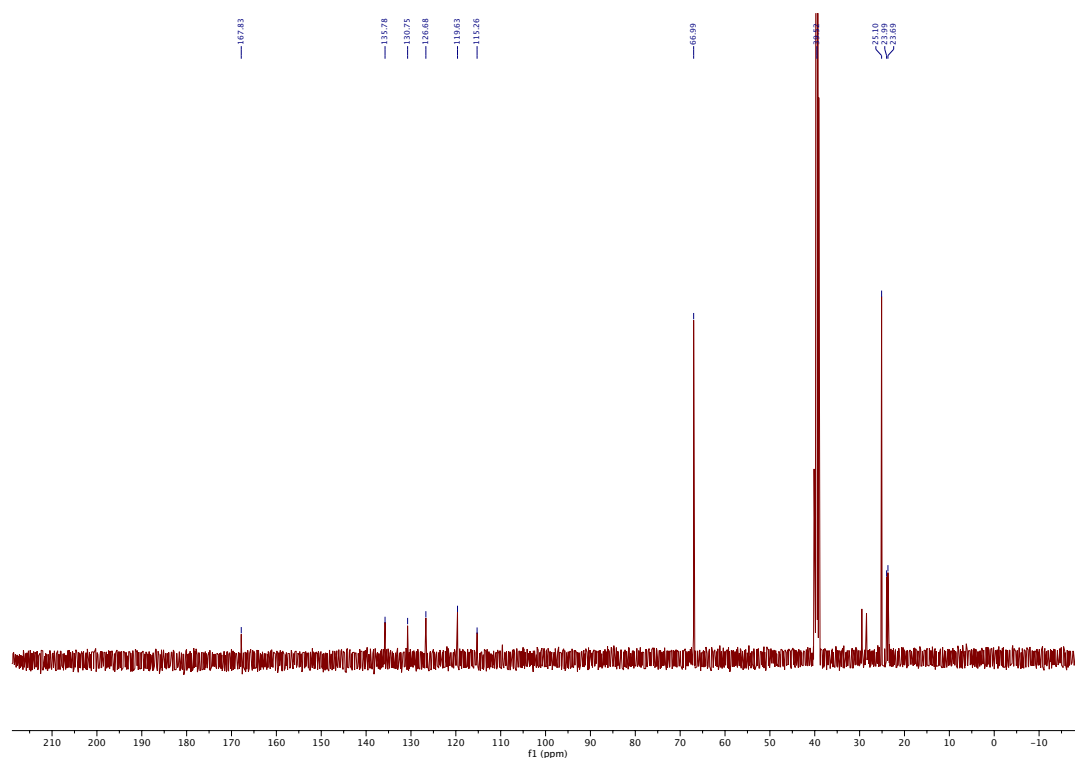


Figure S8. ¹³C NMR of (R-H₈-Binol)₃SmNa₃ in DMSO-*d*₆.

NMR Spectrum (S-H₈-Binol)₃TbNa₃

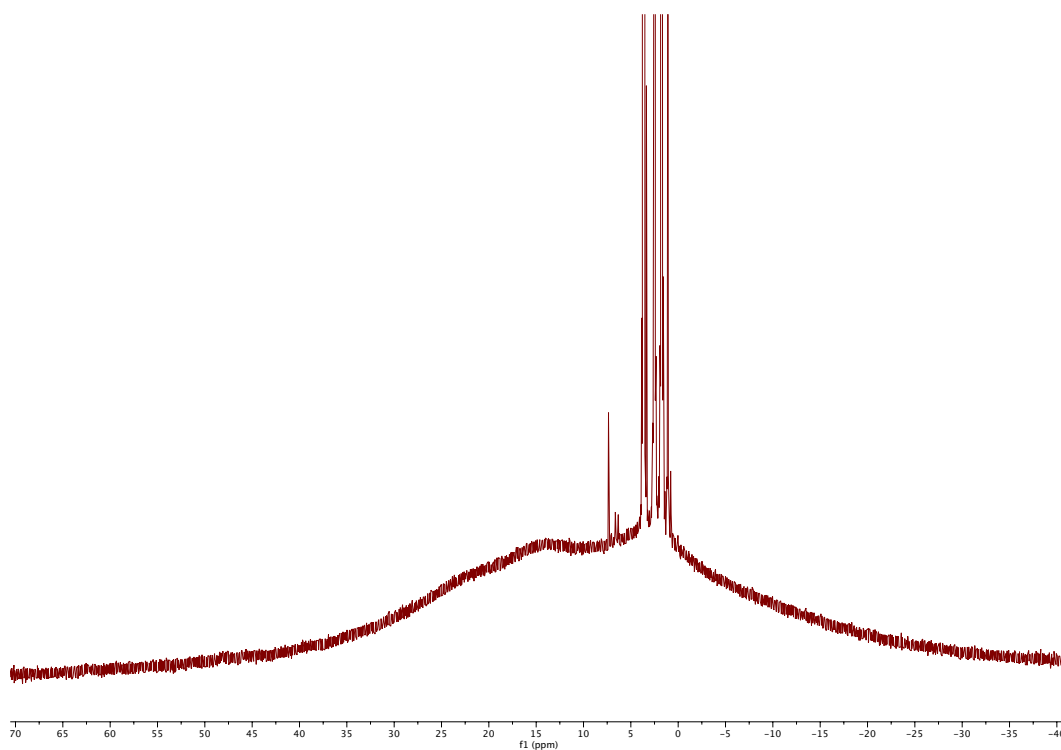


Figure S9. ¹H NMR of (S-H₈-Binol)₃TbNa₃ in DMSO-*d*₆.

NMR Spectrum of (R-H₈-Binol)₃TbNa₃

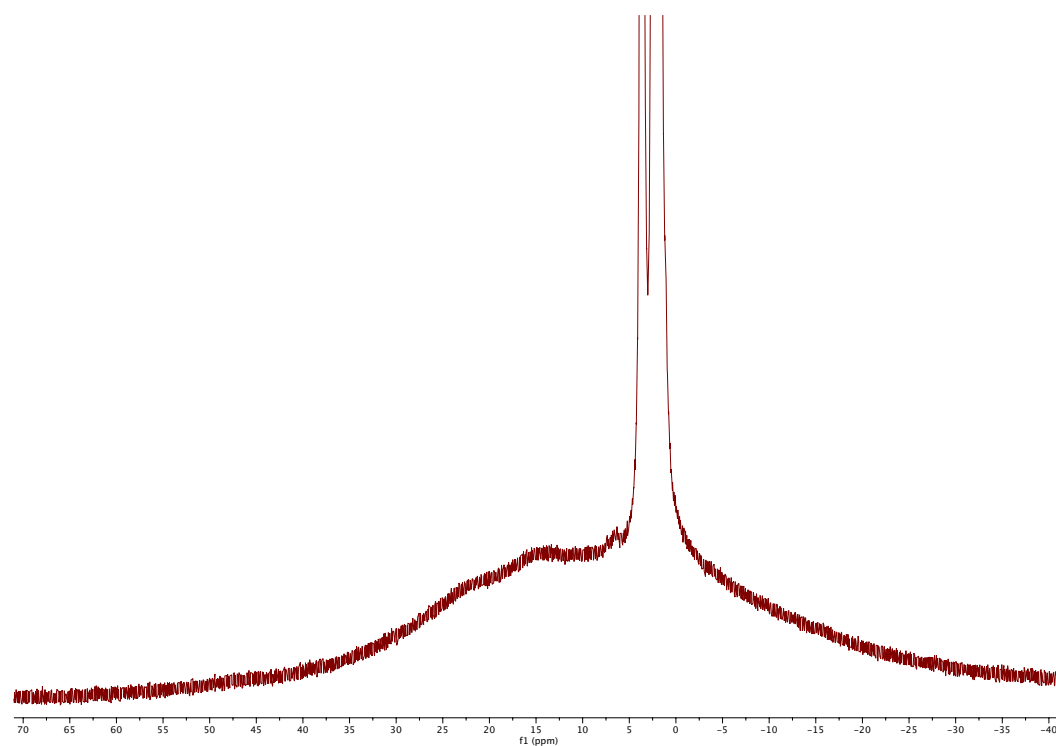


Figure S10. ¹H NMR of (R-H₈-Binol)₃TbNa₃ in DMSO-*d*₆.

NMR Spectrum of (S-H₈-Binol)₃DyNa₃

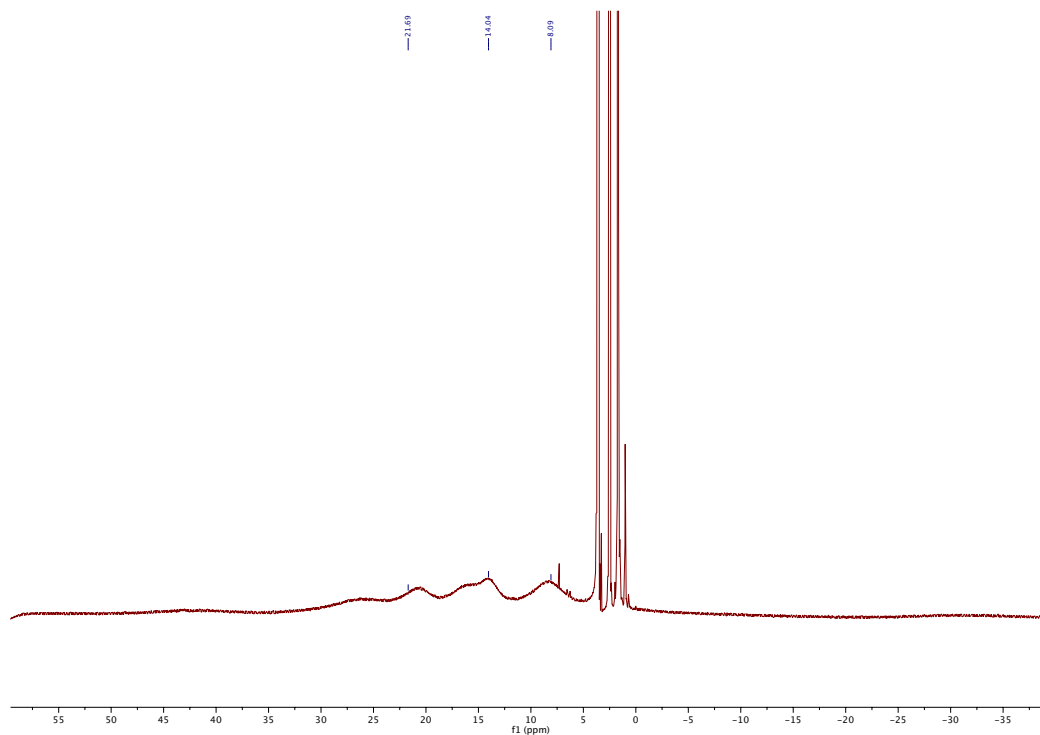


Figure S11. ¹H NMR of (S-H₈-Binol)₃DyNa₃ in DMSO-*d*₆.

NMR Spectrum of (R-H₈-Binol)₃DyNa₃

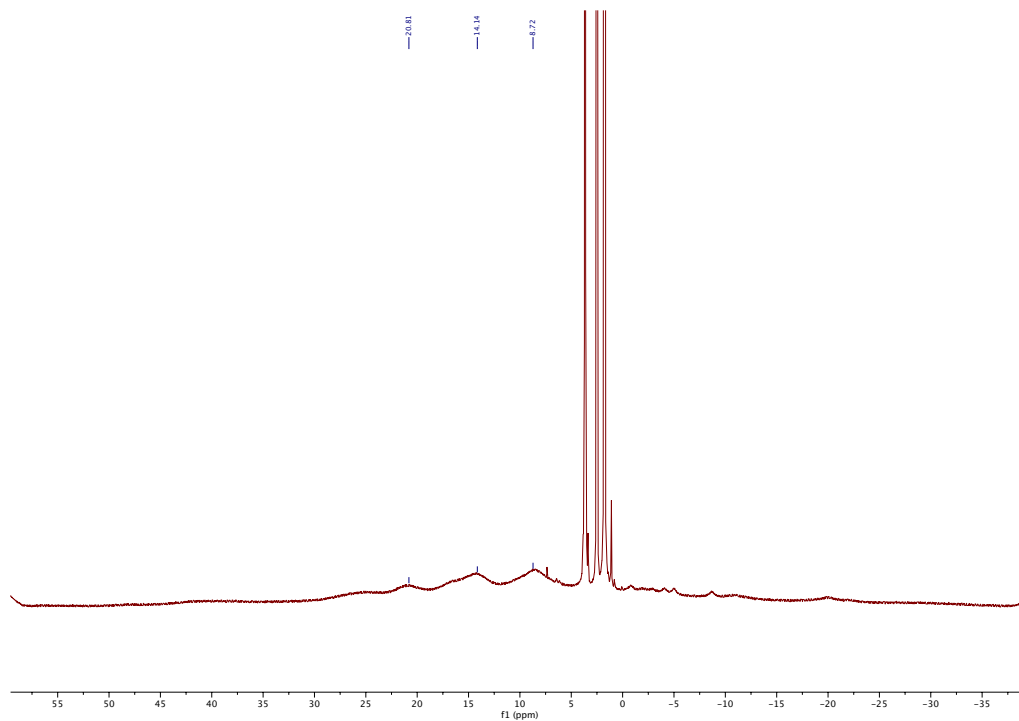


Figure S12. ¹H NMR of (R-H₈-Binol)₃DyNa₃ in DMSO-*d*₆.

Absorption, Excitation and Emission Spectra of Sm Complexes

(S-H₈-Binol)₃SmNa₃

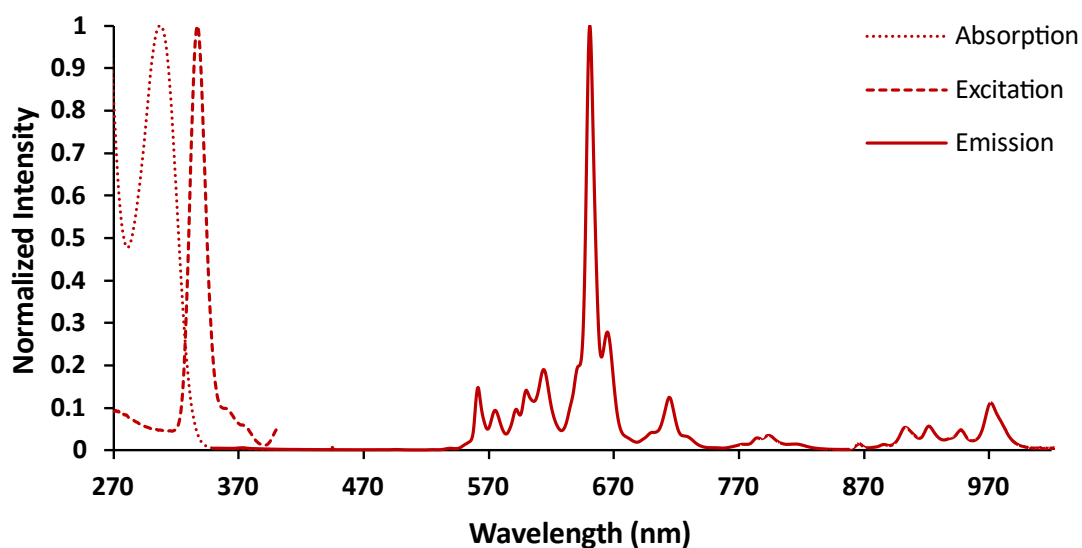


Figure S13. Normalized Absorption (dotted line), Excitation (dashed line) and Emission (solid line) spectra for (S-H₈-Binol)₃SmNa₃ complex in THF. Absorption was measured at 1.3×10^{-5} M, while Excitation and Emission were measured at 1.3×10^{-5} M. Slit widths for absorption 5 nm, for excitation 10 nm EX and EM, and for emission 5 nm EX and EM.

(R-H₈-Binol)₃SmNa₃

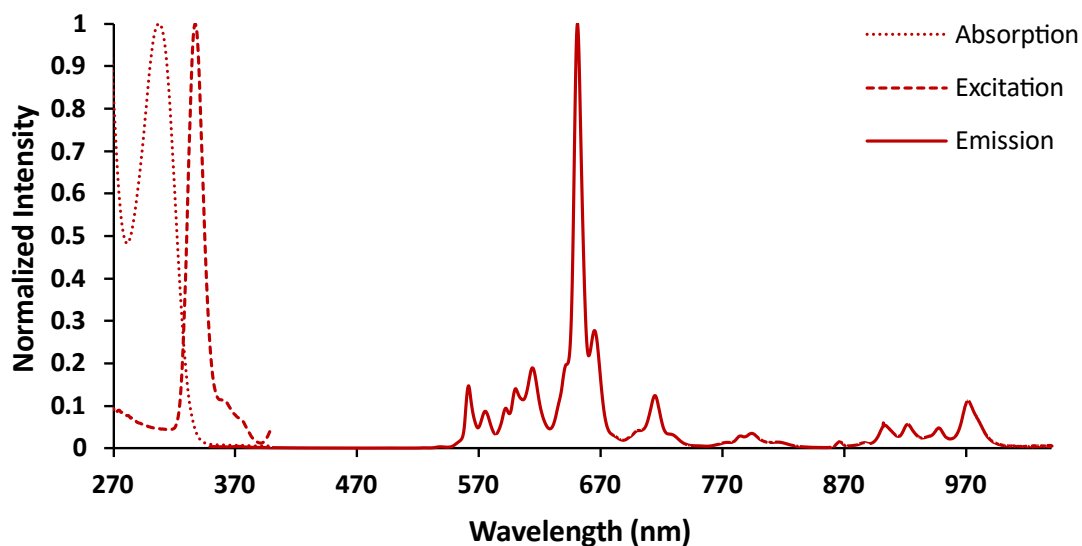


Figure S14. Normalized Absorption (dotted line), Excitation (dashed line) and Emission (solid line) spectra for (R-H₈-Binol)₃SmNa₃ complex in THF. Absorption was measured at 1.3×10^{-5} M, while Excitation and Emission were measured at 1.3×10^{-5} M. Slit widths for absorption 5 nm, for excitation 10 nm EX and EM, and for emission 5 nm EX and EM.

Absorption, Excitation and Emission Spectra of Tb Complexes

(S-H₈-Binol)₃TbNa₃

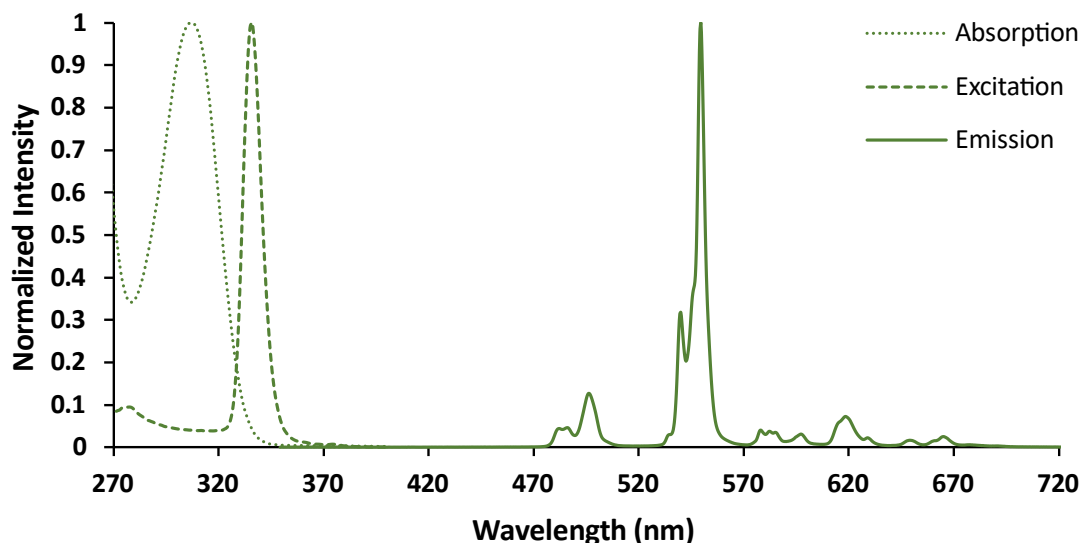


Figure S15. Normalized Absorption (dotted line), Excitation (dashed line) and Emission (solid line) spectra for (S-H₈-Binol)₃TbNa₃ complex in THF. Absorption was measured at 1.3×10^{-5} M, while Excitation and Emission were measured at 1.3×10^{-5} M. Slit widths for absorption 5 nm, for excitation 3 nm EX and EM, and for emission 2 nm EX and EM.

(R-H₈-Binol)₃TbNa₃

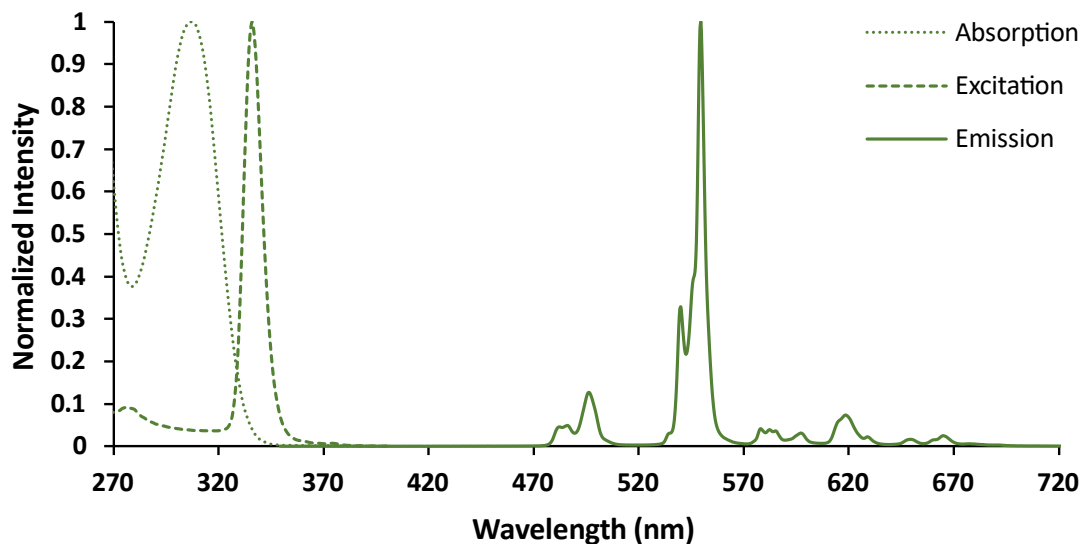


Figure S16. Normalized Absorption (dotted line), Excitation (dashed line) and Emission (solid line) spectra for (R-H₈-Binol)₃TbNa₃ complex in THF. Absorption was measured at 1.3×10^{-5} M, while Excitation and Emission were measured at 1.3×10^{-5} M. Slit widths for absorption 5 nm, for excitation 3 nm EX and EM, and for emission 2 nm EX and EM.

Absorption, Excitation and Emission Spectra of Dy Complexes

(S-H₈-Binol)₃DyNa₃

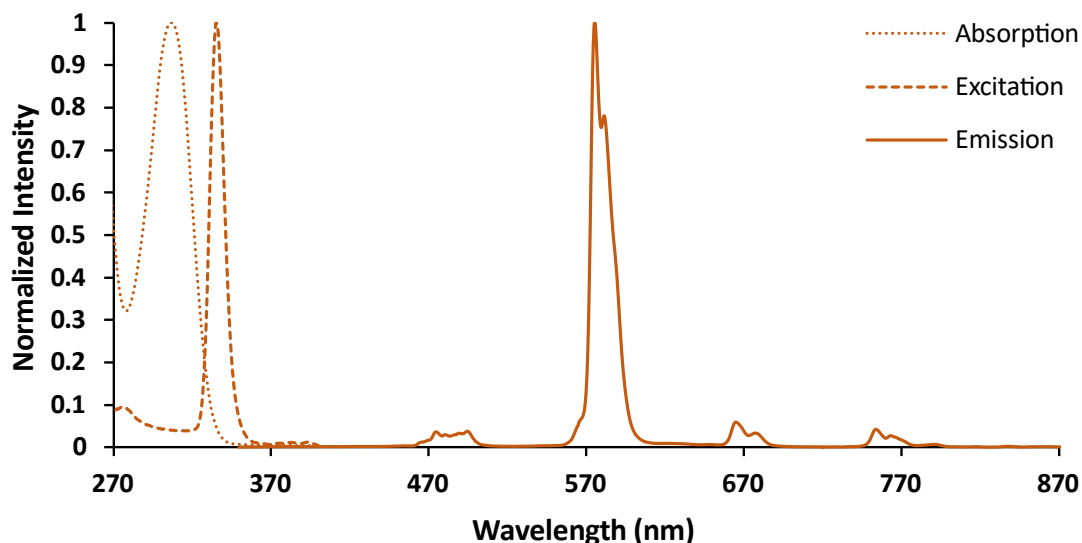


Figure S17. Normalized Absorption (dotted line), Excitation (dashed line) and Emission (solid line) spectra for (S-H₈-Binol)₃DyNa₃ complex in THF. Absorption was measured at 1.3×10^{-5} M, while Excitation and Emission were measured at 1.3×10^{-5} M. Slit widths for absorption 5 nm, for excitation 5 nm EX and EM, and for emission 3 nm EX and EM.

(R-H₈-Binol)₃DyNa₃

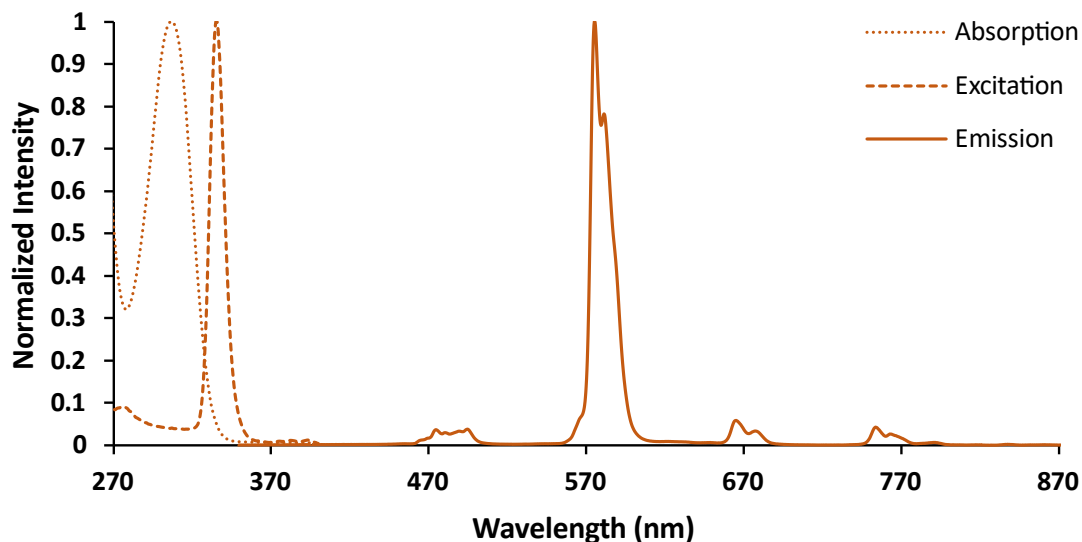


Figure S18. Normalized Absorption (dotted line), Excitation (dashed line) and Emission (solid line) spectra for (S-H₈-Binol)₃DyNa₃ complex in THF. Absorption was measured at 1.3×10^{-5} M, while Excitation and Emission were measured at 1.3×10^{-5} M. Slit widths for absorption 5 nm, for excitation 5 nm EX and EM, and for emission 3 nm EX and EM.

Note: The absorption maximum (dotted lines in Figure S13–S18) is at 310 nm, while the excitation spectra (dashed lines in Figure S13–S18) display bathochromically shifted maximum at 335 nm. These shifts and peaks similarity are reminiscent of ligand-centered sensitization of emissive lanthanide complexes reported by de Bettencourt-Dias.² Excitation at 335 nm gave us the best emission for (H₈-Binol)₃LnNa₃ complexes. However, we chose to use 340 nm LED for CPL measurements because of the limitation of light sources.

Emission Spectrum of Eu Complex

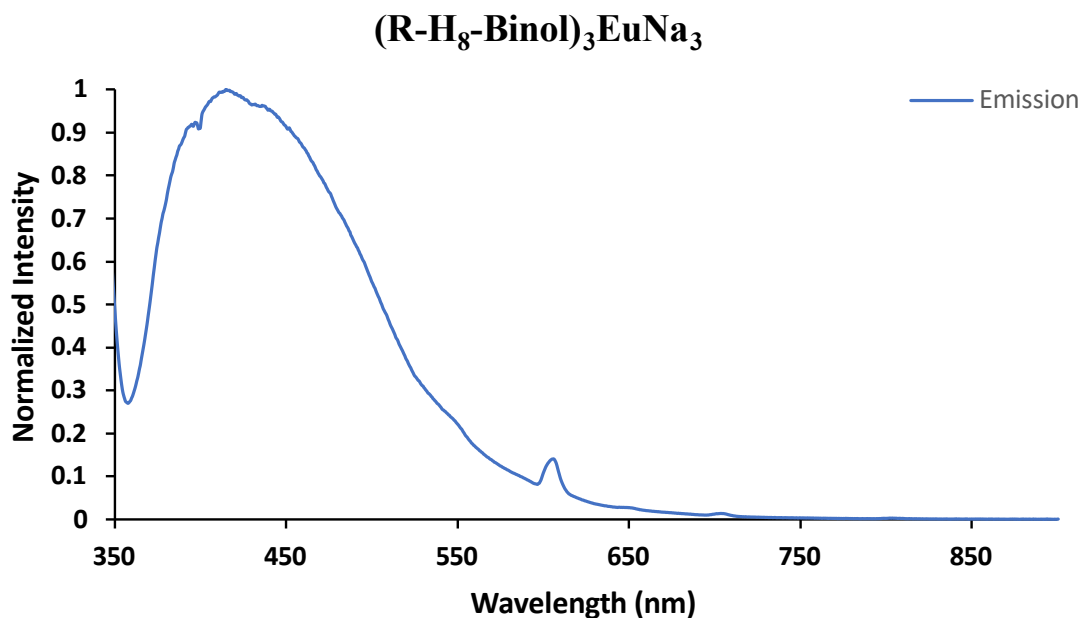


Figure S19. Normalized Emission (solid line) spectrum for (R-H₈-Binol)₃EuNa₃ complex in THF at 1.3 x 10⁻⁵ M. The enantiomer (S-H₈-Binol)₃EuNa₃ emission spectrum is identical. Slit widths: 5 nm EX and EM.

CPL g_{lum} for (S/R-H₈Binol)₃SmNa₃

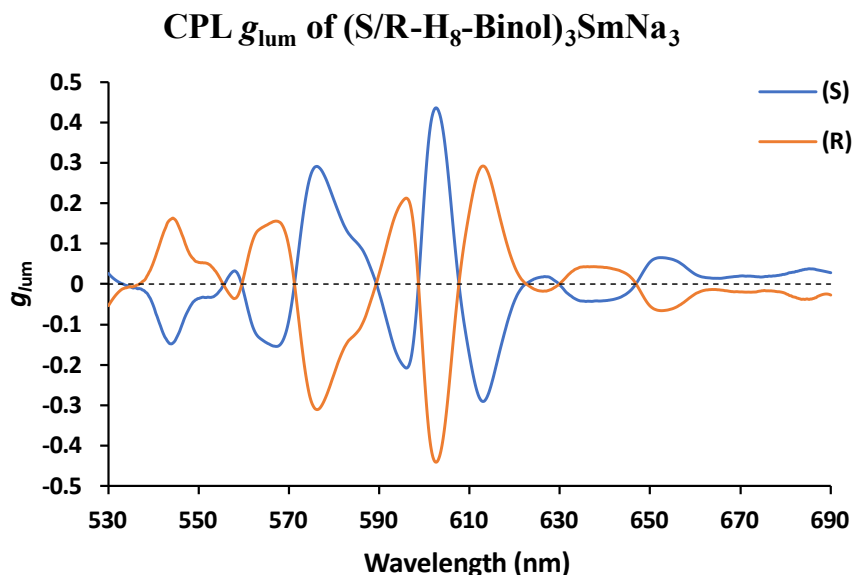


Figure S20. g_{lum} as a function of wavelength for (S/R-H₈-Binol)₃SmNa₃ complexes in THF at 1.3×10^{-3} M. Bandpass: 5 nm. Excitation at 340 nm. Spectra are taken as an average of 100 scans with 0.25 nm increments and 1 second integration time from 530–690 nm.

CPL g_{lum} for (S/R-H₈Binol)₃TbNa₃

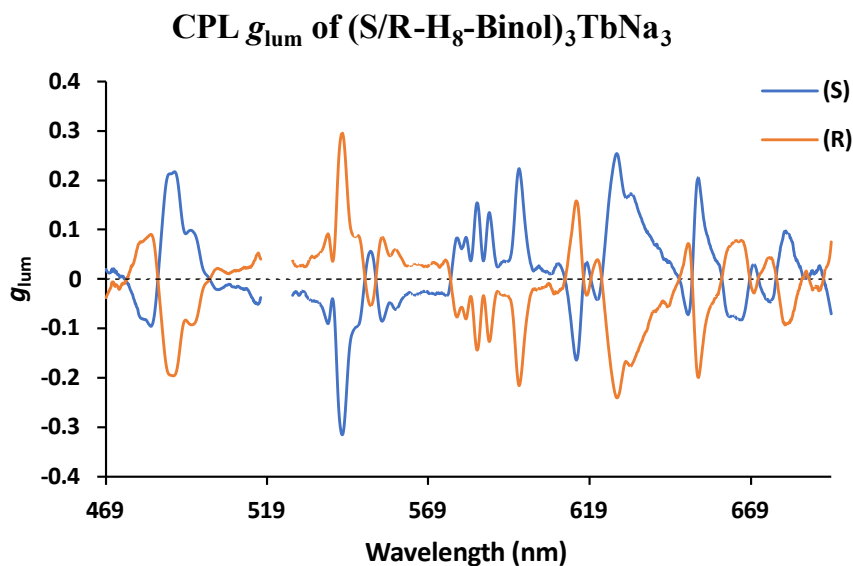


Figure S21. g_{lum} as a function of wavelength for (S/R-H₈-Binol)₃TbNa₃ complexes in THF at 1.3×10^{-3} M. Bandpass: 1.5 nm. Excitation at 340 nm. Spectra are taken as an average of 19 scans with 0.25 nm increments and 1 second integration time from 469–517 nm and 527–694 nm.

CPL g_{lum} for (S/R-H₈-Binol)₃DyNa₃

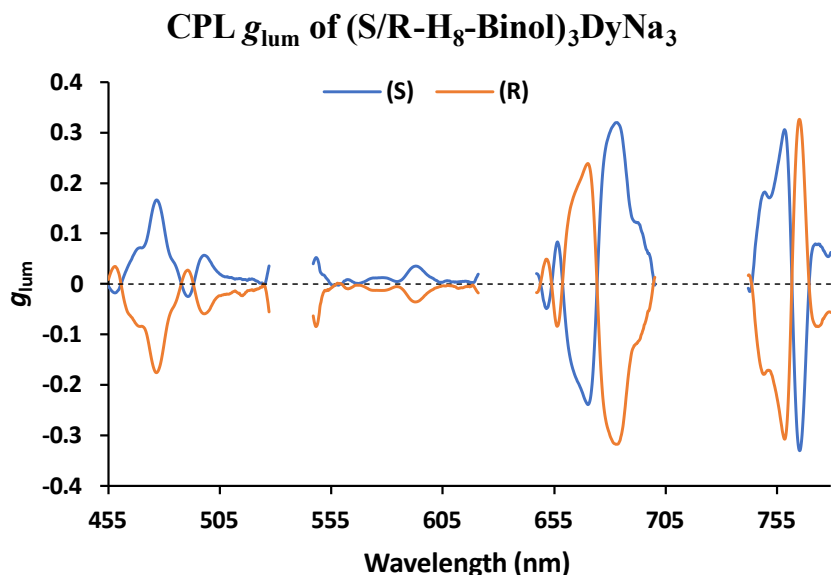


Figure S22. g_{lum} as a function of wavelength for (S/R-H₈-Binol)₃DyNa₃ complexes in THF at 1.3×10^{-3} M. Bandpass: 5 nm. Excitation at 340 nm. Spectra are taken as an average of 33 scans with 0.25 nm increments and 1 second integration time from 455–527 nm, 547–621 nm, 647–700 nm, and 742–779 nm.

Lifetime Plot of (R-H₈-Binol)₃SmNa₃ Complex

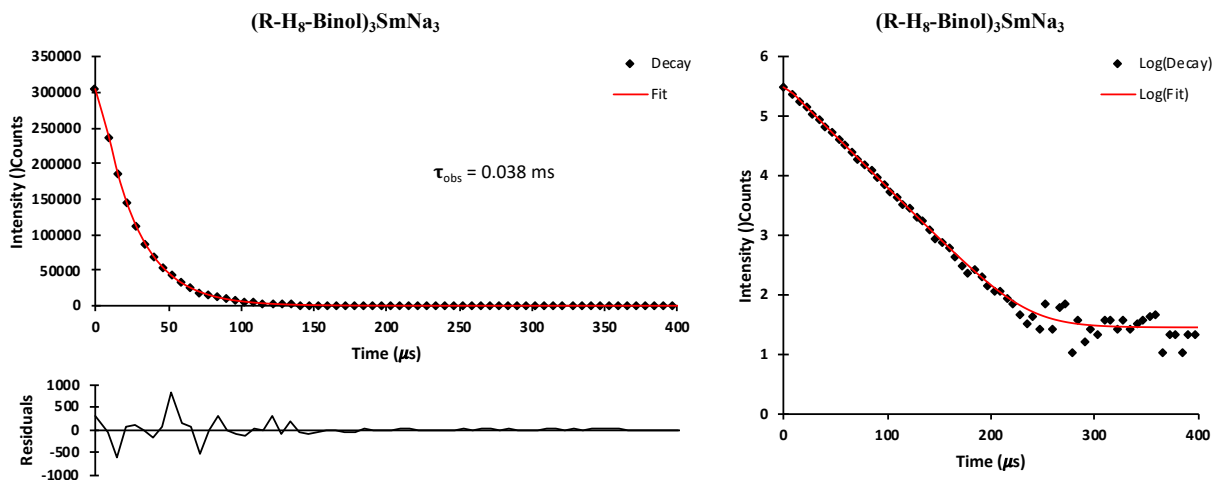


Figure S23. Lifetime exponential (left) and log (right) plots of (R-H₈-Binol)₃SmNa₃ complex for 650 nm. Excited with 340 nm LED, with a gate width of 300 (625 μs window), 200 μs delay, 200 μs LED pulse width, and 1000 events (points) taken over a 1000 μs total cycle time. Plot is an average of 30 individual runs for better resolution. The lifetime for the enantiomer is identical as expected.

Lifetime Plot of (R-H₈-Binol)₃TbNa₃ Complex

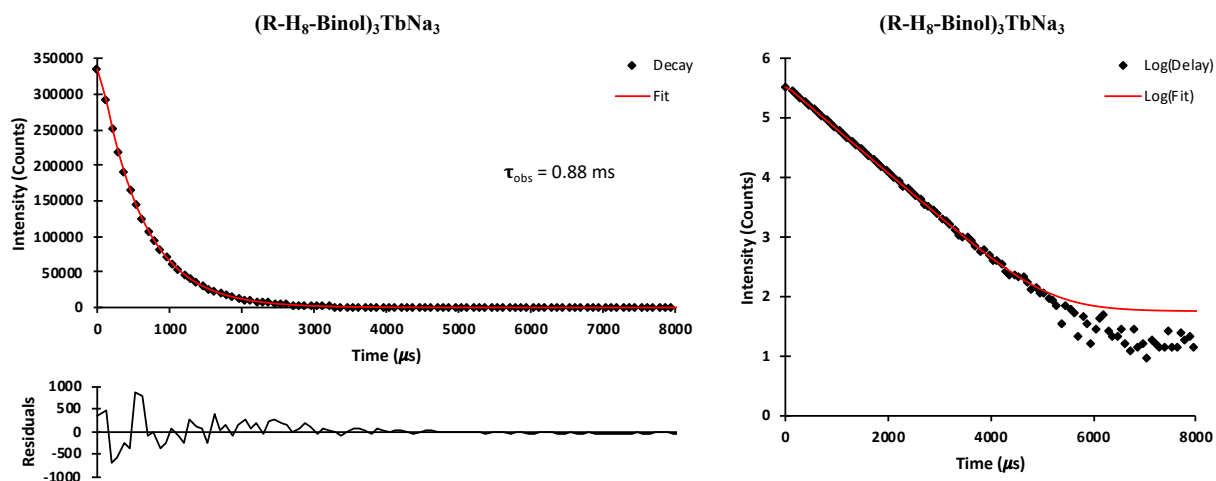


Figure S24. Lifetime exponential (left) and log (right) plots of (R-H₈-Binol)₃TbNa₃ complex for 550 nm. Excited with 340 nm LED, with a gate width of 4000 (8333 μs window), 200 μs delay, 200 μs LED pulse width, and 500 events (points) taken over a 9000 μs total cycle time. Plot is an average of 10 individual runs for better resolution. The lifetime for the enantiomer is identical as expected.

Lifetime Plot of (R-H₈-Binol)₃DyNa₃ Complex

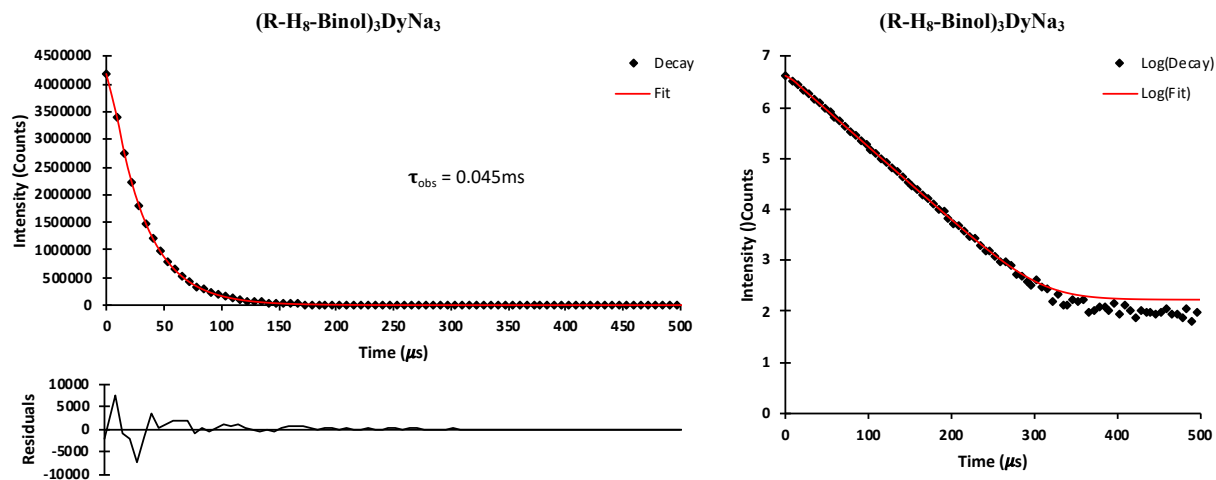


Figure S25. Lifetime exponential (left) and log (right) plots of (R-H₈-Binol)₃DyNa₃ complex for 575 nm. Excited with 340 nm LED, with a gate width of 300 (625 μs window), 500 μs delay, 500 μs LED pulse width, and 1000 events (points) taken over a 1700 μs total cycle time. Plot is an average of 30 individual runs for better resolution. The lifetime for the enantiomer is identical as expected.

XRD Table and XRD Polyhedron Picture for (R-H₈-Binol)₃LaNa₃

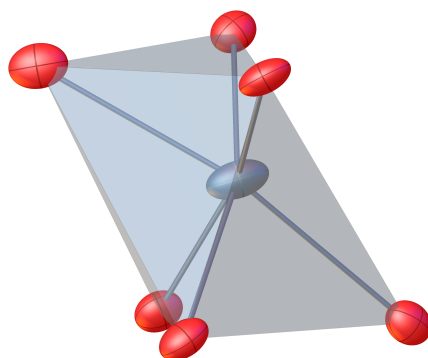


Figure S26. XRD Polyhedron Picture for (R-H₈-Binol)₃LaNa₃. Red: oxygen; Blue: lanthanum.

Table S1. Crystal data and structure refinement for (R-H₈-Binol)₃LaNa₃.

| | |
|---|---|
| Identification code | (R-H ₈ -Binol) ₃ LaNa ₃ |
| Empirical formula | C _{88.19} H _{116.39} LaNa ₃ O _{13.05} |
| Formula weight | 1593.14 |
| Temperature/K | 109(13) |
| Crystal system | orthorhombic |
| Space group | P2 ₁ 2 ₁ 2 |
| a/Å | 28.4265(7) |
| b/Å | 27.2114(9) |
| c/Å | 10.4341(3) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å ³ | 8071.0(4) |
| Z | 4 |
| ρ _{calc} /cm ³ | 1.311 |
| μ/mm ⁻¹ | 0.608 |
| F(000) | 3360.0 |
| Crystal size/mm ³ | 0.334 × 0.296 × 0.227 |
| Radiation | MoKα (λ = 0.71073) |
| 2θ range for data collection/° | 4.714 to 58.862 |
| Index ranges | -38 ≤ h ≤ 35, -32 ≤ k ≤ 36, -14 ≤ l ≤ 14 |
| Reflections collected | 75037 |
| Independent reflections | 19396 [R _{int} = 0.0724, R _{sigma} = 0.0842] |
| Data/restraints/parameters | 19396/109/1004 |
| Goodness-of-fit on F ² | 1.099 |
| Final R indexes [I ≥ 2σ (I)] | R ₁ = 0.0633, wR ₂ = 0.1235 |
| Final R indexes [all data] | R ₁ = 0.0805, wR ₂ = 0.1310 |
| Largest diff. peak/hole / e Å ⁻³ | 1.22/-0.56 |
| Flack parameter | 0.011(5) |

CPL Brightness

Table S2. Photophysical Parameters and B_{CPL} of $(R\text{-}H_8\text{-Binol})_3LnNa_3$ ($Ln = Sm, Tb, Dy$)

| $(H_8\text{-Binol})_3LnNa_3$ | $\epsilon/M^{-1}cm^{-1}$ (λ_{abs}/nm) | Φ | Transition | $ g_{lum} $ (λ/nm) | β | $B_{CPL}/M^{-1}cm^{-1}$ |
|------------------------------|--|--------|------------------------------------|------------------------------|---------|-------------------------|
| Ln = Sm | 27000 (310) | 0.04 | $^4G_{5/2} \rightarrow ^6H_{5/2}$ | 0.31 (576) | 0.08 | 13.4 |
| | | | $^4G_{5/2} \rightarrow ^6H_{7/2}$ | 0.44 (603) | 0.16 | 38.0 |
| | | | $^4G_{5/2} \rightarrow ^6H_{9/2}$ | 0.07 (653) | 0.48 | 18.1 |
| Ln = Tb | 27000 (310) | 0.27 | $^5D_4 \rightarrow ^7F_6$ | 0.21 (490) | 0.13 | 99.5 |
| | | | $^5D_4 \rightarrow ^7F_5$ | 0.32 (542) | 0.67 | 782 |
| | | | $^5D_4 \rightarrow ^7F_4$ | 0.22 (597) | 0.07 | 56.1 |
| | | | $^5D_4 \rightarrow ^7F_3$ | 0.25 (628) | 0.08 | 72.9 |
| Ln = Dy | 27000 (310) | 0.17 | $^4F_{9/2} \rightarrow ^6H_{15/2}$ | 0.18 (477) | 0.06 | 24.8 |
| | | | $^4F_{9/2} \rightarrow ^6H_{13/2}$ | 0.03 (594) | 0.82 | 56.5 |
| | | | $^4F_{9/2} \rightarrow ^6H_{11/2}$ | 0.32 (668) | 0.05 | 36.7 |
| | | | $^4F_{9/2} \rightarrow ^6H_{9/2}$ | 0.33 (756) | 0.04 | 30.3 |

B_{CPL} values are calculated according to the equation: $B_{CPL} = \frac{1}{2} \beta \times \epsilon_{\lambda} \times \Phi \times g_{lum}$ (unit: $M^{-1}cm^{-1}$).³

Table S3. Photophysical Parameters and B_{CPL} of $(bmpbp)Ln(OTf)_3$ ($Ln = Sm, Eu, Tb, Dy$)⁴

| $(bmpbp)Ln(OTf)_3$ | $\epsilon/M^{-1}cm^{-1}$ (λ_{abs}/nm) | Φ | Transition | $ g_{lum} $ (λ/nm) | β | $B_{CPL}/M^{-1}cm^{-1}$ |
|--------------------|--|--------|------------------------------------|------------------------------|---------|-------------------------|
| Ln = Sm | 24000 (305) | 0.0047 | $^4G_{5/2} \rightarrow ^6H_{5/2}$ | 0.25 (577) | 0.08 | 1.13 |
| | | | $^4G_{5/2} \rightarrow ^6H_{7/2}$ | 0.16 (598) | 0.44 | 3.97 |
| | | | $^4G_{5/2} \rightarrow ^6H_{9/2}$ | 0.03 (646) | 0.26 | 0.440 |
| Ln = Eu | 24000 (305) | 0.16 | $^5D_0 \rightarrow ^7F_1$ | 0.06 (592) | 0.14 | 16.1 |
| | | | $^5D_0 \rightarrow ^7F_2$ | 0.05 (620) | 0.31 | 29.8 |
| | | | $^5D_0 \rightarrow ^7F_3$ | 0.22 (653) | 0.04 | 16.9 |
| | | | $^5D_0 \rightarrow ^7F_4$ | 0.03 (703) | 0.38 | 21.9 |
| Ln = Tb | 24000 (305) | 0.32 | $^5D_4 \rightarrow ^7F_6$ | 0.05 (492) | 0.22 | 42.2 |
| | | | $^5D_4 \rightarrow ^7F_5$ | 0.19 (543) | 0.42 | 306 |
| | | | $^5D_4 \rightarrow ^7F_4$ | 0.05 (587) | 0.20 | 38.4 |
| | | | $^5D_4 \rightarrow ^7F_3$ | 0.21 (625) | 0.09 | 72.6 |
| Ln = Dy | 24000 (305) | 0.0033 | $^4F_{9/2} \rightarrow ^6H_{15/2}$ | 0.03 (485) | 0.40 | 0.475 |
| | | | $^4F_{9/2} \rightarrow ^6H_{13/2}$ | 0.03 (571) | 0.42 | 0.499 |
| | | | $^4F_{9/2} \rightarrow ^6H_{11/2}$ | 0.26 (673) | 0.03 | 0.309 |

B_{CPL} values are calculated according to the equation: $B_{CPL} = \frac{1}{2} \beta \times \epsilon_{\lambda} \times \Phi \times g_{lum}$ (unit: $M^{-1}cm^{-1}$).³

Table S4. Photophysical Parameters and B_{CPL} of $(tpdac)Ln(OTf)_3$ ($Ln = Sm, Eu, Tb, Dy$)⁵

| $(tpdac)Ln(OTf)_3$ | $\epsilon/M^{-1}cm^{-1}$ (λ_{abs}/nm) | Φ | Transition | $ g_{lum} $ (λ/nm) | β | $B_{CPL}/M^{-1}cm^{-1}$ |
|--------------------|--|--------|-----------------------------------|------------------------------|---------|-------------------------|
| Ln = Sm | 3300 (260) | 0.0017 | $^4G_{5/2} \rightarrow ^6H_{5/2}$ | 0.13 (563) | 0.12 | 0.0438 |
| | | | $^4G_{5/2} \rightarrow ^6H_{7/2}$ | 0.06 (597) | 0.54 | 0.0909 |
| | | | $^4G_{5/2} \rightarrow ^6H_{9/2}$ | 0.05 (643) | 0.34 | 0.0477 |
| Ln = Eu | 3600 (260) | 0.018 | $^5D_0 \rightarrow ^7F_1$ | 0.06 (591) | 0.17 | 0.330 |
| | | | $^5D_0 \rightarrow ^7F_2$ | 0.06 (615) | 0.31 | 0.603 |

| | | | | | | |
|---------|---------------|--------|------------------------------------|------------|------|--------|
| | | | $^5D_0 \rightarrow ^7F_3$ | 0.09 (648) | 0.05 | 0.146 |
| | | | $^5D_0 \rightarrow ^7F_4$ | 0.07 (690) | 0.46 | 1.04 |
| Ln = Tb | 5600 (260) | 0.28 | $^5D_4 \rightarrow ^7F_6$ | 0.02 (489) | 0.22 | 3.45 |
| | | | $^5D_4 \rightarrow ^7F_5$ | 0.17 (542) | 0.44 | 58.6 |
| | | | $^5D_4 \rightarrow ^7F_4$ | 0.07 (582) | 0.21 | 11.5 |
| | | | $^5D_4 \rightarrow ^7F_3$ | 0.10 (622) | 0.10 | 7.84 |
| Ln = Dy | 5600 (260) | 0.0043 | $^4F_{9/2} \rightarrow ^6H_{15/2}$ | 0.05 (479) | 0.44 | 0.265 |
| | | | $^4F_{9/2} \rightarrow ^6H_{13/2}$ | 0.02 (575) | 0.51 | 0.123 |
| | | | $^4F_{9/2} \rightarrow ^6H_{11/2}$ | 0.15 (665) | 0.05 | 0.0903 |

B_{CPL} values are calculated according to the equation: $B_{CPL} = \frac{1}{2} \beta \times \varepsilon_{\lambda} \times \Phi \times g_{lum}$ (unit: $M^{-1}cm^{-1}$).³

Table S5. Photophysical Parameters and B_{CPL} of $[LnBnMeH22IAM]^+$ (Ln = Sm, Dy)⁶

| $[LnBnMeH22IAM]^+$ | $\varepsilon/M^{-1}cm^{-1}$ (λ_{abs}/nm) | Φ | Transition | $ g_{lum} $ (λ/nm) | β | $B_{CPL}/M^{-1}cm^{-1}$ |
|--------------------|---|--------|------------------------------------|------------------------------|---------|-------------------------|
| Ln = Sm | 25000 (346) | 0.008 | $^4G_{5/2} \rightarrow ^6H_{5/2}$ | 0.027 (565) | 0.10 | 0.270 |
| | | | $^4G_{5/2} \rightarrow ^6H_{7/2}$ | 0.028 (597) | 0.40 | 1.12 |
| Ln = Dy | 25000 (346) | 0.013 | $^4F_{9/2} \rightarrow ^6H_{11/2}$ | 0.013 (669) | 0.09 | 0.190 |

B_{CPL} values are calculated according to the equation: $B_{CPL} = \frac{1}{2} \beta \times \varepsilon_{\lambda} \times \Phi \times g_{lum}$ (unit: $M^{-1}cm^{-1}$).³

Note: The other papers cited in the manuscript lack information for doing circularly polarized luminescence brightness calculations, therefore, we only included several examples we could get.

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