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.

**3₃Eu:** 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.

**4₃Eu:** 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 3₃Eu (top), 4₃Eu (middle) and calculated mass spectrum for L₃Eu (bottom).
Figure S2: Absorption spectra of $\text{3}_{\text{3}}\text{Eu}$ and $\text{4}_{\text{3}}\text{Eu}$ in D$_2$O (A & B), H$_2$O (C & D) and CH$_3$CN (E & F).
Figure S3: Excitation spectra (Emission at 615 nm) of $^{3}$Eu and $^{4}$Eu in D$_2$O (A & B), H$_2$O (C & D) and CH$_3$CN (E & F).
Figure S4: Fluorescence emission spectra of $^{3}_{3}\text{Eu}$ and $^{4}_{3}\text{Eu}$ in D$_2$O (A & B), H$_2$O (C & D) and CH$_3$CN (E & F).
Figure S5: Phosphorescence emission spectra (excitation at 281 nm) of 3\textsubscript{3}Eu and 4\textsubscript{3}Eu in D\textsubscript{2}O (A & B), H\textsubscript{2}O (C & D) and CH\textsubscript{3}CN (E & F).

Lifetime graphs

Figure S6: Lifetimes of 3\textsubscript{3}Eu in D\textsubscript{2}O, H\textsubscript{2}O and CH\textsubscript{3}CN and their corresponding fits.
Figure S7: Lifetimes of $^{43}\text{Eu}$ in D$_2$O, H$_2$O and CH$_3$CN and their corresponding fits.

Table 1: Summary of lifetimes and hydration states for $^{33}\text{Eu}$ and $^{43}\text{Eu}$ (made as solids ($^a$) and in situ ($^b$))

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<th>$\tau_{\text{MeCN}}$</th>
<th>$\tau_{\text{D}_2\text{O}}$</th>
<th>$\tau_{\text{H}_2\text{O}}$</th>
<th>% population</th>
<th>q</th>
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| $^{33}\text{Eu}^a$ | 2.162                  | 3.907                       | 1.683                       | 70%          | 0.1
|       |                        |                             | 0.308                       | 30%          |    |
| $^{43}\text{Eu}^a$ | 1.772                  | 3.777                       | 1.672                       | 71%          | 0.1
|       |                        |                             | 0.309                       | 29%          |    |
| $^{33}\text{Eu}^b$ | 0.917                  | 2.760                       | 1.683                       | 67%          | 0  |
|       |                        |                             | 0.304                       | 33%          |    |
| $^{43}\text{Eu}^b$ | 0.892                  | 3.395                       | 1.665                       | 64%          | 0.11
|       |                        |                             | 0.306                       | 36%          |    |

Figure S8: CD spectra of complexes $^{33}\text{Eu}$ (red) and $^{43}\text{Eu}$ (blue) in CH$_3$CN.
Figure S9: CD spectra of ligands 3 and 4 in CH₃CN.

Figure S10: MM2 calculations showing the most stable species of L₃.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 Eu(CF$_3$SO$_3$)$_3$.

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