Supporting Information for

Stereocontrolled Self-Assembly and Photochromic Transformation of Lanthanide Supramolecular Helicates

Li-Xuan Cai, Liang-Liang Yan, Shao-Chuan Li, Li-Peng Zhou and Qing-Fu Sun*

1 State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, People’s Republic of China
Corresponding Email: qfsun@fjirsm.ac.cn

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3. References
1. Synthetic Procedures

**Synthesis of 4,4’-(4,4’-(perfluorocyclopent-1-ene-1,2-diyl)bis(5-methylthiophene-4,2-diyl))bis(ethyne-2,1-diyl))dianiline (2)**

A mixture of perfluoro-1,2-bis(2-iodo-5-methyl-4-yl)cyclopentene$^\text{S1}$ (620.1 mg, 1 mmol), 4-ethenylbenzenamine (351.4 mg, 3 mmol), CuI (28.6 mg, 0.15 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (69.2 mg, 0.1 mmol) and degassed triethylamine (25 mL) was combined in an oven-dried Schlenk tube and stirred at 90 °C for 20 h. After removal of NEt$_3$ by distillation, CH$_2$Cl$_2$ was added and the solution was washed with water and brine, dried over anhydrous MgSO$_4$ and concentrated in vacuo. The crude product was purified by column chromatography (silica) using CH$_2$Cl$_2$/petroleum ether (1:1) as eluents to give a green solid (239.4 mg, 0.4 mmol) in 40% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.31 (d, $J$ = 8.6 Hz, 4H), 7.18 (s, 2H), 6.63 (d, $J$ = 8.6 Hz, 4H), 3.86 (s, 4H), 1.91 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 147.08 (s), 142.63 (s), 133.17 (s), 130.57 (s), 124.74 (s), 122.69 (s), 114.82 (s), 111.81 (s), 94.82 (s), 79.45 (s), 14.61 (s). HR-MS (ESI) calcd for C$_{31}$H$_{20}$F$_6$N$_2$S$_2$ [M+H]$^{+}$: 599.1045, found 599.1040.

2. Supplemental Figures

Figure S 1 $^1$H NMR spectrum of 2 (CDCl$_3$, 400 MHz, 293 K).
Figure S 2 $^{13}$C NMR spectrum of 2 (CDCl$_3$, 100 MHz, 293 K).

Figure S 3 $^1$H NMR spectrum of o-L$^{ER}$ (DMSO-$_d_6$, 400 MHz, 293 K).
Figure S 4 $^1$H-$^1$H COSY NMR spectrum of $o$-L$^\text{RR}$ (DMSO-$d_6$, 400MHz, 293K).

Figure S 5 $^{13}$C NMR spectrum of $o$-L$^\text{RR}$ (DMSO-$d_6$, 100 MHz, 293 K).
Figure S 6 ESI-TOF-MS spectrum for ligand o-L^RR.
Figure S 7 $^1$H NMR spectrum of [Eu$_2$(o-L$^{RR}$)$_3$](ClO$_4$)$_6$ (CD$_3$CN, 400 MHz, 293 K).

Figure S 8 $^1$H NMR spectrum of [Eu$_2$(o-L$^{SS}$)$_3$](ClO$_4$)$_6$ (CD$_3$CN, 400 MHz, 293 K).
Figure S 9 $^1$H-$^1$H COSY NMR spectrum of $[\text{Eu}_2(\text{o-L}^{SS})_2](\text{ClO}_4)_6$ (CD$_3$CN, 400 MHz, 293 K).

Figure S 10 $^1$H NMR (400 MHz, CD$_3$CN, 298 K) titration spectra of titrating $\text{o-L}^{SS}$ (3.3 mg/mL) with Eu(ClO$_4$)$_3$ with M/L ratio varying from 0 to 1.5.
Figure S 11 UV-Vis titration spectra for ligand $o$-$L^{RR}$ ($3.0 \times 10^{-2}$ M; 2:3 v/v of CHCl$_3$/CH$_3$CN) and Eu(ClO$_4$)$_3$ with M/L ratio varying from 0 to 1.2.

Figure S 12 $^1$H NMR (400 MHz, CD$_3$CN, 298 K) dilution spectra of the complex Eu$_2$(o-$L^{RR}$)$_3$(ClO$_4$)$_6$ at different ligand concentration [o-$L^{RR}$] = 10 mg/mL (a), 5 mg/mL (b) and 1 mg/mL (c).
Simulated molecular models of four helicates based on $\alpha$-$L^{RR}$ ligands with the same metal centered chirality ($\Lambda\Lambda$). The molecular mechanic modeling by Materials Studio program was employed to optimize the structures. First, we imported the crystal structure with the same chiral-inducing group and metal stereogenic center into the program and then changed the center linkers to our DTE units. We kept the periphery metal stereogenic center as rigid Motion Groups and only central DTE units are geometrically optimized. Based on the energy differences between the final optimized structure for the four possible conformational isomers as shown above, the M-(\Lambda\Lambda)-(\text{pro}-S, S)-\text{Eu}_2(\alpha-L^{RR})_3 isomer was obtained as the most reasonable structure.
Figure S 14 $^1$H NMR enantiomeric differentiation experiments for the enantiomers of $(\Lambda\Lambda)$-Eu$_2$(o-$L^{SS}$)$_3$, and $(\Delta\Delta)$-Eu$_2$(o-$L^{RR}$)$_3$ by addition of 3 equiv. chiral resolving agent $\Delta$-TRISPHAT.

Figure S 15 The photochromic process of the ligand $L^{RR}$. 
Figure S 16 $^1$H NMR spectrum of c-L$^{RR}$ (CDCl$_3$, 400 MHz, 293 K).

Figure S 17 $^1$H NMR spectrum of photochromic process of ligands (CDCl$_3$, 400 MHz, 293 K).
Figure S 18 The photochromic process of the helicate [Eu₂(β-L_{RR})₃](ClO₄)₆.

Figure S 19 $^1$H NMR spectra of photochromic process of the helicate [Eu₂(β-L_{RR})₃](ClO₄)₆ (CD₃CN, 400 MHz, 293 K).
Figure S 20 UV-Vis spectra changes of $o$-$\text{L}^{RR}$ in CHCl$_3$ solution upon irradiation of 334 nm light (a) and corresponding $c$-$\text{L}^{RR}$ upon irradiation of 630 nm light (b); UV-Vis spectra changes of Eu$_2(o$-$\text{L}^{RR})_3(\text{ClO}_4)_6$ in CH$_3$CN solution upon irradiation of 334 nm light (c) and corresponding Eu$_2(c$-$\text{L}^{RR})_3(\text{ClO}_4)_6$ upon irradiation of 630 nm light (d).

Figure S 21 UV-Vis absorbance changes of Eu$_2(o$-$\text{L}^{SS})_3(\text{ClO}_4)_6$ in CH$_3$CN solution on alternate excitation at 334 and 630 nm over six cycles at 293 K.
Figure S 22 CD spectra of the extracted ring-closed ligands $c\cdot L_{RR}$ (black line) and $c\cdot L_{SS}$ (red line) from the helicates ($5 \times 10^{-5}$M, CHCl$_3$, 293K).

Figure S 23 ESI-TOF-MS spectrum for the ring-closure helicate Eu$_2$(c-$L_{RR}$)$_3$(ClO$_4$)$_6$. 
Figure S 24 Excitation and emission spectra of $o$-$L^{55}$ (black) and corresponding ring-closure product $c$-$L^{55}$ upon irradiation of 334 nm in CHCl$_3$ (3×10$^{-4}$ M).

Figure S 25 Emission spectra of Eu$_2$(o-$L^{55}$)$_3$(ClO$_4$)$_6$ and corresponding ring-closure product Eu$_2$(c-$L^{55}$)$_3$(ClO$_4$)$_6$ in CH$_3$CN solution (1×10$^{-4}$ M) ($\lambda_{\text{ex}} = 270$ nm).

Figure S 26 Emission spectra of ring-closure product Eu$_2$(c-$L^{55}$)$_3$(ClO$_4$)$_6$ when exited at 441nm.

3. References