

Supplementary Information for:

Chiral triptycene-pyrene π -conjugated chromophores with circularly polarized luminescence

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Synthesis

2. 4-Ethynylbenzoic acid (326 mg, 2.23 mmol), **1** (300 mg, 1.06 mmol) and *N,N*-dimethyl-4-aminopyridine (272 mg, 2.23 mmol) were dissolved in anhydrous *N,N*-dimethylformamide (5.3 mL) and the solution was cooled to 0 °C. To this solution was added 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (427 mg, 2.28 mmol) and the mixture was stirred at room temperature for 10 h. The mixture was diluted with hexane/ethyl acetate (1/1, v/v), washed with 1 N HCl aqueous solution, saturated sodium hydrogen carbonate aqueous solution and water, and then dried over Na₂SO₄. The solvent was removed under reduced pressure and the crude product was purified by silica gel chromatography using hexane/acetone (3/2, v/v) as the eluent to give *rac*-**2** as a pale yellow solid (541 mg, 94% yield). The enantiomers were resolved by chiral high-performance liquid chromatography (HPLC) on Chiralpak IG (column dimensions: 25 cm × 2.0 cm (i.d.); eluent: ethyl acetate; flow rate 10 mL min⁻¹; temperature 20 °C) to give (*R,R*)-**2** (146 mg, 0.27 mmol) and (*S,S*)-**2** (143 mg, 0.26 mmol) as a pale yellow solid. The enantiomeric excess of the resulting enantiomers were confirmed to be more than 99.7% by chiral HPLC using a Chiralpak IG (column dimensions: 25 cm × 0.46 cm (i.d.); eluent: ethyl acetate; flow rate 0.4 mL min⁻¹; temperature 20 °C; *t*_{(*R,R*)-**2**} = 10.1 min, *t*_{(*S,S*)-**2**} = 16.2 min). *rac*-**2**: ¹H NMR (500 MHz, DMSO-*d*₆, rt): δ 10.24 (s, 2H, NH), 7.93 (d, *J* = 2.0 Hz, 2H, ArH), 7.91 (d, *J* = 8.5 Hz, 4H, ArH), 7.61 (d, *J* = 8.0 Hz, 4H, ArH), 7.46 (dd, *J* = 5.5, 3.0 Hz, 2H, ArH), 7.42 (d, *J* = 8.0 Hz, 2H, ArH), 7.30 (dd, *J* = 8.0, 1.7 Hz, 2H, ArH), 7.01 (dd, *J* = 5.5, 3.0 Hz, 2H, ArH), 5.61 (s, 2H, CH), 4.41 (s, 2H, C≡CH). HRMS (DART): *m/z* calcd for C₃₈H₂₄N₂O₂ (M+H⁺), 541.1911; found 541.1906. (*R,R*)-**2**: Mp: 203.6–204.1 °C. [*α*]_D²⁵ +391.5 (*c* 0.2, THF). ¹H NMR (500 MHz, CDCl₃, rt): δ 7.91 (s, 2H, ArH), 7.80 (s, 2H, NH), 7.76 (d, *J* = 8.0 Hz, 4H, ArH), 7.55 (d, *J* = 8.0 Hz, 4H, ArH), 7.37 (m, 2H, ArH), 7.31 (d, *J* = 8.0 Hz, 2H, ArH), 7.04 (d, *J* = 7.5 Hz, 2H, ArH), 7.00 (m, 2H, ArH), 5.40 (s, 2H, CH), 3.22 (s, 2H, C≡CH). HRMS (DART): *m/z* calcd for C₃₈H₂₄N₂O₂ (M+H⁺), 541.1911; found 541.1916. (*S,S*)-**2**: Mp: 203.9–204.3 °C. [*α*]_D²⁵ -393.0 (*c* 0.2, THF). ¹H NMR (500 MHz, CDCl₃, rt): δ 7.94 (s, 2H, NH), 7.87 (d, *J* = 2.0 Hz, 2H, ArH), 7.72 (d, *J* = 8.5 Hz, 4H, ArH), 7.50 (d, *J* = 8.0 Hz, 4H, ArH), 7.34 (m, 2H, ArH), 7.24 (d, *J* = 8.0 Hz, 2H, ArH), 7.03 (dd, *J* = 8.0, 2.5 Hz, 2H, ArH), 6.99 (m, 2H, ArH), 5.35 (s, 2H, CH), 3.21 (s, 2H, C≡CH). HRMS (DART): *m/z* calcd for C₃₈H₂₄N₂O₂ (M+H⁺), 541.1911; found 541.1903.

2-(Tributylstannyl)-4,5-didecylthiophene. To a solution of 2,3-didecylthiophene (322 mg, 0.883 mmol) in anhydrous THF (27 mL) was added dropwise *n*-butyllithium (1.6 M in hexane, 580 μL, 0.927 mmol) via syringe at -78 °C under nitrogen atmosphere. After stirring at -78 °C

for 2 h, tributyltin chloride (310 μ L, 1.15 mmol) was added. The mixture was warmed to room temperature and stirred for 2 h. After quenching the reaction with water, the volatile species were evaporated in vacuo. The residue was extracted with hexane, and the organic layer was washed with water, dried over anhydrous Na_2SO_4 and concentrated. The target compound (1.12 g) was obtained as a pale yellow oil and was used for the next step without further purification. ^1H NMR (500 MHz, CDCl_3 , rt): δ 6.85 (s, 1H, ArH), 2.72 (t, $J = 7.7$ Hz, 2H, ArCH_2), 2.51 (t, $J = 7.7$ Hz, 2H, ArCH_2), 1.68-1.47 (m, 10H, CH_2), 1.43-1.21 (m, 34H, CH_2), 1.15-0.99 (m, 6H, CH_2), 0.95-0.81 (m, 15H, CH_3).

4. To a solution of 2-(tributylstannyl)-4,5-didecylthiophene (1.2 g) and 2,6-diiodopyrene (594 mg, 1.3 mmol) in anhydrous toluene (10 mL) was added $\text{Pd}(\text{PPh}_3)_4$ (55 mg, 0.048 mmol). The solution was stirred at 120 $^\circ\text{C}$ for 10 h. After cooling to room temperature, the solvent was removed by evaporation and the crude product was purified by silica gel chromatography using hexane as the eluent to give the desired product as a pale yellow solid (112 mg, 17% yield). ^1H NMR (500 MHz, CDCl_3 , rt): δ 8.63 (d, $J = 9.2$ Hz, 1H, ArH), 8.51 (d, $J = 8.0$ Hz, 1H, ArH), 8.30 (d, $J = 9.2$ Hz, 1H, ArH), 8.20 (d, $J = 8.0$ Hz, 1H, ArH), 8.14-8.09 (m, 2H, ArH), 8.02 (d, $J = 9.2$ Hz, 1H, ArH), 7.85 (d, $J = 8.0$ Hz, 1H, ArH), 7.09 (s, 1H, ArH), 2.83 (t, $J = 7.7$ Hz, 2H, ArCH_2), 2.62 (t, $J = 7.7$ Hz, 2H, ArCH_2), 1.74 (quint, $J = 7.6$ Hz, 2H, ArCH_2CH_2), 1.67 (quint, $J = 7.6$ Hz, 2H, ArCH_2CH_2), 1.51-1.19 (m, 28H, CH_2), 0.93-0.82 (m, 6H, CH_3).

rac-3. The title compound was prepared from *rac*-2 in the same way as (*R,R*)-3 and obtained in 29% yield as a yellow solid. Mp: 247.6–248.0 $^\circ\text{C}$. ^1H NMR (500 MHz, CDCl_3 , rt): δ 8.62-8.50 (m, 4H, ArH), 8.18-7.92 (m, 16H, ArH, NH), 7.85 (d, $J = 8.6$ Hz, 4H, ArH), 7.73 (d, $J = 8.0$ Hz, 4H, ArH), 7.40 (dd, $J = 5.0, 3.5$ Hz, 2H, ArH), 7.27 (d, $J = 8.0$ Hz, 2H, ArH), 7.10 (dd, $J = 8.0, 1.7$ Hz, 2H, ArH), 7.08 (s, 2H, ArH), 7.03 (dd, $J = 5.0, 3.0$ Hz, 2H, ArH), 5.42 (s, 2H, CH), 2.83 (t, $J = 7.7$ Hz, 4H, ArCH_2), 2.62 (t, $J = 7.7$ Hz, 4H, ArCH_2), 1.74 (quint, $J = 7.6$ Hz, 4H, CH_2), 1.66 (quint, $J = 7.6$ Hz, 4H, CH_2), 1.52-1.20 (m, 56H, CH_2), 0.93-0.83 (m, 12H, CH_3). ^{13}C NMR (125 MHz, CDCl_3 , rt): δ 165.10, 146.37, 144.91, 141.54, 140.59, 138.54, 137.43, 135.02, 134.18, 132.34, 131.84, 131.37, 130.24, 130.00, 129.85, 128.65, 128.53, 128.47, 127.29, 127.18, 126.33, 125.36, 125.23, 124.62, 124.55, 124.27, 124.07, 123.67, 117.03, 116.67, 116.45, 94.24, 91.61, 53.63, 32.03, 31.93, 30.98, 29.67, 29.64, 29.59, 29.52, 29.49, 29.39, 28.43, 28.02, 22.71, 14.15. IR (KBr, cm^{-1}): 3418 (N-H), 2207 ($\text{C}\equiv\text{C}$), 1651 ($\text{C}=\text{O}$). Calcd for $\text{C}_{118}\text{H}_{124}\text{N}_2\text{O}_2\text{S}_2 \cdot 0.2\text{H}_2\text{O}$: C, 84.87; H, 7.51; N, 1.68. Found: C, 84.60; H, 7.48; N, 1.71.

Supporting data

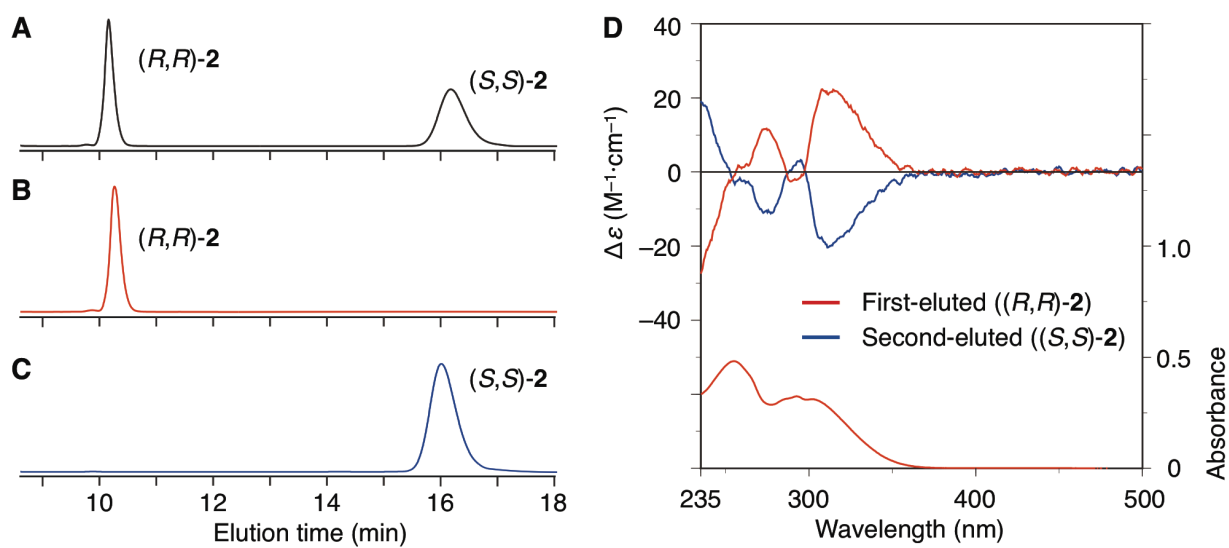


Fig. S1 Resolution results of *rac*-**2** (A), *(R,R)*-**2** (B) and *(S,S)*-**2** (C) on Chiralpak IG (column, 25 cm $\times$ 0.46 cm (i.d.). The chromatograms depict UV traces recorded at 300 nm; eluent, ethyl acetate; flow rate, 0.4 mL min⁻¹; temperature, *ca.* 20 °C). (D) CD and absorption spectra of the first- (red line) and second-eluted (blue line) components in THF at room temperature. [**2**] = 1.0×10^{-5} M.

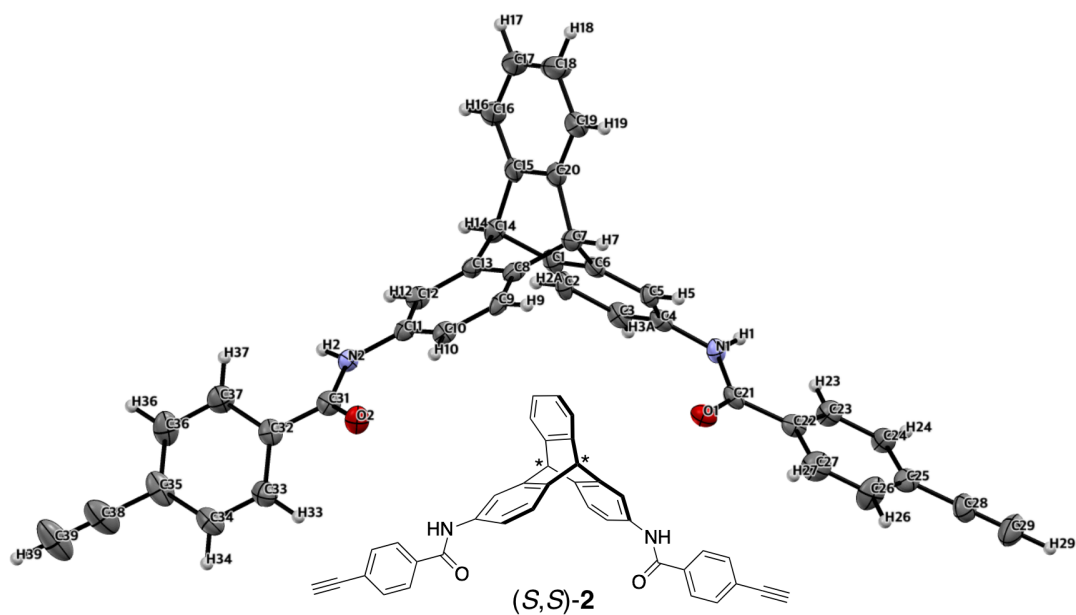


Fig. S2 ORTEP drawing of *(S,S)*-**2** (the second-eluted component in Fig. S1A) with a full atom-numbering scheme determined by X-ray analysis (CCDC deposit number 1546462). Thermal ellipsoids are drawn at the 50% probability level.

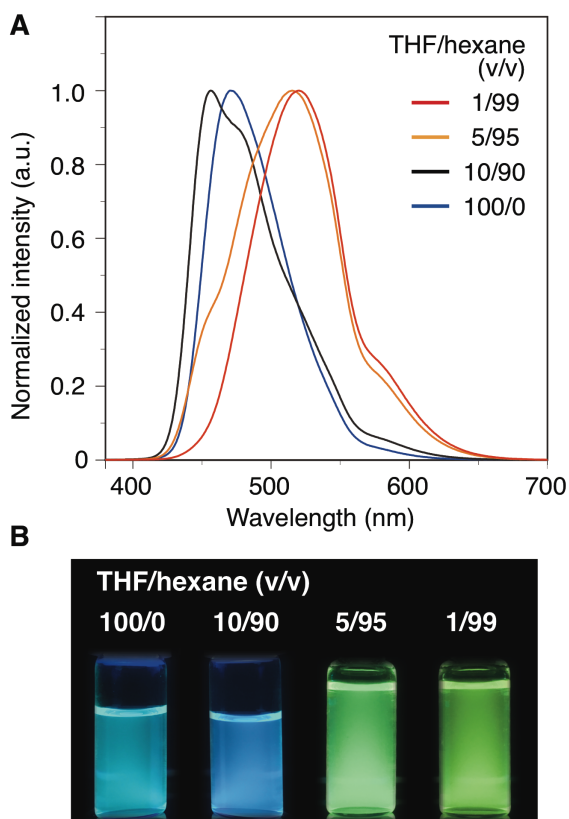


Fig. S3 (A) PL spectra of (S,S) -3 ($\lambda_{\text{ex}} = 365$ nm) in THF/hexane (100/0–1/99, v/v) at room temperature. $[3] = 1.0 \times 10^{-5}$ M. (B) Photograph of the corresponding solutions under UV irradiation (365 nm).

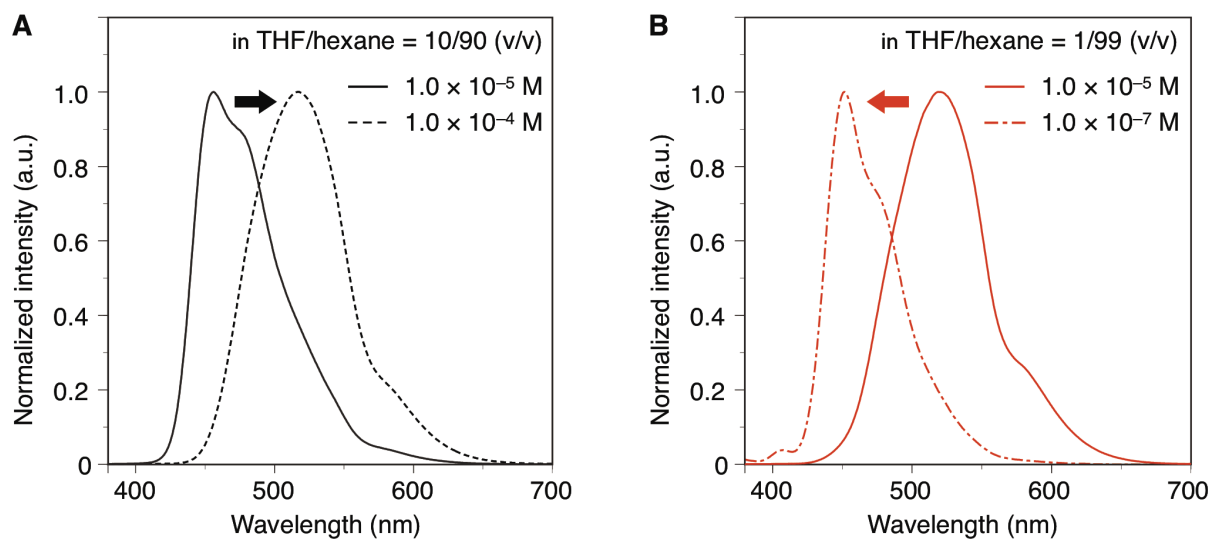


Fig. S4 (A) PL spectra of (R,R) -3 ($\lambda_{\text{ex}} = 365$ nm, room temperature) in THF/hexane (10/90 (A) and 1/99 (B), v/v) at various concentrations.

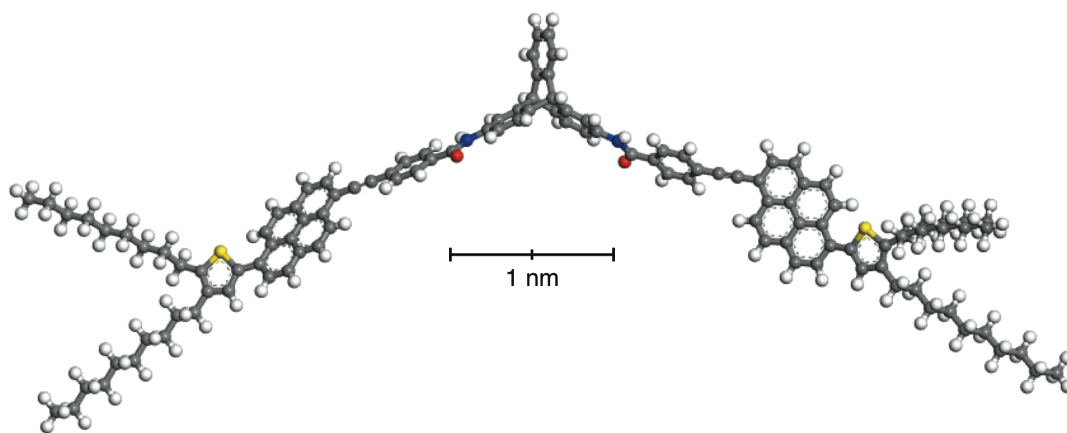


Fig. S5 Computer-generated molecular model of (*S,S*)-**3** represented by the ball-and-stick model.

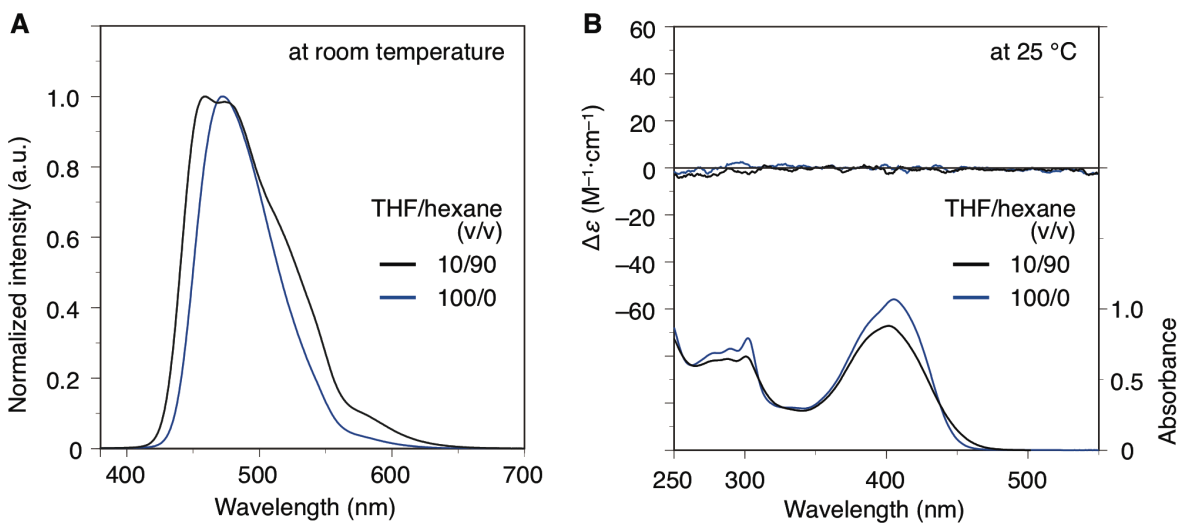


Fig. S6 (A) PL ($\lambda_{\text{ex}} = 365$ nm) and (B) CD and absorption spectra of *rac*-**3** in THF and THF/hexane (10/90, v/v). $[\mathbf{3}] = 1.0 \times 10^{-5}$ M.

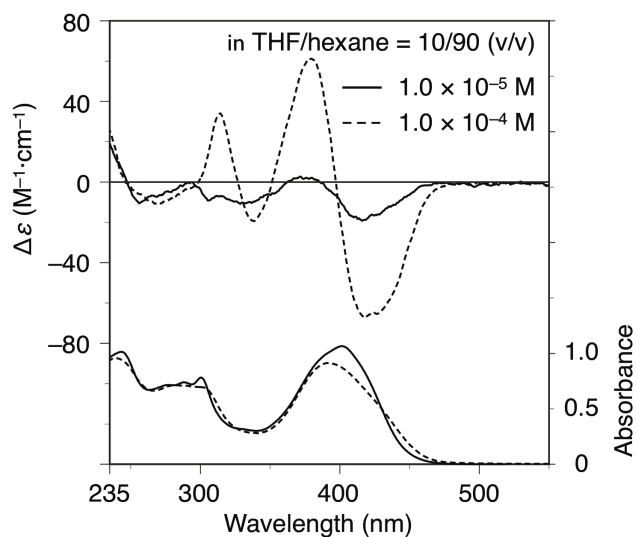


Fig. S7 CD and absorption spectra of (*S,S*)-**3** in THF/hexane (10/90, v/v) at 25 °C. The spectra indicated by solid and dashed lines were obtained from the solutions of 1.0×10^{-5} M (cell length: 10 mm) and 1.0×10^{-4} M (cell length: 1.0 mm), respectively.

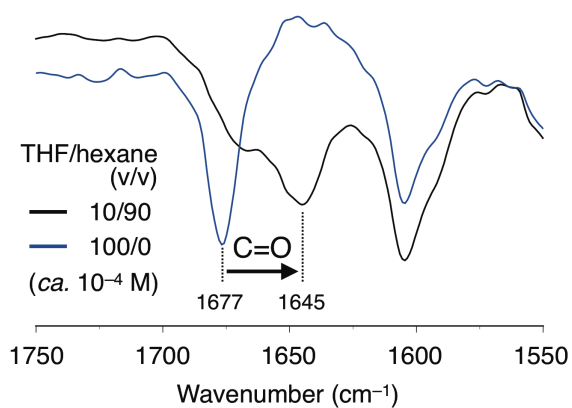


Fig. S8 IR spectra of (*S,S*)-**3** in THF and THF/hexane (10/90, v/v) at room temperature.

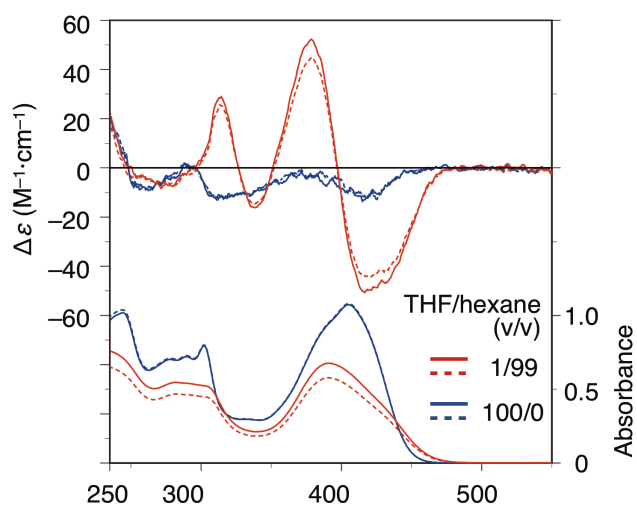


Fig. S9 CD and absorption spectra of (*S,S*)-**3** in THF and THF/hexane (1/99, v/v) at 25 °C before (solid line) and after (dashed line) filtration through a membrane filter with a pore size of 0.20 μm . $[\mathbf{3}] = 1.0 \times 10^{-5}$ M.

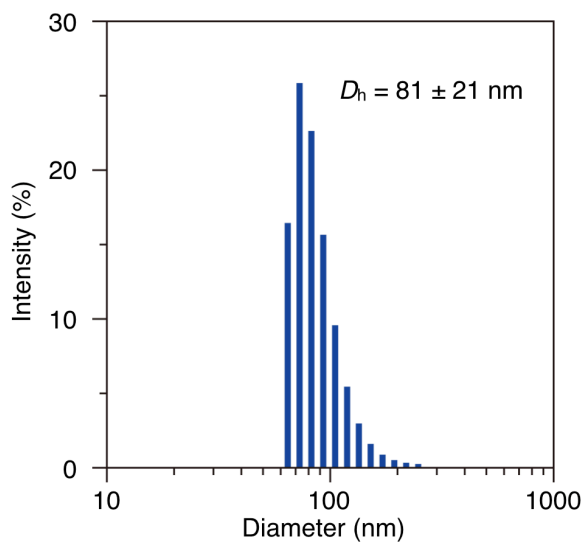


Fig. S10 Histogram analysis of the DLS measurements of (*S,S*)-**3** in THF/hexane (1/99, v/v) at 25 °C. $[\mathbf{3}] = 1.0 \times 10^{-5}$ M.

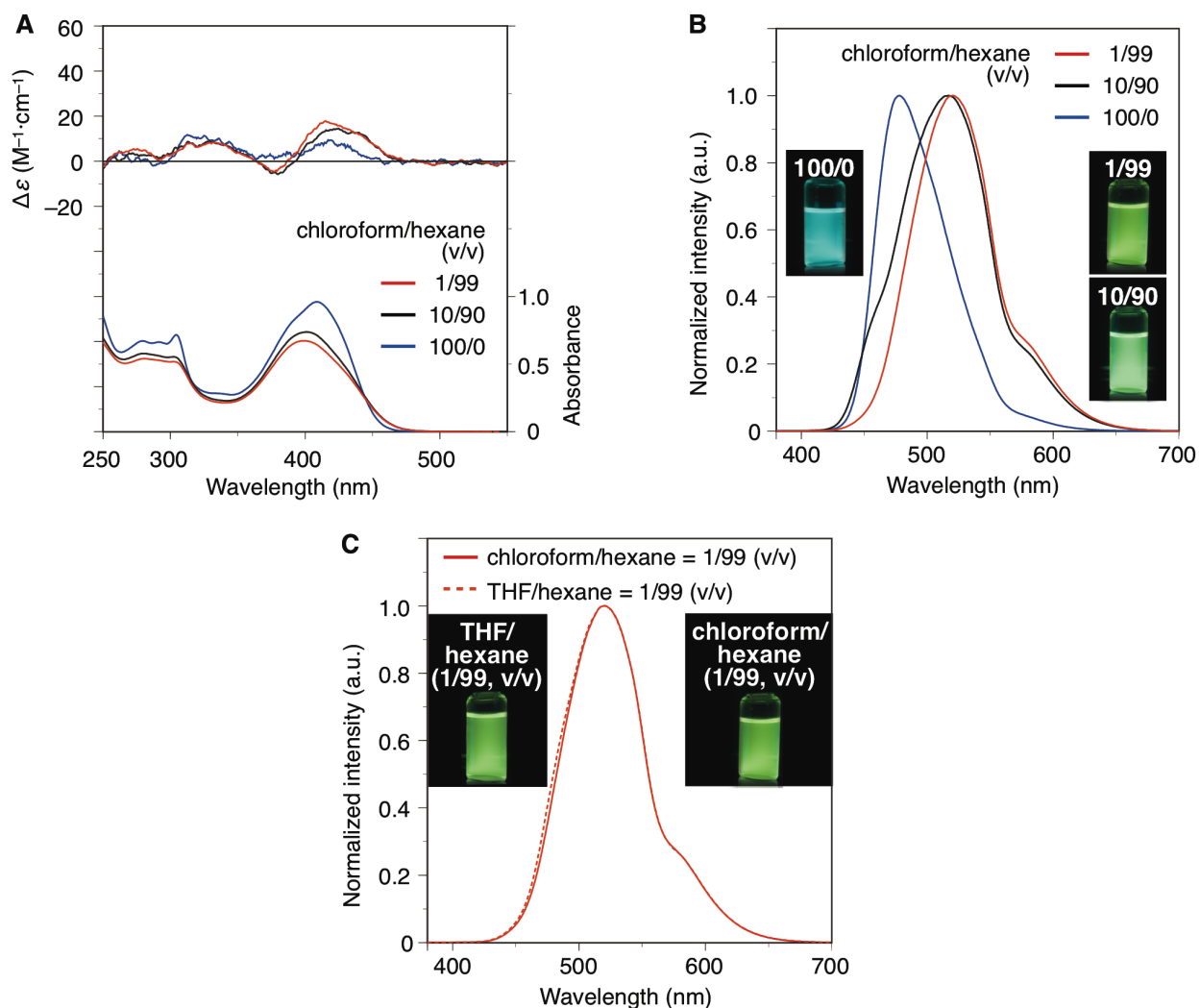


Fig. S11 (A) CD and absorption spectra of (R,R) -**3** in chloroform/hexane (100/0–1/99, v/v) at 25 °C. (B) PL spectra of (R,R) -**3** ($\lambda_{ex} = 365$ nm) in chloroform/hexane (100/0–1/99, v/v) at room temperature. (C) Comparison of the PL spectra of (R,R) -**3** measured in chloroform/hexane (1/99, v/v) and THF/hexane (1/99, v/v). $[3] = 1.0 \times 10^{-5}$ M. Insets: Photographs of the corresponding solutions under irradiation at 365 nm.

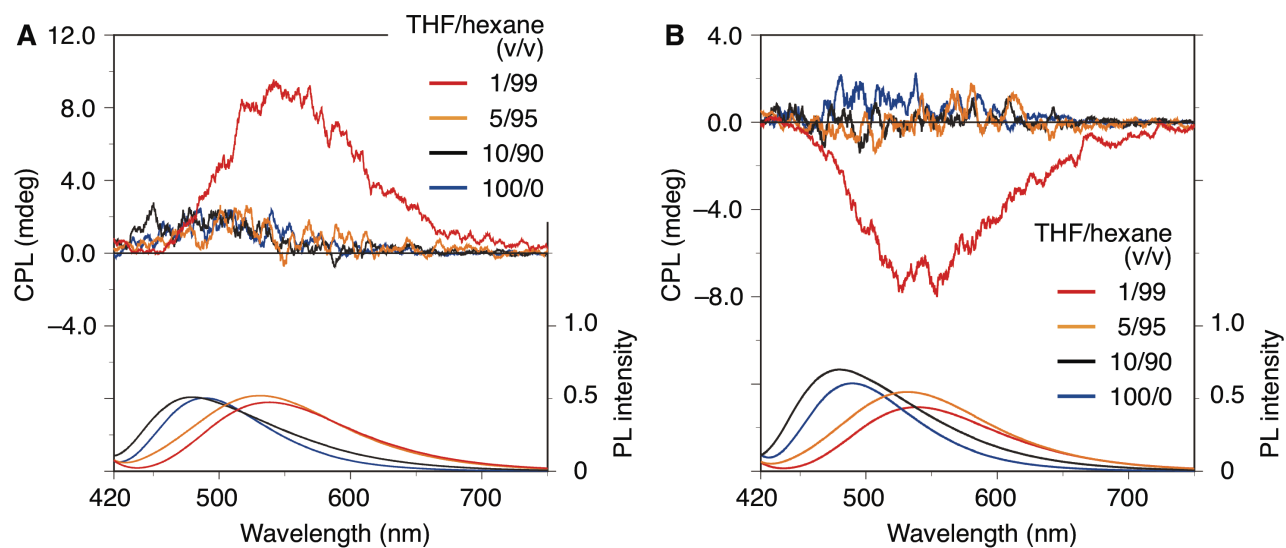


Fig. S12 PL (not normalized) (bottom) and CPL (unprocessed) (top) spectra of *(R,R)*-**3** (A) and *(S,S)*-**3** (B) in THF/hexane (100/0–1/99, v/v) at room temperature. $[\mathbf{3}] = 1.0 \times 10^{-5}$ M.

NMR spectral data

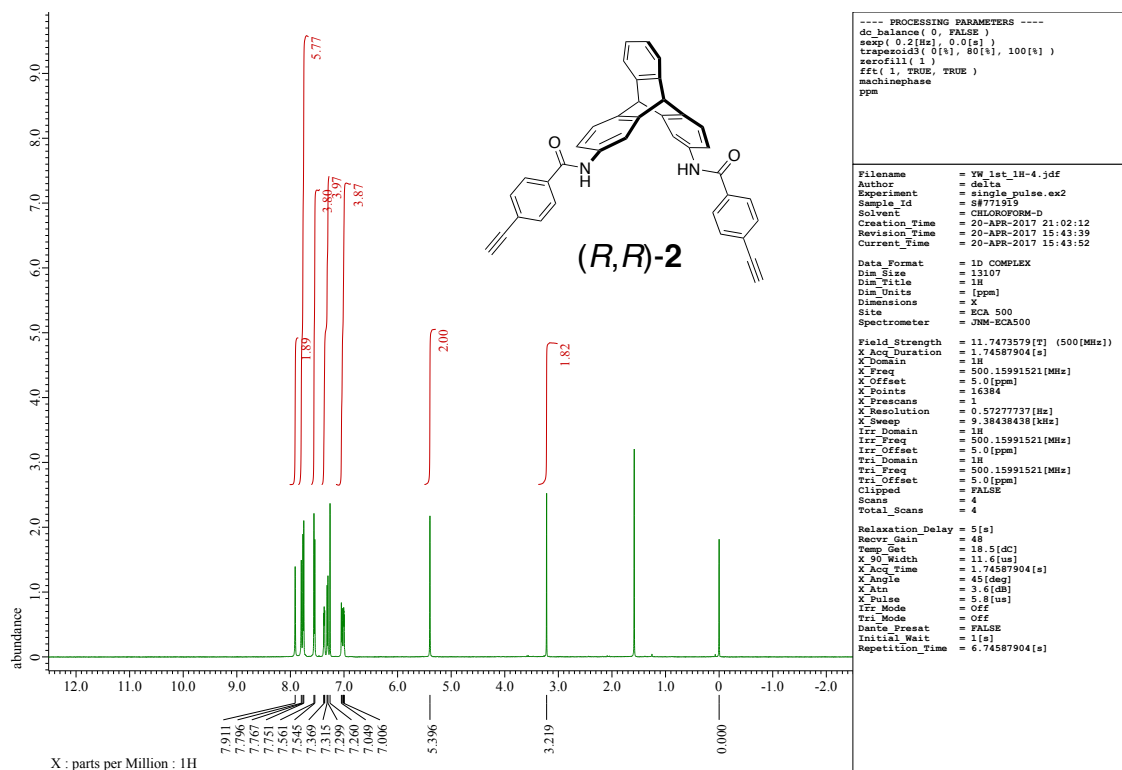


Fig. S13 ^1H NMR (500 MHz, CDCl_3 , rt) spectrum of (R,R)-2.

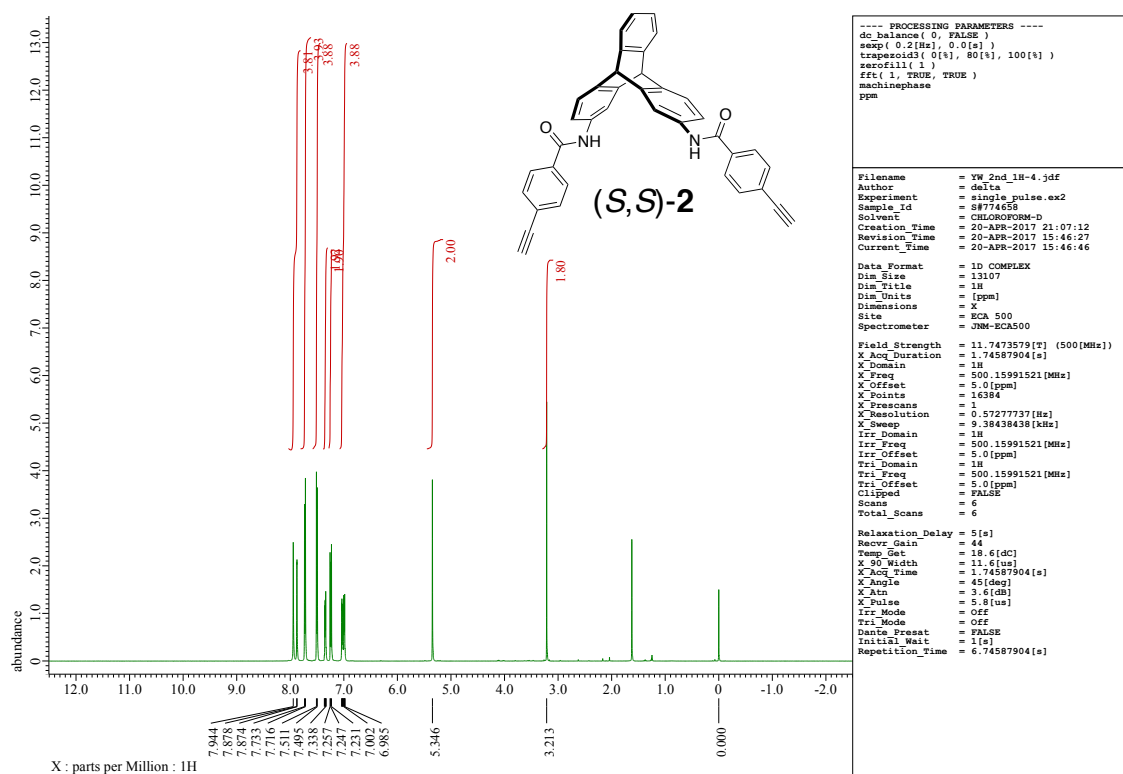


Fig. S14 ^1H NMR (500 MHz, CDCl_3 , rt) spectrum of (S,S)-2.

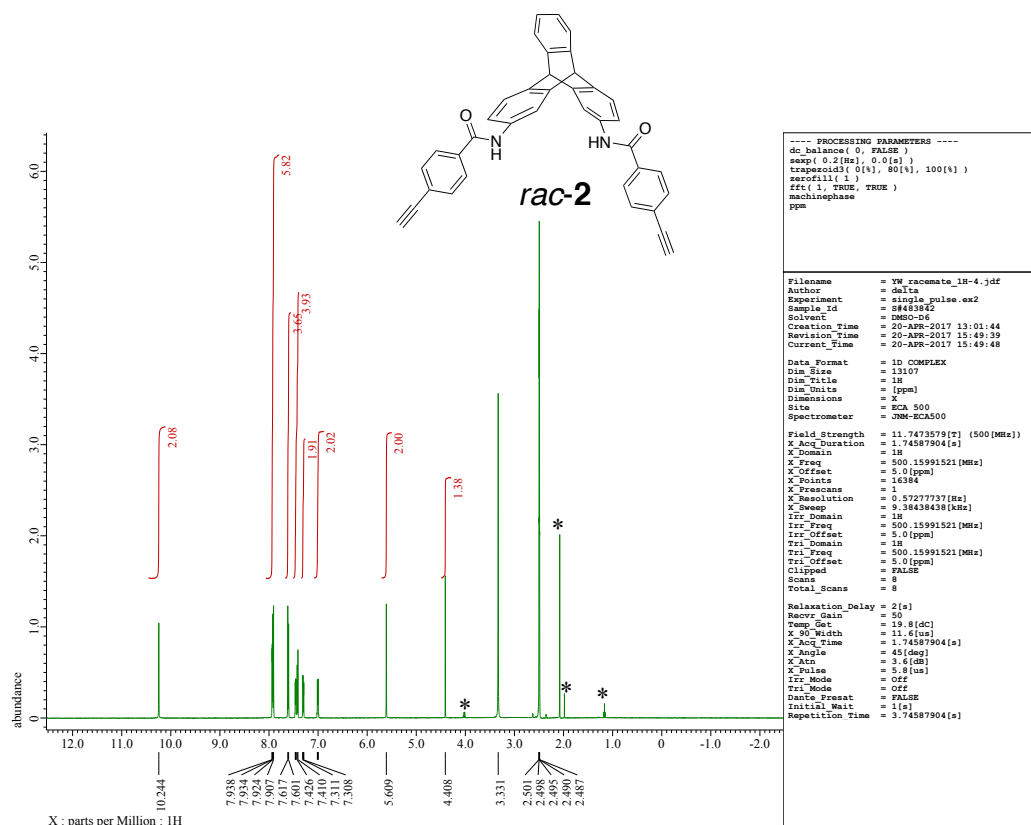


Fig. S15 ^1H NMR (500 MHz, $\text{DMSO}-d_6$, rt) spectrum of *rac-2*. Asterisks denote residual solvent peaks.

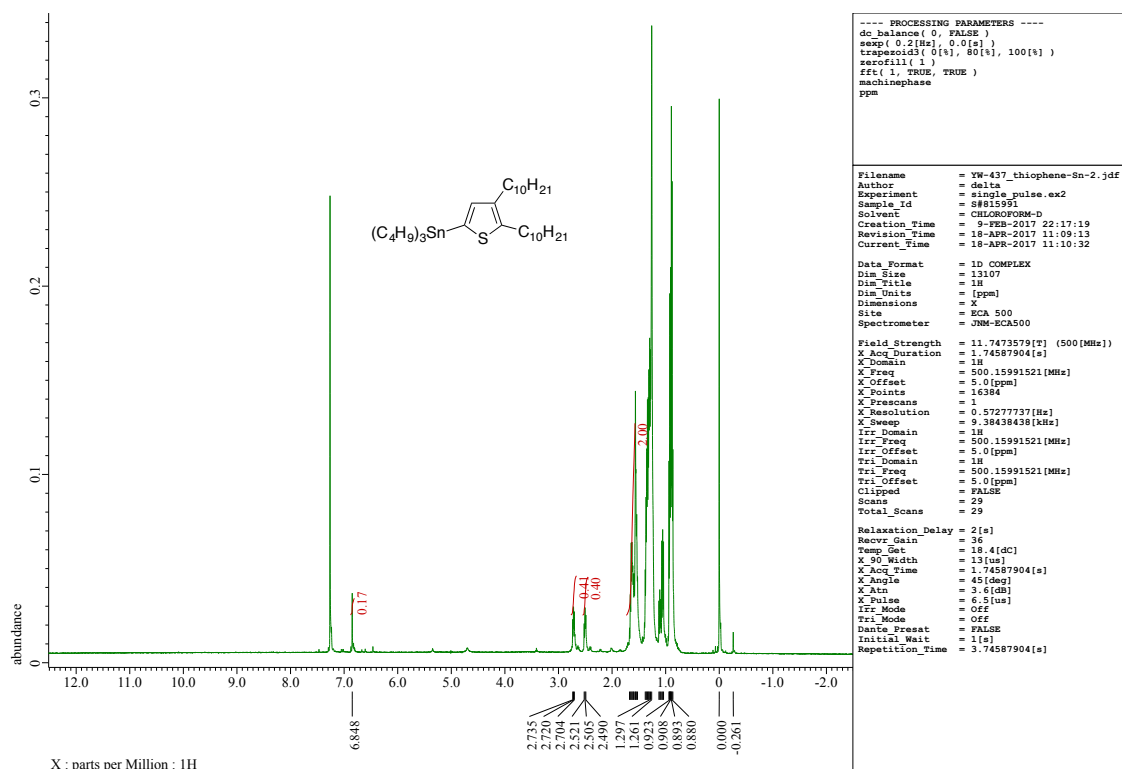


Fig. S16 ^1H NMR (500 MHz, CDCl_3 , rt) spectrum of 2-(tributylstannyl)-4,5-didecylthiophene.

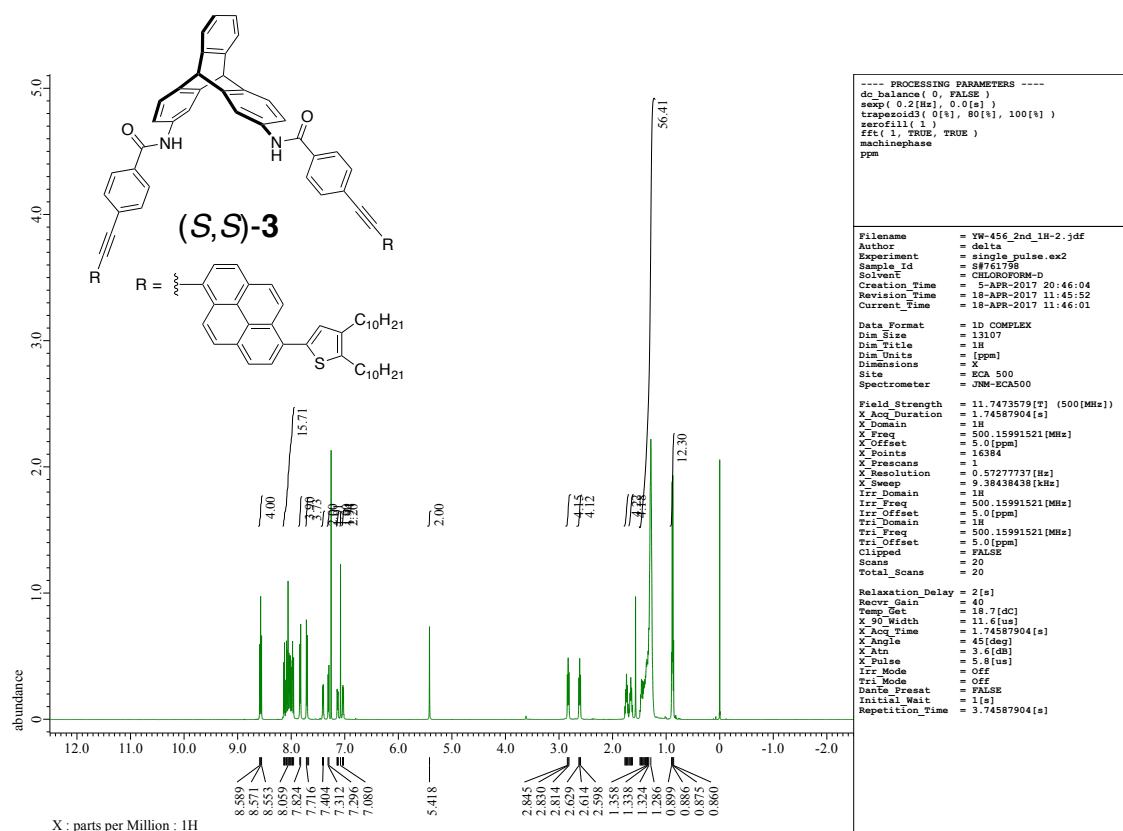


Fig. S19 ^1H NMR (500 MHz, CDCl_3 , rt) spectrum of (S,S)-3.

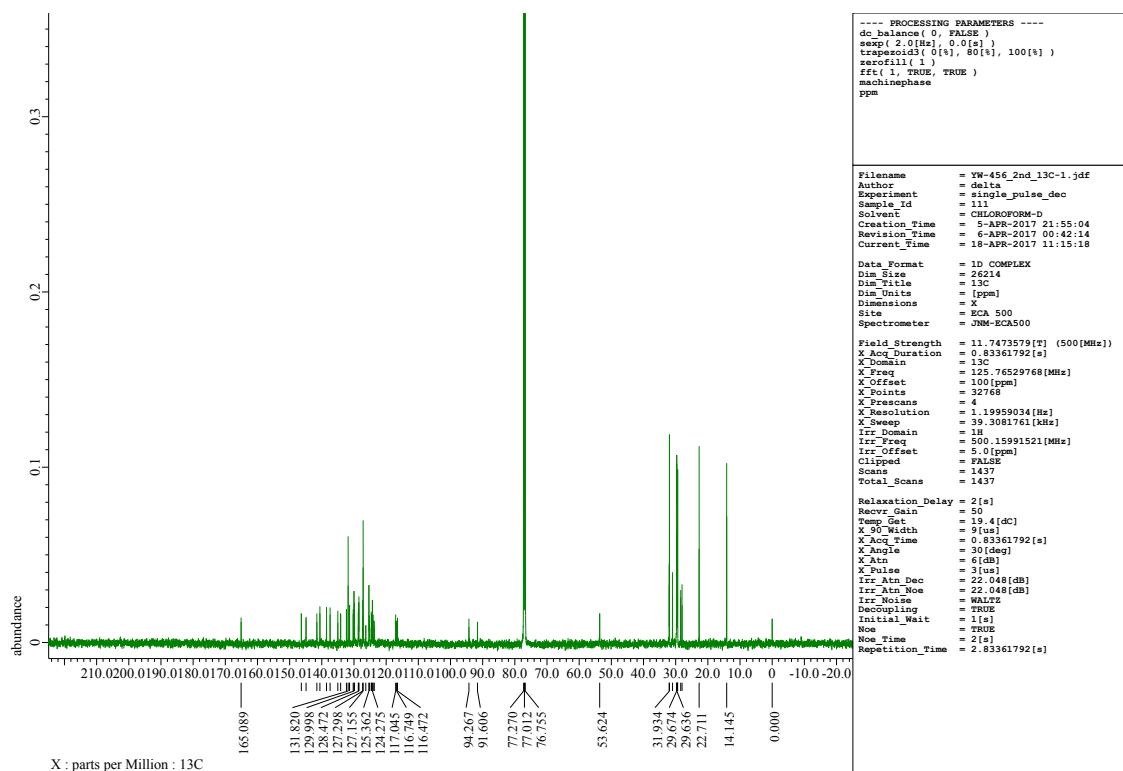


Fig. S20 ^{13}C NMR (125 MHz, CDCl_3 , rt) spectrum of (S,S)-3.

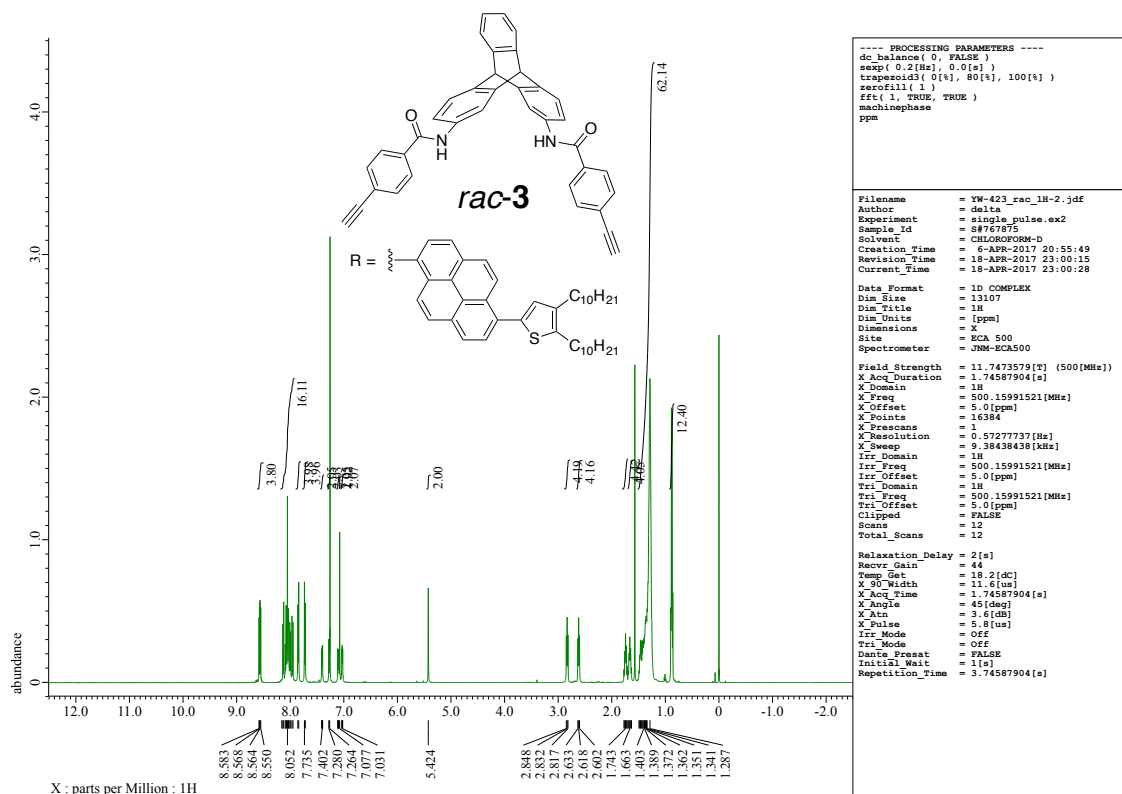


Fig. S21 ^1H NMR (500 MHz, CDCl_3 , rt) spectrum of *rac-3*.

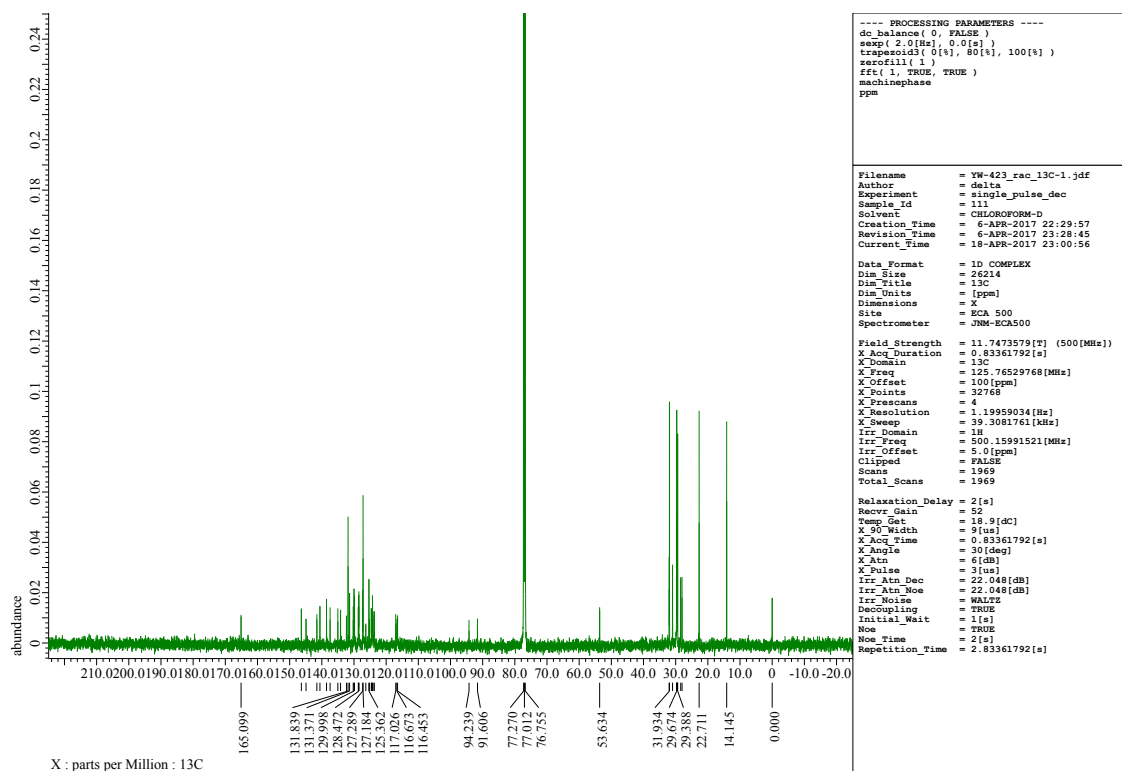


Fig. S22 ^{13}C NMR (125 MHz, CDCl_3 , rt) spectrum of *rac-3*.