

## Supplementary Information

### Ancillary ligand modulated stereoselective self-assembly of triple-stranded Eu(III) helicate featuring circularly polarized luminescence

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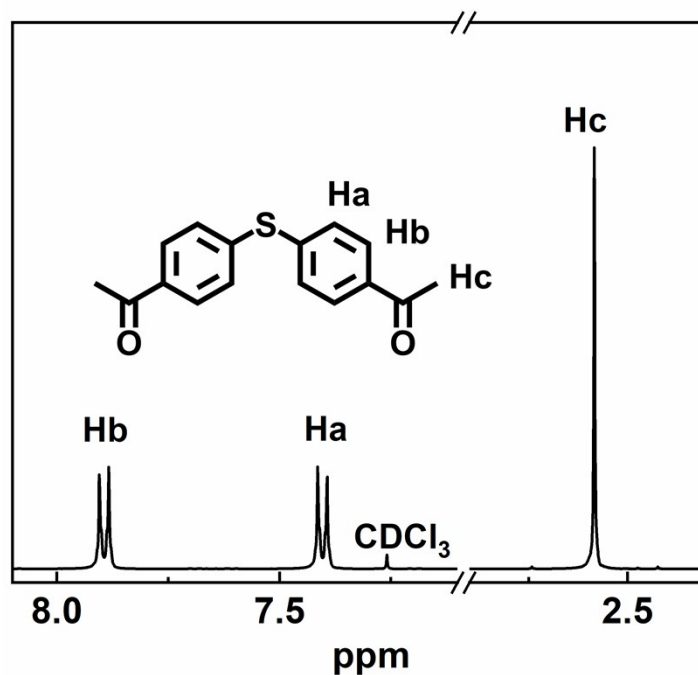


Figure S1. <sup>1</sup>H NMR spectrum of 4,4'-diacetyldiphenyl sulphide in CDCl<sub>3</sub>.

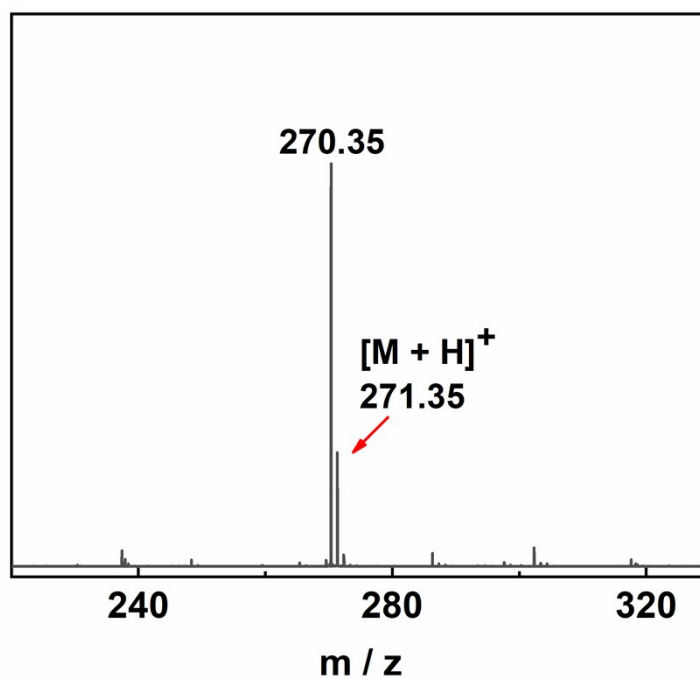


Figure S2. EI-MS of 4,4'-diacetyldiphenyl sulphide.

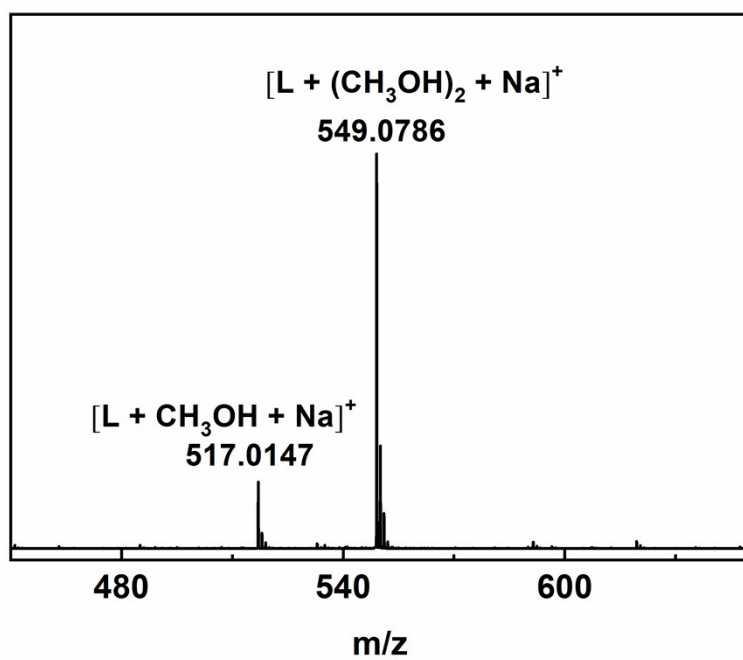


Figure S3. ESI-TOF-MS of L.

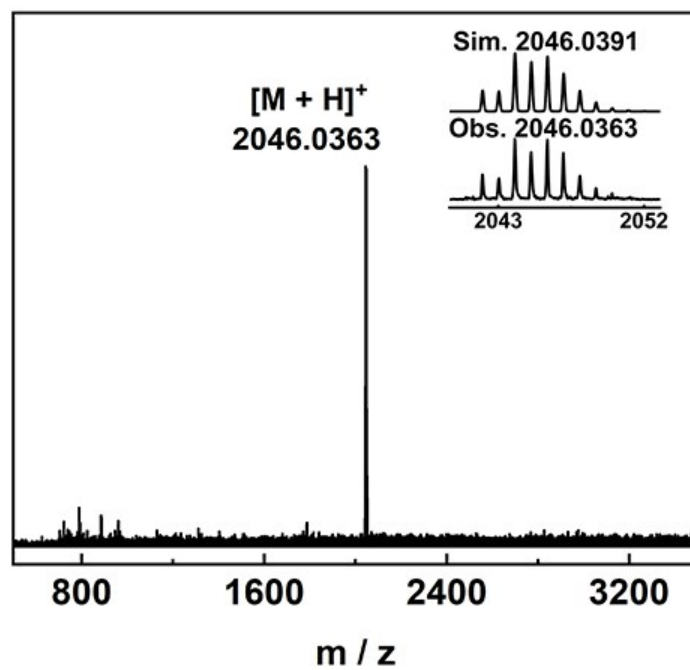


Figure S4. ESI-TOF-MS of  $\text{Eu}_2\text{L}_3(\text{Phen})_2$ .

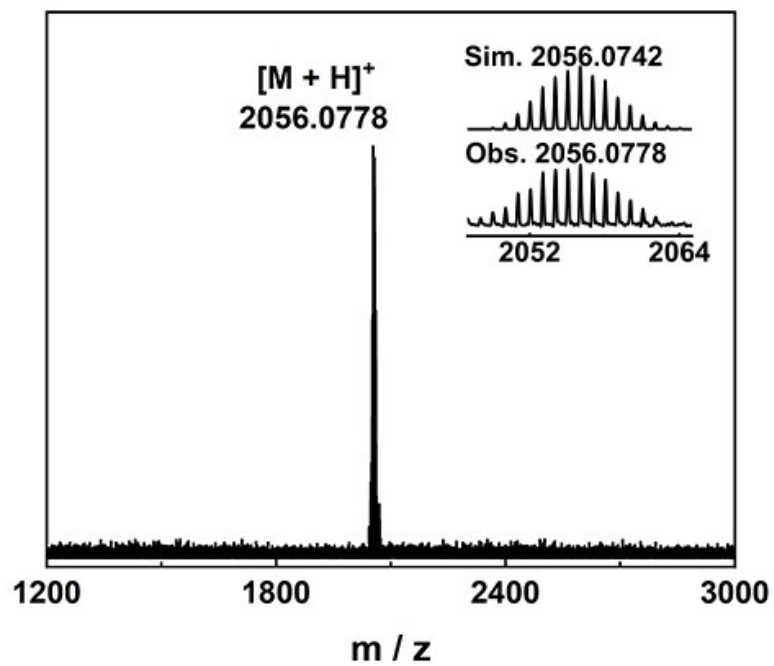


Figure S5. ESI-TOF-MS of  $\text{Gd}_2\text{L}_3(\text{Phen})_2$ .

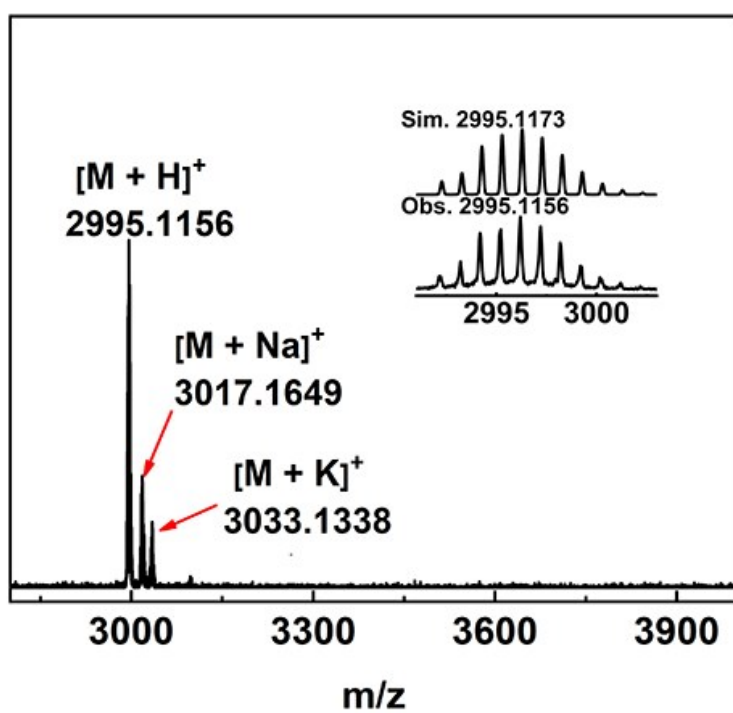


Figure S6. ESI-TOF-MS of  $\text{Eu}_2\text{L}_3(\text{R-BINAPO})_2$ .

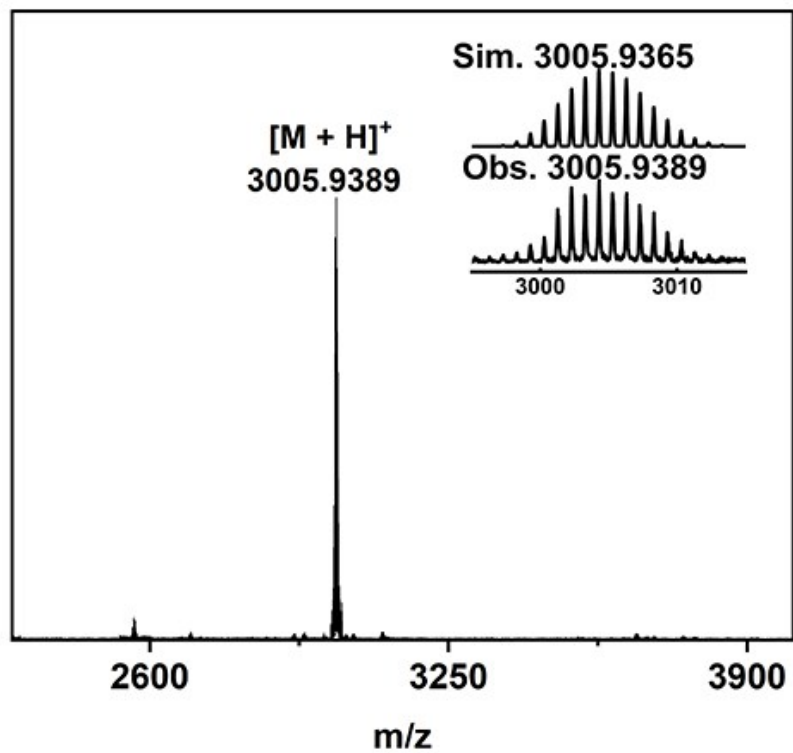


Figure S7. ESI-TOF-MS of  $Gd_2L_3(R-BINAPO)_2$ .

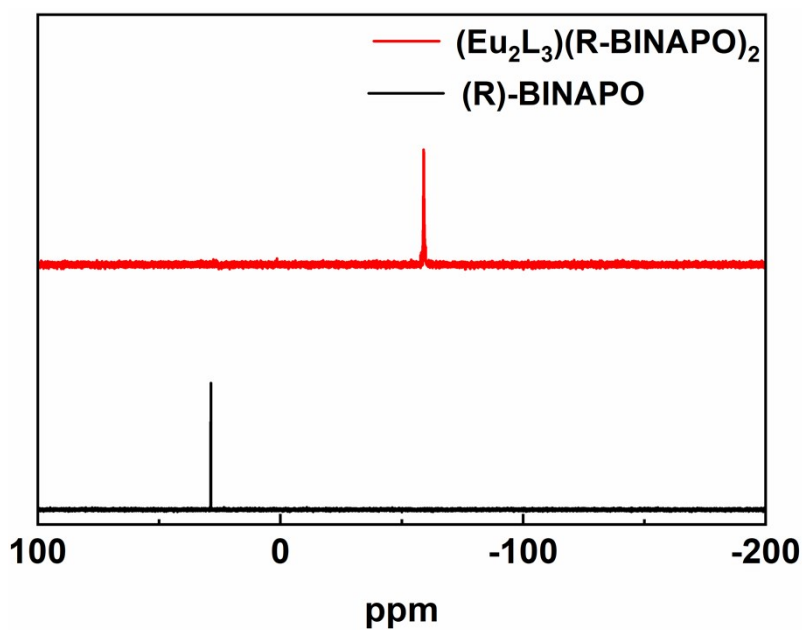
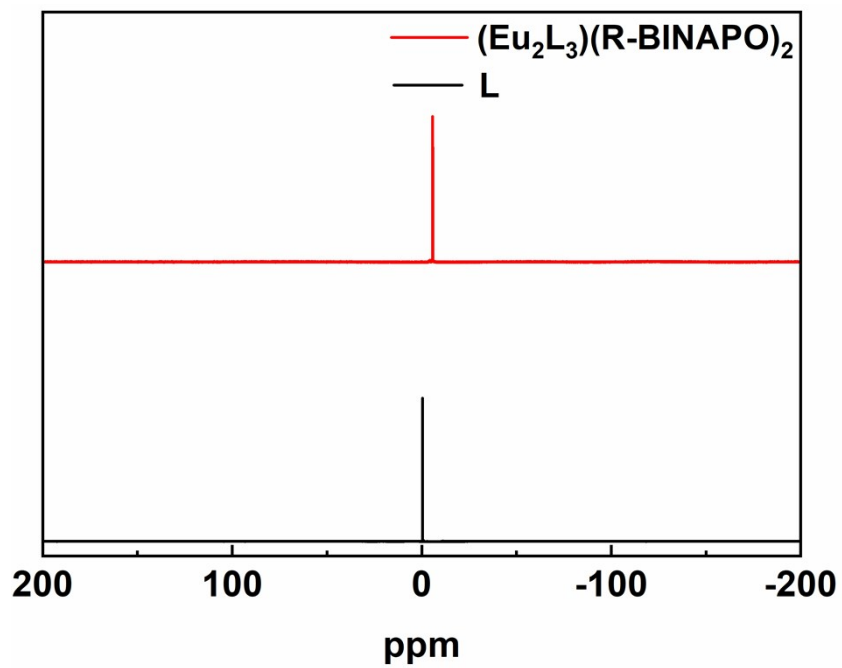
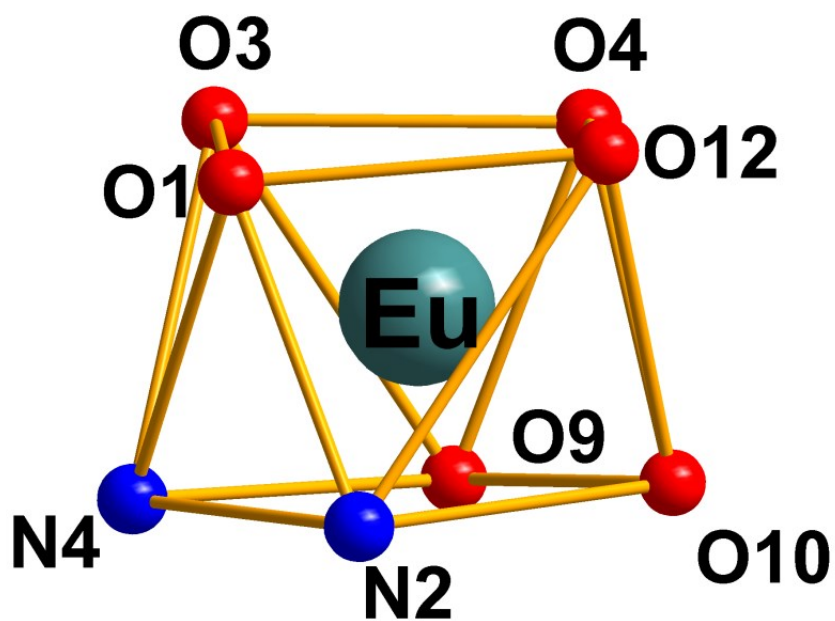


Figure S8.  $^{31}P$  NMR spectrum of  $Eu_2L_3(R-BINAPO)_2$  (red line) and  $(R)-BINAPO$  (black line) in  $THF-d_8$ .



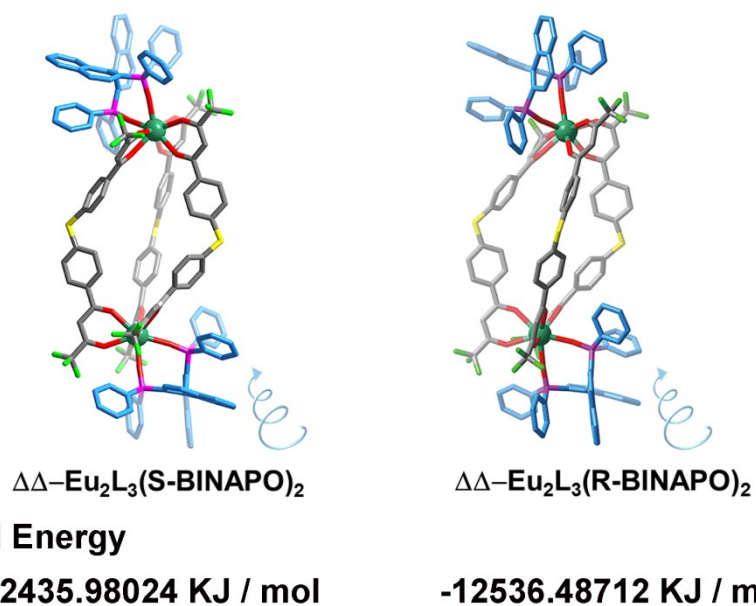
**Figure S9.**  $^{19}\text{F}$  NMR spectrum of  $\text{Eu}_2\text{L}_3(\text{R-BINAPO})_2$  (red line) and L (black line) in  $\text{THF-}d_8$ .



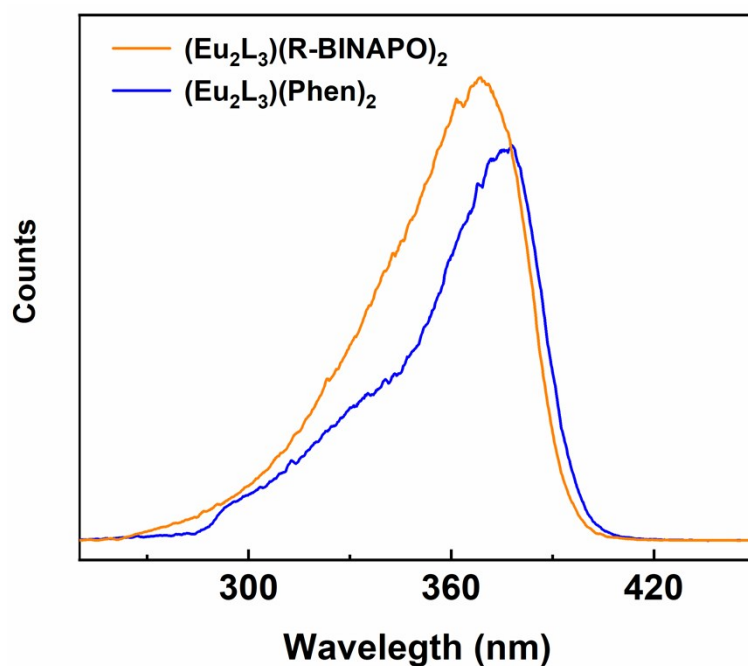
**Figure S10.** The coordination polyhedron of  $\text{Eu}_2\text{L}_3(\text{Phen})_2$ .

**Table S1. Crystallographic data for the Complex of Eu<sub>2</sub>L<sub>3</sub>(phen)<sub>2</sub>**

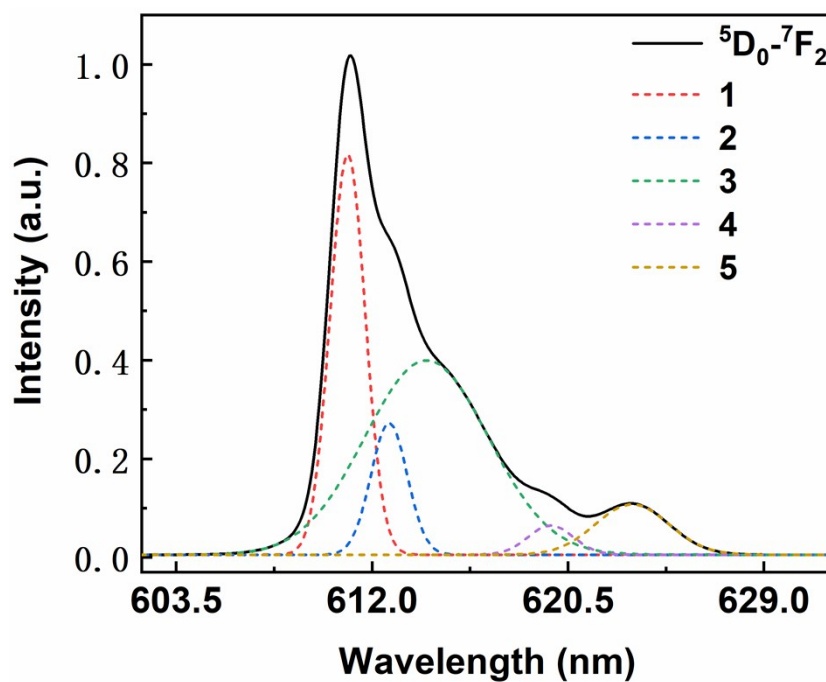
Complex	Eu <sub>2</sub> L <sub>3</sub> (phen) <sub>2</sub>
CCDC number	994501
Empirical formula	C <sub>94.5</sub> H <sub>58</sub> Eu <sub>2</sub> F <sub>18</sub> N <sub>4</sub> O <sub>12</sub> S <sub>3</sub>
color	Colorless
Formula weight	2183.55
Temperature/K	293.0
Crystal system	triclinic
Space group	P-1
a/Å	17.5629(7)
b/Å	18.0137(7)
c/Å	18.8460(6)
$\alpha$ /°	105.518(3)
$\beta$ /°	96.587(3)
$\gamma$ /°	118.352(4)
Volume/Å <sup>3</sup>	4846.0(4)
Z	2
$\rho_{\text{calc}}$ /cm <sup>-3</sup>	1.496
$\mu$ /mm <sup>-1</sup>	1.441
F(000)	2170.0
Crystal size/mm <sup>3</sup>	0.015 × 0.01 × 0.01
Radiation	Mo K $\alpha$ ( $\lambda$ = 0.71073)
2 $\Theta$ range for data collection/°	6.03 to 50.00
Index ranges	-20 ≤ h ≤ 19 -21 ≤ k ≤ 21 -22 ≤ l ≤ 22
Reflections collected	34920
Completeness to theta	99.7%
Independent reflections	17033 [R <sub>int</sub> = 0.0283, R <sub>sigma</sub> = 0.0482]
Data/restraints/parameters	17033/442/1312
Goodness-of-fit on F <sup>2</sup>	1.044
Final R indexes [I ≥ 2 $\sigma$ (I)]	R <sub>1</sub> = 0.0470, wR <sub>2</sub> = 0.1242
Final R indexes [all data]	R <sub>1</sub> = 0.0716, wR <sub>2</sub> = 0.1416
Largest diff. peak/hole / e Å <sup>-3</sup>	1.24/-0.57



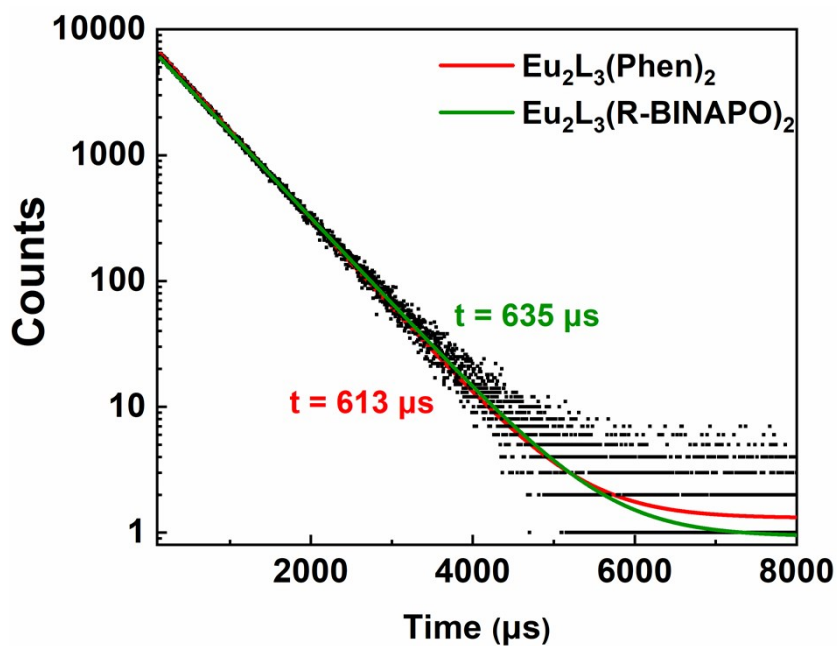
**Figure S11.** Optimized structures of  $\Delta\Delta\text{-Eu}_2\text{L}_3(\text{R-BINAPO})_2$  and  $\Delta\Delta\text{-Eu}_2\text{L}_3(\text{S-BINAPO})_2$ , and the total energy of each possible helicate. The molecular mechanic modeling was built by using the MOPAC 2016 program implemented in the LUMPAC 3.0 software with a Sparkle/RM1 model.



**Figure S12.** Excitation spectra of  $\text{Eu}_2\text{L}_3(\text{R-BINAPO})_2$  (orange line) and  $\text{Eu}_2\text{L}_3(\text{Phen})_2$  (blue line) recorded by monitoring the emission band of  $\text{Eu}^{3+}$  ions at 612 nm in THF ( $1.0 \times 10^{-5}$  M).

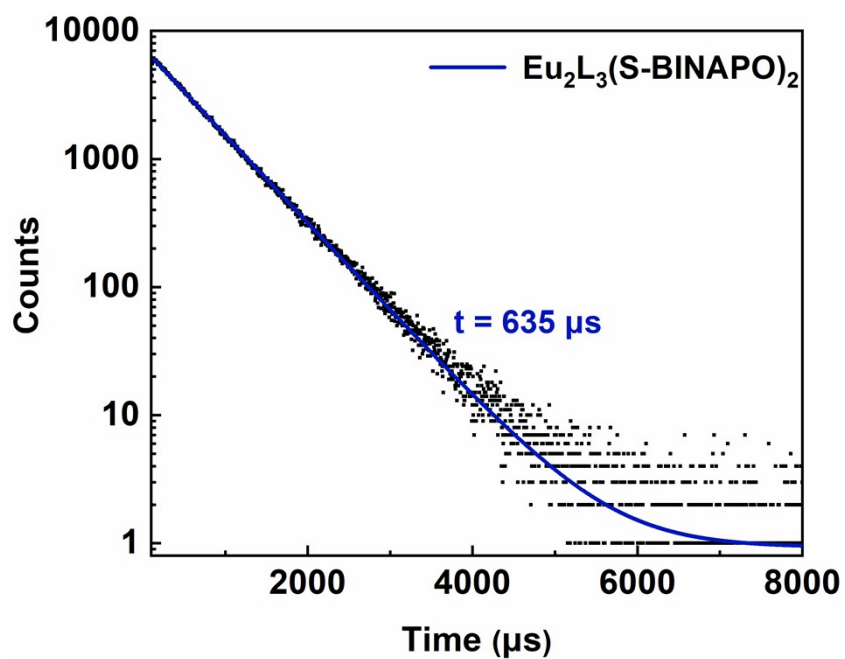


**Figure S13.** Emission spectra of the deconvolution analyses of  ${}^5D_0 \rightarrow {}^7F_2$  transitions with the five peaks at 612 nm of  $\text{Eu}_2\text{L}_3(\text{R-BINAPO})_2$  in THF.

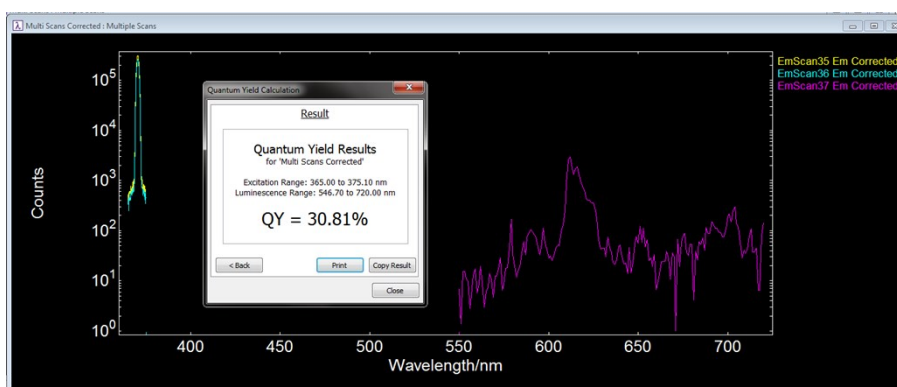


**Figure S14.** Luminescence decay curves of  $\text{Eu}_2\text{L}_3(\text{Phen})_2$  (red line) and  $\text{Eu}_2\text{L}_3(\text{R-BINAPO})_2$  (green line) in THF monitored at 613 nm.

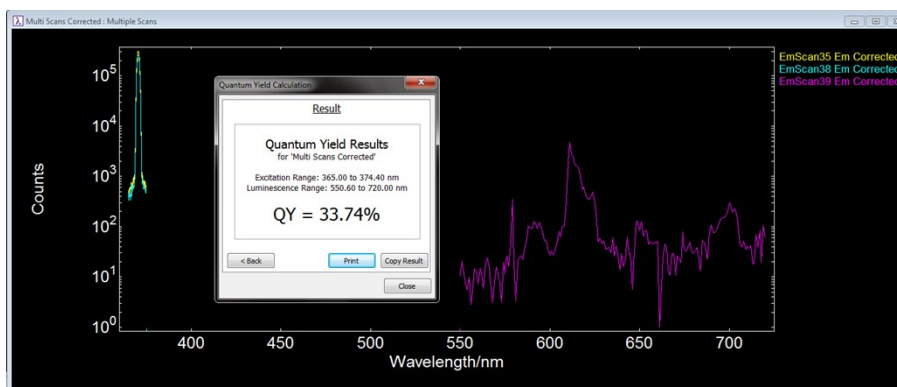




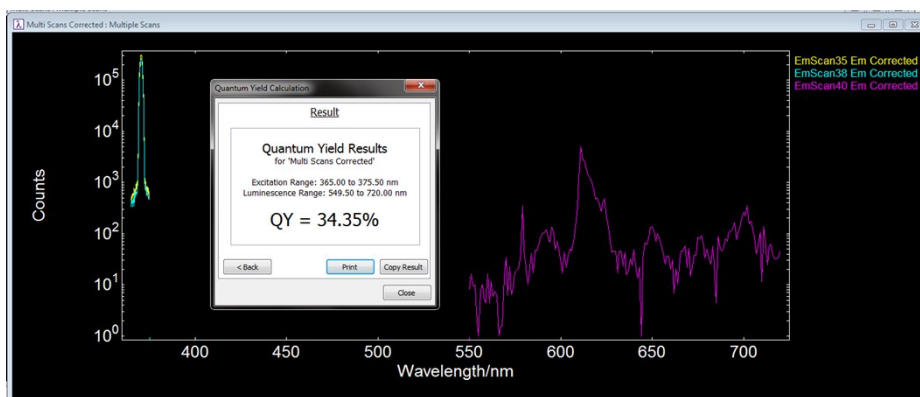
**Figure S15** Luminescence decay curves of  $\text{Eu}_2\text{L}_3(\text{S-BINAPO})_2$  (blue line) in THF monitored at 613 nm.



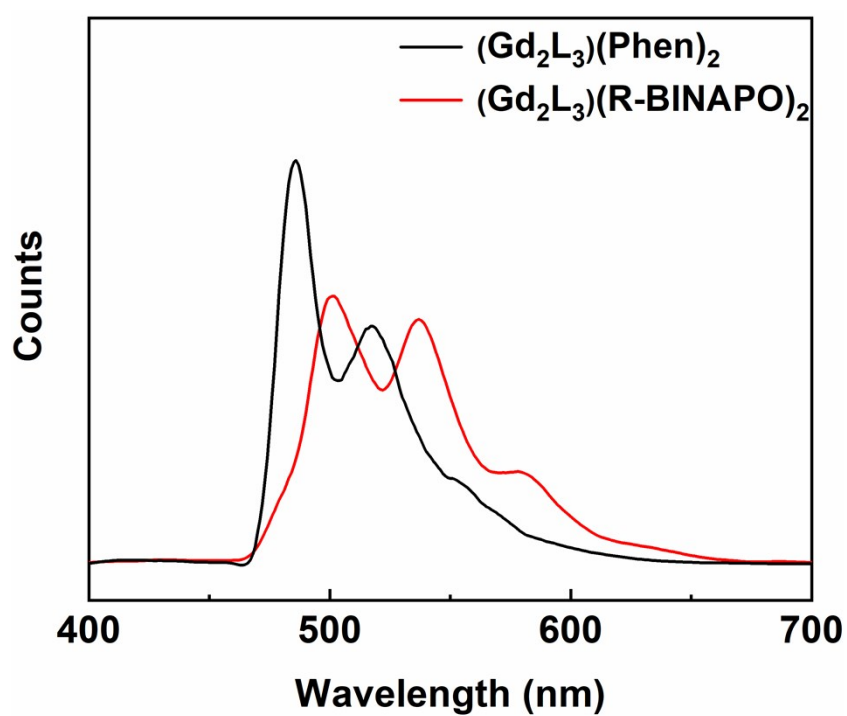
**Figure S16.** The screenshot of the luminescence quantum yield measurement of  $\text{Eu}_2\text{L}_3(\text{Phen})_2$ .



**Figure S17.** The screenshot of the luminescence quantum yield measurement of  $\text{Eu}_2\text{L}_3(\text{R-BINAPO})_2$



**Figure S18.** The screenshot of the luminescence quantum yield measurement of  $\text{Eu}_2\text{L}_3(\text{S-BINAPO})_2$



**Figure S19.** Phosphorescence spectra of  $\text{Gd}_2\text{L}_3(\text{Phen})_2$  (black line)  $\text{Gd}_2\text{L}_3(\text{R-BINAPO})_2$  (red line) in THF at 77 K.