

Electronic Supplementary Information for:

Lanthanide directed self-assembly synthesis and photophysical evaluation of chiral Eu(III) luminescent “half-helicates”

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Synthesis

Ligands **3** or **4** (35 mg, 0.10 mmol) in 5 mL MeCN had solid Eu(CF₃SO₃)₃ (20 mg, 0.03 mmol) added and the resulting solutions were heated at 95°C under microwave irradiation for 10 minutes. The resulting clear yellow solutions were subjected to vapour diffusion of diethyl ether yielding off-white solids.

3₃.Eu₁: obtained as an off-white solid, 24 mg (72%); HR-MALDI-MS: 1133.2395 ([Eu(**3**)₃·Na]⁺ requires 1133.2358). δ_H (400 MHz, CD₃CN), 10.64, 10.08, 8.35, 7.59, 7.46, 6.86, 5.97, 5.29, 4.53, 4.38, 4.11, 1.31. IR(neat): 3290, 3095, 2989, 1619 (C=O), 1590, 1560, 1439, 1380, 1276, 1240, 1225, 1165, 1029, 934, 847, 800, 755, 730, 662 cm⁻¹.

4₃.Eu₁: Obtained as an off-white solid, 27 mg (82%). HR-MALDI-MS: 1133.2393 ([Eu(**4**)₃·Na]⁺ requires 1133.2358). δ_H (400 MHz, CD₃CN) 10.66, 10.11, 8.36, 7.59, 7.47, 6.86, 6.22, 5.92, 5.28, 4.67, 4.36, 4.11, 1.32. IR(neat): 3299, 3093, 1621 (C=O), 1592, 1561, 1440, 1398, 1277, 1241, 1225, 1164, 1029, 935, 847, 800, 757, 731, 662 cm⁻¹.

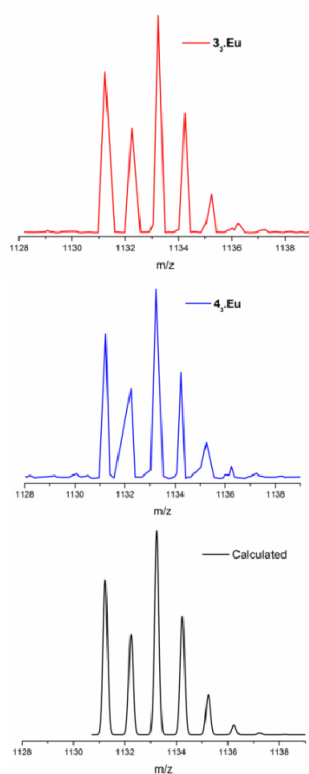


Figure S1: Observed mass spectra for **3₃.Eu** (top), **4₃.Eu** (middle) and calculated mass spectrum for **L₃.Eu** (bottom).

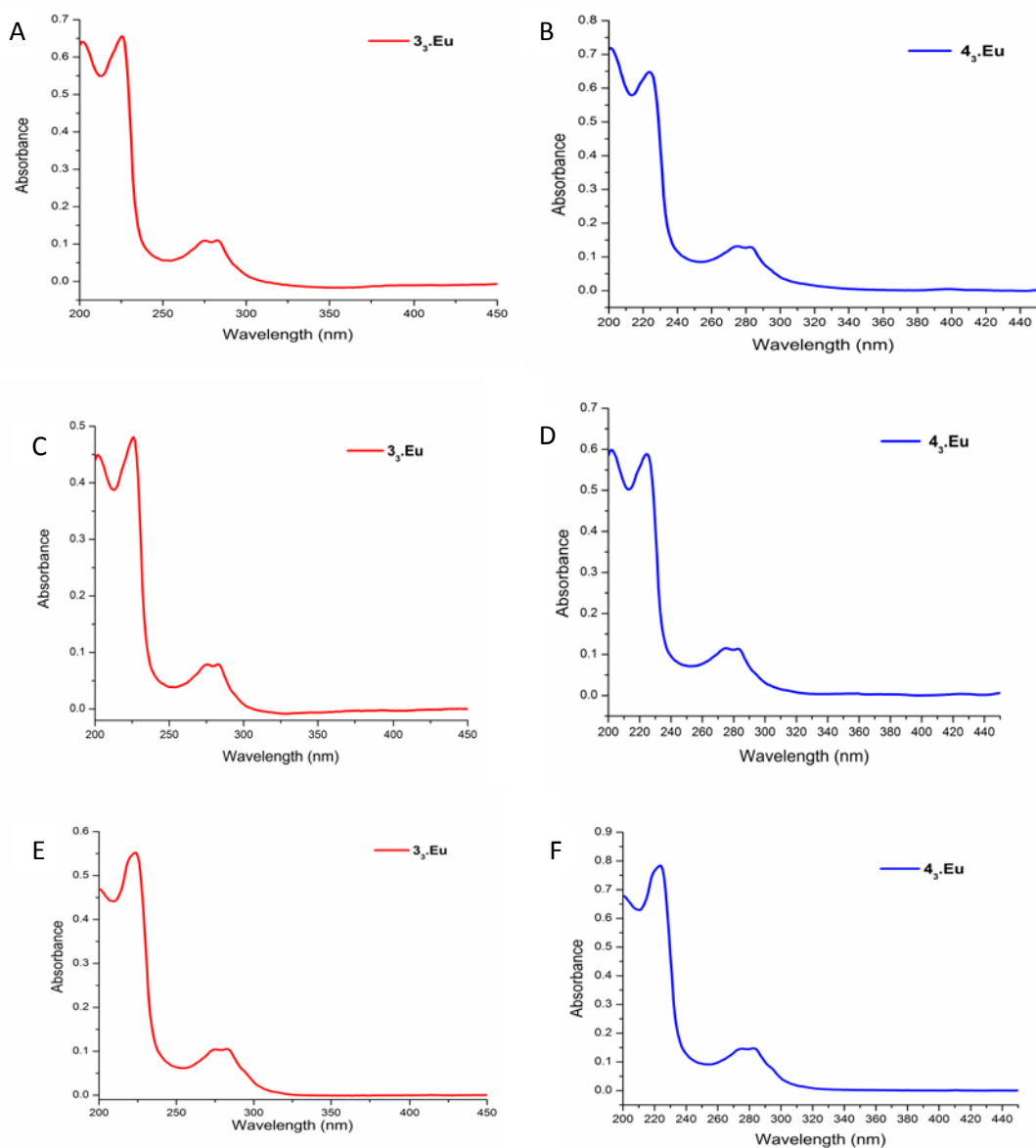


Figure S2: Absorption spectra of 3_3 .Eu and 4_3 .Eu in D_2O (A & B), H_2O (C & D) and CH_3CN (E & F).

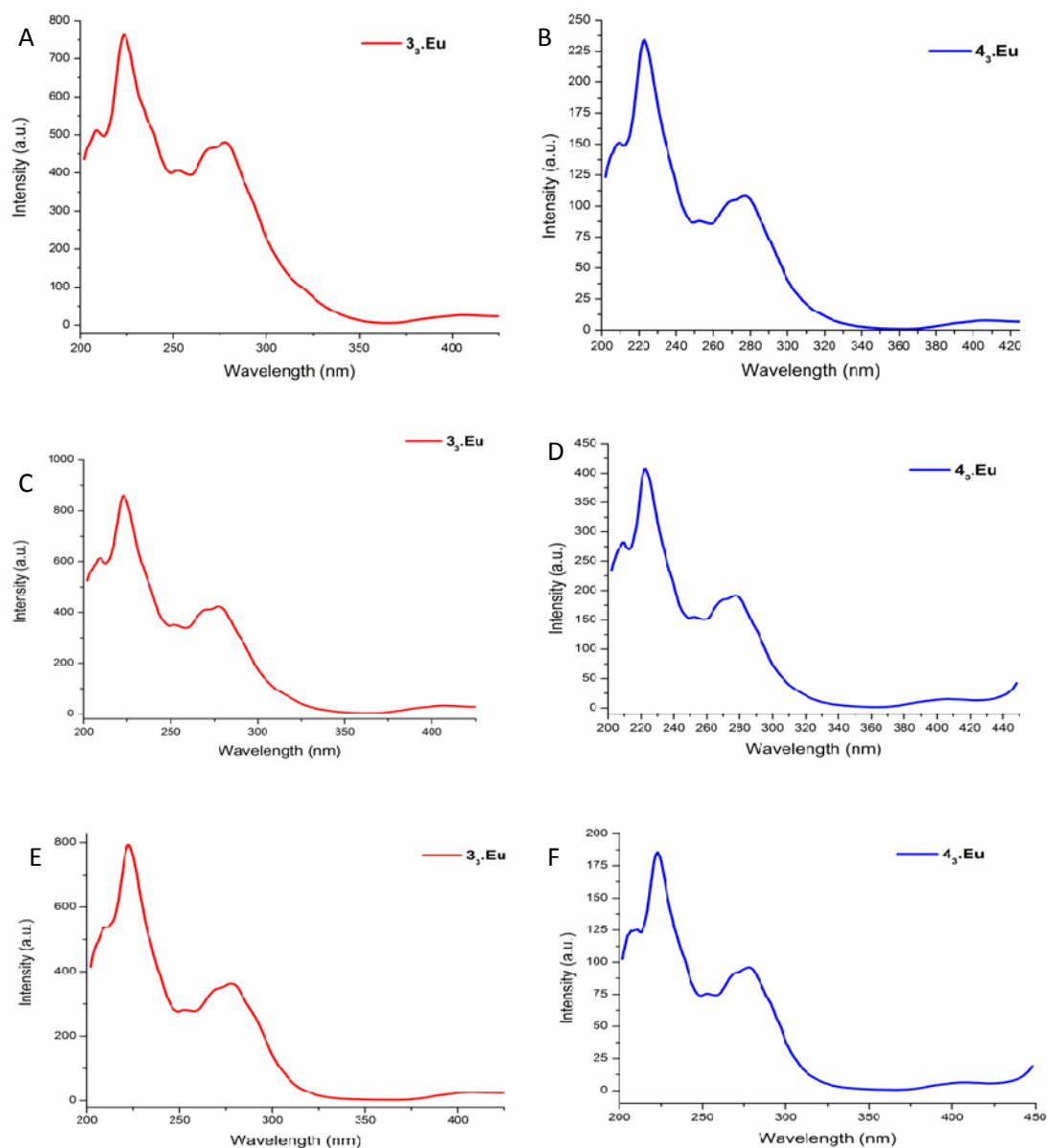


Figure S3: Excitation spectra (Emission at 615 nm) of 3_3 .Eu and 4_3 .Eu in D_2O (A & B), H_2O (C & D) and CH_3CN (E & F).

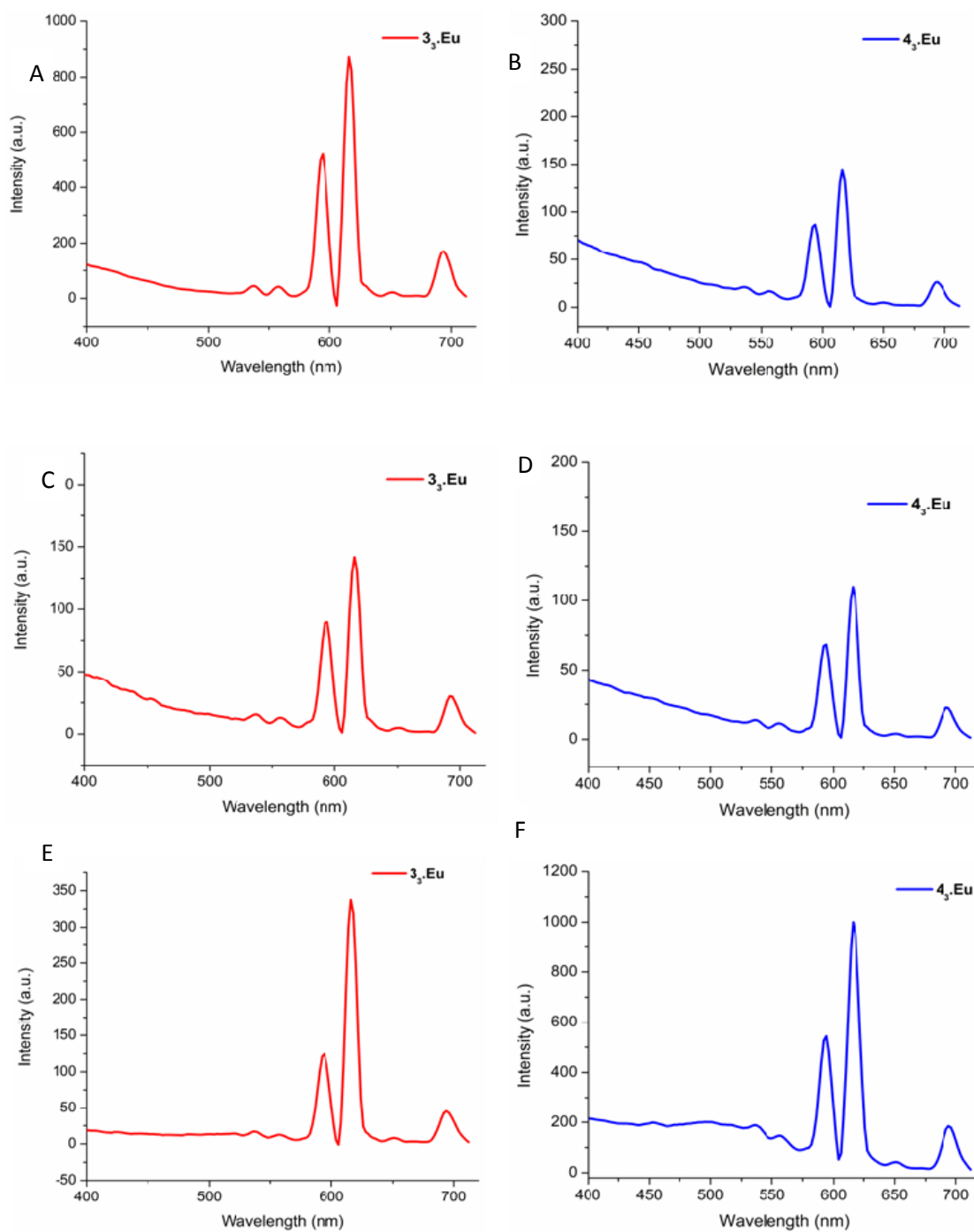


Figure S4: Fluorescence emission spectra of 3_3Eu and 4_3Eu in D_2O (A & B), H_2O (C & D) and CH_3CN (E & F).

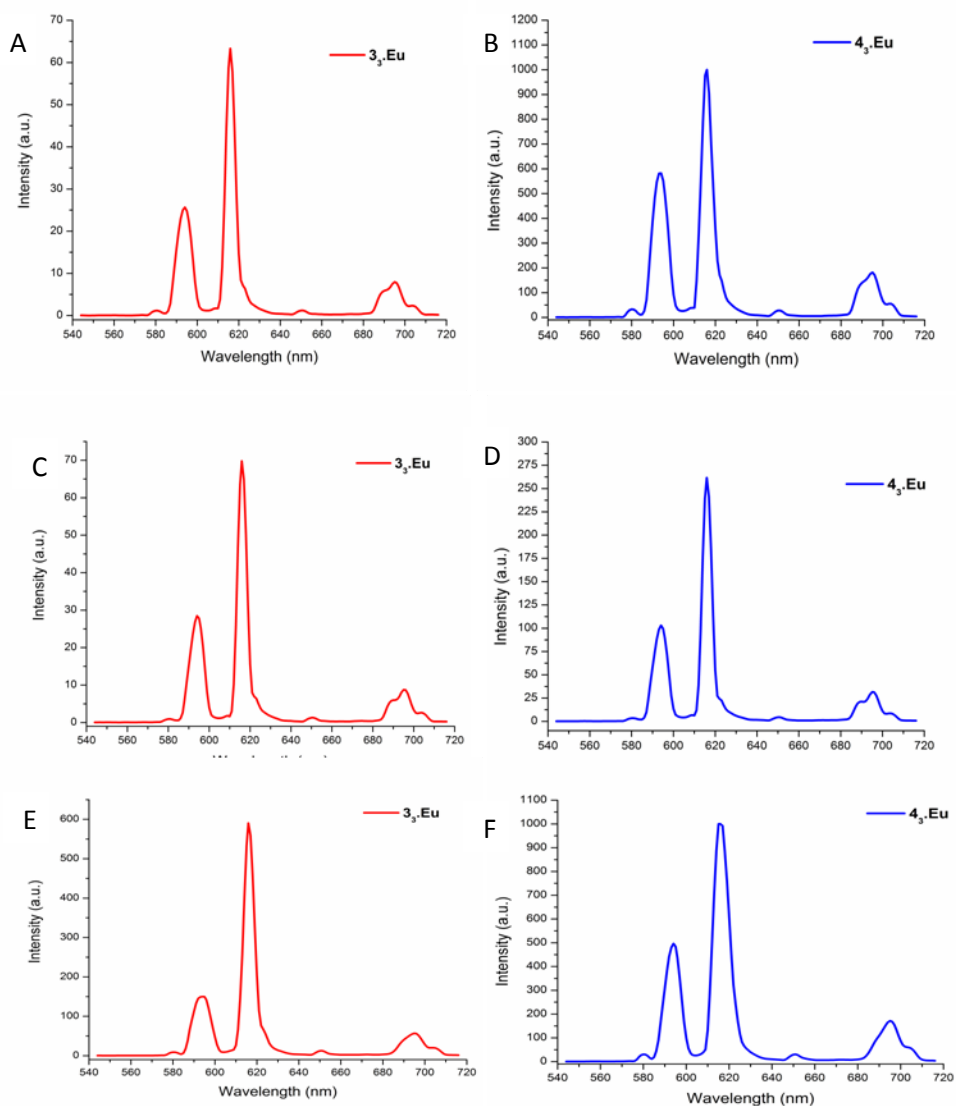


Figure S5: Phosphorescence emission spectra (excitation at 281 nm) of 3_3 .Eu and 4_3 .Eu in D_2O (A & B), H_2O (C & D) and CH_3CN (E & F).

Lifetime graphs

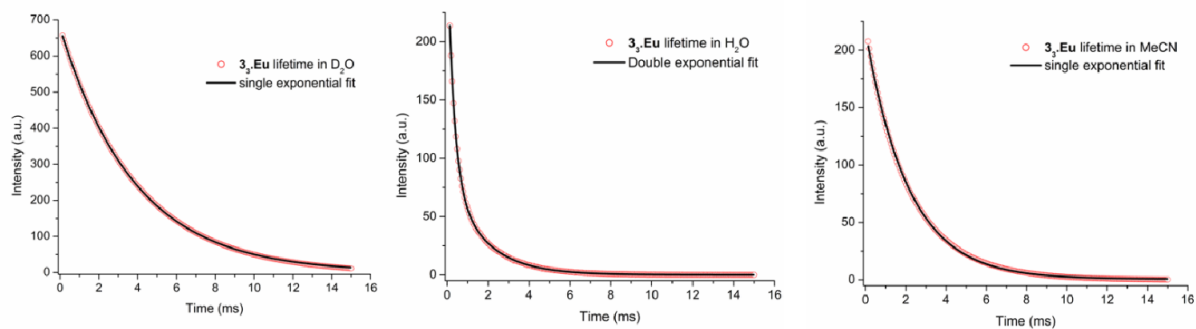


Figure S6: Lifetimes of 3_3 .Eu in D_2O , H_2O and CH_3CN and their corresponding fits.

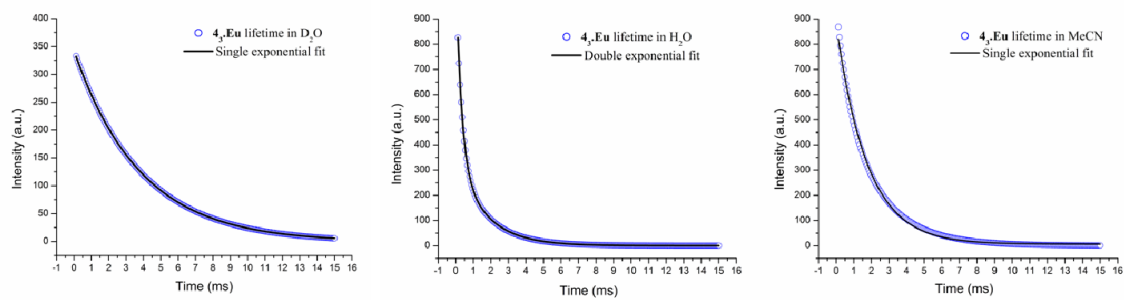


Figure S7: Lifetimes of **4₃.Eu** in D₂O, H₂O and CH₃CN and their corresponding fits.

Table 1: Summary of lifetimes and hydration states for **3₃.Eu** and **4₃.Eu** (made as solids (^a) and *in situ* (^b))

	τ_{MeCN}	τ_{D2O}	τ_{H2O} % population		q
3₃.Eu^a	2.162	3.907	1.683	0.308	0.1
			70%	30%	
4₃.Eu^a	1.772	3.777	1.672	0.309	0.1
			71%	29%	
3₃.Eu^b	0.917	2.760	1.683	0.304	0
			67%	33%	
4₃.Eu^b	0.892	3.395	1.665	0.306	0.11
			64%	36%	

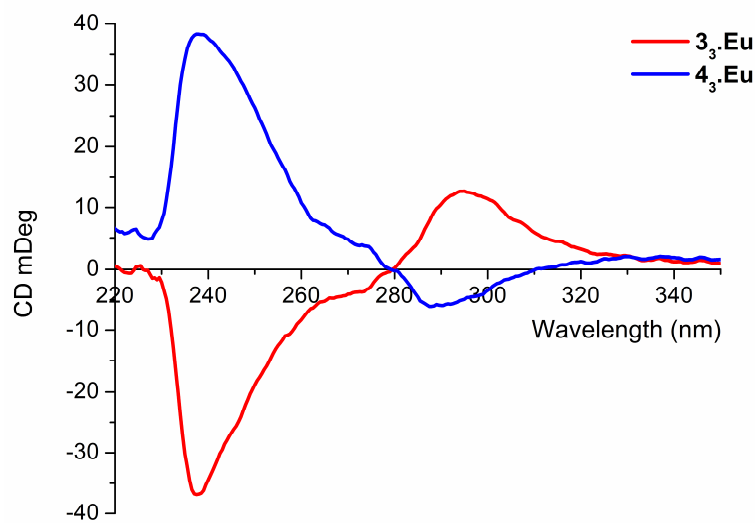


Figure S8: CD spectra of complexes **3₃.Eu** (red) and **4₃.Eu** (blue) in CH₃CN.

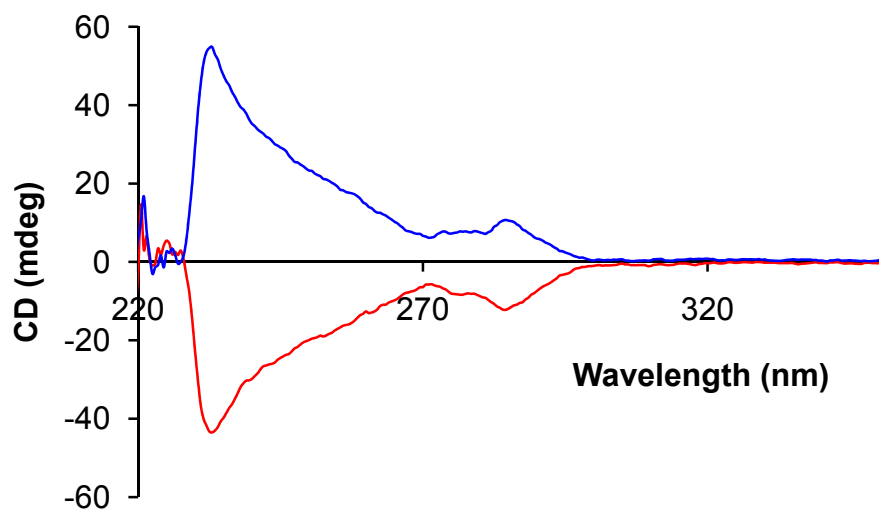


Figure S9: CD spectra of ligands **3** and **4** in CH_3CN .

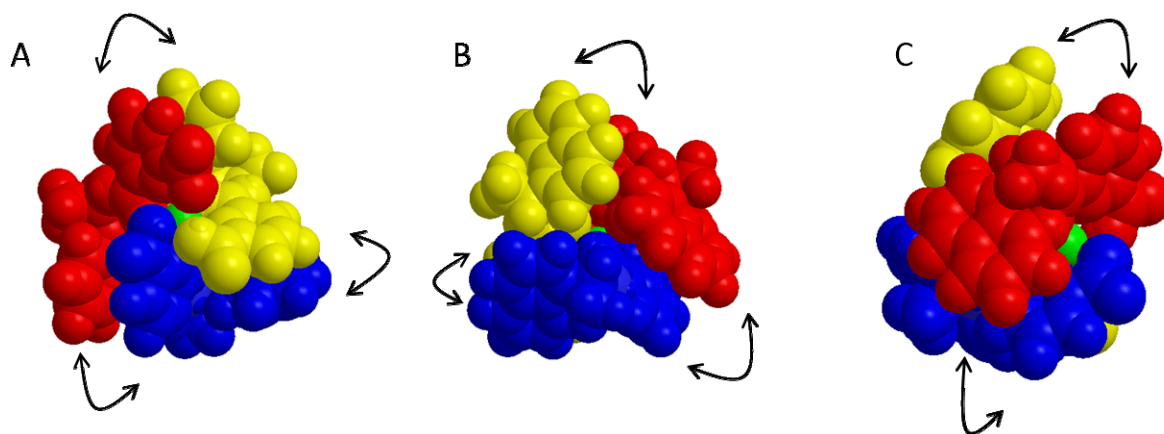


Figure S10: MM2 calculations showing the most stable species of $\text{L}_3\text{.Eu}$ with three different views: A = view of carboxylate plane, B = view of naphthyl plane and C = view of lateral plane. Arrows denote π - π stacking.

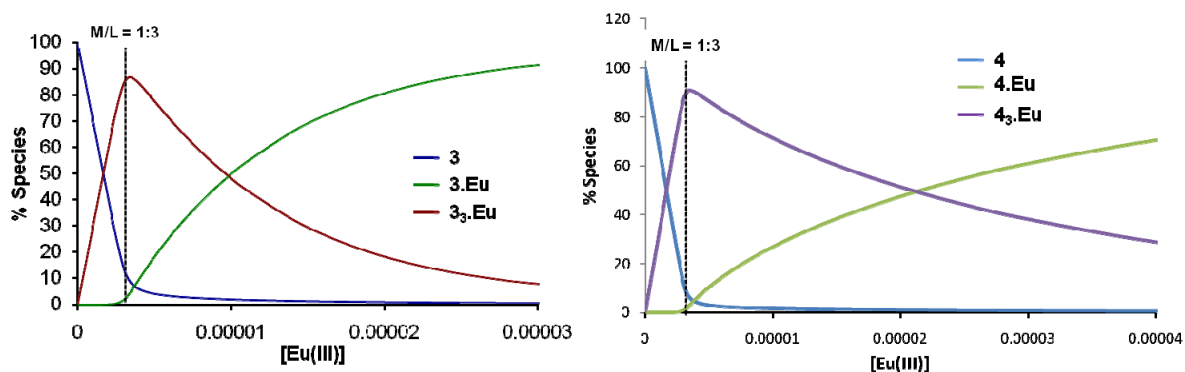


Figure S11: Speciation-distribution diagrams obtained from the titration of **3** (left) and **4** (right) with $\text{Eu}(\text{CF}_3\text{SO}_3)_3$.

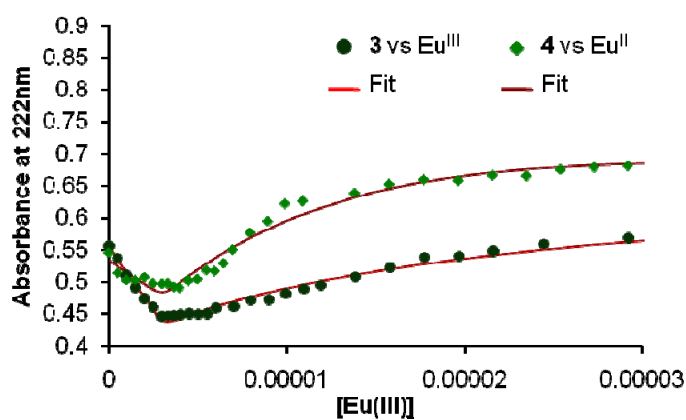


Figure S12: Experimental binding isotherms for the changes in the absorbance spectra upon titrating **3** and **4** with $\text{Eu}(\text{SO}_3\text{CF}_3)_3$ in CH_3CN at room temperature and their corresponding fit by means of SPECFIT.