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# **Supporting Information**

# Solvent and counterion cooperatively induced inversion of stereocenter $\Delta/\Lambda$ and CPL in a mononuclear Eu(III) complex

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## **1. Experimental section**

### 1.1 Materials and measurements

Unless otherwise stated, all chemicals were obtained from commercial sources and used as received. 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>. Electrospray time-of-flight (ESI-TOF) mass spectra were recorded on a Bruker maXis mass spectrometer, and EI-MS for small molecule mass was recorded using an Agilent 5975N. The <sup>1</sup>H NMR, NOESY and <sup>1</sup>H-<sup>1</sup>H DOSY spectra were recorded with a Bruker AVANCE III 400 MHz spectrometer, and the chemical shifts were referenced internally to tetramethylsilane (TMS) or solvents in parts per million (ppm): 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). Abbreviations for signal multiplicity of <sup>1</sup>H NMR spectra are shown as following: s: singlet, d: doublet, t: triplet, m: multiplet.

## **Optical Measurements**

The UV-vis spectra were recorded using a Perkin-Elmer Lambda 25 spectrometer. The CD and CPL spectral data were recorded using an Olis DM245 spectrofluorimeter. The photoluminescence spectra containing the emission, excitation and luminescence lifetime measurements were recorded using an Edinburgh FLS 980 spectrophotometer, and the luminescence quantum yields ( $\Phi$ ) were estimated by an integrating sphere equipped on this instrument. The values reported were the average of three independent determinations for each sample. The  $\Phi$  values were calculated using the following equation:

$$\Phi = \frac{\int L_{emission}}{\int E_{reference} - \int E_{sample}}$$
(1)

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%.

$$k_r = \frac{1}{\tau_{rad}} = A_{MD,0} n^3 \left(\frac{I_{tot}}{I_{MD}}\right)$$
(2)

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<sub>MD,0</sub> (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 (3).

$$\Phi_{Ln} = \frac{k_r}{k_r + k_{nr}} = \frac{\tau_{\text{obs}}}{\tau_{rad}} \qquad (3)$$

 $\tau_{obs}$  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.

$$\Phi_{overall} = \eta_{sen} \Phi_{Ln} \qquad (4)$$

### X-ray crystallography

Crystallographic data of Cs[Eu( $L^L$ )<sub>4</sub>] and NMe<sub>4</sub>[Eu( $L^L$ )<sub>4</sub>] are given in Table S8. Single crystals of suitable dimensions of Cs[Eu( $L^L$ )<sub>4</sub>] and (NMe<sub>4</sub>)[Eu( $L^L$ )<sub>4</sub>] were selected for single-crystal X-ray diffraction analysis. Crystallographic data were collected at 100 K on a Xcalibur, Eos, Gemini diffractometer with Mo K $\alpha$  radiation ( $\lambda$  = 0.71073/0.71076 Å). The structures were solved by direct methods and refined by the full-matrix least-squares method based on  $F^2$  with anisotropic thermal parameters for all non-hydrogen atoms by using the SHELXS (direct methods) and refined by SHELXL 2018 (full matrix least-squares techniques) in the Olex2 package.<sup>1,2</sup> The crystallographic data in CIF format were deposited at the Cambridge Crystallographic Data Centre with CCDC Nos. 2386518 and 2386501. These data are available free of charge from 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 and complexes



Scheme S1. Synthetic routes of ligands  $L^{L/D}$ .

Synthesis of (1R,2S,5R)-(-)-menthol mesylate (L-1) and (1S,2R,5S)-(+)-menthol mesylate (D-1). At room temperature, L/D-menthol (30.00 g, 0.19 mol) and triethylamine (30.80 mL, 0.22 mol) were sequentially dissolved in a flask containing 120 mL of dichloromethane solvent. Methylsulfonyl chloride (16.40 mL, 0.21 mol) was slowly added (20 drops/min) to the solution at 0 °C and stirred for 8 h at the same temperature. After the reaction was completed, the reaction mixture was poured into 100 mL of water, the organic layer was washed repeatedly with water until neutralized, dried with anhydrous sodium sulfate, filtered under reduced pressure, and a yellow oily liquid was obtained after removal of the solvent.

L-1: Yield: 35.70 g, 79%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  4.57–4.50 (td, J = 12.0, 4.0 Hz, 1H), 3.00 (s, 3H), 2.26–2.23 (d, J = 12.0 Hz, 1H), 2.09–2.03 (m, 1H), 1.73–1.66 (m, 2H), 1.48–1.38 (m, 2H), 1.30–1.21 (q, J = 12.0 Hz, 1H), 1.10–1.03 (td, J = 16.0, 4.0 Hz, 1H), 0.93–0.91 (dd, J = 3.2, 4.0 Hz, 6H), 0.88–0.85 (m, 1H), 0.83–0.81 (d, J = 8.0 Hz, 3H) ppm. D-1: Yield: 36.20 g, 80%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  4.57–4.50 (td, J = 8.0, 2.0 Hz, 1H), 3.00 (s, 3H), 2.26–2.23 (d, J = 12.0 Hz, 1H), 2.09–2.02 (m, 1H), 1.73–1.66 (m, 2H), 1.48–1.38 (m, 2H), 1.30–1.22 (q, J = 12.0 Hz, 1H), 1.07–0.99 (td, J = 12.0, 4.0 Hz, 1H), 0.94–0.91 (dd, J = 6.4, 3.3 Hz, 6H), 0.89–0.86 (m, 1H), 0.83–0.82 (d, J = 4.0 Hz, 3H) ppm.

The synthesis of 3,5-bis((1S,2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy-acetophenone (L-2) and 3,5bis((1R,2R,5S)-2-isopropyl-5-methylcyclohexyl)oxy-acetophenone (D-2). Under the protection of N<sub>2</sub> gas, 3,5dihydroxyacetophenone (3.00 g, 0.02 mol) was dissolved in 180 mL of anhydrous DMF, and Cs<sub>2</sub>CO<sub>3</sub> (51.39 g, 0.16 mol) was added to stir for 15 minutes. The solution changed from colorless to yellow-green. The prepared intermediate L/D-1 (46.21 g, 0.20 mol) was added to the above reaction system and refluxed for 12 h. Subsequently, the reaction mixture was cautiously poured into 300 mL ice water, and the pH value of the solution was adjusted to 2–3 with hydrochloric acid (2.0 M), and then extracted with dichloromethane (3 × 30 mL). The organic layer was washed repeatedly with water (4 × 50 mL) and then dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated by vacuum filtration. The yellow oily liquid was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1). L-2: Yield: 2.85 g, 34%. IR (KBr, cm<sup>-1</sup>): 2956, 1690, 1593, 1446, 1153, 1046. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.04 (s, 2H), 6.62 (s, 1H), 4.66 (s, 2H), 2.57 (s, 3H), 2.12–2.09 (d, J = 12.0 Hz, 2H), 1.77–1.74 (m, 4H), 1.70–1.64 (m, 4H), 1.60–1.57 (m, 1H), 1.54–1.51 (m, 1H), 1.08–1.04 (m, 3H), 1.01 (s, 1H), 0.99–0.97 (m, 2H), 0.94–0.92 (d, J = 8.0 Hz, 6H), 0.87–0.85 (d, J = 8.0 Hz, 6H), 0.83–0.82 (d, J = 4.0 Hz, 6H) ppm. ESI-MS (m/z): calculated for C<sub>28</sub>H<sub>44</sub>O<sub>3</sub> [M + Na]<sup>+</sup> 451.3188, found 451.3147. D-2: Yield: 3.10 g, 37%. IR (KBr, cm<sup>-1</sup>): 2960, 1687, 1599, 1450, 1147, 1041. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.04–7.03 (d, J = 4.0 Hz, 2H), 6.62–6.61 (t, J = 2.1 Hz, 1H), 4.66 (s, 2H), 2.57 (s, 3H), 2.12–2.08 (d, J = 16.0 Hz, 2H), 1.80–1.64 (m, 8H), 1.58–1.51 (m, 2H), 1.09–1.02 (m, 3H), 1.01 (s, 1H), 0.99–0.96 (m, 2H), 0.94–0.92 (d, J = 8.0 Hz, 6H), 0.87–0.86 (d, J = 4.0 Hz, 6H), 0.83–0.82 (d, J = 4.0 Hz, 6H) ppm. ESI-MS (m/z): calculated for C<sub>28</sub>H<sub>44</sub>O<sub>3</sub> [M + Na]<sup>+</sup> 451.3188, found 451.3147. D-2.58 (d, J = 4.0 Hz, 2H), 1.09–1.02 (m, 3H), 1.01 (s, 1H), 0.99–0.96 (m, 2H), 0.94–0.92 (d, J = 8.0 Hz, 6H), 0.87–0.86 (d, J = 4.0 Hz, 6H), 0.83–0.82 (d, J = 4.0 Hz, 6H) ppm. ESI-MS (m/z): calculated for C<sub>28</sub>H<sub>44</sub>O<sub>3</sub> [M + Na]<sup>+</sup> 451.3188, found 451.3247.

**Synthesis of ligands L<sup>L</sup> and L<sup>D</sup>.** Sodium methoxide (0.31 g, 5.65 mmol) and ethyl heptafluorobutyrate (1.37 g, 5.65 mmol) were dissolved in 30 mL ethylene glycol dimethyl ether, and then intermediates L/D-2 (1.21 g, 2.82 mmol) was added and stirred at room temperature for 24 h. Afterwards, the reaction solution was poured into 100 mL of water, and the pH of the solution was adjusted to 2–3 with dilute hydrochloric acid (2.0 M). The organic layer was washed repeatedly with water to neutral, vacuum dried to obtain yellow oily liquid.

L<sup>L</sup>: Yield: 1.50 g, 85%. IR (KBr, cm<sup>-1</sup>): 2954, 1583, 1354, 1235, 1164, 1048, 793. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  15.39 (s, 1H), 7.00–6.99 (d, *J* = 4.0 Hz, 2H), 6.67 (s, 1H), 6.54 (s, 2H), 4.67 (s, 2H), 2.11–2.08 (d, *J* = 12.0 Hz, 2H), 1.80–1.76 (m, 4H), 1.70–1.62 (m, 4H), 1.56–1.51 (m, 1H), 1.10–1.04 (m, 4H), 1.01 (s, 1H), 0.98–0.97 (d, *J* = 4.0 Hz, 2H), 0.95–0.93 (d, *J* = 8.0 Hz, 6H), 0.88–0.86 (d, *J* = 8.0 Hz, 6H), 0.85–0.83 (d, *J* = 8.0 Hz, 6H) ppm. ESI-MS (*m*/*z*): calculated for C<sub>32</sub>H<sub>43</sub>F<sub>7</sub>O<sub>4</sub> [M – H]<sup>-</sup> 623.2971, found 623.2968. L<sup>D</sup>: Yield: 1.53 g, 87%. IR (KBr, cm<sup>-1</sup>): 2956, 1582, 1353, 1238, 1163, 1047, 792. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  15.41 (s, 1H), 7.01–7.00 (d, *J* = 4.0 Hz, 2H), 6.67 (s, 1H), 6.53 (s, 2H), 4.66 (s, 2H), 2.11–2.08 (d, *J* = 12.0 Hz, 2H), 1.80–1.75 (m, 4H), 1.70–1.62 (m, 4H), 1.56–1.51 (m, 1H), 1.09–1.03 (m, 4H), 1.02 (s, 1H), 0.98–0.97 (d, *J* = 4.0 Hz, 2H), 0.95–0.93 (d, *J* = 8.0 Hz, 6H), 0.88–0.86 (d, *J* = 8.0 Hz, 2H), 6.81 (s, 1H), 6.79–6.78 (s, 1H), 4.77 (s, 2H), 2.04–2.01 (d, *J* = 12.0 Hz, 2H), 1.78–1.75 (d, *J* = 12.0 Hz, 4H), 1.66–1.59 (m, 4H), 1.56–1.52 (m, 2H), 1.11–1.03 (m, 4H), 0.99–0.95 (m, 2H), 0.93–0.92 (d, *J* = 4.0 Hz, 6H), 0.86–0.85 (d, *J* = 4.0 Hz, 6H), 0.82–0.80 (d, *J* = 8.0 Hz, 6H) ppm. ESI-MS (*m*/*z*): calculated for C<sub>32</sub>H<sub>4</sub>F<sub>7</sub>O<sub>4</sub> [M – H]<sup>-</sup> 623.2971, found 623.2982.

Synthesis of complexes (NMe<sub>4</sub>)[Eu( $L^{L/D}$ )<sub>4</sub>]. The ligands  $L^{L/D}$  (0.30 g, 0.48 mmol) and tetramethylammonium hydroxide aqueous solution (25 % w/w, 0.48 mmol) were dissolved in 80 mL acetonitrile, and then Eu(OTf)<sub>3</sub> (Ln = Eu and Gd; 0.12 mmol) acetonitrile solution was added and refluxed for 12 h. Finally, the solution was dropped into 20 mL 1,4-dioxane and slowly volatilized to obtain a colorless block crystal.

(NMe<sub>4</sub>)[Eu(L<sup>L</sup>)<sub>4</sub>]. Yield: 0.24 g, 73%. Anal. calc. for C<sub>132</sub>H<sub>180</sub>Eu<sub>1</sub>F<sub>28</sub>N<sub>1</sub>O<sub>16</sub> (2720.80): C, 58.27; H, 6.67; N, 0.51. Found: C, 58.26; H, 6.62; N, 0.53. IR (KBr, cm<sup>-1</sup>): 2952, 1627, 1592, 1512, 1345, 1231, 1154, 784. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):  $\delta$  6.21 (s, 1H), 6.01 (s, 2H), 4.45 (s, 2H), 4.21 (s, 1H), 3.09 (s, 3H), 1.75–1.66 (m, 7H), 1.52–1.43 (m, 4H), 0.97–0.94 (m, 5H), 0.89–0.87 (d, *J* = 8.0 Hz, 7H), 0.84–0.83 (d, *J* = 4.0 Hz, 7H), 0.71–0.69 (d, *J* = 8.0 Hz, 6H) ppm. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  16.53 (s, 3H), 6.44–6.40 (m, 3H), 4.73 (s, 2H), 2.68 (s, 1H), 1.88–1.78 (m, 5H), 1.74–1.67 (m, 4H), 1.60–1.57 (d, *J* = 12.0 Hz, 2H), 1.14–1.04 (m, 10H), 0.96 (s, 2H), 0.92–0.87 (m, 13H) ppm. ESI-MS (*m*/*z*): calculated for C<sub>136</sub>H<sub>192</sub>Eu<sub>1</sub>F<sub>28</sub>N<sub>2</sub>O<sub>16</sub> [Eu(L<sup>L</sup>)<sub>4</sub> + 2 (NMe<sub>4</sub>)]<sup>+</sup> 2794.3101, found 2794.3147.

(NMe<sub>4</sub>)[Eu(L<sup>D</sup>)<sub>4</sub>]. Yield: 0.25 g, 76%. Anal. calc. for C<sub>132</sub>H<sub>180</sub>Eu<sub>1</sub>F<sub>28</sub>N<sub>1</sub>O<sub>16</sub> (2720.80): C, 58.27; H, 6.67; N, 0.51. Found: C, 58.22; H, 6.64; N, 0.50. IR (KBr, cm<sup>-1</sup>): 2948, 1627, 1591, 1509, 1346, 1230, 1153, 785. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN): δ 6.21 (s, 1H), 6.01 (s, 2H), 4.45 (s, 2H), 4.22 (s, 1H), 3.09 (s, 3H), 1.75–1.66 (m, 7H), 1.52–1.43 (m, 4H), 0.97-0.94 (m, 5H), 0.89-0.87 (d, J = 8.0 Hz, 7H), 0.84-0.83 (d, J = 4.0 Hz, 7H), 0.71-0.69 (d, J = 8.0 Hz, 6H) ppm. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  16.53 (s, 3H), 6.44-6.40 (m, 3H), 4.73 (s, 2H), 2.68 (s, 1H), 1.88-1.78 (m, 5H), 1.74-1.67 (m, 4H), 1.60-1.53 (m, 2H), 1.14-1.04 (m, 10H), 0.96 (s, 2H), 0.92-0.87 (m, 13H) ppm. ESI-MS (*m/z*): calculated for C<sub>136</sub>H<sub>192</sub>Eu<sub>1</sub>F<sub>28</sub>N<sub>2</sub>O<sub>16</sub> [Eu(L<sup>D</sup>)<sub>4</sub> + 2 (NMe<sub>4</sub>)]<sup>+</sup> 2794.3101, found 2794.3100.

Synthesis of complexes Cs[Ln( $L^{L/D}$ )<sub>4</sub>] [Ln = Eu, Gd and Lu]. Ligands  $L^{L/D}$  (0.30 g, 0.48 mmol) and cesium hydroxide aqueous solution (50 % w/w, 0.48 mmol) were dissolved in 120 mL of acetonitrile until the solution became transparent. Then, an acetonitrile solution of Ln(OTf)<sub>3</sub> (Ln = Eu, Gd and Lu; 0.12 mmol) was added, and the mixture was refluxed with stirring for 14 hours. After the reaction, the reaction solution was poured into water to precipitate, filtered and washed, and vacuum dried to obtain a white solid.

**Cs[Eu(L<sup>L</sup>)<sub>4</sub>].** Yield: 0.24 g, 72%. Anal. calc. for C<sub>128</sub>H<sub>168</sub>Eu<sub>1</sub>Cs<sub>1</sub>F<sub>28</sub>O<sub>16</sub> (2779.56): C, 55.31; H, 6.09. Found: C, 55.26; H, 6.02. IR (KBr, cm<sup>-1</sup>): 2948, 1625, 1591, 1513, 1346, 1234, 1150, 790. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):  $\delta$  6.22 (s, 1H), 6.00 (s, 2H), 4.46 (s, 2H), 4.21 (s, 1H), 1.76–1.67 (m, 7H), 1.50–1.46 (m, 4H), 1.00–0.94 (m, 5H), 0.90–0.88 (d, *J* = 8.0 Hz, 6H), 0.85–0.84 (d, *J* = 4.0 Hz, 8H), 0.71–0.69 (d, *J* = 8.0 Hz, 6H) ppm. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  6.20 (s, 1H), 6.02 (s, 2H), 4.78 (s, 2H), 2.39 (s, 1H), 2.20–2.17 (d, *J* = 12.0 Hz, 3H), 1.75–1.72 (m, 6H), 1.60–1.51 (m, 4H), 1.10–1.08 (m, 2H), 1.02–1.01 (d, *J* = 4.0 Hz, 6H), 0.97–0.96 (d, *J* = 4.0 Hz, 8H), 0.90 (s, 1H), 0.78–0.76 (d, *J* = 8.0 Hz, 6H) ppm. ESI-MS (*m*/*z*): calculated for C<sub>128</sub>H<sub>168</sub>Eu<sub>1</sub>F<sub>28</sub>O<sub>16</sub> [Eu(L<sup>L</sup>)<sub>4</sub>]<sup>-</sup> 2646.1162, found 2646.1158.

**Cs[Eu(L<sup>D</sup>)<sub>4</sub>].** Yield: 0.25 g, 75%. Anal. calc. for C<sub>128</sub>H<sub>168</sub>Eu<sub>1</sub>Cs<sub>1</sub>F<sub>28</sub>O<sub>16</sub> (2779.56): C, 55.31; H, 6.09. Found: C, 55.34; H, 6.04. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):  $\delta$  6.21 (s, 1H), 5.98 (s, 2H), 4.44 (s, 2H), 4.21 (s, 1H), 1.76–1.66 (m, 7H), 1.50–1.47 (m, 4H), 1.00–0.95 (m, 5H), 0.90–0.88 (d, *J* = 8.0 Hz, 6H), 0.85–0.84 (d, *J* = 4.0 Hz, 8H), 0.72–0.70 (d, *J* = 8.0 Hz, 6H) ppm. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  6.20 (s, 1H), 6.02 (s, 2H), 4.78 (s, 2H), 2.39 (s, 1H), 2.20–2.17 (d, *J* = 12.0 Hz, 3H), 1.75–1.72 (m, 6H), 1.60–1.51 (m, 4H), 1.10–1.08 (m, 2H), 1.02–1.01 (d, *J* = 4.0 Hz, 6H), 0.97–0.96 (d, *J* = 4.0 Hz, 8H), 0.90 (s, 1H), 0.78–0.76 (d, *J* = 8.0 Hz, 6H) ppm. ESI-MS (*m*/*z*): calculated for C<sub>128</sub>H<sub>168</sub>Eu<sub>1</sub>F<sub>28</sub>O<sub>16</sub>Cs<sub>2</sub> [Eu(L<sup>D</sup>)<sub>4</sub> + 2Cs]<sup>+</sup> 2911.9192, found 2911.9174.

**Cs**[**Gd**(**L**<sup>L</sup>)<sub>4</sub>]. Yield: 0.27 g, 82%. Anal. calc for  $C_{128}H_{168}Lu_1Cs_1F_{28}O_{16}$  (2784.85): C, 55.21; H, 6.08. Found: C, 55.26; H, 6.04. ESI-MS (*m/z*): calculated for  $C_{128}H_{168}Gd_1Cs_2F_{28}O_{16}$  [Gd(**L**<sup>L</sup>)<sub>4</sub> + 2Cs]<sup>+</sup> 2916.9363, found 2916.9367.

**Cs[Lu(L<sup>L</sup>)<sub>4</sub>].** Yield: 0.24 g, 71%. Anal. calc for  $C_{128}H_{168}Gd_1Cs_1F_{28}O_{16}$  (2802.04): C, 54.68; H, 6.04. Found: C, 54.66; H, 6.08. ESI-MS (*m/z*): calculated for  $C_{128}H_{168}Lu_1F_{28}O_{16}$  [Lu(L<sup>L</sup>)<sub>4</sub>]<sup>-</sup> 2669.1294, found 2669.1284.

# 1.3 Characterization of intermediates and ligands





Figure S1. <sup>1</sup>H NMR spectrum (400 MHz, 298 K, CDCl<sub>3</sub>) of L-1.





Figure S2. <sup>1</sup>H NMR spectrum (400 MHz, 298 K, CDCl<sub>3</sub>) of D-1.



Figure S3. <sup>1</sup>H NMR spectrum (400 MHz, 298 K, CDCl<sub>3</sub>) of L-2.

# $\begin{array}{c} 7.26\\ 6.61\\ 6.67\\ 7.03\\ 6.66\\ 7.03\\$



Figure S4. <sup>1</sup>H NMR spectrum (400 MHz, 298 K, CDCl<sub>3</sub>) of D-2.



Figure S5. ESI-MS spectrum of L-2.



Figure S6. ESI-MS spectrum of D-2.



Chemical shift (ppm)

Figure S7. <sup>1</sup>H NMR spectrum (400 MHz, 298 K, CDCl<sub>3</sub>) of L<sup>L</sup>.

### 15.39 7.000 7.000 7.000 7.000 7.000 7.000 7.000 7.000 1.77 1.761.7



Figure S8. <sup>1</sup>H NMR spectrum (400 MHz, 298 K, CDCl<sub>3</sub>) of L<sup>D</sup>.



Figure S9. <sup>1</sup>H NMR spectrum (400 MHz, 298 K, CD<sub>3</sub>CN) of L<sup>D</sup>.



Figure S10. ESI-MS spectrum of L<sup>L</sup>.



Figure S11. ESI-MS spectrum of L<sup>D</sup>.





Figure S12.<sup>1</sup>H NMR spectrum (400 MHz, 298 K, CDCl<sub>3</sub>) of (NMe<sub>4</sub>)[Eu(L<sup>D</sup>)<sub>4</sub>].



Figure S13.<sup>1</sup>H NMR spectrum (400 MHz, 298 K, CD<sub>3</sub>CN) of (NMe<sub>4</sub>)[Eu(L<sup>D</sup>)<sub>4</sub>].



Figure S14. <sup>1</sup>H DOSY spectrum of  $(NMe_4)[Eu(L^L)_4]$  in CDCl<sub>3</sub>.



Figure S15. NOESY spectrum (400 MHz, 298 K) of (NMe<sub>4</sub>)[Eu(L<sup>L</sup>)<sub>4</sub>] in CDCl<sub>3</sub>.



Figure S16. ESI-MS spectrum of (NMe<sub>4</sub>)[Eu(L<sup>L</sup>)<sub>4</sub>] in CHCl<sub>3</sub>.







Figure S18.<sup>1</sup>H NMR spectrum (400 MHz, 298 K, CDCl<sub>3</sub>) of Cs[Eu(L<sup>D</sup>)<sub>4</sub>].



Figure S19.<sup>1</sup>H NMR spectrum (400 MHz, 298 K, CD<sub>3</sub>CN) of Cs[Eu(L<sup>D</sup>)<sub>4</sub>].



Figure S20. <sup>1</sup>H DOSY spectrum (400 MHz, 298 K, CDCl<sub>3</sub>) of Cs[Eu(L<sup>L</sup>)<sub>4</sub>].



Figure S21. NOESY spectrum (400 MHz, 298 K, CDCl<sub>3</sub>) of Cs[Eu(L<sup>L</sup>)<sub>4</sub>].



Figure S22. ESI-MS spectrum of  $Cs[Eu(L^D)_4]$  in CHCl<sub>3</sub>.



Figure S23. ESI-MS spectrum of  $Cs[Gd(L^L)_4]$  in CHCl<sub>3</sub>.



Figure S24. ESI-MS spectrum of  $Cs[Lu(L^L)_4]$  in  $CH_3CN$ .



Figure S25. <sup>1</sup>H NMR spectrum (400 MHz, 298 K, CD<sub>3</sub>CN) of (NMe<sub>4</sub>)OTf.

# 2. Photophysical properties



Figure S26. UV-visible absorption spectra of  $L^{L}$  ( $c = 1.0 \times 10^{-5}$  M) and (NMe<sub>4</sub>)[Eu( $L^{L}$ )<sub>4</sub>] ( $c = 2.5 \times 10^{-6}$  M) in CHCl<sub>3</sub>.



Figure S27. UV-visible absorption spectra of  $L^{L}$  ( $c = 1.0 \times 10^{-5}$  M) and (NMe<sub>4</sub>)[Eu( $L^{L}$ )<sub>4</sub>] ( $c = 2.5 \times 10^{-6}$  M) in CH<sub>3</sub>CN.



Figure S28. Excitation spectra of (NMe<sub>4</sub>)[Eu( $L^{L}$ )<sub>4</sub>] in CHCl<sub>3</sub> (blue) and CH<sub>3</sub>CN (red) ( $c = 1.0 \times 10^{-5}$  M).



Figure S29. CD spectra of (NMe<sub>4</sub>)[Eu( $L^L$ )<sub>4</sub>] and (NMe<sub>4</sub>)[Eu( $L^D$ )<sub>4</sub>] ( $c = 1.0 \times 10^{-4}$  M) in CHCl<sub>3</sub> (blue) and CH<sub>3</sub>CN (red).



Figure S30. Emission spectra of (NMe<sub>4</sub>)[Eu( $L^{L}$ )<sub>4</sub>] in CHCl<sub>3</sub> (blue) and CH<sub>3</sub>CN (red) ( $c = 1.0 \times 10^{-5}$  M).



Figure S31. CPL spectra of (NMe<sub>4</sub>)[Eu( $L^{L}$ )<sub>4</sub>] and (NMe<sub>4</sub>)[Eu( $L^{D}$ )<sub>4</sub>] ( $c = 1.0 \times 10^{-5}$  M) in CHCl<sub>3</sub> (blue) and CH<sub>3</sub>CN (red).



Figure S32. Luminescence decay curve of  $(NMe_4)[Eu(L^L)_4]$  in CHCl<sub>3</sub> ( $c = 1.0 \times 10^{-5}$  M) monitored at 612 nm.



Figure S33. Luminescence decay curve of (NMe<sub>4</sub>)[Eu( $L^{D}$ )<sub>4</sub>] in CHCl<sub>3</sub> ( $c = 1.0 \times 10^{-5}$  M) monitored at 612 nm.



Figure S34. Luminescence decay curve of  $(NMe_4)[Eu(L^L)_4]$  in CH<sub>3</sub>CN ( $c = 1.0 \times 10^{-5}$  M) monitored at 612 nm.



Figure S35. Luminescence decay curve of  $(NMe_4)[Eu(L^D)_4]$  in CH<sub>3</sub>CN ( $c = 1.0 \times 10^{-5}$  M) monitored at 612 nm.



Figure S36. The screenshots of the luminescence quantum yields of  $(NMe_4)[Eu(L^L)_4]$  (top) and  $(NMe_4)[Eu(L^D)_4]$  (bottom) in CHCl<sub>3</sub>.



Figure S37. The screenshots of the luminescence quantum yields of  $(NMe_4)[Eu(L^L)_4]$  (top) and  $(NMe_4)[Eu(L^D)_4]$  (bottom) in CH<sub>3</sub>CN.



Figure S38. UV-visible absorption spectra of  $L^{L}$  ( $c = 1.0 \times 10^{-5}$  M) and Cs[Eu( $L^{L}$ )<sub>4</sub>] ( $c = 2.5 \times 10^{-6}$  M) in CHCl<sub>3</sub>.



Figure S39. UV-visible absorption spectra of  $L^{L}$  ( $c = 1.0 \times 10^{-5}$  M) and Cs[Eu( $L^{L}$ )<sub>4</sub>] ( $c = 2.5 \times 10^{-6}$  M) in CH<sub>3</sub>CN.



Figure S40. CD spectra of Cs[Eu( $L^{L}$ )<sub>4</sub>] and Cs[Eu( $L^{D}$ )<sub>4</sub>] ( $c = 1.0 \times 10^{-4}$  M) in CHCl<sub>3</sub>.



Figure S41. CD spectra of Cs[Eu( $L^{L}$ )<sub>4</sub>] and Cs[Eu( $L^{D}$ )<sub>4</sub>] ( $c = 1.0 \times 10^{-4}$  M) in CH<sub>3</sub>CN.



Figure S42. Excitation spectrum of Cs[Eu( $L^L$ )<sub>4</sub>] ( $c = 1.0 \times 10^{-5}$  M) in CHCl<sub>3</sub>.



Figure S43. Excitation spectrum of Cs[Eu( $L^L$ )<sub>4</sub>] ( $c = 1.0 \times 10^{-5}$  M) in CH<sub>3</sub>CN.



Figure S44. Emission spectra of Cs[Eu( $L^L$ )<sub>4</sub>] in CHCl<sub>3</sub> (blue) and CH<sub>3</sub>CN (red) ( $c = 1.0 \times 10^{-5}$  M).



Figure S45. CPL spectra of Cs[Eu( $L^{L}$ )<sub>4</sub>] and Cs[Eu( $L^{D}$ )<sub>4</sub>] ( $c = 1.0 \times 10^{-5}$  M) in CHCl<sub>3</sub>.



Figure S46. CPL spectra of Cs[Eu( $L^{L}$ )<sub>4</sub>] and Cs[Eu( $L^{D}$ )<sub>4</sub>] ( $c = 1.0 \times 10^{-5}$  M) in CH<sub>3</sub>CN.

![](_page_28_Figure_2.jpeg)

Figure S47. Phosphorescence emission spectrum of  $Cs[Gd(L^L)_4]$  in THF.

![](_page_29_Figure_0.jpeg)

Figure S48. Luminescence decay curve of Cs[Eu( $L^L$ )<sub>4</sub>] in CHCl<sub>3</sub> ( $c = 1.0 \times 10^{-5}$  M) monitored at 612 nm.

![](_page_29_Figure_2.jpeg)

Figure S49. Luminescence decay curve of Cs[Eu( $L^{D}$ )<sub>4</sub>] in CHCl<sub>3</sub> ( $c = 1.0 \times 10^{-5}$  M) monitored at 612 nm.

![](_page_30_Figure_0.jpeg)

Figure S50. Luminescence decay curve of Cs[Eu( $L^L$ )<sub>4</sub>] in CH<sub>3</sub>CN ( $c = 1.0 \times 10^{-5}$  M) monitored at 612 nm.

![](_page_30_Figure_2.jpeg)

Figure S51. Luminescence decay curve of Cs[Eu( $L^{D}$ )<sub>4</sub>] in CH<sub>3</sub>CN ( $c = 1.0 \times 10^{-5}$  M) monitored at 612 nm.

![](_page_31_Figure_0.jpeg)

Figure S52. The screenshots of the luminescence quantum yields of  $Cs[Eu(L^L)_4]$  (top) and  $Cs[Eu(L^D)_4]$  (bottom) in CHCl<sub>3</sub>.

![](_page_31_Figure_2.jpeg)

Figure S53. The screenshots of the luminescence quantum yields of  $Cs[Eu(L^L)_4]$  (top) and  $Cs[Eu(L^D)_4]$  (bottom) in  $CH_3CN$ .

![](_page_32_Figure_0.jpeg)

Figure S54. Variations of <sup>1</sup>H NMR (400 MHz, 298 K) spectra of  $Cs[Eu(L^L)_4]$  with increasing of CDCl<sub>3</sub> content in  $CD_3CN$ .

![](_page_32_Figure_2.jpeg)

Figure S55. Variations of <sup>1</sup>H NMR spectra of  $Cs[Lu(L^L)_4]$  with increasing of CDCl<sub>3</sub> content in CD<sub>3</sub>CN.

**Table S1.** Radiative (k<sub>r</sub>) and nonradiative (k<sub>nr</sub>) decay rates, observed luminescence lifetime of Eu<sup>3+</sup> ( $\tau_{obs}$ ), intrinsic quantum yield ( $\Phi_{Eu}$ ), sensitization efficiency ( $\eta_{sens}$ ) and quantum yield of Eu<sup>3+</sup> ( $\Phi_{overall}$ ). Error in  $\tau_{obs}$ : ±0.05 ms; 10% relative error in the other values;  $\lambda_{ex} = 347$  nm. g<sub>lum</sub> values for  ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$  of Eu<sup>3+</sup> ion. (CHCl<sub>3</sub> and CH<sub>3</sub>CN)

Complexes	k <sub>r</sub>	k <sub>nr</sub>	$ au_{ m obs}$	$arPsi_{ ext{Ln}}$	$\Phi_{ m Ln}$ $\eta_{ m sens}$	$arPsi_{ m overall}$	$g_{lum} {}^{5}D_{0} \rightarrow {}^{7}F_{J} (J = 0, 1, 2, 3, 4)$					
Complexes	$(s^{-1})$	$(s^{-1})$	(µs)	(%)	(%)	(%)	J = 0	J = 1	J = 2	J = 3	J = 4	
$(NMe_4)[Eu(L^L)_4](CHCl_3)$	781	1073	539	42	85	36	+0.008	+0.197	-0.009	+0.025	-0.005	
$(NMe_4)[Eu(L^D)_4](CHCl_3)$	781	1073	539	42	86	36	-0.008	-0.191	+0.008	-0.028	+0.002	
$(NMe_4)[Eu(L^L)_4](CH_3CN)$	886	952	545	48	92	44	+0.008	+0.142	-0.008	+0.026	-0.008	
$(NMe_4)[Eu(L^D)_4](CH_3CN)$	886	948	545	48	90	43	-0.007	-0.136	+0.007	-0.022	+0.007	

**Table S2.** Radiative (k<sub>r</sub>) and nonradiative (k<sub>nr</sub>) decay rates, observed luminescence lifetime of Eu<sup>3+</sup> ( $\tau_{obs}$ ), intrinsic quantum yield ( $\Phi_{Eu}$ ), sensitization efficiency ( $\eta_{sens}$ ) and quantum yield of Eu<sup>3+</sup> ( $\Phi_{overall}$ ). Error in  $\tau_{obs}$ : ±0.05 ms; 10% relative error in the other values;  $\lambda_{ex} = 351$  nm (CHCl<sub>3</sub>),  $\lambda_{ex} = 347$  nm (CH<sub>3</sub>CN). g<sub>lum</sub> values for <sup>5</sup>D<sub>0</sub>  $\rightarrow$  <sup>7</sup>F<sub>J</sub> of Eu<sup>3+</sup> ion. (CHCl<sub>3</sub> and CH<sub>3</sub>CN)

Comulayor	$k_{\rm r}$ $k_{\rm nr}$		$ au_{ m r}$ $ au_{ m obs}$ $ au_{ m L}$		$\eta_{\rm sens}$	$arPsi_{ m overall}$	$g_{lum} {}^{5}D_{0} \rightarrow {}^{7}F_{J} (J = 0, 1, 2, 3, 4)$					
Complexes	$(s^{-1})$	$(s^{-1})$	(µs)	(%)	(%) (%)	(%)	(%)	(%)	J = 0	J = 1	J = 3	J = 4
$Cs[Eu(L^L)_4]$ (CHCl <sub>3</sub> )	717	798	660	47	76	36	+0.005	-0.125	+0.006	-0.020	+0.009	
$Cs[Eu(L^D)_4]$ (CHCl <sub>3</sub> )	721	790	654	47	76	36	-0.008	+0.122	-0.007	+0.023	-0.007	
Cs[Eu(L <sup>L</sup> ) <sub>4</sub> ] (CH <sub>3</sub> CN)	882	942	547	48	92	45	+0.007	+0.147	-0.006	+0.019	-0.003	
$Cs[Eu(L^D)_4]$ (CH <sub>3</sub> CN)	877	947	548	48	92	44	-0.006	-0.143	+0.005	-0.016	+0.005	

# 3. Calculation of Cs[Eu(L<sup>L</sup>)<sub>4</sub>]

# 3.1 DFT calculation of Cs[Eu(L<sup>L</sup>)<sub>4</sub>]

### **Calculation Details**

All DFT calculations are performed using the Gaussian16 Revision C.01 program package.<sup>3</sup> Geometry optimizations under different solvents were conducted by the DFT calculations with PBE0-D3(BJ) functional.<sup>4</sup> Relativistic effective core potential SDD was used for the europium atom, and 6-31G\* was adopted for all the other atoms.<sup>5,6</sup> The solvent effects of acetonitrile and chloroform solvent were considered by SMD solvation model.<sup>7</sup> All the optimizations were confirmed to be stationary points by the absence of imaginary frequencies. Different from geometry optimizations, for calculating more accurate energy, the basis set of the calculated energy is increased from 6-31G\* to  $6-311G^{**}/6-311+G^{**}$  ( $\beta$ -diketone part).<sup>8</sup> The stable = opt command ensures that the complexes converges to a stable wavefunction.

![](_page_34_Figure_4.jpeg)

Figure S56. DFT-optimized structures of  $\Delta$ -[Eu(L<sup>L</sup>)<sub>4</sub>]<sup>-</sup> (a) and (b)  $\Lambda$ -[Eu(L<sup>L</sup>)<sub>4</sub>]<sup>-</sup>.

![](_page_34_Figure_6.jpeg)

Figure S57. DFT-optimized structures of  $\Delta$ -Cs[Eu(L<sup>L</sup>)<sub>4</sub>] (a) and (b)  $\Lambda$ -Cs[Eu(L<sup>L</sup>)<sub>4</sub>].

The ratio of different configurations were calculated based on Boltzmann distribution at 298 K.<sup>9,10</sup> The relative Gibbs free energies ( $\Delta G$ ) and Boltzmann weighting ( $P_i$ %) are shown in Table S3. [Eu( $\mathbf{L}^L$ )<sub>4</sub>]<sup>-</sup> includes two configuration ( $\Delta$ -[Eu( $\mathbf{L}^L$ )<sub>4</sub>]<sup>-</sup>,  $\Lambda$ -[Eu( $\mathbf{L}^L$ )<sub>4</sub>]<sup>-</sup>); Cs[Eu( $\mathbf{L}^L$ )<sub>4</sub>] includes two configuration ( $\Delta$ -Cs[Eu( $\mathbf{L}^L$ )<sub>4</sub>],  $\Lambda$ -Cs[Eu( $\mathbf{L}^L$ )<sub>4</sub>]).

**Table S3.** Relative Gibbs free energies ( $\Delta G$ ) and Boltzmann weighting ( $P_i$  %) for different configurations of

	complexes	
Configuration	$\Delta G$ (kJ/mol)	$P_{i}\%$
$\Delta$ -[Eu(L <sup>L</sup> ) <sub>4</sub> ] <sup>-</sup>	0.00	98.70
$\Lambda$ -[Eu(L <sup>L</sup> ) <sub>4</sub> ] <sup>-</sup>	10.73	1.30
$\Delta$ -Cs[Eu(L <sup>L</sup> ) <sub>4</sub> ]	7.18	5.23
$\Lambda$ -Cs[Eu(L <sup>L</sup> )4]	0.00	94.77

# 3.2 Independent gradient model (IGM) analysis of Cs[Eu(L<sup>L</sup>)<sub>4</sub>]

Independent gradient model (IGM) analysis carried out with the Multiwfn 3.8 program was employed to investigate the intermolecular weak interactions and visualized with VMD 1.9.39.<sup>11</sup> To quantitatively investigate and visualize the supramolecular interaction in compounds  $\Delta/\Lambda$ -Cs[Eu(L<sup>L</sup>)<sub>4</sub>], Hirshfeld surface analysis was performed utilizing Multiwfn 3.8 program.

![](_page_35_Figure_5.jpeg)

Figure S59. IGM analysis of between a ligand and other components in complexes  $\Delta$ -Cs[Eu(L<sup>L</sup>)<sub>4</sub>] (a) and  $\Lambda$ -Cs[Eu(L<sup>L</sup>)<sub>4</sub>] (b) ( $\delta g_{inter} = 0.009$ ).

# 3.3 Hirshfeld surfaces of Cs[Eu(L<sup>L</sup>)<sub>4</sub>]

The Hirshfeld surface highlights the supramolecular interactions between  $Cs^+$  and  $[Eu(L^L)_4]^-$  and between adjacent ligands. For the  $Cs^+$ , Hirshfeld surface analysis showed that the intermolecular force was dominated by  $Cs\cdots$ H contacts, which accounted for 34.0% and 41.2% in  $\Delta$ -Cs $[Eu(L^L)_4]$  and  $\Lambda$ -Cs $[Eu(L^L)_4]$ , respectively. Subsequently, the  $Cs\cdots$ F interactions (i.e.,  $Cs\cdots$ F contacts) emerge as the second prominent interactions, comprising 35.0% and 36.2 % for  $\Delta$ -Cs $[Eu(L^L)_4]$  and  $\Lambda$ -Cs $[Eu(L^L)_4]$ . The Cs $\cdots$ O interaction (i.e., Cs $\cdots$ O contacts) accounts for 16.9% and 17.5%. (Figure S61).

In addition, taking one ligand as a representative example, the Hirshfeld surface and fingerprint plots between adjacent ligands of  $\Delta/\Lambda$ -Cs[Eu(L<sup>L</sup>)<sub>4</sub>] are shown in Figure S62. The contribution percentage of the average interaction between the adjacent ligands are shown in Figure S62e, 62f. Firstly, in  $\Lambda$ -Cs[Eu(L<sup>L</sup>)<sub>4</sub>], the interactions between the ligands are dominated by the inter ligand H···H contacts, accounting for 46.5%. Subsequently, H···F contacts emerge as the second prominent interactions, accounting for 36.6%. There are twelve different contacts exist in  $\Lambda$ -Cs[Eu(L<sup>L</sup>)<sub>4</sub>] (H···H 46.5%, H···F 36.6%, F···F 4.5%, C···H 4.2%, O···O 2.6%, Cs···F 1.1%, C···F 1.8%, O···Eu 1.0%, O···F 1.0%, H···O 0.3%, Cs···O 0.3%, C···O 0.1%). There are also twelve different contacts exist in  $\Delta$ -Cs[Eu(L<sup>L</sup>)<sub>4</sub>] (H···H 41.8%, H···F 39.4%, F···F 4.7%, C···H 5.0%, O···O 2.4%, Cs···F 1.8%, C···F 1.6%, O···Eu 1.1%, O···F 0.8%, H···O 0.8%, Cs···O 0.3%).

Each dot in this fingerprint map is a vertex on a Hirshfeld surface and is colored according to the density of the distribution of the dots on the fingerprint map, with denser areas colored yellow and sparser areas colored purple.

![](_page_36_Figure_4.jpeg)

Figure S60. Color-coded sign scale bar. (a) Hirshfeld surface. (b) finger-print map.

![](_page_37_Figure_0.jpeg)

**Figure S61.** (a, b) Hirshfeld surfaces of  $\Delta$ -Cs[Eu(L<sup>L</sup>)<sub>4</sub>] and  $\Lambda$ -Cs[Eu(L<sup>L</sup>)<sub>4</sub>], with Cs<sup>+</sup> as the central molecule. (c, d) 2D fingerprint plots for  $\Delta$ -Cs[Eu(L<sup>L</sup>)<sub>4</sub>] and  $\Lambda$ -Cs[Eu(L<sup>L</sup>)<sub>4</sub>]. (e, f) Percentage contributions of the average interactions for  $\Delta$ -Cs[Eu(L<sup>L</sup>)<sub>4</sub>] and  $\Lambda$ -Cs[Eu(L<sup>L</sup>)<sub>4</sub>]. (cs<sup>---</sup>H 34.0%, Cs<sup>---</sup>F 35.0%, Cs<sup>---</sup>C 14.1%); for  $\Lambda$ -Cs[Eu(L<sup>L</sup>)<sub>4</sub>], (Cs<sup>---</sup>H 41.2%, Cs<sup>---</sup>F 36.2%, Cs<sup>---</sup>C 5.1%), not distinguish inside and outside elements.

![](_page_38_Figure_0.jpeg)

**Figure S62.** (a, b) Hirshfeld surfaces of  $\Delta$ -Cs[Eu(L<sup>L</sup>)<sub>4</sub>] and  $\Lambda$ -Cs[Eu(L<sup>L</sup>)<sub>4</sub>], with a ligand as the central molecule. (c, d) 2D fingerprint plots for  $\Delta$ -Cs[Eu(L<sup>L</sup>)<sub>4</sub>] and  $\Lambda$ -Cs[Eu(L<sup>L</sup>)<sub>4</sub>]. (e, f) Percentage contributions of the average interactions for  $\Delta$ -Cs[Eu(L<sup>L</sup>)<sub>4</sub>] and  $\Lambda$ -Cs[Eu(L<sup>L</sup>)<sub>4</sub>]. For  $\Delta$ -Cs[Eu(L<sup>L</sup>)<sub>4</sub>], (H···H 41.8%, H···F 39.4%, C···H 5.0%, O···H 0.8%, other 13.0%); for  $\Lambda$ -Cs[Eu(L<sup>L</sup>)<sub>4</sub>], (H···H 46.5%, H···F 36.6%, C···H 4.3%, O···H 0.3%, other 12.3%), not distinguish inside and outside elements.

# 4. Exchange constants determination

NMR titrations were conducted on a Bruker Avance III 400 MHz spectrometer and the chemical shifts are referenced internally to tetramethylsilane (TMS) or solvents in parts per million (ppm). In all cases, NMR titrations were performed maintaining the concentration (usually around  $4.0 \times 10^{-3}$  M) of the host constant in CD<sub>3</sub>CN/CDCl<sub>3</sub> (1:9, v/v).

In an NMR tube, CsTFPB (10 eq) was dissolved in CD<sub>3</sub>CN/CDCl<sub>3</sub> (1:9, v/v) solution and then by addition of various equivalents of Cs<sup>+</sup> salt into (NMe<sub>4</sub>)[Eu( $L^L$ )<sub>4</sub>] in CD<sub>3</sub>CN/CDCl<sub>3</sub> (1:9, v/v), delivered accurately using 10 µL pipette. The formation of the host-guest species could be easily followed looking at the chemical shift for proton (Hb) of the benzene ring.

The data were analysed with the Bindfit web-based app at Supramolecular.org - Binding Constant Calculators | Supramolecular. <sup>12-15</sup>

![](_page_39_Figure_4.jpeg)

**Figure S63.** Changes of <sup>1</sup>H NMR spectral with adding various equivalents of CsTFPB to the solution of (NMe<sub>4</sub>)[Eu(L<sup>L</sup>)<sub>4</sub>] (400 MHz, 298 K, CD<sub>3</sub>CN/CDCl<sub>3</sub> = 1:9).

	[H]	[G]	d (ppm)
1	4.000E-03	0.000E+00	6.2460
2	4.000E-03	8.000E-04	6.2197
3	4.000E-03	2.000E-03	6.1898
4	4.000E-03	2.800E-03	6.1550
5	4.000E-03	3.600E-03	6.1425
6	4.000E-03	4.400E-03	6.1229
7	4.000E-03	6.000E-03	6.1137
8	4.000E-03	6.800E-03	6.1015
9	4.000E-03	8.000E-03	6.0774
10	4.000E-03	1.200E-02	6.0578
711	4.000E-03	1.600E-02	6.0336
12	4.000E-03	1.800E-02	6.0311
13	4.000E-03	2.000E-02	6.0272
14	4.000E-03	2.400E-02	6.0218

Table S4. Titration dates for (NMe<sub>4</sub>)[Eu(L<sup>L</sup>)<sub>4</sub>]

![](_page_40_Figure_2.jpeg)

Figure S64. The job plot and residuals of (NMe<sub>4</sub>)[Eu(L<sup>L</sup>)<sub>4</sub>] with Cs<sup>+</sup> salt in CD<sub>3</sub>CN/CDCl<sub>3</sub> (1:9, v/v, 4mM)

We fit the data to this model:

$$y = y_0 + \frac{A}{w\sqrt{\pi/2}} e^{-2\frac{(x-x_c)^2}{w^2}}$$

 Table S5. The nonlinear regression presents the best-fit value for each parameter, along with a standard error and 95% confidence interval

F	Parameter			Best-fi	t value		Standard E	rror		95%	CI		
	<i>Y</i> 0			-0.04	1309		0.00507		-0.05	414 to	-0.032	04	
	$x_{ m c}$			0.45	342		0.01003		0.43	157 to	0.4752	28	
	A			0.10	009		0.00606		0.08	689 to	0.1133	0	
	W			0.79	379		(constant	)					
-7.26							-3.20	-1.94	1.94	1.78			
			a    -N	<u>+</u>									
							a	CD		)	^		
'.5 7.0	6.5	6.0	5.5	5.0	4.5 Che	4.0 mical :	3.5 3.0 shift (ppm)	2.5	2.0	1.5	1.0	0.5	0

![](_page_41_Figure_4.jpeg)

7.63
7.26
7.26
7.26
7.195
1.95
1.81

![](_page_42_Figure_1.jpeg)

Figure S66. <sup>1</sup>H NMR spectrum of CsTFPB (400 MHz, 298 K, CD<sub>3</sub>CN/CDCl<sub>3</sub> = 1: 9).

![](_page_42_Figure_3.jpeg)

Figure S67. Changes of CD spectral with adding various equivalents of  $Cs^+$  ( $c = 7.0 \times 10^{-3}$  M) to the solution of  $(NMe_4)[Eu(L^L)_4]$  ( $c = 1.0 \times 10^{-4}$  M) in CH<sub>3</sub>CN/CHCl<sub>3</sub> (1:9, v/v).

![](_page_43_Figure_0.jpeg)

Figure S68. Changes of CPL spectral with adding various equivalents of  $Cs^+$  ( $c = 1.5 \times 10^{-3}$  M) to the solution of (NMe<sub>4</sub>)[Eu(L<sup>L</sup>)<sub>4</sub>] ( $c = 1.0 \times 10^{-5}$  M) in CH<sub>3</sub>CN/CHCl<sub>3</sub> (1:9, v/v).

![](_page_43_Figure_2.jpeg)

Figure S69. Changes of  $g_{lum}$  value with adding various equivalents of CsTFPB ( $c = 1.5 \times 10^{-3}$  M) to the solution of  $(NMe_4)[Eu(L^L)_4]$  ( $c = 1.0 \times 10^{-5}$  M) in CH<sub>3</sub>CN/CHCl<sub>3</sub> (1:9, v/v).

![](_page_44_Figure_0.jpeg)

Figure S70. Changes of emission spectral with adding various equivalents of  $Cs^+$  ( $c = 1.5 \times 10^{-3}$  M) to the solution of  $(NMe_4)[Eu(L^L)_4]$  ( $c = 1.0 \times 10^{-5}$  M) in CH<sub>3</sub>CN/CHCl<sub>3</sub> (1:9, v/v).

# 5. X-ray Crystallography

![](_page_45_Picture_1.jpeg)

Figure S71. Coordination polyhedra of  $\Lambda$ -(NMe<sub>4</sub>)[Eu(L<sup>L</sup>)<sub>4</sub>].

Table S6. Shape analysis of (NMe<sub>4</sub>)[Eu(L<sup>L</sup>)<sub>4</sub>] using SHAPE 2.1 software.

Complexes	Square antiprism	Biaugmented trigonal prism	Triangular dodecahedron
$\Lambda$ -(NMe <sub>4</sub> )[Eu(L <sup>L</sup> ) <sub>4</sub> ]	0.334	1.995	1.477

![](_page_45_Figure_5.jpeg)

Figure S72. Coordination polyhedra of (a)  $\Delta$ -Cs[Eu(L<sup>L</sup>)<sub>4</sub>] (Eu1); (b)  $\Lambda$ -Cs[Eu(L<sup>L</sup>)<sub>4</sub>] (Eu2).

Complexes	Triangular dodecahedron	Biaugmented trigonal prism	Square antiprism
$\Delta$ -Cs[Eu(L <sup>L</sup> ) <sub>4</sub> ] (Eu1)	0.354	2.232	2.768
$\Lambda$ -Cs[Eu(L <sup>L</sup> ) <sub>4</sub> ] (Eu2)	0.143	2.201	2.397

	$Cs[Eu(L^L)_4]$	$(NMe_4)[Eu(L^L)_4]$
CCDC Numbers	2386518	2386501
Empirical formula	C258H344Cs2Eu2F56O34	$C_{132}H_{180}EuF_{28}NO_{16}$
Formula weight	5623.05	2720.75
Color	Colorless	Colorless
Crystal system	monoclinic	Orthorhombic
Space group	<i>C</i> 2	$P2_{1}2_{1}2$
a (Å)	39.133(3)	15.8406(17)
<i>b</i> (Å)	13.2872(11)	37.007(4)
<i>c</i> (Å)	27.8939(19)	13.8562(13)
$\alpha$ (deg)	90	90
$\beta$ (deg)	94.471(3)	90
γ (deg)	90	90
$V(Å^3)$	14459.9(19)	8122.7(15)
Ζ	2	2
$ ho_{calc}g/cm^3$	1.291	1.181
$\mu$ (mm <sup>-1</sup> )	0.774	0.474
F (000)	5808.0	3033.0
$R_{1}, [I > 2\sigma(I)]$	0.0803	0.0543
$wR_2, [I > 2\sigma(I)]$	0.2186	0.1448
$R_1$ , (all data)	0.0976	0.0689
wR <sub>2</sub> , (all data)	0.2357	0.1560
GOF on $F^2$	1.110	1.042

Table S8. Crystal datas of complexes Cs[Eu( $L^L$ )<sub>4</sub>] and (NMe<sub>4</sub>)[Eu( $L^L$ )<sub>4</sub>]

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