

Supplementary Information for:

A cellulose-based chiral fluorescent sensor for aromatic nitro compounds with central, axial and planar chirality

Tomoyuki Ikai,*^a Daisuke Suzuki,^a Ken-ichi Shinohara,^b Katsuhiro Maeda^a and Shigeyoshi Kanoh^a

^aGraduate School of Natural Science and Technology, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan.

^bSchool of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Asahi-dai, Nomi 923-1292, Japan

*To whom correspondence should be addressed. E-mail: ikai@se.kanazawa-u.ac.jp.

Table of content:

1. Materials	S-2
2. Instruments	S-2
3. Synthesis	S-3
Supporting data	S-8
NMR spectral data	S-16
Captions for supporting movies	S-24
References	S-24

1. Materials

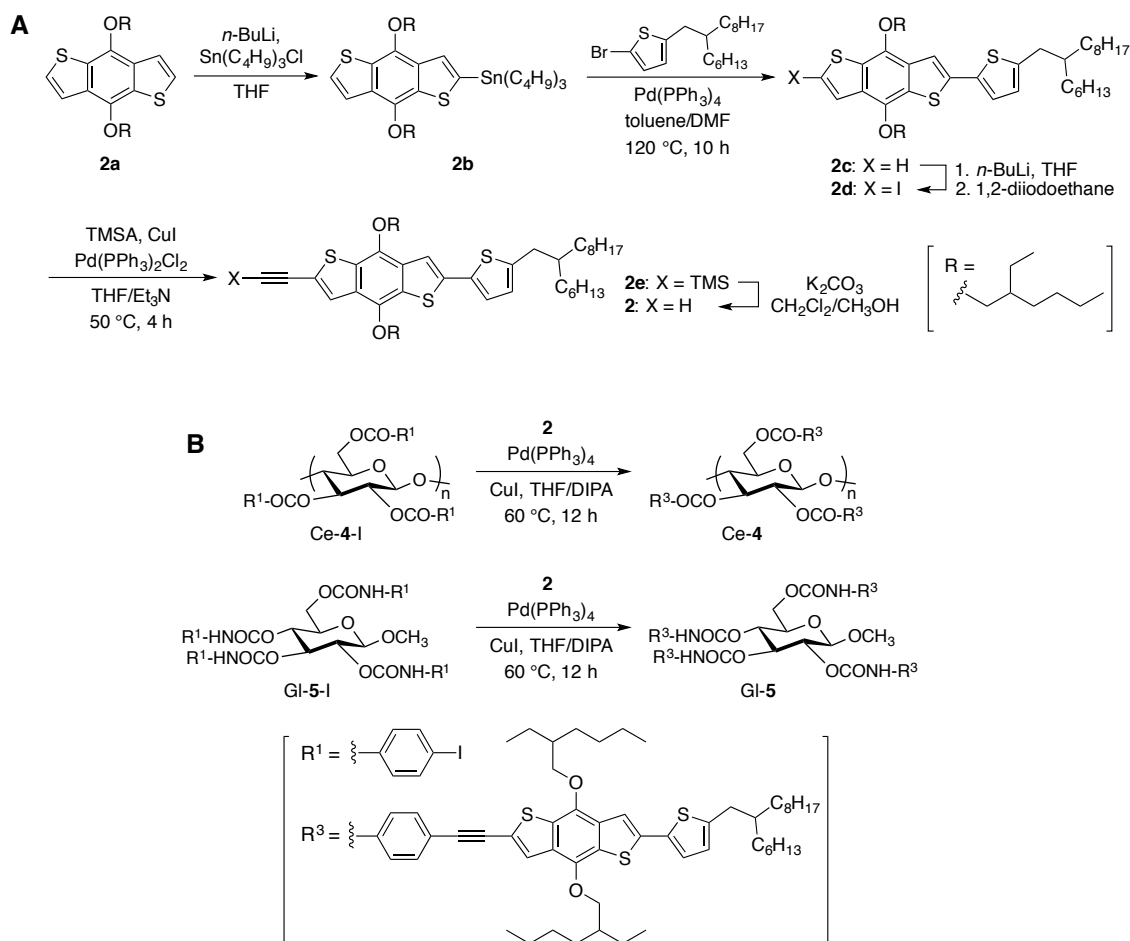
Anhydrous solvents (toluene, *N,N*-dimethylformamide (DMF), dichloromethane and tetrahydrofuran (THF)) and common organic solvents were purchased from Kanto Kagaku (Tokyo, Japan). Tributyltin chloride and copper (I) iodide (CuI) were from Sigma-Aldrich (St. Louis, MO, USA). Trimethylacetylene (TMSA), *trans*-dichlorobis(triphenylphosphine)palladium(II) (Pd(PPh₃)₂Cl₂), 1,2-diiodoethane, diisopropylamine (DIPA), nitrobenzene, anthracene and *n*-butyllithium (1.6 M in hexane) were purchased from Wako Pure Chemical Industries (Osaka, Japan). Tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄) and *rac*-4-hydroxy[2.2]paracyclophane were purchased from Nacalai (Kyoto, Japan). Triethylamine was obtained from Kishida (Osaka, Japan). Chiralpak IA (25 cm × 2.0 cm (i.d.) and 25 cm × 0.46 cm (i.d.)) were purchased from Daicel (Tokyo, Japan). 2-Bromo-5-(2-hexyldecyl)thiophene,^{S1} Ce-4-I,^{S1} Gl-5-I,^{S1} aromatic nitro compounds (**6–12**)^{S1,S2} and 4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b'*]dithiophene (**2a**)^{S3} were prepared according to literature procedures.

2. Instruments

NMR spectra were taken on a JNM-ECA 500 (JEOL, Tokyo, Japan) (500 MHz for ¹H, 125 MHz for ¹³C) spectrometer in CDCl₃ using tetramethylsilane as the internal standard. Melting points were measured on a Yanako melting point apparatus and were uncorrected. IR spectra were obtained using a JASCO (Hachioji, Japan) Fourier Transform IR-460 spectrophotometer with a KBr pellet. Absorption and circular dichroism (CD) spectra were measured at 25 °C using a JASCO V-570 and a JASCO J-725 spectrometers, respectively, with a quartz cell of 1.0 or 10 mm path length. The temperature was controlled using a JASCO ETC-505T (absorption spectroscopy) and a JASCO PTC-348WI apparatus (CD spectroscopy). Dynamic light scattering (DLS) measurements were performed on a Nano partica SZ-100 (Horiba, Kyoto, Japan) equipped with a 10 mW diode pumped solid state laser (532 nm) at 25 °C. Fluorescence emission spectra were measured with a JASCO FP-6300. The photoluminescence quantum yield was evaluated by using Quantaaurus-QY (Hamamatsu Photonics, Shizuoka, Japan). Elemental analyses were performed by the Research Institute for Instrumental Analysis of Advanced Science Research Center, Kanazawa University, Kanazawa, Japan.

3. Synthesis

A benzo[1,2-*b*:4,5-*b'*]dithiophene derivative (**2**) and cellulose (Ce-**4**) and glucose (Gl-**5**) derivatives were prepared according to Scheme S1. An aromatic nitro compound (**13**) was synthesized thorough a common addition reaction using the corresponding alcohol and isocyanate as starting materials.



Scheme S1 Synthesis of a benzo[1,2-*b*:4,5-*b'*]dithiophene derivative (**2**) (A) and cellulose (Ce-**4**) and glucose (Gl-**5**) derivatives (B).

2b. To a solution of **2a** (5.79 g, 12.9 mmol) in anhydrous THF (46 mL) was added dropwise *n*-butyllithium (1.6 M in hexane, 8.1 mL, 13 mmol) via syringe at $-78\text{ }^{\circ}\text{C}$ under nitrogen atmosphere. After the mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 2 h, tributyltin chloride (5.52 g, 16.9 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 chloroform, and the organic layer was washed with

brine, dried over anhydrous Na₂SO₄ and concentrated. Compound **2b** (10.3 g) was obtained as a pale yellow oil and was used for the next step without further purification. ¹H NMR (500 MHz, CDCl₃, rt): δ 7.51 (s, 1H, ArH), 7.46 (d, *J* = 5.5 Hz, 1H, ArH), 7.33 (d, *J* = 5.5 Hz, 1H, ArH), 4.19 (dd, *J* = 8.0, 5.5 Hz, 4H, OCH₂), 1.88-1.76 (m, 2H, CH), 1.76-0.98 (m, 34H, CH₂) 0.97-0.86 (m, 21H, CH₃).

2c. To a solution of **2b** (10.3 g) and 2-bromo-5-(2-hexyldecyl)thiophene (4.31 g, 11.1 mmol) in toluene/DMF (4/1, v/v) (48 mL) was added Pd(PPh₃)₄ (0.39 g, 0.34 mmol). The solution was stirred at 120 °C for 10 h. After cooling to room temperature, the reaction mixture was diluted with hexane/ethyl acetate (1/1, v/v), washed with brine, and then dried over Na₂SO₄. After removing the solvent by evaporation, the crude product was purified by silica gel chromatography using hexane/dichloromethane (20/1, v/v) as the eluent to give the desired product as a yellow oil (5.99 g, 72% yield). ¹H NMR (500 MHz, CDCl₃, rt): δ 7.44 (d, *J* = 6.0 Hz, 1H, ArH), 7.42 (s, 1H, ArH), 7.34 (d, *J* = 5.5 Hz, 1H, ArH), 7.14 (d, *J* = 3.5 Hz, 1H, ArH), 6.71 (d, *J* = 3.0 Hz, 1H, ArH), 4.17 (d, *J* = 5.5 Hz, 4H, OCH₂), 2.76 (d, *J* = 7.0 Hz, 2H, CH₂), 1.80-1.76 (m, 3H, CH), 1.76-1.14 (m, 40H, CH₂), 1.06-0.98 (m, 6H, CH₃), 0.98-0.92 (m, 6H, CH₃), 0.91-0.82 (m, 6H, CH₃).

2d. To a solution of **2c** (4.77 g, 6.33 mmol) in anhydrous THF (23 mL) was added dropwise *n*-butyllithium (1.6 M in hexane, 3.9 mL, 6.2 mmol) via syringe at -78 °C under nitrogen atmosphere. The mixture was stirred at -78 °C for 30 min and then at room temperature for 30 min. After the mixture was cooled to -78 °C again, 1,2-diiodoethane (2.13 g, 7.56 mmol) was added. The mixture was warmed to room temperature and stirred for 2 h. After quenching the reaction with water, the reaction mixture was diluted with ethyl acetate, washed with brine, and then dried over Na₂SO₄. After removing the solvent by evaporation, the crude product was purified by silica gel chromatography using hexane/dichloromethane (10/1, v/v) as the eluent to give the desired product as a yellow oil (4.79 g, 86% yield). ¹H NMR (500 MHz, CDCl₃, rt): δ 7.61 (s, 1H, ArH), 7.38 (s, 1H, ArH), 7.13 (d, *J* = 3.5 Hz, 1H, ArH), 6.71 (d, *J* = 3.5 Hz, 1H, ArH), 4.13 (t, *J* = 5.0 Hz, 4H, OCH₂), 2.76 (d, *J* = 6.0 Hz, 2H, CH₂), 1.79 (m, 3H, CH), 1.73-1.06 (m, 40H, CH₂), 1.07-0.79 (m, 18H, CH₃).

2e. To a solution of **2d** (4.79 g, 5.44 mmol), Pd(PPh₃)₂Cl₂ (0.19 g, 0.27 mmol) and CuI (51 mg, 0.27 mmol) in degassed THF/triethylamine (3/1, v/v) (480 mL) was added TMSA (0.56 g, 5.70 mmol). The solution was stirred at 50 °C for 4 h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate, washed with 1 N HCl

aqueous solution and brine, and then dried over Na₂SO₄. After removing the solvent by evaporation, the crude product was purified by silica gel chromatography using hexane/dichloromethane (20/1, v/v) as the eluent to give the desired product as a yellow oil (4.6 g, >99% yield). ¹H NMR (500 MHz, CDCl₃, rt): δ 7.55 (s, 1H, ArH), 7.39 (s, 1H, ArH), 7.14 (d, *J* = 3.5 Hz, 1H, ArH), 6.71 (d, *J* = 3.0 Hz, 1H, ArH), 4.14 (dd, *J* = 10.5, 6.0 Hz, 4H, OCH₂), 2.76 (d, *J* = 7.0 Hz, 2H, CH₂), 1.86-1.74 (m, 3H, CH), 1.74-1.09 (m, 40H, CH₂), 1.07-0.77 (m, 18H, CH₃), 0.29 (s, 9H, TMS).

2. To a solution of **2e** (4.6 g, 5.44 mmol) in dichloromethane/methanol (1/1, v/v) (150 mL) was added potassium carbonate (1.31 g, 9.48 mmol) under nitrogen atmosphere. After the mixture was stirred at room temperature for 10 h, the volatile species were evaporated in *vacuo*. The residue was extracted with ethyl acetate, and the organic layer was washed with water, dried over anhydrous Na₂SO₄. After removing the solvent by evaporation, the crude product was purified by silica gel chromatography using hexane/dichloromethane (10/1, v/v) as the eluent to give the desired product as a brown oil (3.38 g, 80% yield). ¹H NMR (500 MHz, CDCl₃, rt): δ 7.61 (s, 1H, ArH), 7.39 (s, 1H, ArH), 7.14 (d, *J* = 3.5 Hz, 1H, ArH), 6.72 (d, *J* = 3.5 Hz, 1H, ArH), 4.19-4.10 (m, 4H, OCH₂), 3.47 (s, 1H, C≡CH), 2.76 (d, *J* = 6.5 Hz, 2H, CH₂), 1.85-1.75 (m, 3H, CH), 1.74-1.11 (m, 40H, CH₂), 1.08-0.74 (m, 18H, CH₃). ¹³C NMR (125 MHz, CDCl₃, rt): δ 145.85, 144.36, 143.62, 137.91, 134.82, 133.55, 130.32, 130.21, 128.83, 126.75, 126.14, 125.24, 120.81, 114.80, 83.04, 77.57, 76.18, 75.94, 40.64, 40.02, 34.65, 33.17, 31.93, 31.91, 30.46, 30.37, 29.97, 29.65, 29.36, 29.25, 29.19, 26.60, 26.58, 23.85, 23.83, 23.18, 23.14, 22.71, 14.21, 14.18, 14.15, 11.33. IR (KBr, cm⁻¹): 3311 (≡CH), 2103 (C≡C). Calcd for C₄₈H₇₂O₂S₃·0.2H₂O: C, 73.83; H, 9.35. Found: C, 73.65; H, 9.41.

Ce-4. The title compound was prepared from **Ce-4-I** in the same way as **Ce-3** and obtained in 18% yield as a brown solid. ¹H NMR (500 MHz, CDCl₃, 55 °C): δ 8.02-6.09 (br, 24H, ArH), 5.66-3.00 (br, 19H, OCH₂, glucose protons), 2.83-2.39 (br, 6H, CH₂), 1.80-0.40 (br, 183H, CH, CH₂, CH₃). IR (KBr, cm⁻¹): 2200 (C≡C), 1733 (C=O). Calcd for C₁₇₁H₂₃₂O₁₄S₉·1.2H₂O: C, 72.78; H, 8.37. Found: C, 72.51; H, 8.14.

Gl-5. The title compound was prepared from **Gl-5-I** in the same way as **Ce-3** and obtained in 62% yield as a brown solid. ¹H NMR (500 MHz, CDCl₃, rt): δ 7.60-7.27 (m, 24H, ArH), 7.15-7.08 (m, 4H, ArH), 6.98-6.76 (br, 4H, NH), 6.73-6.66 (m, 4H, ArH), 5.33 (t, *J* = 10.0 Hz, 1H, glucose proton), 5.20 (t, *J* = 9.5 Hz, 1H, glucose proton), 5.13-5.02 (m, 1H, glucose proton), 4.61-4.49 (m, 2H, glucose protons), 4.46-4.36 (m, 1H, glucose proton),

4.19-4.03 (m, 16H, OCH₂), 3.90 (m, 1H, glucose proton), 3.59 (s, 3H, OCH₃), 2.82-2.66 (m, 8H, CH₂), 1.89-1.72 (m, 12H, CH), 1.71-1.09 (m, 160H, CH₂), 1.06-0.76 (m, 72H, CH₃). IR (KBr, cm⁻¹): 3324 (N-H), 2202 (C≡C), 1717 (C=O). Calcd for C₂₂₇H₃₁₄O₁₈S₁₂: C, 72.29; H, 8.39; N, 1.49. Found: C, 72.10; H, 8.25; N, 1.48.

[2.2]Paracyclophan-4-yl *p*-nitrophenylcarbamate (13).

rac-4-Hydroxy[2.2]paracyclophane (100 mg, 0.45 mmol), *p*-nitrophenyl isocyanate (88 mg, 0.53 mmol) and triethylamine (a few drops) were dissolved in anhydrous dichloromethane (4.5 mL) and the solution was stirred at room temperature for 10 h. The volatile species were removed under reduced pressure and the crude product was purified by silica gel chromatography using dichloromethane as the eluent to give the desired racemic product as a white solid (118 mg, 68% yield). The enantiomers were resolved by chiral high-performance liquid chromatography (HPLC) on Chiralpak IA (column dimensions: 25 cm × 2.0 cm (i.d.); eluent: hexane/acetone (4/1, v/v); flow rate 8.0 mL min⁻¹; temperature 20 °C) to give (+)-**13** (37 mg, 0.094 mmol) and (–)-**13** (42 mg, 0.11 mmol) as a white solid. The enantiomeric excess of the optically active **13** was confirmed to be >97% by chiral HPLC using a Chiralpak IA column (column dimensions: 25 cm × 0.46 cm (i.d.); eluent: hexane/acetone (4/1, v/v); flow rate 0.5 mL min⁻¹; temperature 20 °C; *t*₍₊₎₋₁₃ = 17.0 min, *t*_{(–)-13} = 18.3 min). *rac*-**13**: Mp: 195.0–195.3 °C. ¹H NMR (500 MHz, CDCl₃, rt): δ 8.26 (d, *J* = 9.0 Hz, 2H, ArH), 7.66 (d, *J* = 9.0 Hz, 2H, ArH), 7.30 (br, 1H, NH), 6.93-6.85 (m, 1H, ArH), 6.62-6.44 (m, 5H, ArH), 6.12 (s, 1H, ArH), 3.32-2.73 (m, 8H, CH₂). ¹³C NMR (125 MHz, CDCl₃, rt): δ 150.53, 148.21, 143.44, 143.40, 141.94, 139.37, 139.32, 135.52, 133.50, 133.08, 132.33, 131.25, 130.80, 129.31, 127.67, 125.31, 118.03, 35.27, 34.86, 34.43, 31.37. IR (KBr, cm⁻¹): 3278 (N-H), 1713 (C=O). (–)-**13**: Mp: 207.5–207.8 °C. [*α*]_D²⁵ –12.7 (*c* 0.5, CHCl₃). ¹H NMR (500 MHz, CDCl₃, rt): δ 8.24 (d, *J* = 9.5 Hz, 2H, ArH), 7.63 (d, *J* = 9.0 Hz, 2H, ArH), 7.45 (br, 1H, NH), 6.89 (dd, *J* = 8.0, 1.5 Hz, 1H, ArH), 6.59-6.43 (m, 5H, ArH), 6.11 (s, 1H, ArH), 3.31-3.18 (m, 1H, CH₂), 3.15-2.93 (m, 6H, CH₂), 2.83-2.72 (m, 1H, CH₂). ¹³C NMR (125 MHz, CDCl₃, rt): δ 150.67, 148.20, 143.54, 143.29, 141.94, 139.37, 139.31, 135.50, 133.50, 133.08, 132.30, 131.24, 130.77, 129.30, 127.71, 125.27, 118.06, 35.25, 34.83, 34.39, 31.37. IR (KBr, cm⁻¹): 3376 (N-H), 1750 (C=O). Calcd for C₂₃H₂₀N₂O₄: C, 71.12; H, 5.19; N, 7.21. Found: C, 70.92; H, 5.27; N, 7.02. (+)-**13**: Mp: 207.8–208.3 °C. [*α*]_D²⁵ +9.6 (*c* 0.5, CHCl₃). ¹H NMR (500 MHz, CDCl₃, rt): δ 8.25 (d, *J* = 8.0 Hz, 2H, ArH), 7.64 (d, *J* = 8.5 Hz, 2H, ArH), 7.40 (s, 1H, NH), 6.89 (d, *J* = 8.0 Hz, 1H, ArH), 6.60-6.43 (m, 5H, ArH), 6.11 (s, 1H, ArH), 3.29-3.20 (m, 1H, CH₂), 3.15-2.94 (m, 6H, CH₂), 2.82-2.73 (m, 1H, CH₂). ¹³C NMR (125 MHz, CDCl₃, rt): δ 150.62, 148.21,

143.50, 143.34, 141.94, 139.37, 139.31, 135.51, 133.50, 133.08, 132.32, 131.24, 130.78, 129.31, 127.70, 125.28, 118.05, 35.26, 34.84, 34.41, 31.37. IR (KBr, cm^{-1}): 3375 (N-H), 1750 (C=O). Calcd for $\text{C}_{23}\text{H}_{20}\text{N}_2\text{O}_4 \cdot 0.6\text{H}_2\text{O}$: C, 69.20; H, 5.35; N, 7.02. Found: C, 69.20; H, 5.21; N, 6.86.

Supporting data

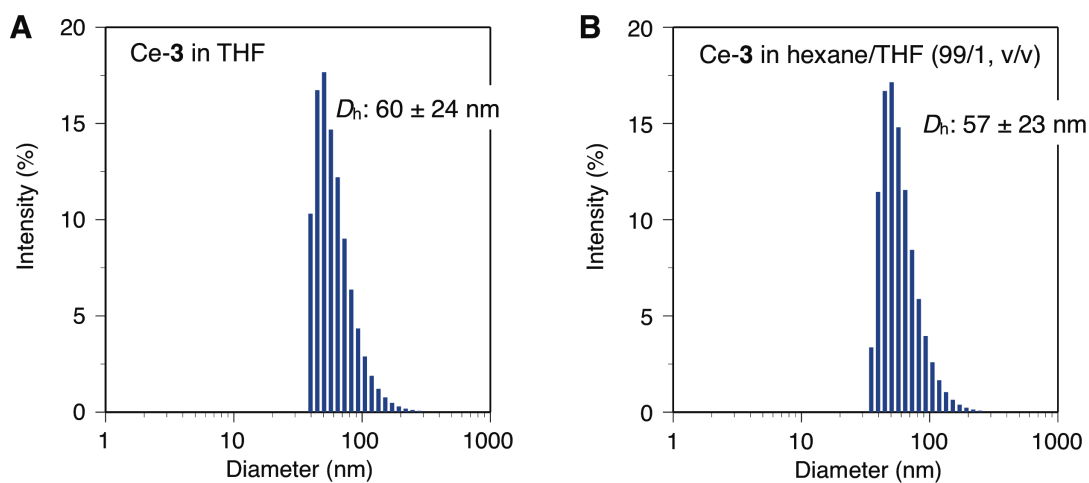


Fig. S1 Histogram analysis of the DLS measurements of Ce-3 in THF (A) and hexane/THF (99/1, v/v) (B) at 30 °C after filtration through a membrane filter with a pore size of 0.45 μm . [Glucose unit] = 1.0×10^{-5} M.

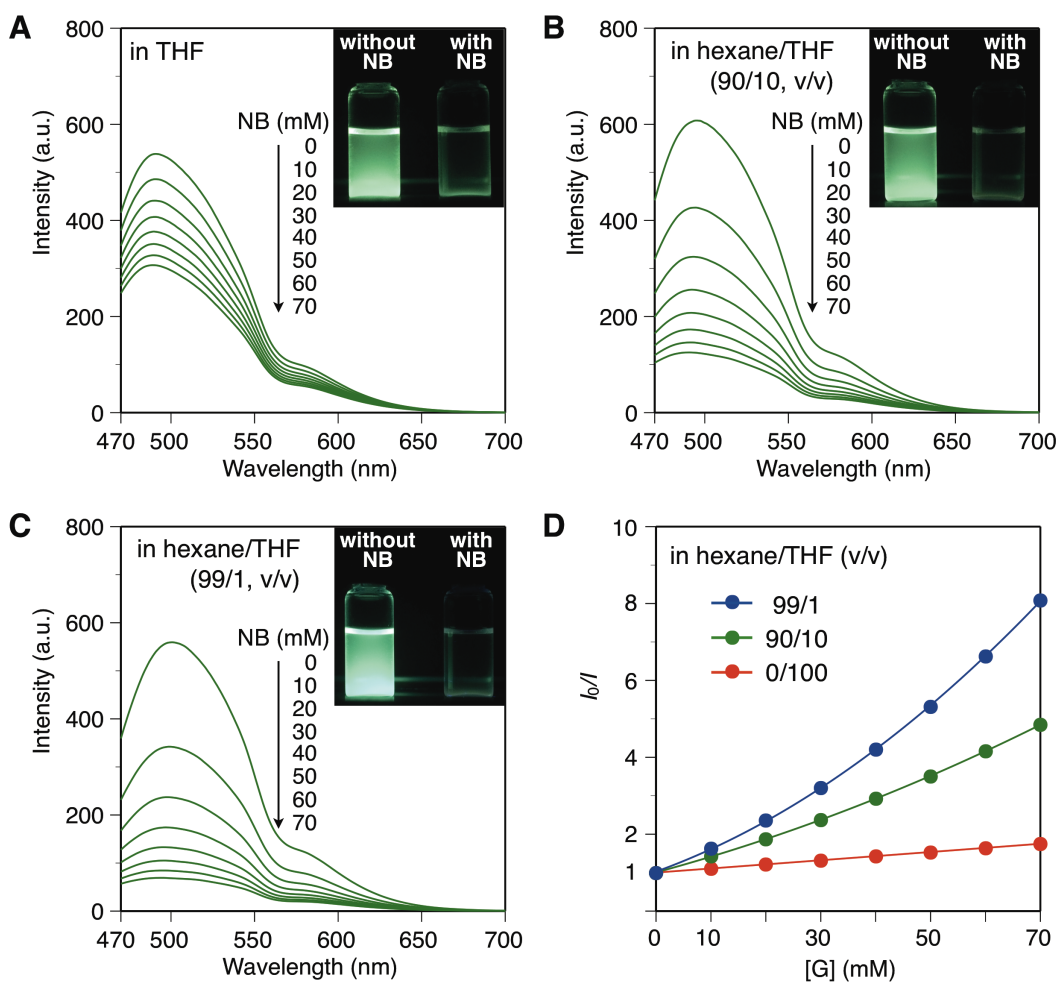


Fig. S2 Fluorescence spectra of Ce-3 ($\lambda_{\text{ex}} = 450$ nm) upon the addition of various amounts of NB (0–70 mM) in THF (A) and hexane/THF (90/10 (B) and 99/1 (C), v/v) at room temperature. [Glucose unit] = 1.0×10^{-5} M. Insets: photographs of the Ce-3 solutions in the absence (left) and presence (right) of NB (70 mM) under irradiation at 365 nm. (D) Stern–Volmer plots for the fluorescence quenching of Ce-3 by NB in hexane/THF (0/100–99/1, v/v).

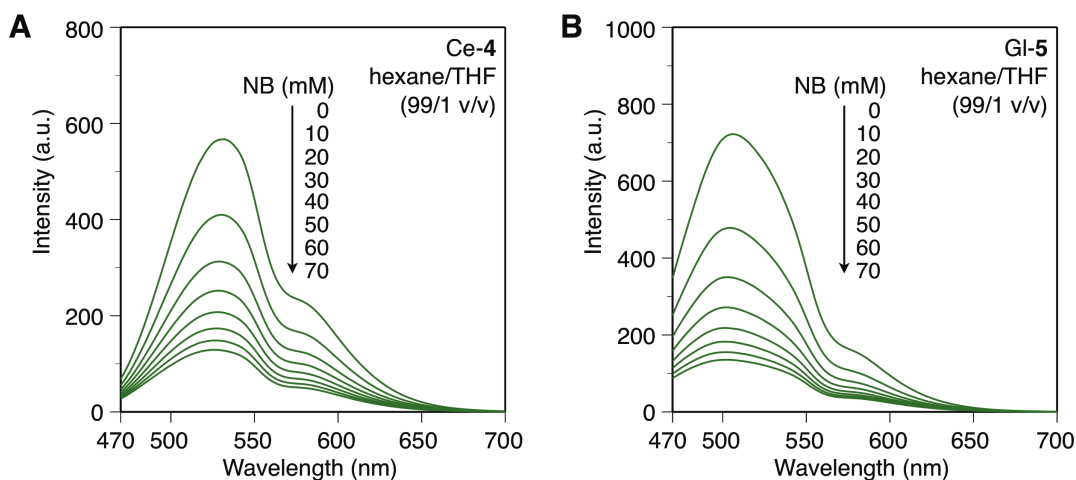


Fig. S3 Fluorescence spectra of Ce-4 (A) and Gl-5 (B) upon the addition of various amounts of NB (0–70 mM) in hexane/THF (99/1, v/v) at room temperature. [Glucose unit] = 1.0×10^{-5} M, $\lambda_{\text{ex}} = 450$ nm.

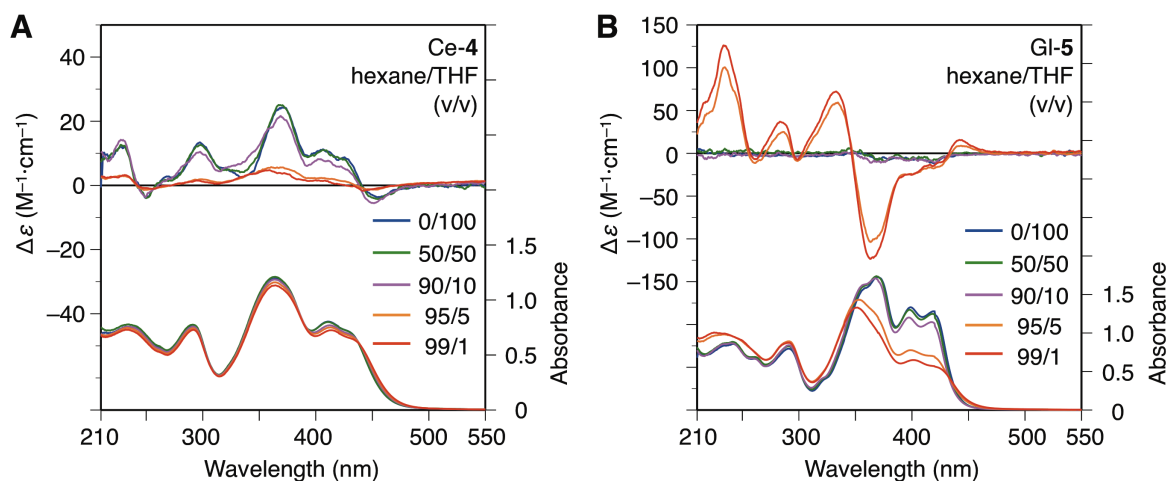


Fig. S4 CD and absorption spectra of Ce-4 (A) and Gl-5 (B) in hexane/THF (0/100–99/1, v/v) at 25 °C. [Glucose unit] = 1.0×10^{-5} M.

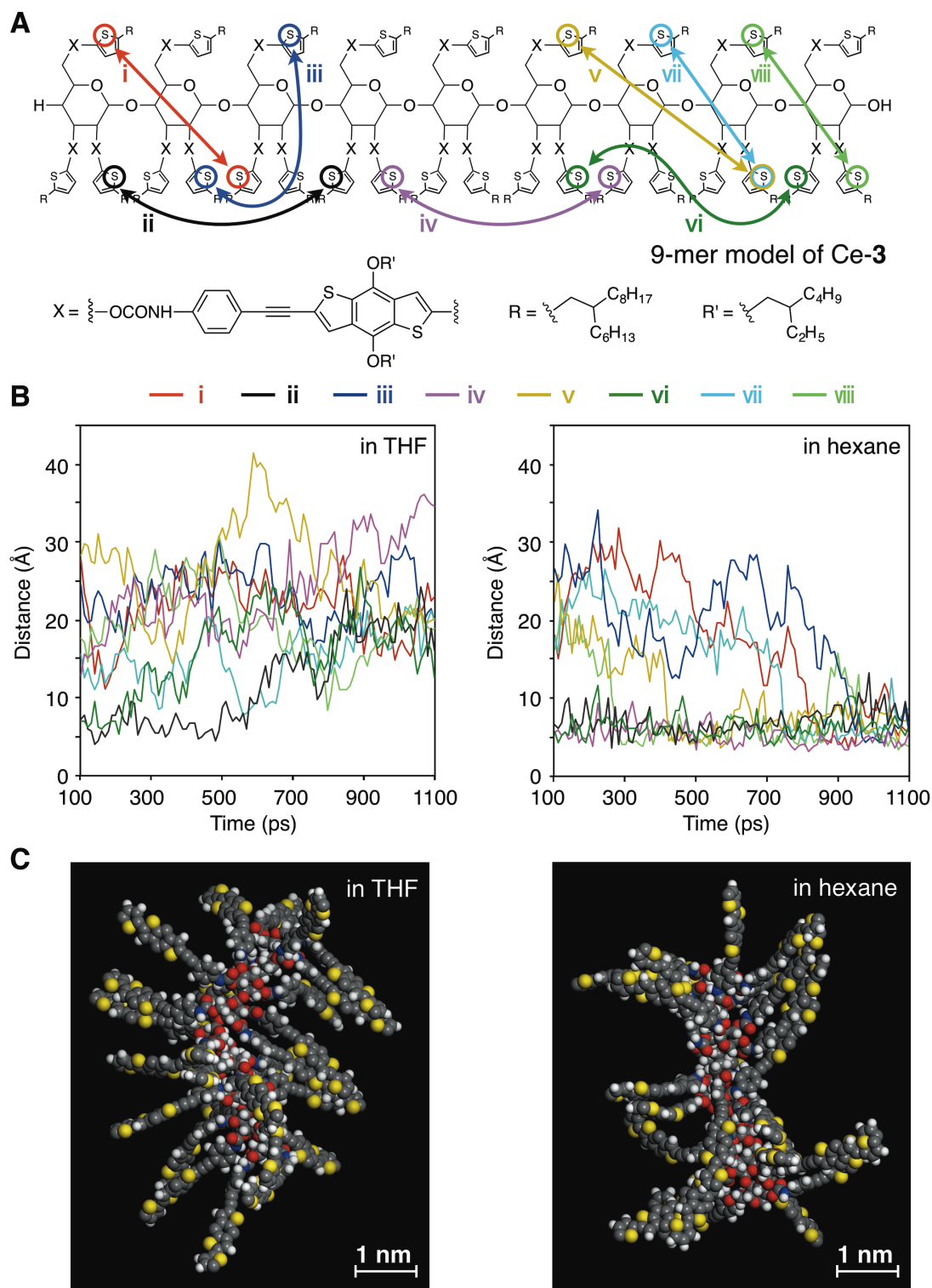


Fig. S5 (A) Structure of the 9-mer model of Ce-3. (B) Plots of the interatomic distances between sulfur atoms indicated by the arrows (i–viii) in (A) in THF (left) and hexane (right), as a function of the calculation time. (C) Molecular models of Ce-3 in THF (left) and hexane (right) at 1100 ps (final states) in MD simulations represented by space-filling models. Alkyl and alkoxy groups and solvent molecules are not displayed to clearly demonstrate the difference in the environment of the π -conjugated pendants.

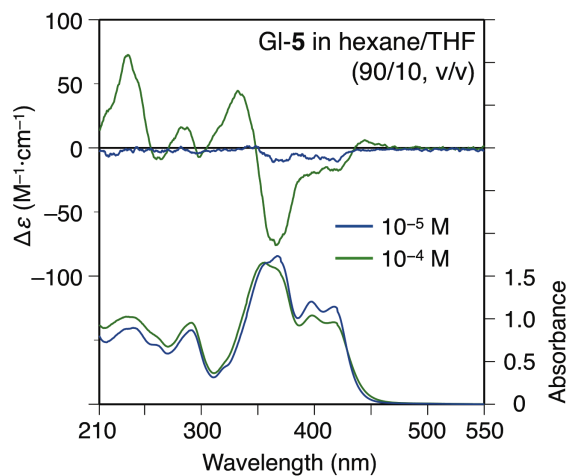


Fig. S6 CD and absorption spectra of GI-5 in hexane/THF (90/10, v/v) at 25 °C. The spectra indicated by blue and green lines were obtained from the solutions of 1.0×10^{-5} M (cell length: 10 mm) and 1.0×10^{-4} M (cell length: 1.0 mm), respectively.

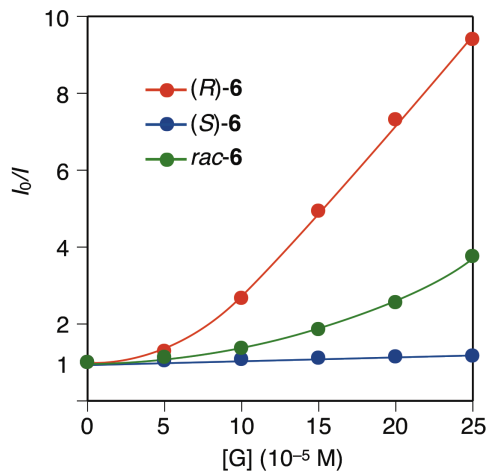


Fig. S7 Stern–Volmer plots for the fluorescence quenching of Ce-3 ($\lambda_{\text{ex}} = 450$ nm) by (*R*)-6 (red), (*S*)-6 (blue) and *rac*-6 (green) in hexane/THF (90/10, v/v) at room temperature. [Glucose unit] = 1.0×10^{-5} M.

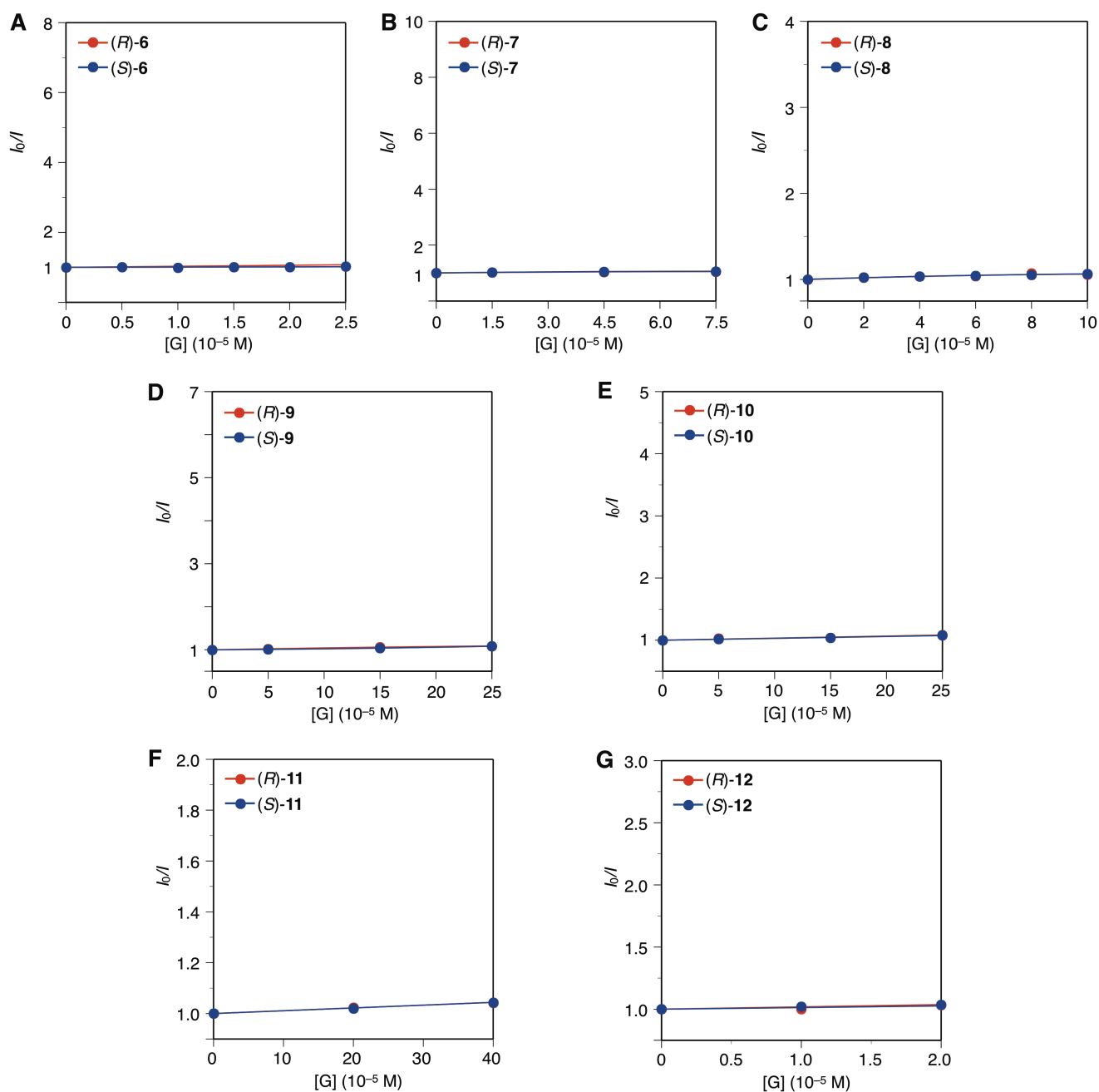


Fig. S8 Stern–Volmer plots for the fluorescence quenching of Ce-4 ($\lambda_{\text{ex}} = 450 \text{ nm}$) by the (R)- (red) and (S)- (blue) isomers of **6** (A), **7** (B), **8** (C), **9** (D), **10** (E), **11** (F) and **12** (G) in hexane/THF (99/1 (A–E) and 90/10 (F, G), v/v) at room temperature. [Glucose unit] = $1.0 \times 10^{-5} \text{ M}$.

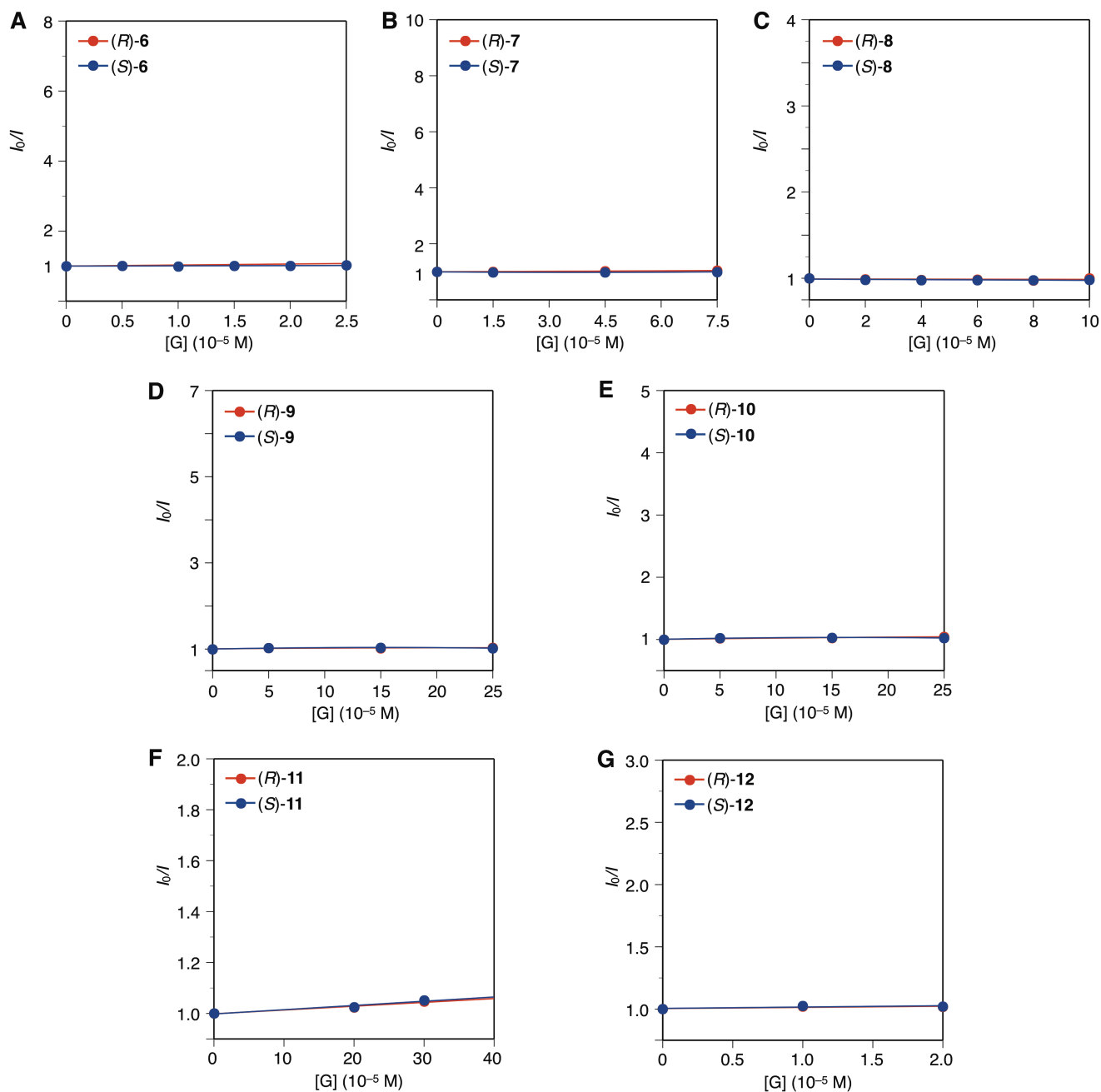


Fig. S9 Stern–Volmer plots for the fluorescence quenching of Gl-5 ($\lambda_{\text{ex}} = 450$ nm) by the *(R)*- (red) and *(S)*- (blue) isomers of **6** (A), **7** (B), **8** (C), **9** (D), **10** (E), **11** (F) and **12** (G) in hexane/THF (99/1 (A–E) and 90/10 (F, G), v/v) at room temperature. [Glucose unit] = 1.0×10^{-5} M.

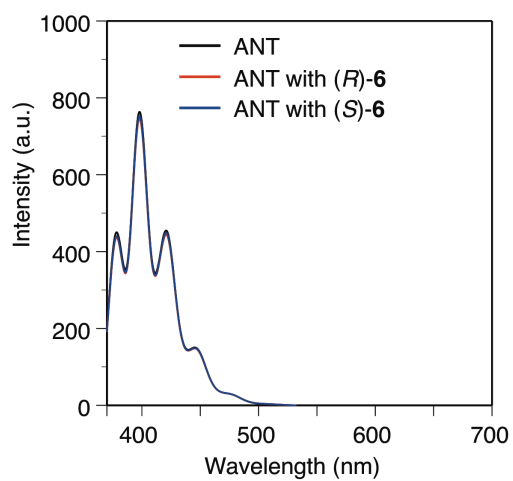


Fig. S10 (A) Fluorescence spectra of ANT in the absence (black line) and presence of (*R*)-**6** (red line) or (*S*)-**6** (blue line) in hexane/THF (99/1, v/v) at room temperature. $\lambda_{\text{ex}} = 360$ nm. $[\text{ANT}] = 6.0 \times 10^{-5}$ M. $[\mathbf{6}] = 2.5 \times 10^{-5}$ M.

NMR spectral data

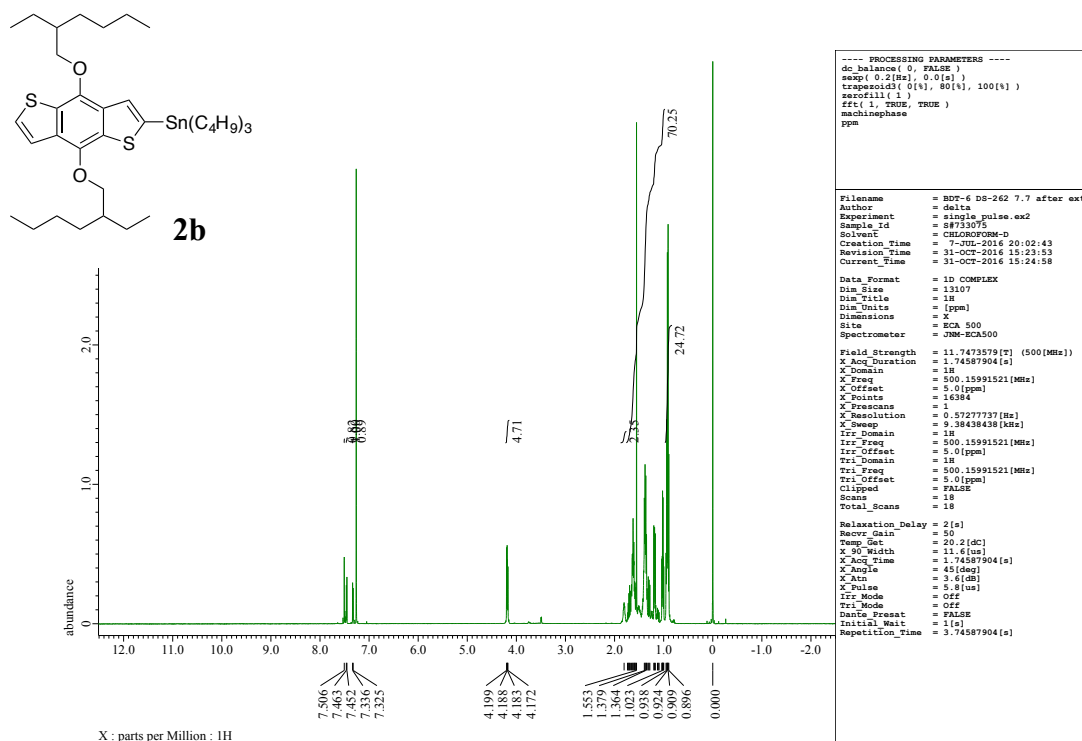


Fig. S11 ^1H NMR (500 MHz, CDCl_3 , rt) spectrum of **2b**.

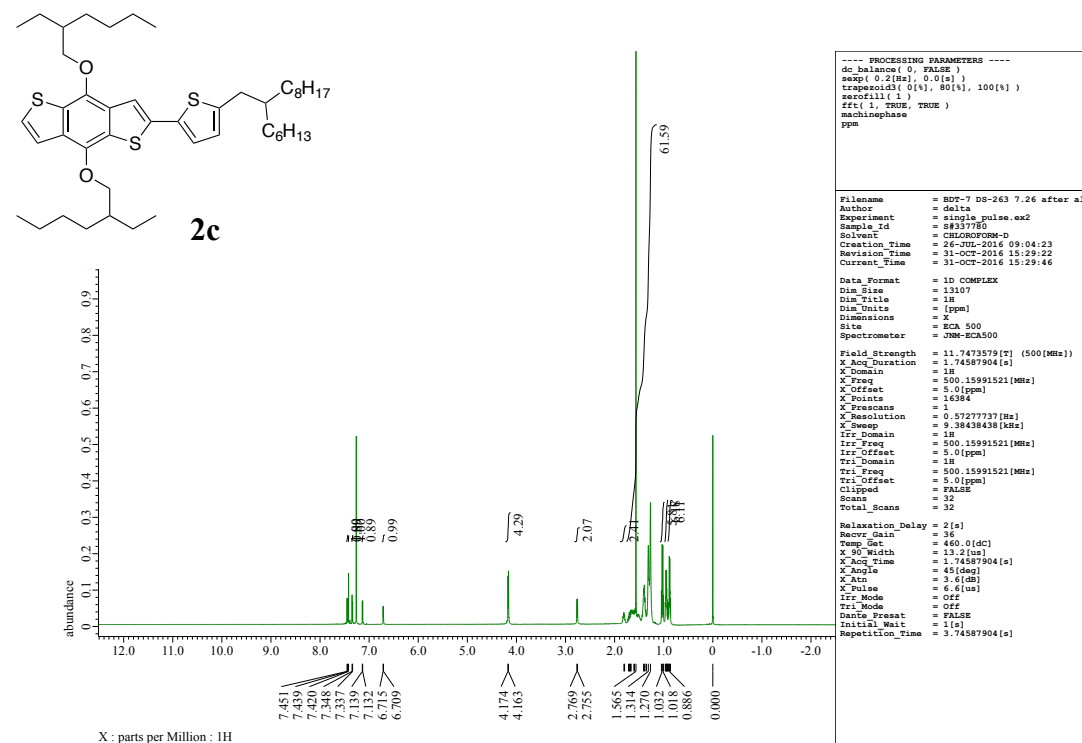


Fig. S12 ^1H NMR (500 MHz, CDCl_3 , rt) spectrum of **2c**.

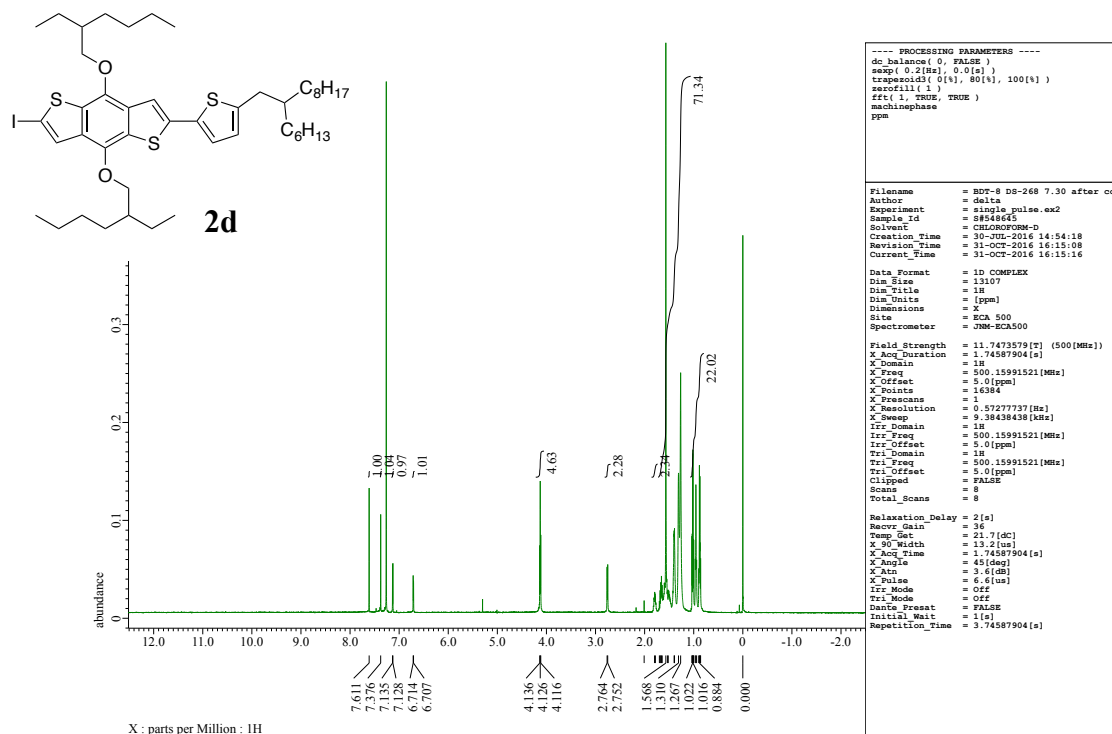


Fig. S13 ^1H NMR (500 MHz, CDCl_3 , rt) spectrum of **2d**.

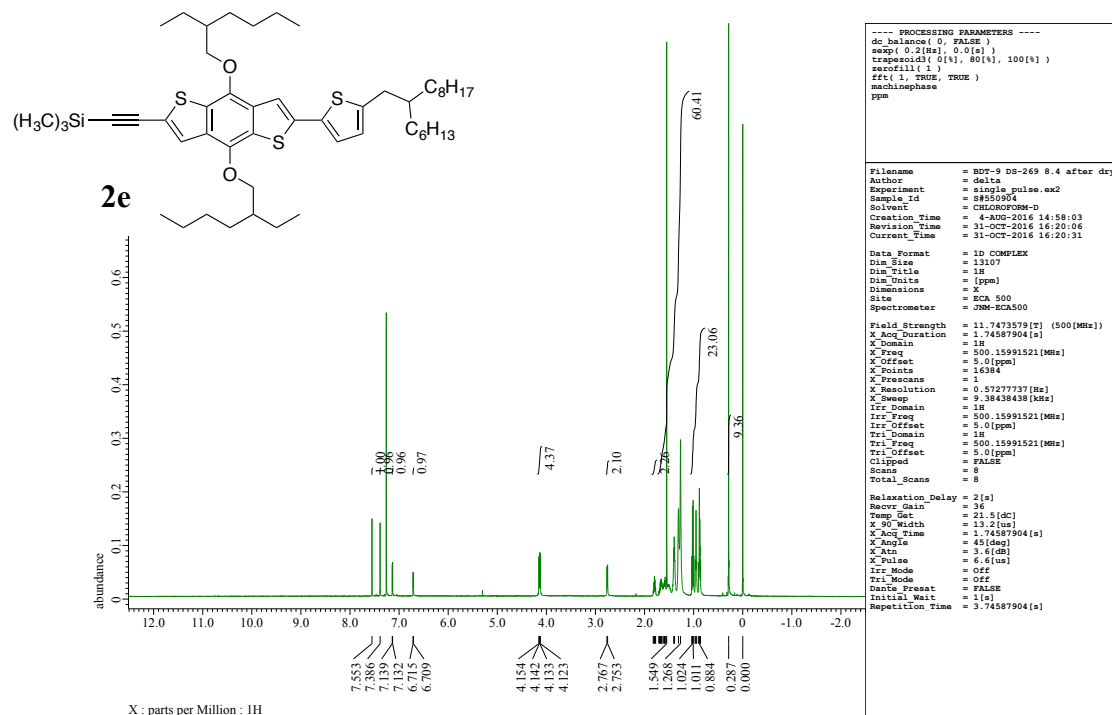


Fig. S14 ^1H NMR (500 MHz, CDCl_3 , rt) spectrum of **2e**.

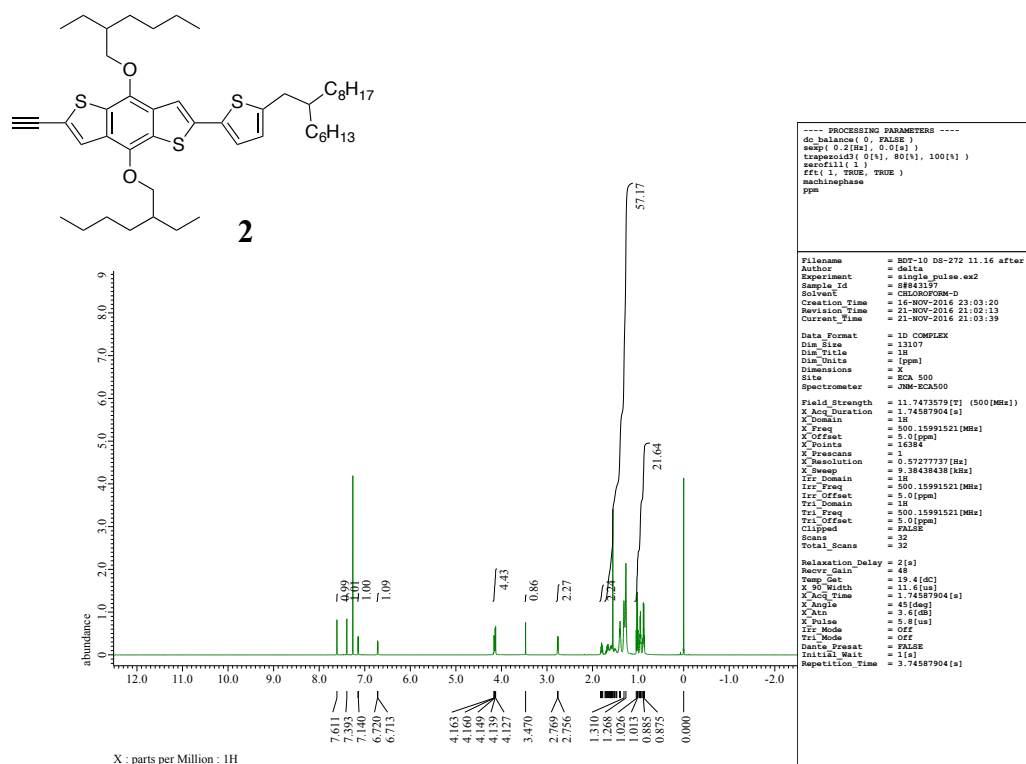


Fig. S15 ^1H NMR (500 MHz, CDCl_3 , rt) spectrum of **2**.

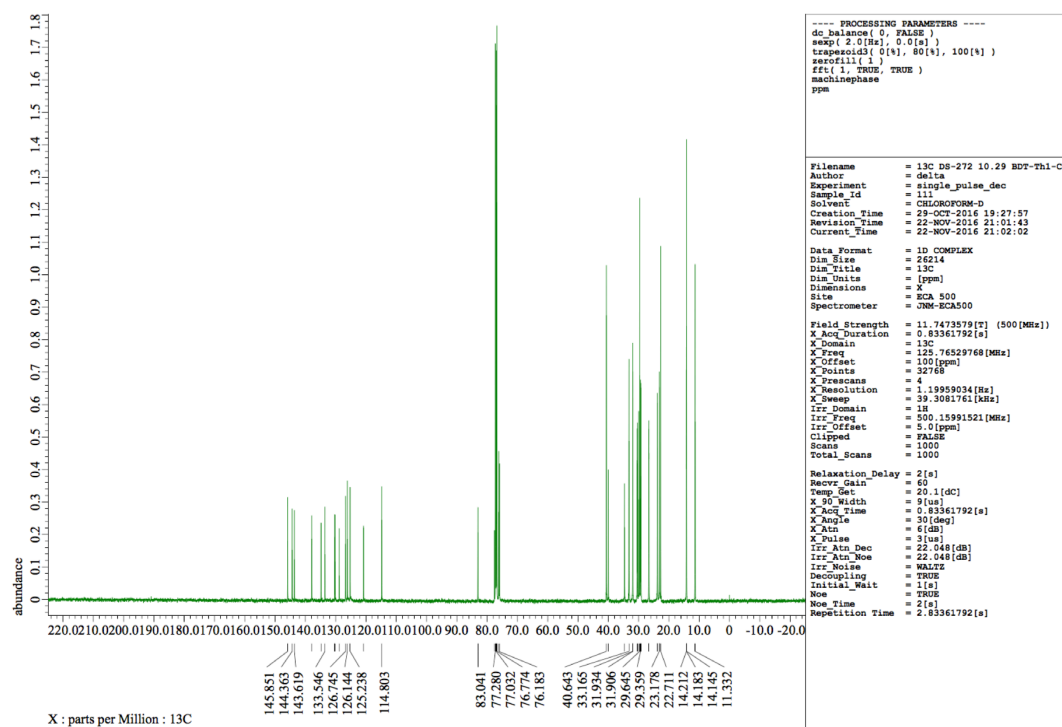


Fig. S16 ^{13}C NMR (125 MHz, CDCl_3 , rt) spectrum of **2**.

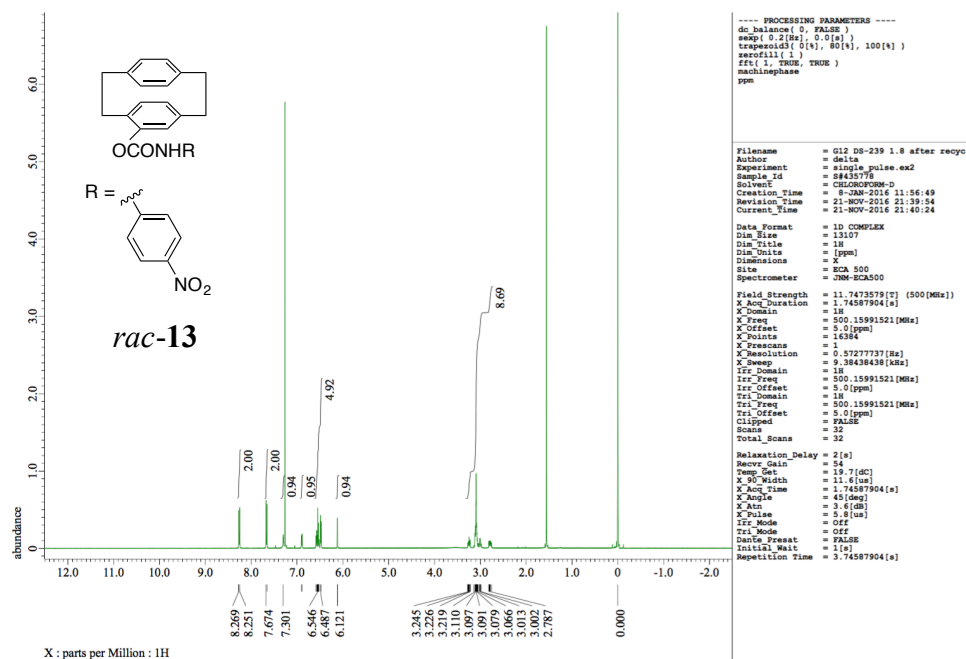


Fig. S17 ^1H NMR (500 MHz, CDCl_3 , rt) spectrum of *rac-13*.

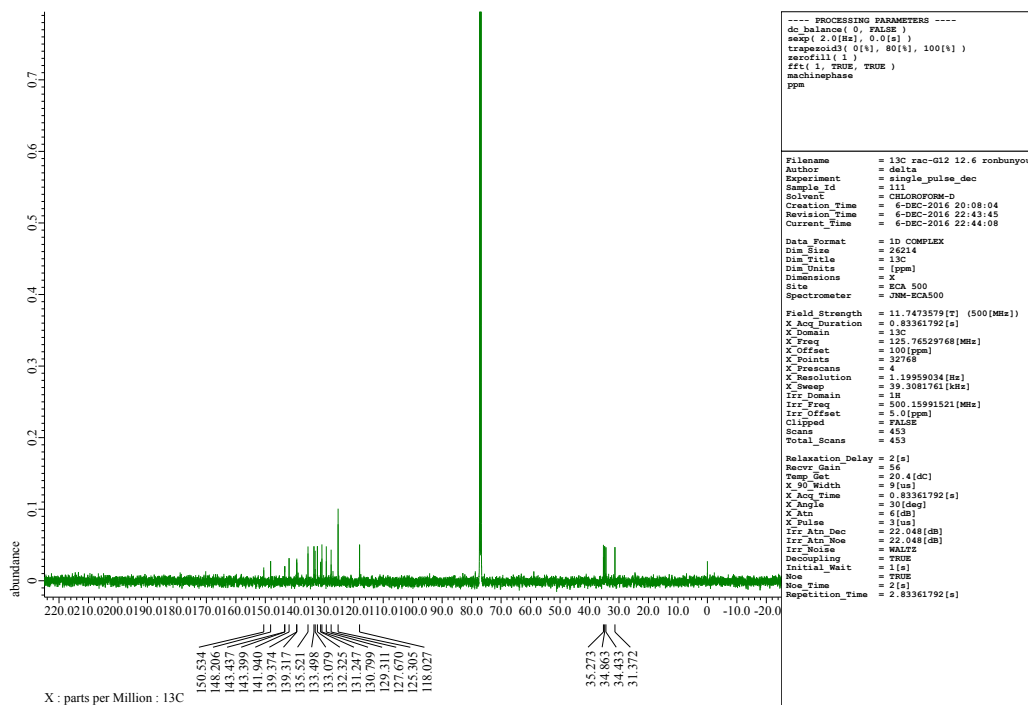


Fig. S18 ^{13}C NMR (125 MHz, CDCl_3 , rt) spectrum of *rac-13*.

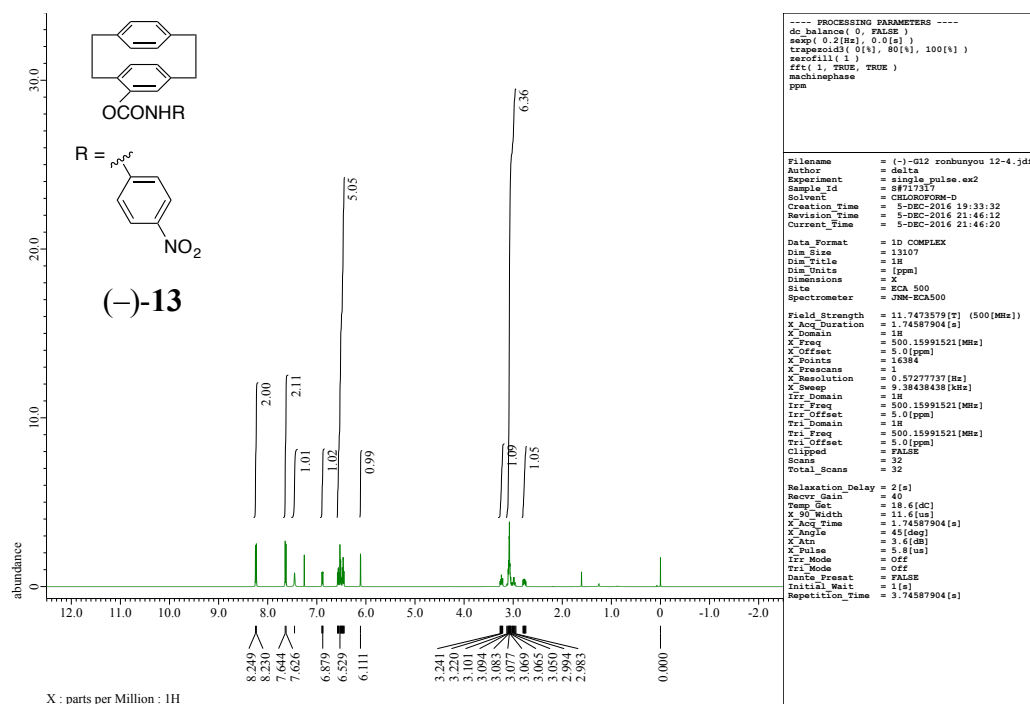


Fig. S19 ¹H NMR (500 MHz, CDCl₃, rt) spectrum of (-)-13.

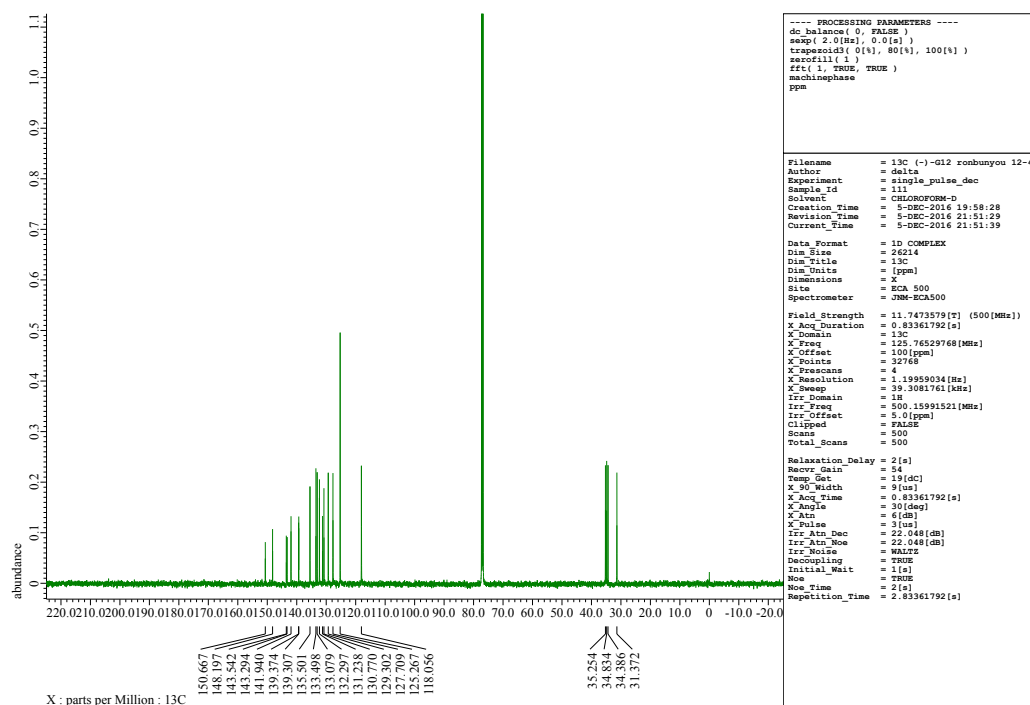


Fig. S20 ¹³C NMR (125 MHz, CDCl₃, rt) spectrum of (-)-13.

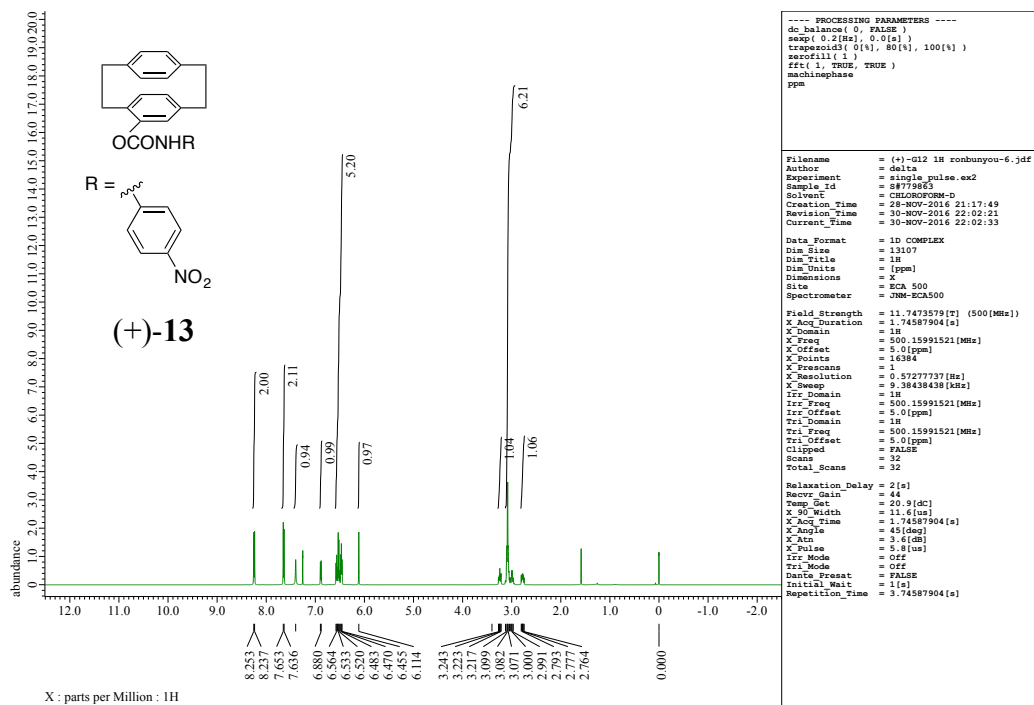


Fig. S21 ¹H NMR (500 MHz, CDCl₃, rt) spectrum of (+)-13.

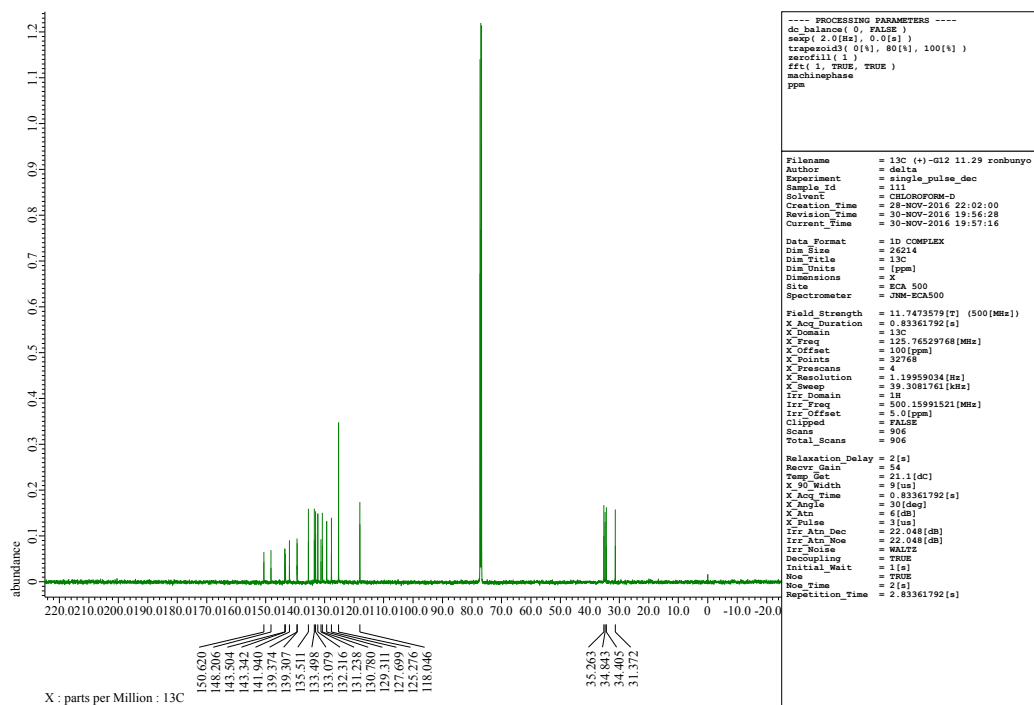


Fig. S22 ¹³C NMR (125 MHz, CDCl₃, rt) spectrum of (+)-13.

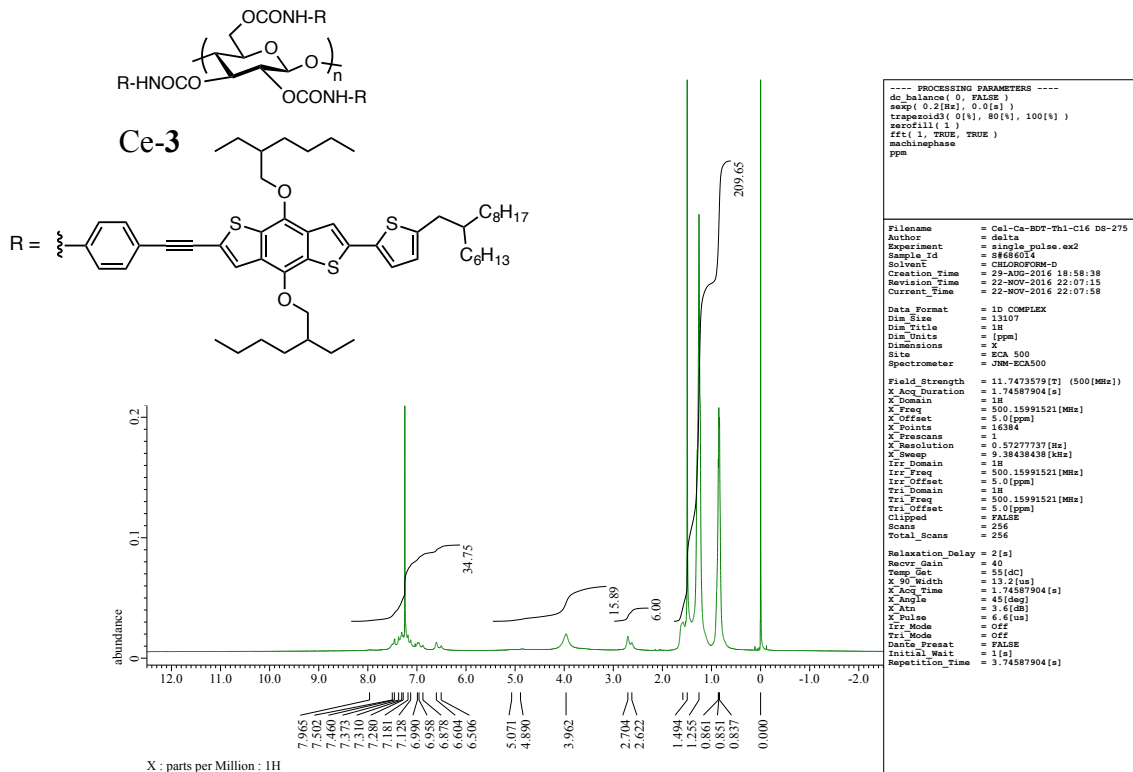


Fig. S23 ^1H NMR (500 MHz, CDCl_3 , 55 $^\circ\text{C}$) spectrum of Ce-3.

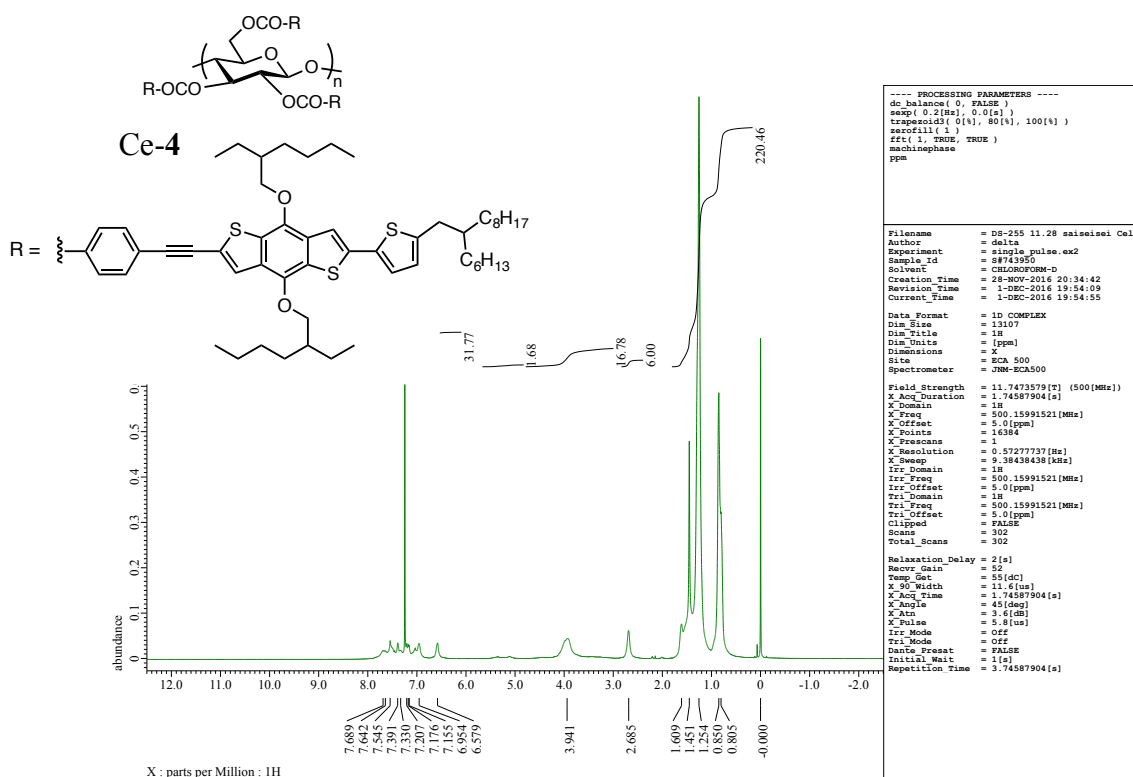


Fig. S24 ^1H NMR (500 MHz, CDCl_3 , 55 $^\circ\text{C}$) spectrum of Ce-4.

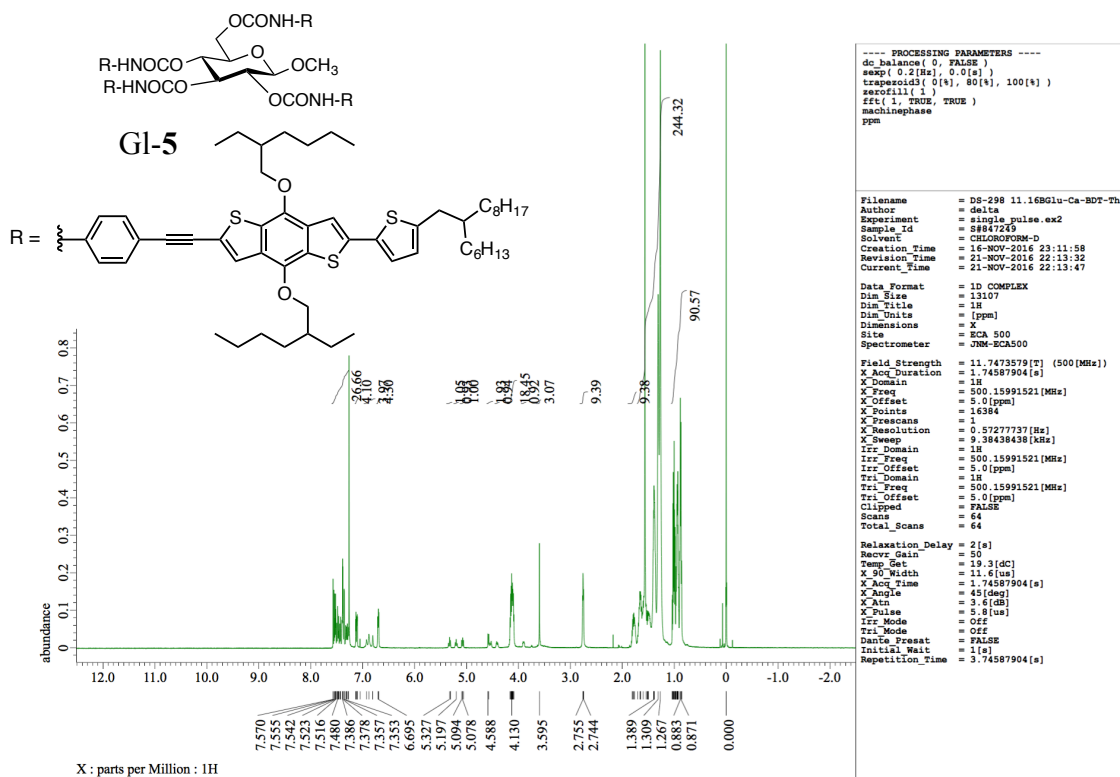


Fig. S25 ¹H NMR (500 MHz, CDCl₃, rt) spectrum of **GI-5**.

Captions for supporting movies

Movie S1 An animation of all-atom MD simulation in the NVT ensemble at 800 K of the 9-mer model of Ce-**3** (CPK model) in THF (stick model, hydrogen atoms are omitted to simplify the view) at 100–1,100 ps as the production run. The cell density and pressure were 0.863 g cm^{-3} and 0.532 GPa.

Movie S2 An animation of all-atom MD simulation in the NVT ensemble at 800 K of the 9-mer model of Ce-**3** (CPK model) in hexane (stick model, hydrogen atoms are omitted to simplify the view) at 100–1,100 ps as the production run. The cell density and pressure were 0.673 g cm^{-3} and 0.379 GPa.

References

- S1 T. Ikai, D. Suzuki, Y. Kojima, C. Yun, K. Maeda and S. Kanoh, *Polym. Chem.*, 2016, **7**, 4793–4801.
- S2 T. Ikai, C. Yun, Y. Kojima, D. Suzuki, K. Maeda and S. Kanoh, *Molecules*, 2016, **21**, 1518–1529.
- S3 Y. Liang, D. Feng, Y. Wu, S.-T. Tsai, G. Li, C. Ray and L. Yu, *J. Am. Chem. Soc.*, 2009, **131**, 7792–7799.