## **Supporting Information**

# Solvent induced self-assembly of dinuclear Eu(III) helicate and emergent strong CPL

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#### 1. Experimental section

#### 1.1 Methods

#### NMR and ESI-TOF-MS

The <sup>1</sup>H NMR, <sup>19</sup>F NMR and <sup>1</sup>H-<sup>1</sup>H DOSY spectra were recorded on a Bruker AVANCE III 400 MHz spectrometer. <sup>1</sup>H NMR chemical shifts are in ppm relative to tetramethylsilane (TMS): CDCl<sub>3</sub> (7.26 ppm for <sup>1</sup>H), CD<sub>3</sub>CN (1.94 ppm for <sup>1</sup>H; 1.32 ppm, 118.26 ppm for <sup>13</sup>C). <sup>1</sup>H-<sup>19</sup>F HOESY spectra were recorded on a JNM-ECZ400S/L1 spectrometer.

High-resolution electrospray ionization mass spectrometry (ESI-TOF-MS) were recorded by using a Bruker maXis mass spectrometer. Data analysis was conducted with the Mass-Lynx Data Analysis software (Version 4.1) and simulations were performed with the MassLynx Isotope Pattern software.

#### **FT-IR** spectra measurements

FT-IR spectra of all samples were performed with a Perkin Elmer Spectrum One spectrophotometer by using KBr disks in the range of 4000–370 cm<sup>-1</sup>.

#### **Photophysical behavior**

UV-vis spectra were recorded in different solvent ratios (CH<sub>3</sub>CN/CHCl<sub>3</sub> = v/v,  $c = 2.5 \times 10^{-6}$  M) at room temperature in 10 mm light path quartz cuvettes on a PerkinElmer Lambda 25 spectrometer.

Excitation and emission spectra were recorded using an Edinburgh FLS 980 fluorescence spectrometer equipped with a red-sensitive photomultiplier detector (Hamamatsu R928). Excitation spectra were measured in CH<sub>3</sub>CN ( $2.5 \times 10^{-6}$  M) with quartz cuvettes of 10 mm path length. Emission spectra were measured in different solvent ratios (CH<sub>3</sub>CN/CHCl<sub>3</sub> = v/v,  $c = 2.5 \times 10^{-6}$  M) with quartz cuvettes of 10 mm path length.

Luminescence lifetimes were recorded on a single photon counting spectrometer from Edinburgh Instruments (FLS 980) with a microsecond pulse lamp as the excitation source.

The luminescence quantum yields ( $\Phi$ ) of the samples were recorded at room temperature through an absolute method using an Edinburgh Instruments integrating sphere coupled to the modular Edinburgh FLS 980 fluorescence spectrometer. The absolute quantum yield was calculated using the following expression:

$$\Phi = \frac{\int L_{emission}}{\int E_{reference} - \int E_{sample}}$$
(S1)

Where  $L_{\text{emission}}$  is the emission spectrum of the sample, collecting using the sphere,  $E_{\text{sample}}$  is the spectrum of the incident light used to excite the sample, collected using the sphere, and  $E_{\text{reference}}$  is the spectrum of the light used for excitation with only the reference in the sphere. The method is accurate within 10%.

$$k_r = \frac{1}{\tau_{rad}} = A_{MD, 0} n^3 \left( \frac{I_{tot}}{I_{MD}} \right)$$
 (S2)

The radiative rate constant  $(k_r)$  is proportional to the intensity ratio of total integrated emission of the  ${}^5D_0 \rightarrow {}^7F_J$  transitions  $(I_{tot})$  to the integrated emission of the  ${}^5D_0 \rightarrow {}^7F_1$  transitions  $(I_{MD})$ .  $A_{MD,0}$  (14.65 s<sup>-1</sup>) is the spontaneous emission probability of the  ${}^5D_0 \rightarrow {}^7F_1$  transition and *n* is the refractive index of the medium.

The radiative transition  $(k_r)$  values and non-radiative transition  $(k_{nr})$  determine the intrinsic quantum yield  $(\Phi_{Ln})$  of Eu<sup>3+</sup> ion emission as shown in eqn (S3).

$$\Phi_{Ln} = \frac{k_r}{k_r + k_{nr}} = \frac{\tau_{obs}}{\tau_{rad}} \qquad (S3)$$

 $\tau_{obs}$  is the observed lifetimes. On the basis of the emission decay curves monitored within the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition. The sensitization efficiencies ( $\eta_{sen}$ ) can be calculated.

#### $\Phi_{overall} = \eta_{sen} \Phi_{Ln} \qquad (S4)$

#### **Chiraloptical measurements**

CD and CPL experiments were performed on an Olis DM245 spectrometer at room temperature. All samples were dissolved in different solvent ratios (CH<sub>3</sub>CN/CHCl<sub>3</sub> = v/v,  $c = 2.5 \times 10^{-6}$  M), and quartz cuvettes with optical pathway of 10 mm were employed. CD spectra were recorded in the range of 250–450 nm in increments of 1 nm, and a slit width of 2 mm for the excitation was utilized. CPL spectra were recorded with a 375 nm laser as light source. The emission of left- and right-handed polarized light were collected in the range of 550–720 nm with the integration time of 1 s and the emission slit width of 0.6 mm.

#### X-ray crystallography

Crystallographic data of  $(NMe_4)_2[Eu_2(L^R)_4]$  is given in Table S2. Single crystals of suitable dimensions of  $(NMe_4)_2[Eu_2(L^R)_4]$  was selected for single-crystal X-ray diffraction analysis. Crystallographic data were collected at 150 K on a Xcalibur, Eos, Gemini diffractometer with Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The structure was solved by direct methods and refined by the full-matrix least-squares method based on  $F^2$  with anisotropic ghermal parameters for all non-hydrogen atoms by using the SHELXS (direct methods) and refined by SHELXL 2018<sup>[1]</sup> (full matrix least-squares techniques) in the Olex2 package.<sup>[2]</sup> The crystallographic data in CIF format were deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21 EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

#### 1.2 Synthetic of ligands $L^{R/S}$ and helicates $(NMe_4)_2[Ln_2(L^{R/S})_4]$ (Ln = Eu, Gd)



Scheme S1. Synthetic route of ligands L<sup>R/S</sup>.

#### The intermediates R/S-1 and R/S-2 were prepared according to the previously reported procedures.<sup>[3]</sup> Synthesis of (R/S)-3,3'-bis(4-acetylphenyl)-2,2'-dimethoxy-1,1'-binaphthalene R/S-3

Under the N<sub>2</sub> atmosphere, R/S-2 (2.50 g, 6.22 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.50 g, 0.44 mmol) and 3bromoacetophenone (2.60 g, 13.06 mmol) were placed in a 100 mL Schlenk flask. THF (50 mL) and an aqueous solution of Na<sub>2</sub>CO<sub>3</sub> (2.0 M, 25 mL) were added to the mixture and stirred at reflux for 24 h. After cooling to room temperature and extracting with ethyl acetate ( $3 \times 50$  mL), the combined organic layers were washed with water and dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude residue purified by silica gel column chromatography (hexane/ethyl acetate = 3:1) afforded R/S-3 as a white solid.

R-**3** Yield: 1.68 g, 49%. <sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>): δ 8.27 (s, 2H), 7.93–7.89 (d, J = 20.0 Hz, 6H), 7.86–7.84 (d, J = 8.0 Hz, 2H), 7.48–7.45 (t, J = 8.0 Hz, 2H), 7.36–7.32 (t, J = 8.0 Hz, 2H), 7.22–7.19 (t, J = 8.0 Hz, 2H), 7.16 (s, 2H), 3.09 (s, 6H), 2.57 (s, 6H) ppm. **ESI-TOF-MS** (m/z): calculated for C<sub>38</sub>H<sub>30</sub>O<sub>4</sub> [M + K]<sup>+</sup> 589.2144, found 589.2106. **IR** (KBr) 740, 1042, 1247, 1350, 1413, 1676, 2932 cm<sup>-1</sup>. S-**3** Yield: 1.64 g, 48%. <sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>): δ 8.27 (s, 2H), 7.93–7.89 (d, J = 20.0 Hz, 6H), 7.86–7.84 (d, J = 8.0 Hz, 2H), 7.48–7.45 (t, J = 8.0 Hz, 2H), 7.36–7.32 (t, J = 8.0 Hz, 2H), 7.22–7.19 (t, J = 8.0 Hz, 2H), 7.16 (s, 2H), 3.09 (s, 6H), 2.57 (s, 6H) ppm. **ESI-TOF-MS** (m/z): calculated for C<sub>38</sub>H<sub>30</sub>O<sub>4</sub> [M + K]<sup>+</sup> 589.2144, found 589.2106. **IR** (KBr) 743, 1040, 1241, 1355, 1415, 1675, 2931 cm<sup>-1</sup>.

#### Synthesis of L<sup>R/S</sup>

Sodium methoxide (0.39 g, 7.27 mmol) and ethyl heptafluorobutyrate (1.76 g, 7.27 mmol) were dissolved in ethylene glycol dimethyl ether (20 mL), and then R/S-**3** (0.50 g, 0.91 mmol) was added and stirred at room temperature for 24 h. The resulting solution was quenched with water and acidified with hydrochloric acid (2.0 M) to pH 2–3. A yellow precipitate was filtered and dried in vacuum.

L<sup>R</sup> Yield: 0.77 g, 89.5%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  15.26 (s, 2H), 8.34 (s, 2H), 8.07–8.05 (d, *J* = 8.0 Hz, 2H), 8.03 (s, 2H), 7.99–7.96 (t, *J* = 8.0 Hz, 4H), 7.64–7.60 (t, *J* = 8.0 Hz, 2H), 7.48–7.44 (t, *J* = 8.0 Hz, 2H), 7.34–7.32 (t, *J* = 8.0 Hz, 2H), 7.24 (s, 2H), 6.70 (s, 2H), 3.19 (s, 2H) ppm. **ESI-TOF-MS** (m/z): calculated for C<sub>46</sub>H<sub>28</sub>F<sub>14</sub>O<sub>6</sub> [M – H]<sup>+</sup> 941.1662, found 941.1621. **IR** (KBr) 748, 1133, 1229, 1346, 1597, 3450 cm<sup>-1</sup>. L<sup>S</sup> Yield: 0.80 g, 93.5%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  15.26 (s, 2H), 8.34 (s, 2H), 8.07–8.05 (d, *J* = 8.0 Hz, 2H), 8.03 (s, 2H), 7.99–7.96 (t, *J* = 8.0 Hz, 4H), 7.64–7.60 (t, *J* = 8.0 Hz, 2H), 7.48–7.44 (t, *J* = 8.0 Hz, 2H), 7.34–7.32 (t, *J* = 8.0 Hz, 2H), 7.24 (s, 2H), 3.19 (s, 2H) ppm. **ESI-TOF-MS** (m/z): calculated for C<sub>46</sub>H<sub>28</sub>F<sub>14</sub>O<sub>6</sub> (t, *J* = 8.0 Hz, 4H), 7.64–7.60 (t, *J* = 8.0 Hz, 2H), 7.48–7.44 (t, *J* = 8.0 Hz, 2H), 7.34–7.32 (t, *J* = 8.0 Hz, 2H), 7.24 (s, 2H), 6.70 (s, 2H), 3.19 (s, 2H) ppm. **ESI-TOF-MS** (m/z): calculated for C<sub>46</sub>H<sub>28</sub>F<sub>14</sub>O<sub>6</sub> [M – H]<sup>+</sup> 941.1662, found 941.1635. **IR** (KBr) 745, 1130, 1226, 1340, 1590, 3446 cm<sup>-1</sup>.

#### Synthesis of $(NMe_4)_2[Ln_2(L^{R/S})_4]$ (Ln = Eu, Gd)

The ligand  $L^{R/S}$  (0.30 g, 0.31 mmol) and tetramethylammonium hydroxide (25% w/w in water, 0.63 mmol) were dissolved in CH<sub>3</sub>CN (20 mL), and heated until the solution became clear and transparent. Ln(OTf)<sub>3</sub> (Ln = Eu, Gd; 0.16 mmol) in 5 mL CH<sub>3</sub>CN was added and stirred at room temperature for 24 h, and then the precipitates ware formed after the addition of water. At last, the produce was filtered and dried in vacuum.

 $(NMe_4)_2[Eu_2(L^R)_4]$ . Yield: 0.25 g, 79%. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN/CDCl<sub>3</sub> = 2:8):  $\delta$  8.81 (s, 4H), 8.60–8.58 (d, J = 8.0 Hz, 2H), 8.18–8.06 (m, 4H), 6.83–6.79 (t, J = 8.0 Hz, 2H), 6.32–6.31 (d, J = 12.0 Hz, 2H), 6.01–5.98 (t, J = 8.0 Hz, 2H), 5.75 (s, 2H), 0.76 (s, 6H), –5.92 (s, 2H) ppm. ESI-TOF-MS (m/z): calculated for C<sub>184</sub>H<sub>104</sub>Eu<sub>2</sub>F<sub>56</sub>O<sub>24</sub>. [Eu<sub>2</sub>(L<sup>R</sup>)<sub>4</sub>]<sup>2–</sup> 2033.2247, found 2033.2244. Elemental analysis: calculated for  $C_{192}H_{128}Eu_2F_{56}N_2O_{24}$ : C, 54.71; H, 3.06; N, 0.66, found: C, 54.86; H, 2.99; N, 0.55. (NMe<sub>4</sub>)<sub>2</sub>[Eu<sub>2</sub>(L<sup>S</sup>)<sub>4</sub>]. Yield: 0.24 g, 74%. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN/CDCl<sub>3</sub> = 2:8):  $\delta$  8.81 (s, 4H), 8.60–8.58 (d, *J* = 8.0 Hz, 2H), 8.18–8.06 (m, 4H), 6.83–6.79 (t, *J* = 8.0 Hz, 2H), 6.32–6.31 (d, *J* = 12.0 Hz, 2H), 6.01–5.98 (t, *J* = 8.0 Hz, 2H), 5.75 (s, 2H), 0.76 (s, 6H), -5.92 (s, 2H) ppm. ESI-TOF-MS (m/z): calculated for C<sub>184</sub>H<sub>104</sub>Eu<sub>2</sub>F<sub>56</sub>O<sub>24</sub>. [Eu<sub>2</sub>(L<sup>S</sup>)<sub>4</sub>]<sup>2–</sup>2033.2247, found 2033.2242. Elemental analysis: calculated for C<sub>192</sub>H<sub>128</sub>Eu<sub>2</sub>F<sub>56</sub>N<sub>2</sub>O<sub>24</sub>: C, 54.71; H, 3.06; N, 0.66, found: C, 54.88; H, 2.95; N, 0.54.

 $(NMe_4)_2[Gd_2(L^R)_4]$ . Yield: 0.24 g, 74%. ESI-TOF-MS (m/z): calculated for  $C_{184}H_{104}Gd_2F_{56}O_{24}$ .  $[Gd_2(L^R)_4]^{2-2}$ 2038.2278, found 2038.2275. Elemental analysis: calculated for  $C_{192}H_{128}Gd_2F_{56}N_2O_{24}$ : C, 54.58; H, 3.05; N, 0.66, found: C, 54.77; H, 2.86; N, 0.61.  $(NMe_4)_2[Gd_2(L^S)_4]$ . Yield: 0.25 g, 76%. ESI-TOF-MS (m/z): calculated for  $C_{184}H_{104}Gd_2F_{56}O_{24}$ .  $[Gd_2(L^S)_4]^{2-2}$  2038.2278, found 2038.2271. Elemental analysis: calculated for  $C_{192}H_{128}Gd_2F_{56}N_2O_{24}$ .  $[Gd_2(L^S)_4]^{2-2}$  2038.2278, found 2038.2271. Elemental analysis: calculated for  $C_{192}H_{128}Gd_2F_{56}N_2O_{24}$ .  $[Gd_2(L^S)_4]^{2-2}$  2038.2278, found 2038.2271. Elemental analysis: calculated for  $C_{192}H_{128}Gd_2F_{56}N_2O_{24}$ .  $[Gd_2(L^S)_4]^{2-2}$  2038.2278, found 2038.2271. Elemental analysis: calculated for  $C_{192}H_{128}Gd_2F_{56}N_2O_{24}$ .  $[Gd_2(L^S)_4]^{2-2}$  2038.2278, found 2038.2271. Elemental analysis: calculated for  $C_{192}H_{128}Gd_2F_{56}N_2O_{24}$ .  $[Gd_2(L^S)_4]^{2-2}$  2038.2278, found 2038.2271. Elemental analysis: calculated for  $C_{192}H_{128}Gd_2F_{56}N_2O_{24}$ .  $[Gd_2(L^S)_4]^{2-2}$  2038.2278, found 2038.2271. Elemental analysis: calculated for  $C_{192}H_{128}Gd_2F_{56}N_2O_{24}$ .  $[Gd_2(L^S)_4]^{2-2}$  2038.2278, found 2038.2271. Elemental analysis: calculated for  $C_{192}H_{128}Gd_2F_{56}N_2O_{24}$ .  $[Gd_2(L^S)_4]^{2-2}$  2038.2278, found 2038.2271. Elemental analysis: calculated for  $C_{192}H_{128}Gd_2F_{56}N_2O_{24}$ .  $[Gd_2(L^S)_4]^{2-2}$  2038.2278, found 2038.228, found 2038, found 2038,

#### 1.3 Characterization of intermediates and ligands







Figure S3. <sup>1</sup>H NMR spectrum (400 MHz, 298 K, CDCl<sub>3</sub>) of L<sup>R</sup>.



Figure S5. ESI-TOF-MS spectrum of  $L^{R}$ .



Figure S7. <sup>19</sup>F NMR spectrum (376 MHz, 298 K, CD<sub>3</sub>CN) of L<sup>R</sup>.





1.4 Characterization of  $(NMe_4)_2[Ln_2(L^{R/S})_4]$  (Ln = Eu, Gd)



Figure S9. ESI-TOF-MS spectrum of  $(NMe_4)_2[Eu_2(L^R)_4]$  in CH<sub>3</sub>CN/CHCl<sub>3</sub> = 2:8 (v/v).



Figure S10. ESI-TOF-MS spectrum of  $(NMe_4)_2[Eu_2(L^S)_4]$  in CH<sub>3</sub>CN/CHCl<sub>3</sub> = 2:8 (v/v).



Figure S11. ESI-TOF-MS spectrum of  $(NMe_4)_2[Gd_2(L^R)_4]$  in  $CH_3CN/CHCl_3 = 2:8$  (v/v).



Figure S12. ESI-TOF-MS spectrum of  $(NMe_4)_2[Gd_2(L^S)_4]$  in  $CH_3CN/CHCl_3 = 2:8$  (v/v).



Figure S13. <sup>1</sup>H NMR spectrum (400 MHz, 298 K) of  $(NMe_4)_2[Eu_2(L^S)_4]$  in CD<sub>3</sub>CN/CDCl<sub>3</sub> = 2:8 (v/v).



Figure S14. <sup>1</sup>H NMR spectrum (400 MHz, 298 K, CD<sub>3</sub>CN) of (NMe<sub>4</sub>)OTf.

## 2. Study of structure control of (NMe<sub>4</sub>)<sub>2</sub>[Eu<sub>2</sub>(L<sup>R</sup>)<sub>4</sub>]



Figure S15. ESI-TOF-MS spectra of  $(NMe_4)_2[Eu_2(L^R)_4]$  in different solvent ratios  $(CH_3CN/CHCl_3 = v/v)$ .



Figure S16. <sup>1</sup>H-<sup>19</sup>F HOESY (400 MHz, 298 K) spectrum of (NMe<sub>4</sub>)<sub>2</sub>[Eu<sub>2</sub>(L<sup>R</sup>)<sub>4</sub>] in CD<sub>3</sub>CN/CDCl<sub>3</sub> = 2:8 (v/v).



Figure S17. ESI-TOF-MS spectrum of  $(NMe_4)_2[Eu_2(L^R)_4]$  in  $CH_3CN/CHCl_3 = 2:8$  (v/v).







Figure S19. <sup>1</sup>H NMR spectra (400 MHz, 298 K) of  $(NMe_4)_2[Eu_2(L^R)_4]$  in different solvent ratios  $(CD_3CN/CDCl_3 = v/v)$ .



Figure S20. <sup>1</sup>H NMR spectra (400 MHz, 233 K) of (NMe<sub>4</sub>)<sub>2</sub>[Eu<sub>2</sub>(L<sup>R</sup>)<sub>4</sub>] in CD<sub>3</sub>CN.



Figure S21. <sup>1</sup>H NMR spectra (400 MHz, 298 K) change of  $(NMe_4)_2[Eu_2(L^R)_4]$  upon the addition of  $(Et_4N)^+$  in  $CD_3CN/CDCl_3 = 2:8 (v/v)$ .



Figure S22. <sup>1</sup>H NMR spectra (400 MHz, 298 K) change of  $(NMe_4)_2[Eu_2(L^R)_4]$  upon the addition of  $(n-Bu_4N)^+$  in  $CD_3CN/CDCl_3 = 2:8 (v/v).$ 



Figure S23. CD spectra of  $(NMe_4)_2[Eu_2(L^{R/S})_4]$  in different solvent ratios  $(CH_3CN/CHCl_3 = v/v, c = 2.5 \times 10^{-6} \text{ M})$ .



Figure S24. CPL spectra of  $(NMe_4)_2[Eu_2(L^{R/S})_4]$  in different solvent ratios  $(CH_3CN/CHCl_3 = v/v, c = 2.5 \times 10^{-6} \text{ M})$ monitored at 612 nm.



Figure S25. The  $g_{lum}$  values of  $(NMe_4)_2[Eu_2(L^R)_4]$  in different solvent ratios  $(CH_3CN/CHCl_3 = v/v, c = 2.5 \times 10^{-6} M)$ .



Figure S26. UV-vis spectra of  $L^{\mathbf{R}}$  in CH<sub>3</sub>CN ( $c = 1.0 \times 10^{-5}$  M) and (NMe<sub>4</sub>)<sub>2</sub>[Eu<sub>2</sub>( $L^{\mathbf{R}}$ )<sub>4</sub>] in different solvent ratios (CH<sub>3</sub>CN/CHCl<sub>3</sub> = v/v,  $c = 2.5 \times 10^{-6}$  M).



Figure S27. Emission spectra of  $(NMe_4)_2[Eu_2(L^R)_4]$  in different solvent ratios  $(CH_3CN/CHCl_3 = v/v, c = 2.5 \times 10^{-6} M)$  monitored at 612 nm.



Figure S28. Excitation spectrum of  $(NMe_4)_2[Eu_2(L^R)_4]$  in CH<sub>3</sub>CN/CHCl<sub>3</sub> = 2:8 (v/v) monitored at 375 nm.



Figure S29. Luminescence decay curve of  $(NMe_4)_2[Eu_2(L^R)_4]$  in CH<sub>3</sub>CN ( $c = 2.5 \times 10^{-6}$  M) monitored at 612 nm.



Figure S30. Luminescence decay curve of  $(NMe_4)_2[Eu_2(L^R)_4]$  in CH<sub>3</sub>CN/CHCl<sub>3</sub> = 2:8 (v/v,  $c = 2.5 \times 10^{-6}$  M) monitored at 612 nm.



Figure S31. The screenshots of the luminescence quantum yields of  $(NMe_4)_2[Eu_2(L^R)_4]$  in CH<sub>3</sub>CN monitored at

612 nm.



Figure S32. The screenshots of the luminescence quantum yields of  $(NMe_4)_2[Eu_2(L^R)_4]$  in CH<sub>3</sub>CN/CHCl<sub>3</sub> = 2:8 (v/v) monitored at 612 nm.

## 3. Cavity volume calculation of (NMe<sub>4</sub>)<sub>2</sub>[Eu<sub>2</sub>(L<sup>R</sup>)<sub>4</sub>]

To determine the available void space within the helicates of  $(NMe_4)_2[Eu_2(L^R)_4]$ , MoloVol calculations based on the crystal structure obtained in this study were performed. The cavity volume were calculated to be 403 Å<sup>3</sup> using the parameters tabulated below. The corresponding graphics were generated with Pymol.<sup>[4]</sup>

Probe mode: two probes

Small probe radius: 1.2 Å

Large probe radius: 3 Å

Grid resolution: 0.1 Å

Optimization depth: 4



Figure S33. Cavity volumes of  $(NMe_4)_2[Eu_2(L^R)_4]$ .

## 4. Coordination polyhedra and X-ray crystallography of $(NMe_4)_2[Eu_2(L^R)_4]$



Figure S34. Coordination polyhedra of  $(NMe_4)_2[Eu_2(L^R)_4]$  (Eu1 and Eu2).

Table S1. Shape analysis of  $(NMe_4)_2[Eu_2(L^R)_4]$  using SHAPE 2.1 software.

Helicate	Square antiprism	Biaugmented trigonal prism	Triangular dodecahedron
(NMe <sub>4</sub> ) <sub>2</sub> [Eu <sub>2</sub> (L <sup>R</sup> ) <sub>4</sub> ] (Eu1)	0.683	2.407	1.860
$(NMe_4)_2[Eu_2(L^R)_4]$ (Eu2)	0.337	2.218	1.848

Table S2.	Crystal	data o	f (NMe <sub>4</sub>	$)_2[Eu_2]$	$(L^R)_4$	₄].
			- (	121	(~ )4	t_I '

$(NMe_4)_2[Eu_2(\mathbf{L}^{\mathbf{R}})_4]$	
2305764	
$C_{194}H_{131}Eu_2F_{56}N_3O_{24}$	
4255.93	
Yellow	
triclinic	
P1	
16.0230 (5)	
19.1998 (6)	
25.5570 (8)	
73.256 (3)	
88.743 (3)	
	$(NMe_4)_2[Eu_2(L^R)_4]$ 2305764 $C_{194}H_{131}Eu_2F_{56}N_3O_{24}$ 4255.93 Yellow triclinic P1 16.0230 (5) 19.1998 (6) 25.5570 (8) 73.256 (3) 88.743 (3)

γ (deg)	79.280 (3)	
$V(Å^3)$	7393.4 (4)	
Ζ	1	
$ ho (\mathrm{g} \mathrm{cm}^3)$	0.956	
$\mu (\mathrm{mm}^{-1})$	0.498	
F(000)	2138.0	
$R_{1},\left[I>2\sigma\left(I\right)\right]$	0.0726	
$wR_2$ , $[I > 2\sigma(I)]$	0.1497	
$R_1$ , (all data)	0.1557	
$wR_2$ , (all data)	0.1894	
GOF on $F^2$	0.903	
Flack parameter	0.040 (10)	

### 5. References

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