Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information for:

Synthesis and chiroptical properties of a π-conjugated polymer containing glucose-linked biphenyl units in the main chain capable of folding into a helical conformation

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1. Materials

Anhydrous solvents (*N*,*N*-dimethylformamide (DMF), dichloromethane, chloroform, acetonitrile and tetrahydrofuran (THF)) and common organic solvents were purchased from Kanto Kagaku (Tokyo, Japan). (+)-(4,6-*O*-Benzylidene)methyl-α-D-glucopyranoside (**1**) and [2-(2-methoxyethoxy)ethoxy]acetic acid were from Tokyo Kasei Kogyo (TCI) (Tokyo, Japan). Potassium fluoride, 5,5′-diiodo-2,2′-bithiophene (**8**) and copper (I) iodide (CuI) were from Sigma-Aldrich (St. Louis, MO, USA). Trimethylsilylacetylene (TMSA), *trans*-dichlorobis(triphenylphosphine)palladium(II) ($Pd(PPh_3)_2Cl_2$), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC-HCl) and *N*,*N*-dimethyl-4-aminopyridine (DMAP) were purchased from Wako Pure Chemical Industries (Osaka, Japan). Tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$) was purchased from Nacalai (Kyoto, Japan). Triethylamine and diisopropylamine (DIPA) were obtained from Kishida (Osaka, Japan). Chiralpak IA (25 cm × 0.46 cm (i.d.)) was purchased from Daicel (Tokyo, Japan). 5,5′-Dibromobiphenyl-2,2′-dicarboxylic acid (**2**),[1] 4-ethynylbenzoic acid (**12**),[2] ethyl 4-ethynylbenzoate (**16**)[2] and silica supported perchloric acid ($HClO_4$-SiO_2)[3] were prepared according to a literature procedure.

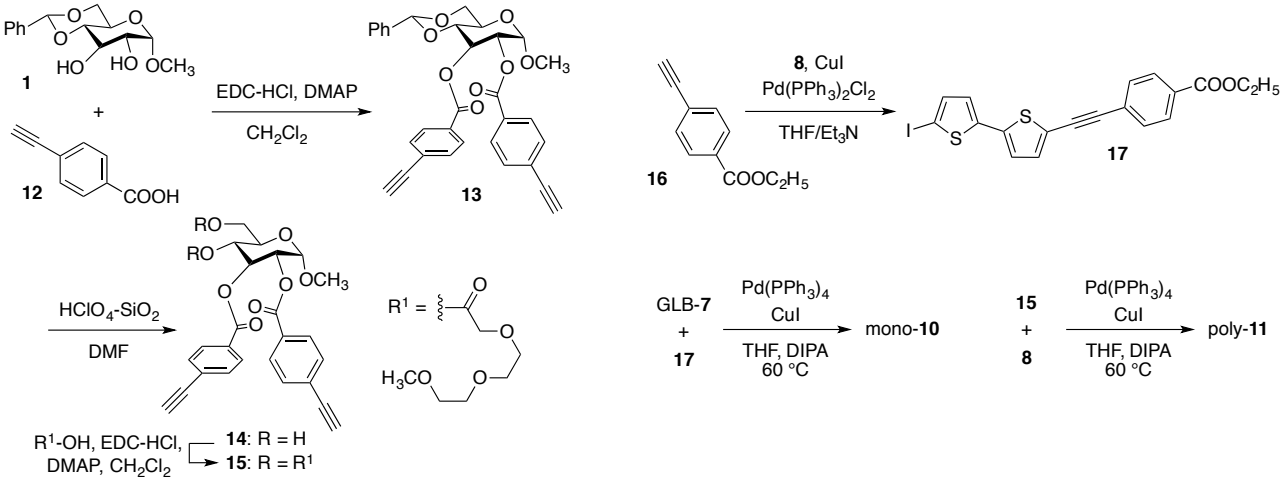
2. Instruments

NMR spectra were taken on a JNA-LA 400 (JEOL, Tokyo, Japan) (400 MHz for ^1H) or a JNM-ECA 500 (JEOL) (500 MHz for ^1H, 125 MHz for ^{13}C) or a JNM-ECA 600 (JEOL) (600 MHz for ^1H) spectrometer in $CDCl_3$ 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. The molecular weights and distributions of the polymers were estimated using size-exclusion chromatography equipped with a TSKgel MultiporeH_{XL}-M column (Tosoh, Tokyo, Japan), a JASCO PU-2080 Plus high-performance liquid chromatography (HPLC) pump and a JASCO UV-970 UV/VIS detector at 254 nm, where chloroform was used as the eluent. The molecular weight calibration curve was obtained with polystyrene standards (Tosoh). The optical rotation was measured at 25 °C with a JASCO P-1030 polarimeter. Absorption and circular dichroism (CD) spectra in solution states were measured using a

JASCO V-570 (a scanning rate of 100 nm min^{-1} and a bandwidth of 0.5 nm) and a JASCO J-725 (a scanning rate of 200 nm min^{-1} and a bandwidth of 1 nm) spectrometers, respectively, with a 0.10, 1.0, or 10 mm in path length quartz cell (UV-grade) (GL Sciences, Tokyo, Japan). The temperature was controlled using a JASCO ETC-505T (absorption spectroscopy) and a JASCO PTC-348WI apparatus (CD spectroscopy). Spin-coated films prepared on quartz substrates (USQ-grade) (Daico MFG, Kyoto, Japan) from a chloroform or a chloroform/acetonitrile (60/40, v/v) solution (10 mg mL^{-1}) were used for solid-state spectral measurements. Fluorescence quantum yields were measured on a JASCO FP-6300 using quinine sulfate in ethanol as a standard material. Chromatographic separations of GLB-**7** diastereomers were performed using a JASCO PU-2080 pump equipped with a JASCO MD-2018 UV/VIS and a JASCO CD-2095 CD detectors at *ca.* 20 °C (column, Chiralpak IA (25 cm × 0.46 cm (i.d.)); eluent, hexane/dichloromethane/ethanol (70/30/1, v/v/v); flow rate, 0.6 mL min^{-1}). The CD spectrum of each diastereomeric component of GLB-**7** was obtained by the stop-flow HPLC-CD analysis. A solution of an analyte was injected into the chromatographic system by a Rheodyne Medel 7125 injector (Rheodyne, Rohnert Park, CA, USA). Elemental analyses were performed by the Research Institute for Instrumental Analysis of Advanced Science Research Center, Kanazawa University, Kanazawa, Japan.

3. Synthesis

An optically active diethynyl compound (GLB-**6**) bearing a glucose-linked biphenyl unit was prepared according to Scheme 1. **15**, mono-**10** and poly-**11** were also synthesized according to Scheme S1.



Scheme S1 Synthesis of mono-**10** and poly-**11**.

GLB-**3**-Br**.** To a solution of **1** (2.83 g, 10.0 mmol), **2** (4.00 g, 10.0 mmol) and DMAP (3.67 g, 30.0 mmol) in dichloromethane (500 mL) was added EDC-HCl (5.76 g, 30.0 mmol) at 0 °C under nitrogen atmosphere. After stirring at 0 °C for 12 h, the mixture was warmed to room temperature and further stirred for 1 h. The reaction system was diluted with dichloromethane and the solution was washed with 1 N HCl aqueous solution and water, and then dried over Na_2SO_4. After filtration, the solvent was removed by evaporation and the crude product was purified by silica gel chromatography using dichloromethane as the eluent to give the desired product as a white solid (4.60 g, 71% yield). ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 7.70-7.48 (m, 6H, ArH), 7.43-7.34 (m, 5H, ArH), 5.73 (t, J = 9.6 Hz, 1H, CH), 5.58 (s, 1H, CH), 5.32 (dd, J = 9.5, 3.5 Hz, 1H, CH), 4.99 (d, J = 3.5, 1H, CH), 4.36 (dd, J = 10.5, 4.5 Hz, 1H, CH), 4.50-3.97 (m, 1H, CH), 3.92 (t, J = 9.5, 1H, CH), 3.85 (t, J = 10.0, 1H, CH), 3.51 (s, 3H, OCH_3).

GLB-**4.** To a solution of GLB-**3**-Br (4.60 g, 7.12 mmol), $Pd(PPh_3)_2Cl_2$ (0.50 g, 0.71 mmol) and CuI (0.14 g, 0.74 mmol) in degassed THF/triethylamine (3/1, v/v) (91 mL) was added TMSA (2.60 mL, 18.4 mmol). The solution was stirred at 60 °C for 12 h. After cooling to room temperature, the reaction mixture was diluted with dichloromethane and the solution was washed with 1 N HCl aqueous solution and water, and then dried over Na_2SO_4. After removing the solvent by evaporation, the crude product was purified by silica gel chromatography using hexane–dichloromethane (3/1, v/v) as the eluent to give the desired product as a pale yellow solid (4.39 g, 91% yield). ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 7.61-7.35 (m, 11H, ArH), 5.73 (t, J = 10.0 Hz, 1H, CH), 5.59 (s, 1H, CH), 5.33 (dd, J = 9.0, 3.5 Hz, 1H, CH), 4.98 (d, J = 3.0 Hz, 1H, CH), 4.36 (dd, J = 10.0, 4.5 Hz, 1H, CH), 4.50-3.98 (m, 1H, CH), 3.93 (t, J = 9.0, 1H, CH), 3.85 (t, J = 10.5, 1H, CH), 3.51 (s, 3H, OCH_3), 0.29-0.24 (m, 18H, TMS).

GLB-**5.** To a solution of GLB-**4** (4.39 g, 6.45 mmol) in DMF (65 mL) was added potassium fluoride (5.61 g, 96.6 mmol). After stirring at room temperature for 3 h, the reaction mixture was diluted with a hexane/ethyl acetate mixture and the solution was washed with water, and then dried over Na_2SO_4. After removing the solvent by evaporation, the crude product was purified by silica gel chromatography using hexane–dichloromethane (3/1, v/v) as the eluent to give the desired product as a white solid (3.19 g, 92% yield). ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 7.64-7.37 (m, 11H, ArH), 5.74 (t, J = 10.0 Hz, 1H, CH), 5.59 (s, 1H, CH), 5.34 (dd, J = 10.0, 4.0 Hz, 1H, CH), 5.00 (d, J = 3.5 Hz, 1H, CH), 4.37 (dd, J = 10.0, 4.5 Hz, 1H, CH), 4.50-3.98 (m, 1H, CH), 3.94 (t, J = 9.0, 1H, CH), 3.86 (t, J =

10.5, 1H, CH), 3.52 (s, 3H, OCH_3), 3.20 (s, 2H, C≡CH).

GLB-**6.** To a solution of GLB-**5** (1.00 g, 1.86 mmol) in acetonitrile (50 mL) was added $HClO_4$-SiO_2 (1.15 g). After stirring at room temperature for 1 h, the reaction mixture was diluted with dichloromethane and passed through a short pad of silica gel using dichloromethane as the eluent to remove $HClO_4$-SiO_2. After removing the solvent by evaporation, the crude product was purified by silica gel chromatography using ethyl acetate as the eluent to give the desired product as a white solid (0.80 g, 96% yield). ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 7.63-7.43 (m, 6H, ArH), 5.54 (t, J = 9.5 Hz, 1H, CH), 5.21 (dd, J = 10.0 Hz, 3.5 Hz, 1H, CH), 4.95 (d, J = 3.5 Hz, 1H, CH), 4.04-3.97 (m, 1H, CH), 3.93-3.85 (br, 1H, CH), 3.85-3.72 (m, 2H, CH), 3.45 (s, 3H, OCH_3), 3.21_1 (s, 1H, C≡CH), 3.20_8 (s, 1H, C≡CH), 2.81 (t, J = 5.5 Hz, 1H, OH).

13. To a solution of **1** (1.00 g, 3.54 mmol), **12** (1.13 g, 7.73 mmol) and DMAP (0.95 g, 7.8 mmol) in dichloromethane (10.6 mL) was added EDC-HCl (1.49 g, 7.79 mmol) at 0 °C under nitrogen atmosphere. After stirring at room temperature for 4 h, the reaction system was diluted with dichloromethane and the solution was washed with 1 N HCl aqueous solution and water, and then dried over Na_2SO_4. After filtration, the solvent was removed by evaporation and the crude product was purified by silica gel chromatography using dichloromethane as the eluent to give the desired product as a white solid (1.75 g, 92% yield). ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 7.96-7.89 (m, 4H, ArH), 7.50-7.40 (m, 6H, ArH), 7.35-7.26 (m, 3H, ArH), 6.03 (t, J = 9.5 Hz, 1H, CH), 5.56 (s, 1H, CH), 5.23 (dd, J = 10.0, 3.5 Hz, 1H, CH), 5.16 (d, J = 4.0 Hz, 1H, CH), 4.37 (dd, J = 10.5, 5.5 Hz, 1H, CH), 4.07 (dt, J = 9.5, 4.5 Hz, 1H, CH), 3.90 (t, J = 10.0 Hz, 1H, CH), 3.86 (t, J = 10.5 Hz, 1H, CH), 3.43 (s, 3H, OCH_3), 3.22 (s, 1H, C≡CH), 3.19 (s, 1H, C≡CH).

14. The title compound was prepared from **13** in the same way as GLB-**6** and obtained in 75% yield as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$, rt): δ 7.92 (dd, J = 9.0, 3.0 Hz, 4H, ArH), 7.48 (d, J = 8.4 Hz, 4H, ArH), 5.72 (t, J = 9.0 Hz, 1H, CH), 5.21 (dd, J = 10.2, 3.6 Hz, 1H, CH), 5.10 (d, J = 3.6 Hz, 1H, CH), 4.00-3.90 (m, 3H, CH), 3.88-3.83 (m, 1H, CH), 3.44 (s, 3H, OCH_3), 3.21_9 (s, 1H, C≡CH), 3.21_6 (s, 1H, C≡CH), 3.00 (d, J = 5.4 Hz, 1H, OH), 2.07-2.03 (m, 1H, OH).

15. The title compound was prepared from **14** in the same way as GLB-**7** and obtained in 86% yield as a white solid. $[\alpha]^{25}_D$ +14.4 (c 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$, rt): δ 7.89 (dd, J = 15.6, 9.0 Hz, 4H, ArH), 7.48 (dd, J = 8.4, 6.6 Hz, 4H, ArH), 5.92 (t, J = 10.2 Hz, 1H, CH), 5.37 (t, J = 9.6 Hz,

1H, CH), 5.20 (dd, J = 10.2, 3.6 Hz, 1H, CH), 5.16 (d, J = 3.6 Hz, 1H, CH), 4.39 (dd, J = 12.6, 4.2 Hz, 1H, CH), 4.30-4.22 (m, 3H, CH, CH_2), 4.17-4.13 (m, 1H, CH), 4.05 (dd, J = 55.8, 17.4 Hz, 2H, CH_2), 3.81-3.64 (m, 6H, CH_2), 3.60-3.46 (m, 10H, CH_2), 3.44 (s, 3H, OCH_3), 3.39 (s, 3H, OCH_3), 3.36 (s, 3H, OCH_3), 3.22 (d, J = 4.2 Hz, 2H, C≡CH). ^{13}C NMR (150 MHz, $CDCl_3$, rt): δ 170.32, 169.45, 165.15, 165.13, 132.31, 132.27, 129.89, 129.76, 128.89, 128.87, 127.54, 127.51, 97.06, 82.73, 82.67, 80.65, 80.61, 72.04, 71.96, 71.91, 71.11, 70.89, 70.79, 70.75, 70.69, 70.57, 70.50, 68.59, 68.48, 68.22, 67.25, 62.13, 59.18, 59.14, 55.86. IR (KBr, cm^{-1}): 2107 (C≡C), 1763 (C=O), 1727 (C=O). Calcd for $C_{39}H_{46}O_{16}$: C, 60.77; H, 6.02. Found: C, 60.75; H, 6.16.

17. To a solution of **16** (0.43 g, 2.5 mmol), $Pd(PPh_3)_4$ (0.17 g, 0.15 mmol) and CuI (0.14 g, 0.74 mmol) in degassed THF/triethylamine (3/1, v/v) (38 mL) was added **8** (1.02 g, 2.44 mmol). The solution was stirred at 50 °C for 6 h. After cooling to room temperature, the reaction mixture was diluted with dichloromethane and passed through Celite to remove the metal catalyst. The solution was washed with 1 N HCl aqueous solution and water, and then dried over Na_2SO_4. After removing the solvent by evaporation, the crude product was purified by silica gel chromatography using hexane–dichloromethane (2/3, v/v) as the eluent to give the desired product as a pale yellow solid (0.37 g, 32% yield). ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 8.03 (d, J = 8.0 Hz, 2H, ArH), 7.56 (d, J = 8.6 Hz, 2H, ArH), 7.20 (d, J = 4.0 Hz, 1H, ArH), 7.03 (d, J = 3.0 Hz, 1H, ArH), 6.88 (d, J = 4.0 Hz, 1H, ArH), 4.39 (q, J = 7.3 Hz, 2H, CH_2), 1.41 (t, J = 6.9 Hz, 3H, CH_3).

mono-**10.** To a solution of GLB-**7** (41 mg, 0.053 mmol), $Pd(PPh_3)_4$ (3.8 mg, 3.3 μmol) and CuI (2.9 mg, 0.015 mmol) in degassed THF/DIPA (5/1, v/v) (38 mL) was added **17** (50 mg, 0.11 mmol). The solution was stirred at 60 °C for 12 h. After cooling to room temperature, the reaction mixture was diluted with dichloromethane and the solution was washed with 1 N HCl aqueous solution and water, and then dried over Na_2SO_4. After filtration, the solvent was removed by evaporation and the crude product was purified by silica gel chromatography using dichloromethane–methanol (15/1, v/v) as the eluent to give the desired product as a yellow solid (31 mg, 41% yield). Mp: 82.4–82.8 °C. $[\alpha]^{25}_D$ +51.2 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 8.03 (d, J = 8.0 Hz, 4H, ArH), 7.73-7.34 (m, 10H, ArH), 7.25-7.21 (m, 4H, ArH), 7.15-7.09 (m, 4H, ArH), 5.66 (t, J = 9.5 Hz, 1H, CH), 5.44-5.33 (m, 2H, CH), 5.02 (d, J = 3.5 Hz, 1H, CH), 4.44-4.06 (m, 10H, CH, CH_2), 3.85-3.49 (m, 20H, CH, CH_2, OCH_3), 3.39 (s, 3H, OCH_3), 3.38 (s, 3H, OCH_3), 1.41 (t, J = 6.5 Hz, 6H, CH_3). ^{13}C NMR (125 MHz,

$CDCl_3$, rt): δ 170.34, 169.21, 168.39, 168.19, 166.12, 138.82, 138.72, 137.14, 136.96, 133.79, 133.68, 132.32, 132.25, 131.29, 130.79, 130.13, 129.66, 127.33, 126.79, 126.55, 126.08, 124.44, 122.24, 122.06, 97.43, 94.15, 93.51, 85.50, 85.30, 75.00, 74.05, 72.02, 72.00, 71.08, 70.73, 70.68, 68.44, 67.81, 67.23, 61.91, 61.35, 59.20, 55.88, 14.46. IR (KBr, cm^{-1}): 2197 (C≡C), 1753 (C=O), 1715 (C=O). Calcd for $C_{77}H_{68}O_{20}S_4 \cdot 0.7H_2O$: C, 63.60; H, 4.81. Found: C, 63.61; H, 4.97.

poly-**11.** The title compound was prepared from **15** in the same way as poly-**9** and obtained in 97% yield as a yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$, 55 °C): δ 7.91 (dd, J = 19.2, 7.8 Hz, 4H, ArH), 7.70-7.30 (m, 4H, ArH), 7.20-6.94 (m, 4H, ArH), 5.92 (t, J = 9.6 Hz, 1H, CH), 5.35 (t, J = 9.6 Hz, 1H, CH), 5.26-5.07 (m, 2H, CH), 4.40-3.95 (m, 7H, CH, CH_2), 3.78-3.61 (m, 6H, CH_2), 3.60-3.45 (m, 10H, CH_2), 3.45 (s, 3H, OCH_3), 3.37 (s, 3H, OCH_3), 3.34 (s, 3H, OCH_3). IR (KBr, cm^{-1}): 2196 (C≡C), 1725 (C=O). Calcd for $C_{47}H_{48}O_{16}S_2 \cdot 0.6H_2O$: C, 59.81; H, 5.25. Found: C, 59.81; H, 5.25.

4. Molecular modeling

The molecular modeling and molecular mechanics (MM) calculations were performed using the CompassII Force Field as implemented in the Material Studio Version 8.0 (Dassault Systèmes BIOVIA, San Diego, CA, USA) on a Windows 7 PC. Before MM simulation, the initial structure of a polymer chain model with a head-to-tail orientation and a degree of polymerization of 20 using the repeating unit was generated.

5. Circularly polarized luminescence measurement

Photoluminescence and circularly polarized luminescence spectra in solution states were recorded at room temperature on a JASCO CPL-300 with 1.0 mm in path length quartz cell (GL Sciences, UV-grade). Spin-coated films prepared on quartz substrates (Daico MFG, USQ-grade) from a chloroform or a chloroform/acetonitrile (60/40, v/v) solution (10 mg mL^{-1}) were used for solid-state spectral measurements. A scanning rate of 50 nm min^{-1}, an excitation bandwidth of 3000 μm, a monitoring bandwidth of 3000 μm, a response time of 8 seconds and single (film state) or 4 times (solution state) accumulation were employed.

Supporting data

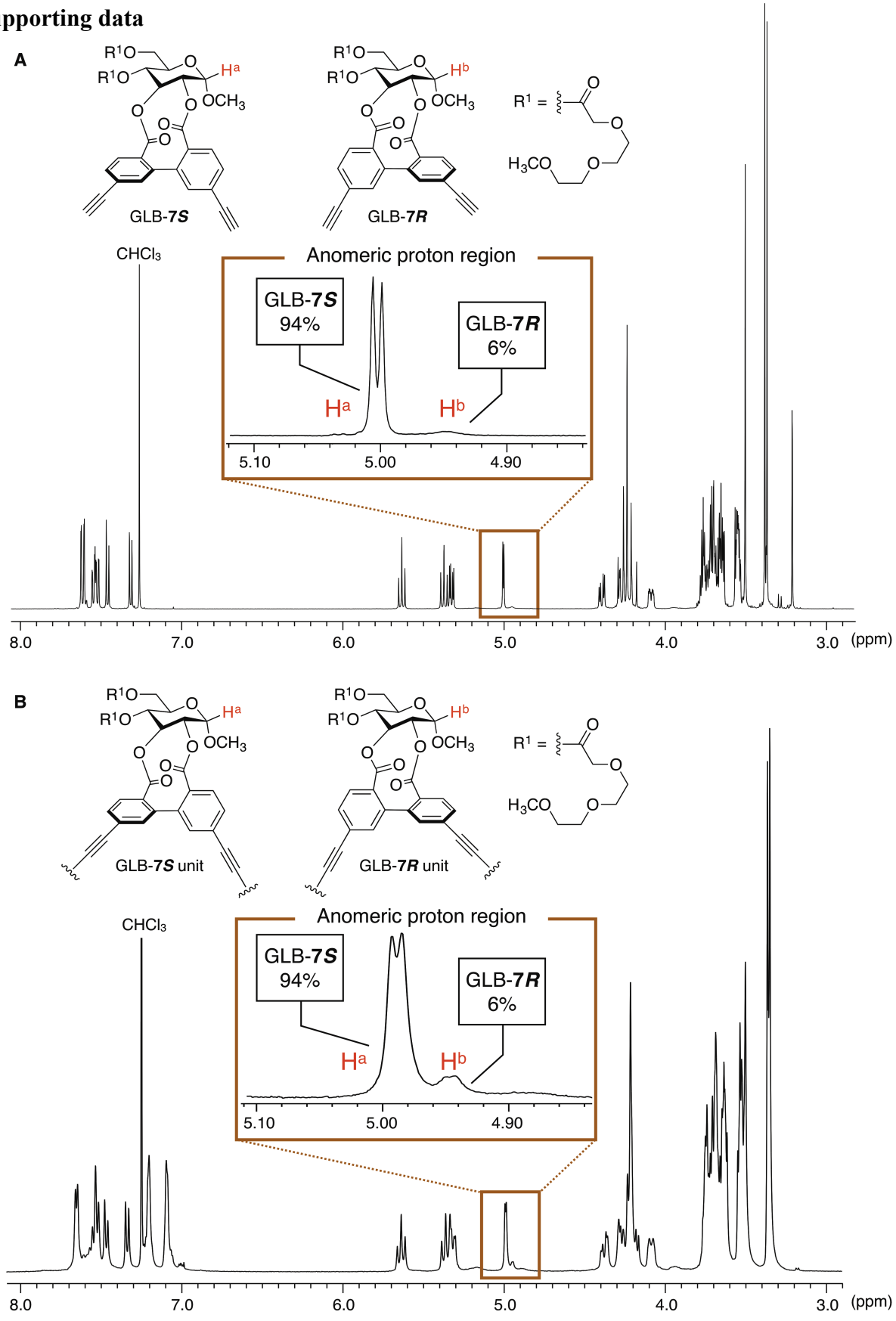


Fig. S1 ^{1}H NMR spectra of GLB-**7** (A) at room temperature and poly-**9** (B) at 55 °C in $CDCl_3$.

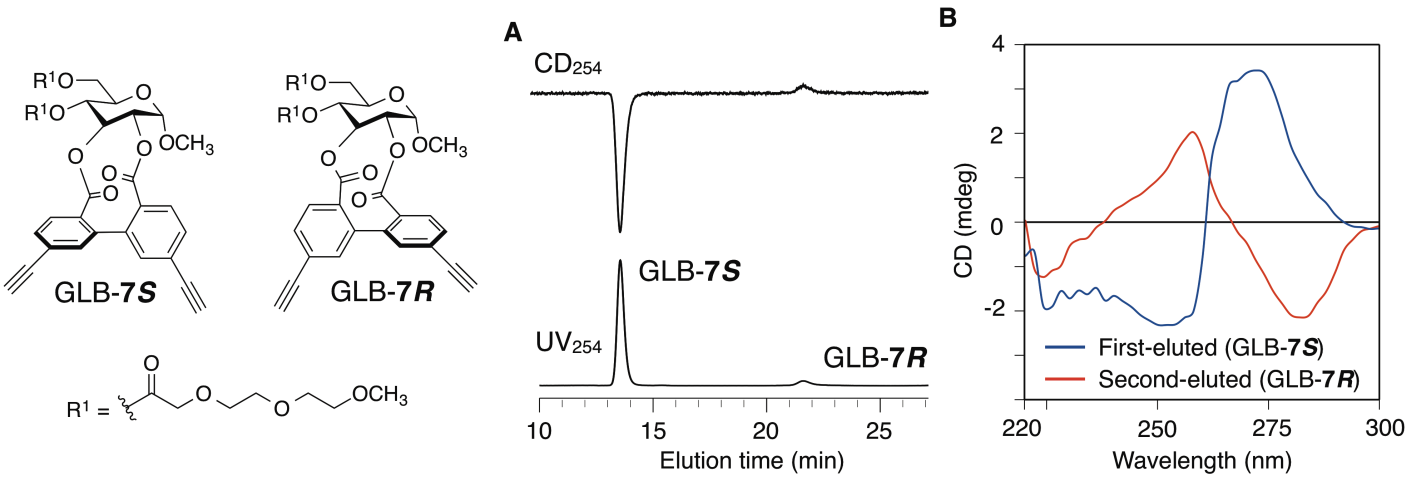


Fig. S2 (A) Chromatograms for the diastereomer separation of GLB-**7** on Chiralpak IA. The chromatograms depict CD (upper) and UV (lower) traces recorded at 254 nm (column, 25 cm × 0.46 cm (i.d.); eluent, hexane/dichloromethane/ethanol (70/30/1, v/v/v); flow rate, 0.6 mL min^{-1}; temperature, *ca.* 20 °C). (B) CD spectra of the first- (blue line) and second-eluted (red line) components in (A), obtained by stop-flow HPLC-CD analysis.

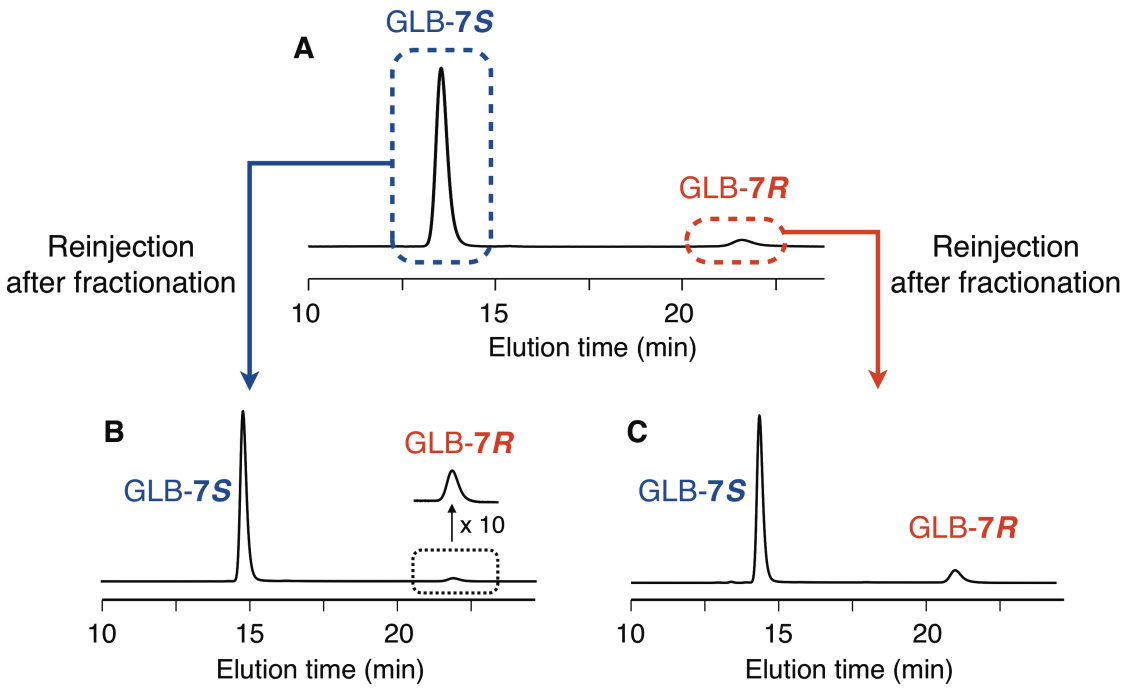


Fig. S3 Chromatograms for the diastereomer separations of GLB-**7** on Chiralpak IA. Separation results of as-synthesized GLB-**7** (A) and fractionated concentrates of the first- (B) and second-eluted (C) components in (A). Detailed chromatographic conditions are given in the caption for Fig. S2.

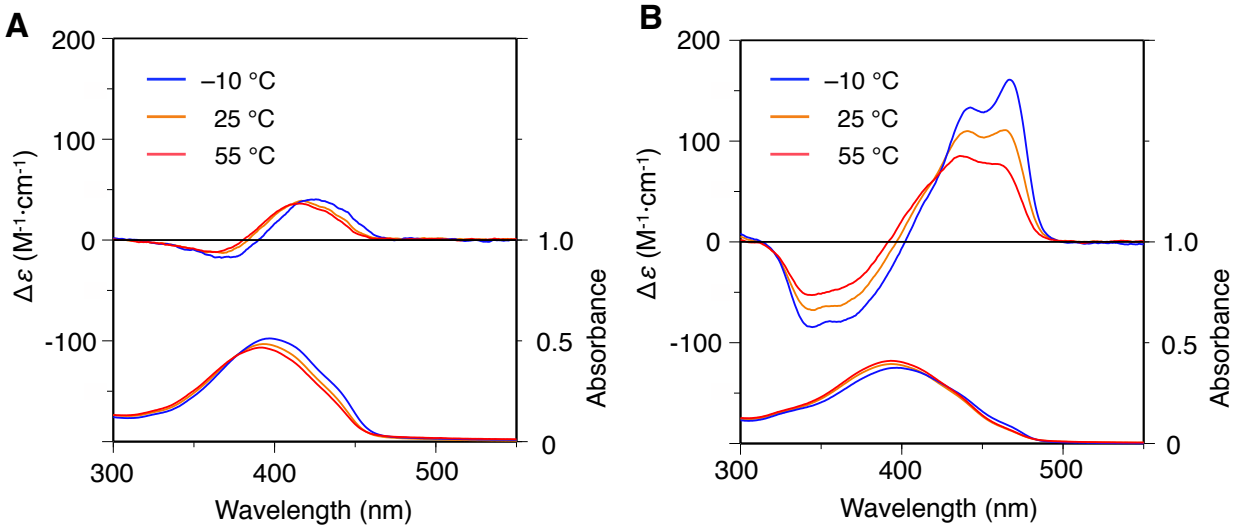


Fig. S4 CD and absorption spectra of poly-**9** in chloroform (A) and chloroform/acetonitrile (60/40, v/v) (B) at various temperatures. [glucose unit] = 1.0×10^{-4} M.

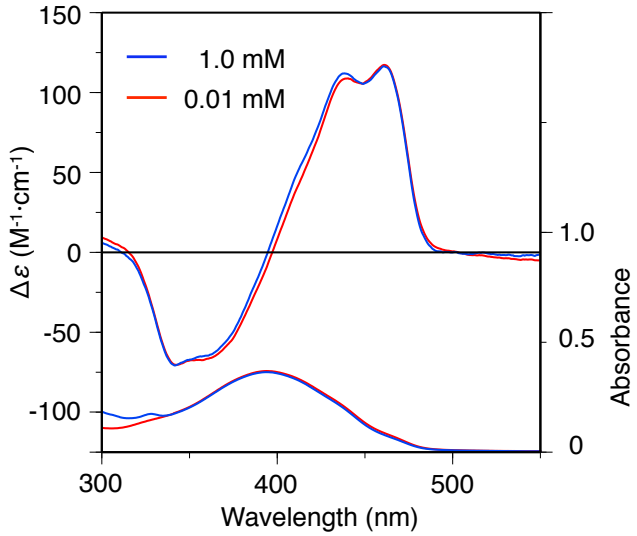


Fig. S5 CD and absorption spectra of poly-**9** in chloroform/acetonitrile (60/40, v/v) at 25 °C. The spectra indicated by red and blue lines were obtained from polymer solutions of 0.01 mM (cell length: 10 mm) and 1.0 mM (cell length: 0.10 mm), respectively.

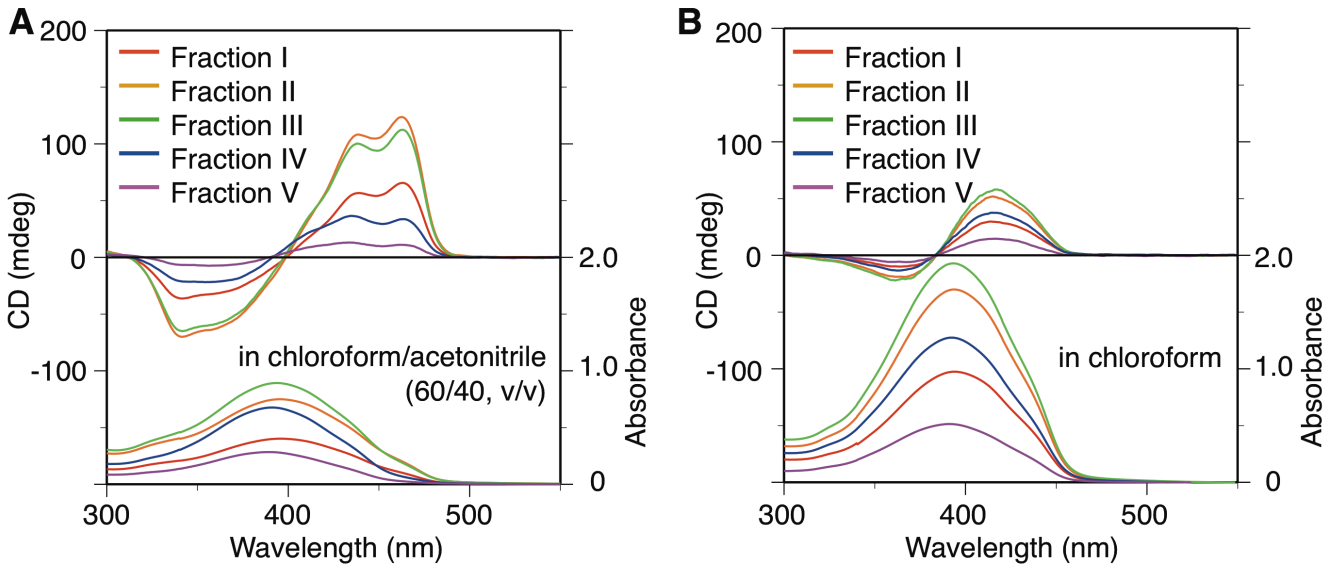


Fig. S6 (A, B) Molecular weight dependency of the CD (unprocessed) and absorption (not normalized) spectra of poly-**9** in chloroform/acetonitrile (60/40, v/v) (A) and chloroform (B) at 25 °C.

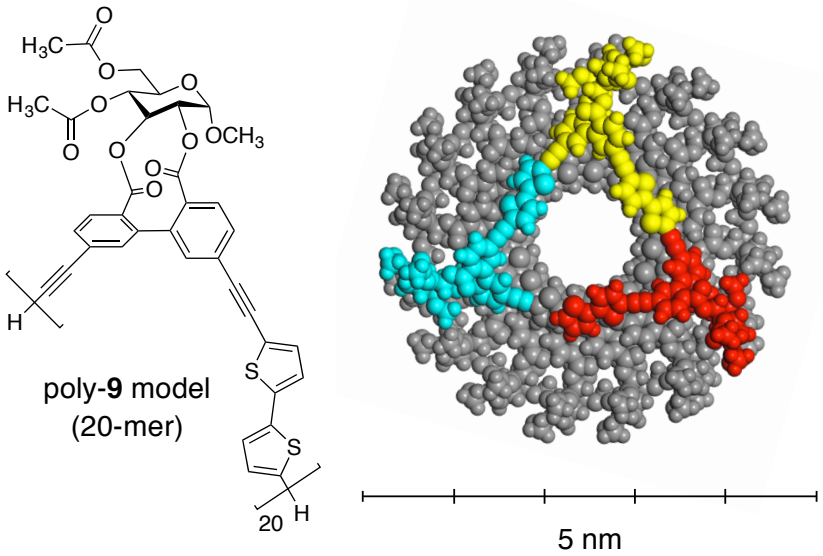


Fig. S7 Computer-generated space-filling model for the left-handed helical structure of the 20-mer model of poly-**9** (top view). The first, second and third repeating units, counting from the front of the model, are shown in red, yellow and blue, respectively, and the other repeating units are shown in grey for clarity.

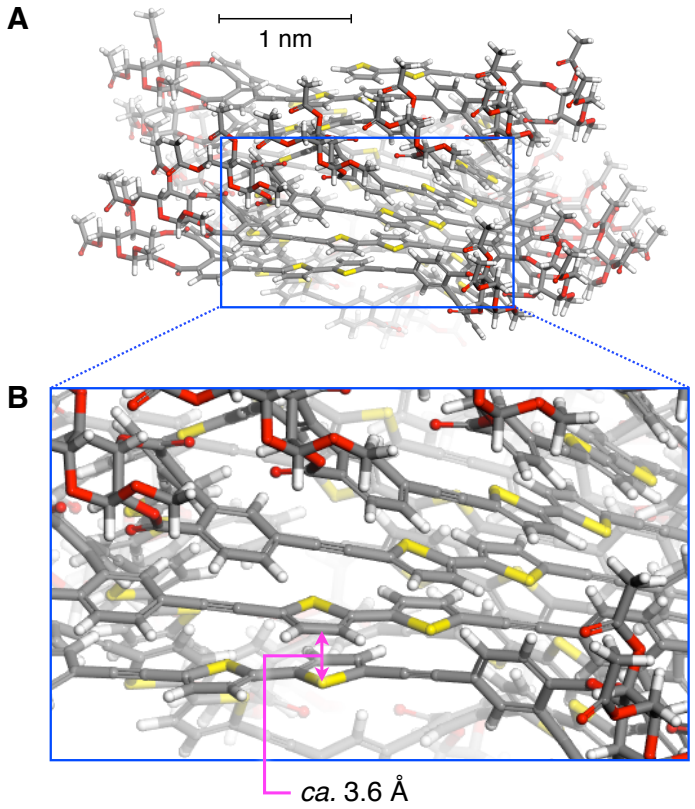


Fig. S8 (A) Computer-generated stick model for the left-handed helical structure of the 20-mer model of poly-**9** (side view). (B) Enlarged image of the region marked with a blue rectangle in (A).

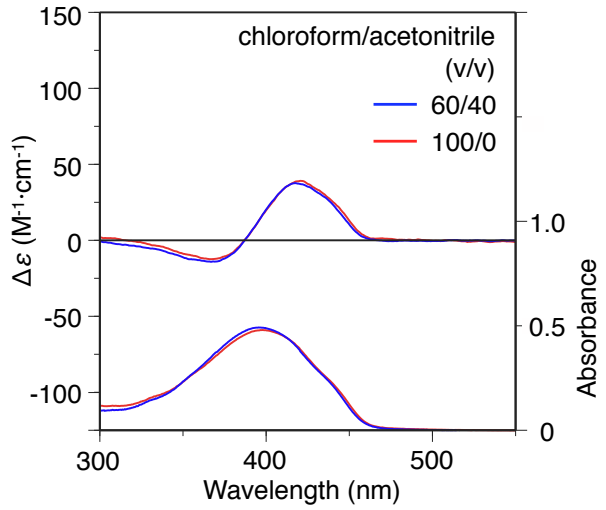


Fig. S9 CD and absorption spectra of poly-**11** in chloroform (red line) and chloroform/acetonitrile (60/40, v/v) (blue line) at 25 °C. [glucose unit] = 1.0×10^{-4} M.

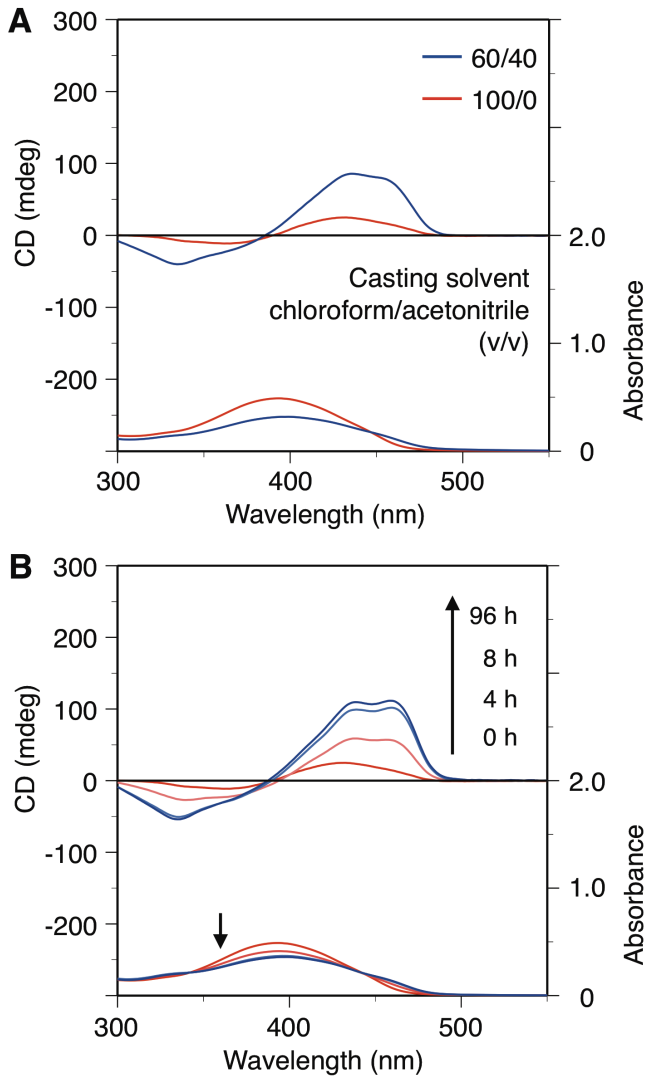


Fig. S10 (A) CD (unprocessed) and absorption (not normalized) spectra of poly-**9** in the film states at room temperature. The spectra indicated by red and blue lines were obtained from the spin-cast poly-**9** films prepared from chloroform and chloroform/acetonitrile (60/40, v/v) solutions, respectively. (B) Time-dependent CD spectral changes of a chloroform-cast film of poly-**9** on exposure to acetonitrile vapor.

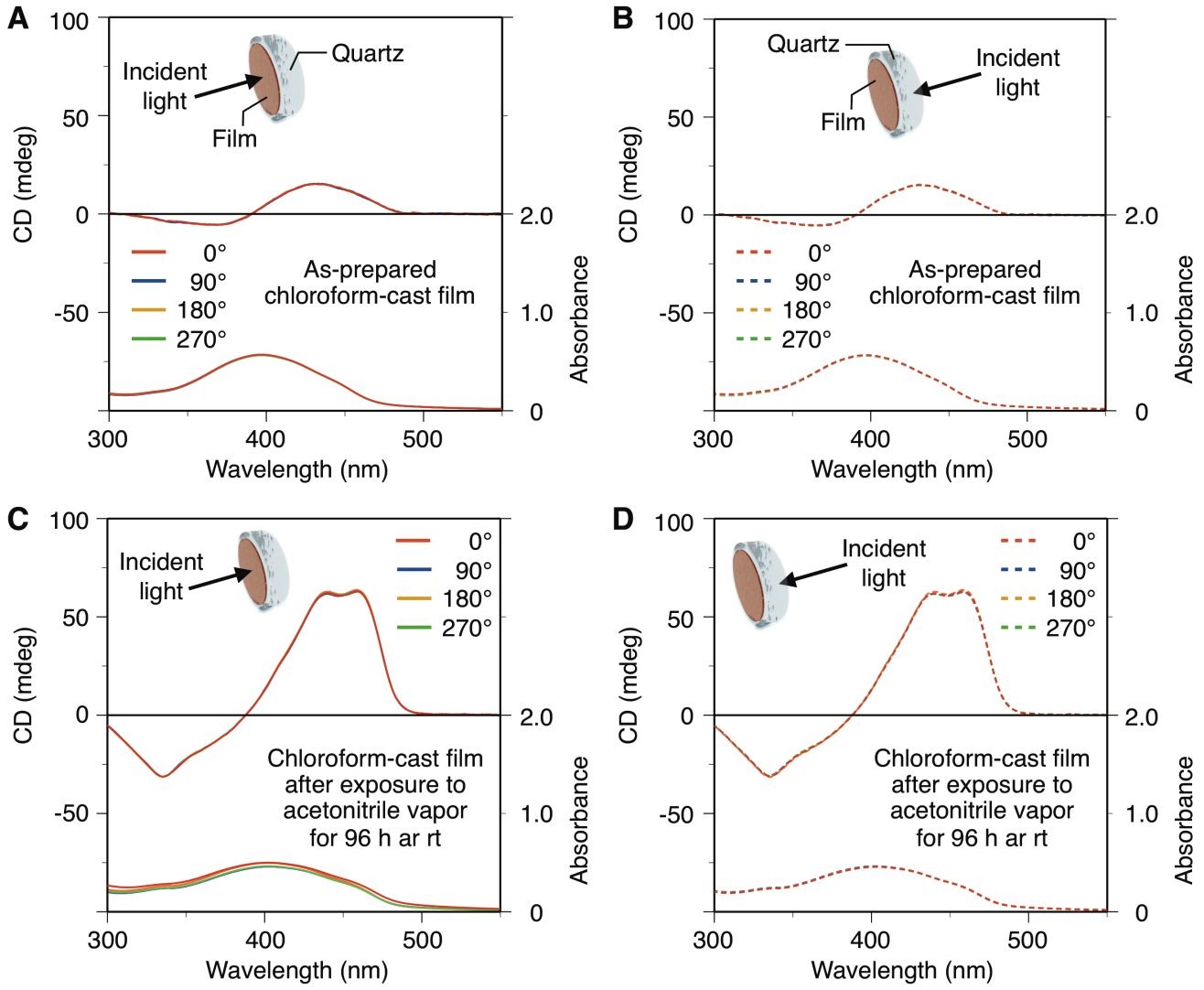


Fig. S11 CD and absorption spectra of poly-**9** in the as-prepared chloroform-cast film (A, B) and the chloroform-cast film after exposure to acetonitrile vapor for 96 h at room temperature (C, D). The spectra were measured at different rotation angles (A, C) and by reversing a quartz plate to be an incident light/quartz/film arrangement (B, D).

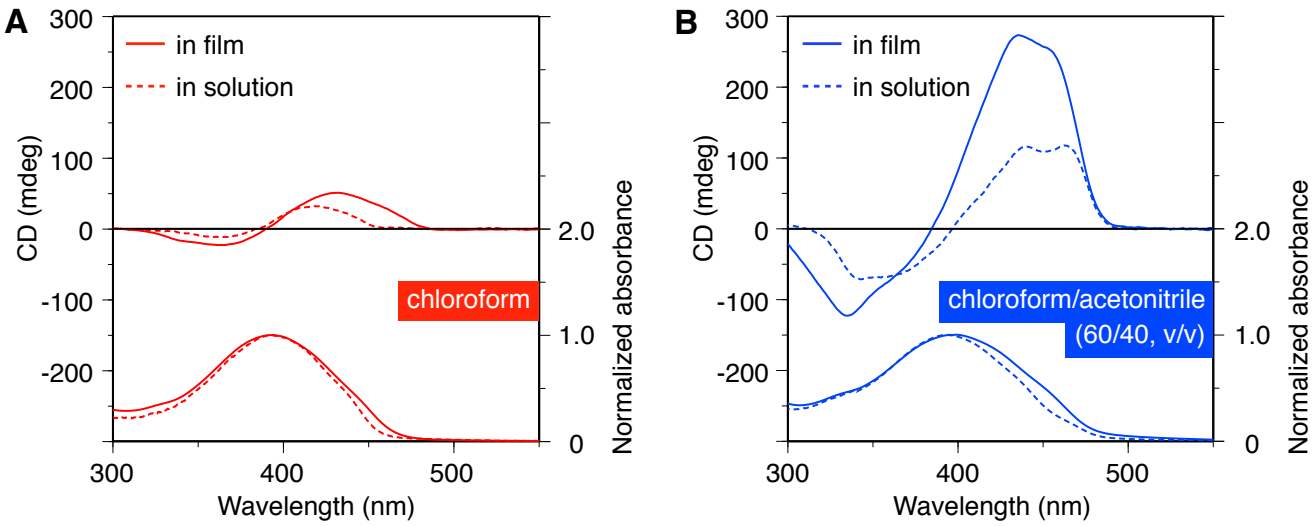


Fig. S12 (A) CD and absorption spectra of poly-**9** ([glucose unit] = 1.0×10^{-4} M) in chloroform at 25 °C (dashed line) and of a poly-**9** cast film prepared from a chloroform solution at room temperature (solid line). (B) CD and absorption spectra of poly-**9** ([glucose unit] = 1.0×10^{-4} M) in chloroform/acetonitrile (60/40, v/v) at 25 °C (dashed line) and of a poly-**9** cast film prepared from a chloroform/acetonitrile (60/40, v/v) solution at room temperature (solid line). To allow comparison of the CD intensities between the solution and film states, the CD spectra were normalized with respect to the absorbance at the absorption maximum wavelength.

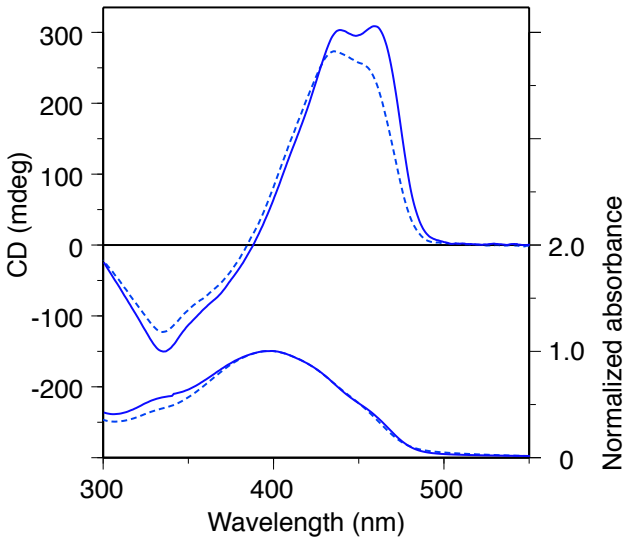


Fig. S13 CD and absorption spectra of the as-prepared poly-**9** cast film prepared from a chloroform/acetonitrile (60/40, v/v) solution (dashed line) and of a chloroform-cast poly-**9** film after exposure to acetonitrile vapor for 96 h (solid line). To allow comparison of the CD intensities between the two films, the CD spectra were normalized with respect to the absorbance at the absorption maximum wavelength.

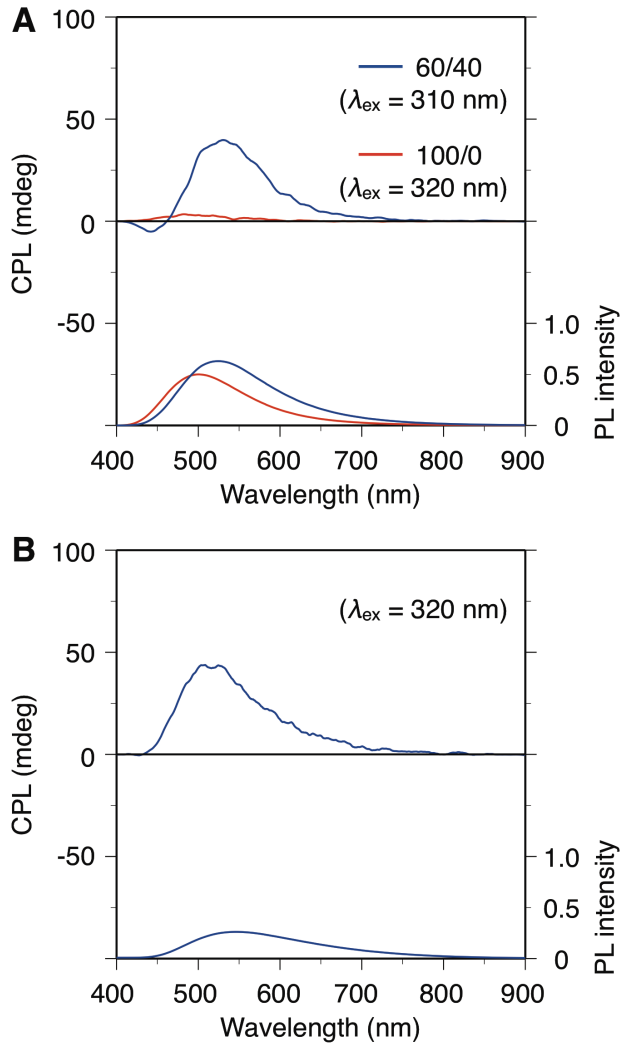


Fig. S14 PL (not normalized) (bottom) and CPL (unprocessed) (top) spectra of poly-**9** (1.0×10^{-4} M) in chloroform/acetonitrile (100/0 or 60/40, v/v) (A) and of a chloroform-cast film of poly-**9** after exposure to acetonitrile vapor for 96 h (B) at room temperature.

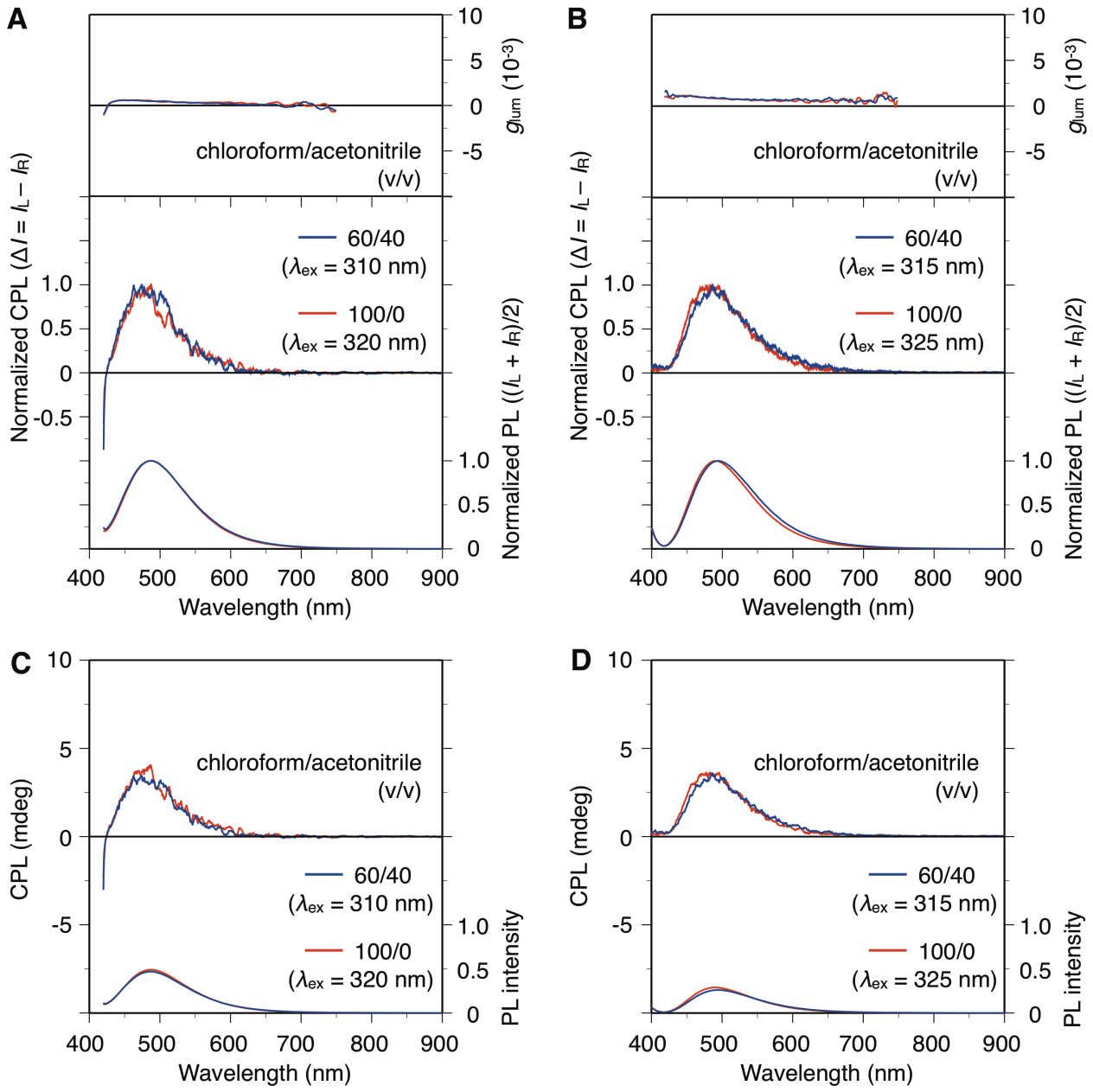


Fig. S15 (A, B) PL (bottom), CPL (middle) and g_{lum} (top) spectra of mono-**10** (A) and poly-**11** (B) in chloroform/acetonitrile (100/0 or 60/40, v/v). [glucose unit] = 1.0×10^{-4} M. (C, D) PL (not normalized) (bottom) and CPL (unprocessed) (top) spectra of mono-**10** (C) and poly-**11** (D) in chloroform/acetonitrile (100/0 or 60/40, v/v). [glucose unit] = 1.0×10^{-4} M.

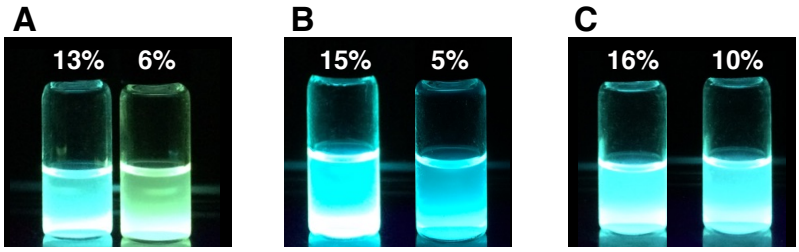


Fig. S16 Photographs of the solutions of poly-**9** (A), poly-**11** (B) and mono-**10** (C) in chloroform (left) and chloroform/acetonitrile (60/40, v/v) (right) under irradiation at 365 nm. The percentage values represent the fluorescence quantum yields in the corresponding solutions. [glucose unit] = 1.0×10^{-4} M.

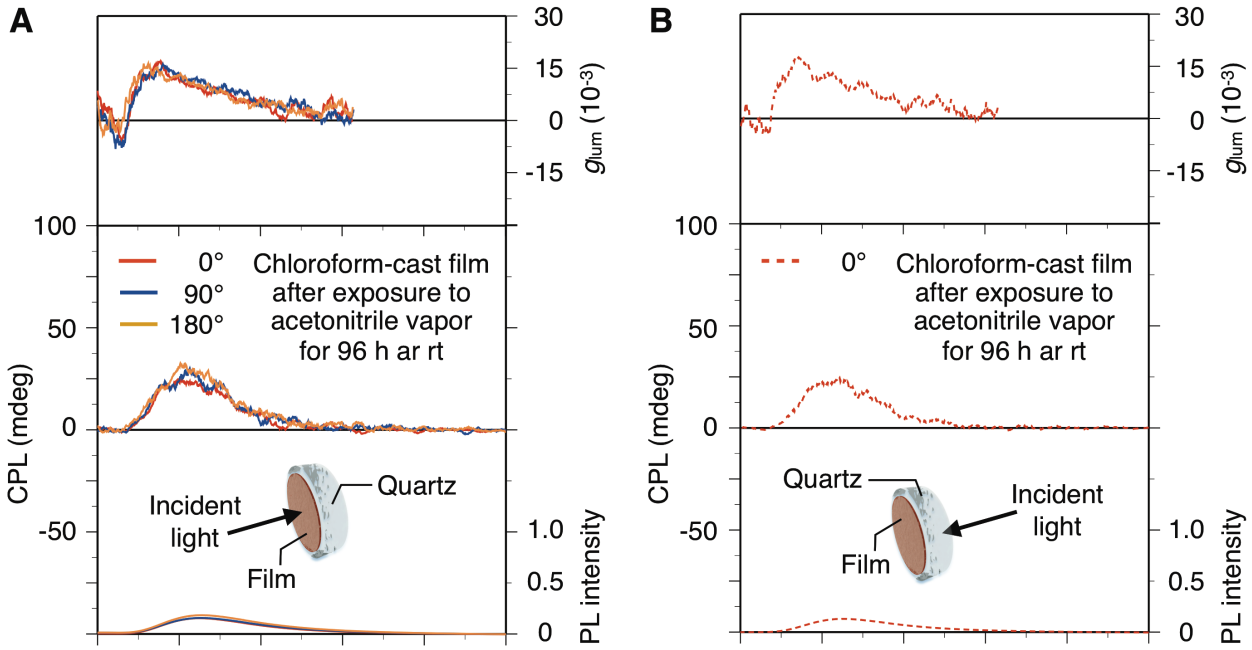


Fig. S17 PL (bottom), CPL (middle) and g_{lum} (top) spectra of a chloroform-cast film of poly-**9** after exposure to acetonitrile vapor for 96 h at room temperature. The spectra were measured at different rotation angles (A) and by reversing a quartz plate to be an incident light/quartz/film arrangement (B).

NMR spectral data

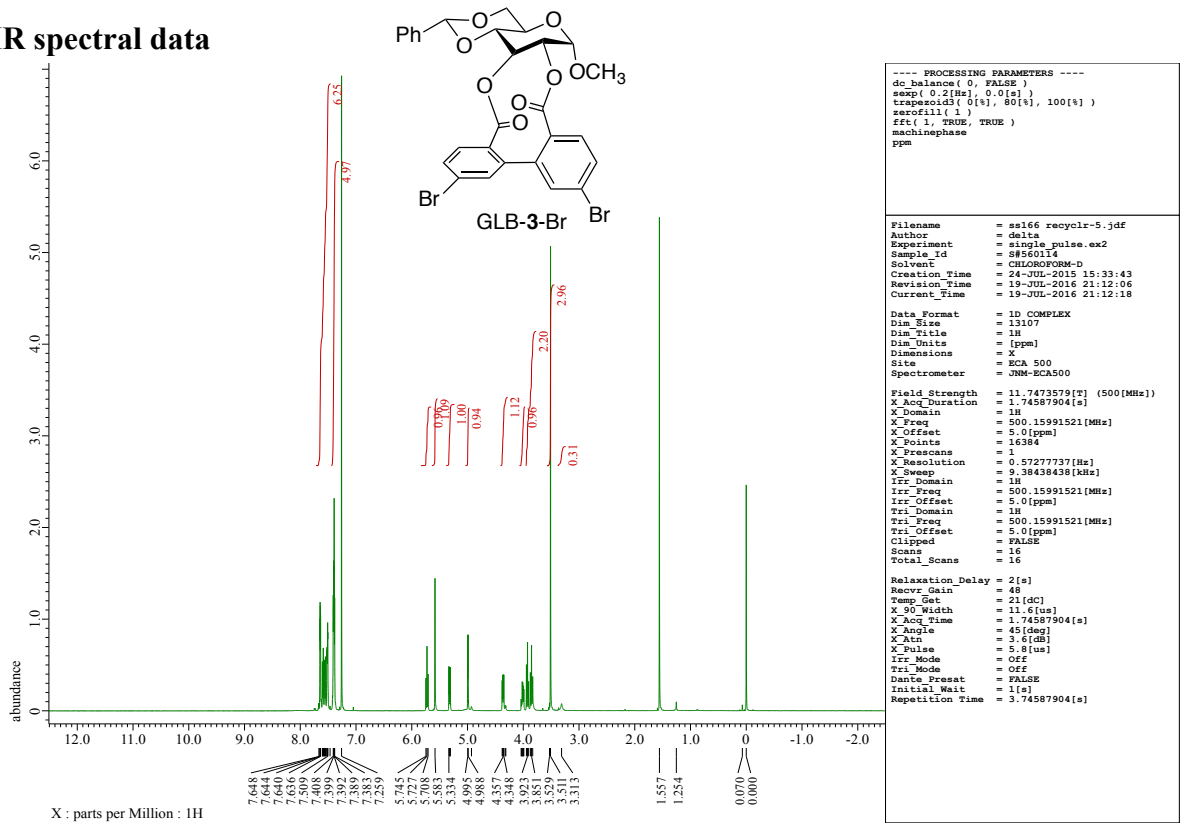


Fig. S18 ^{1}H NMR ($CDCl_3$, 500 MHz, rt) spectrum of GLB-**3**-Br.

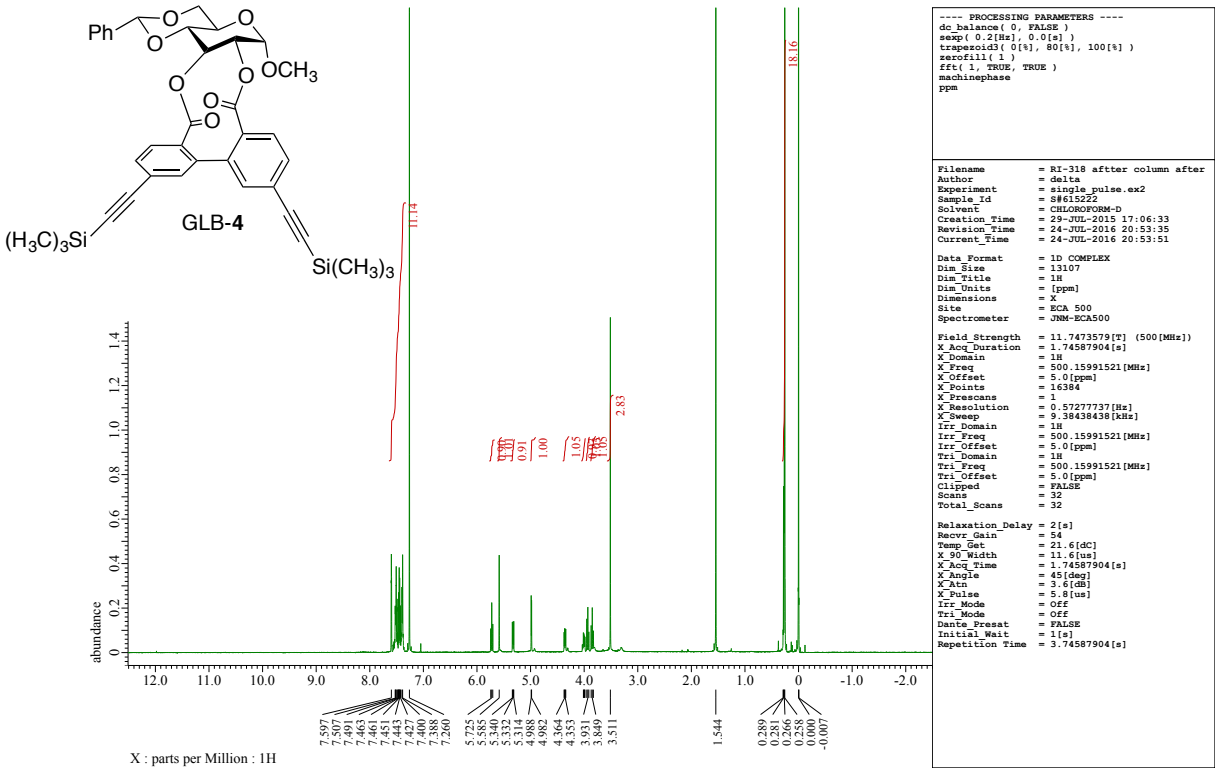


Fig. S19 ^{1}H NMR ($CDCl_3$, 500 MHz, rt) spectrum of GLB-**4**.

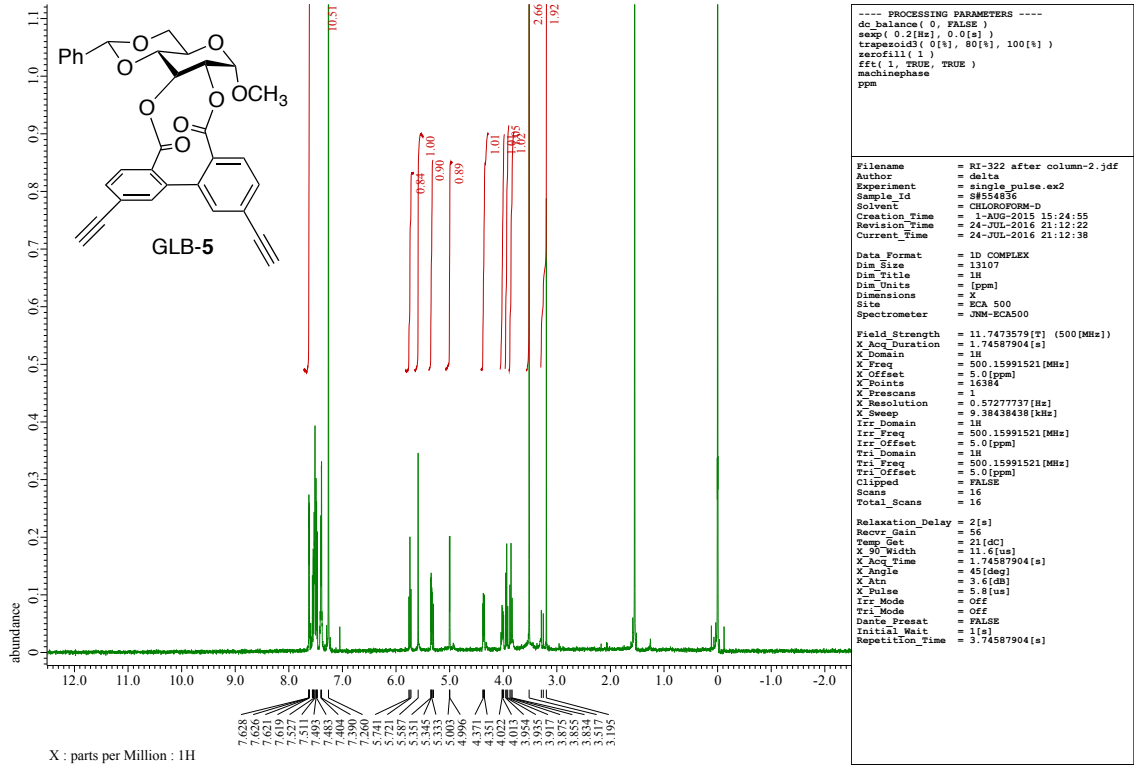


Fig. S20 ^{1}H NMR ($CDCl_3$, 500 MHz, rt) spectrum of GLB-**5**.

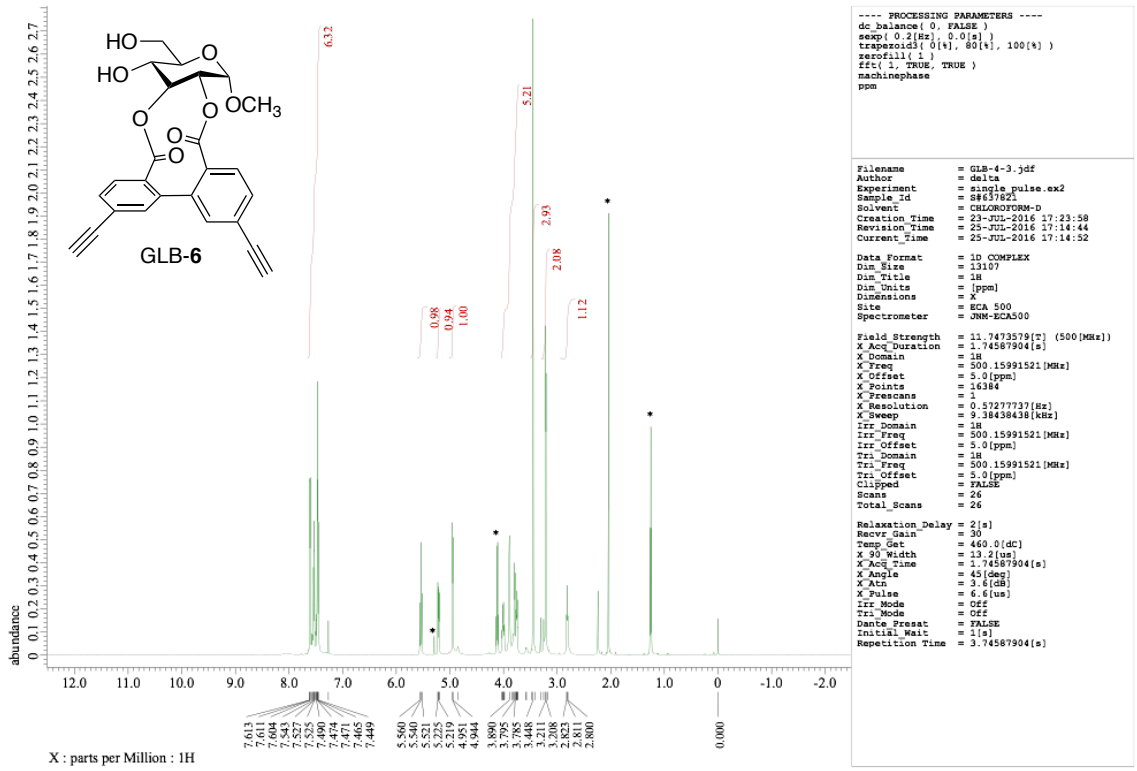


Fig. S21 ^{1}H NMR ($CDCl_3$, 500 MHz, rt) spectrum of GLB-**6**. Asterisks denote residual solvent peaks.

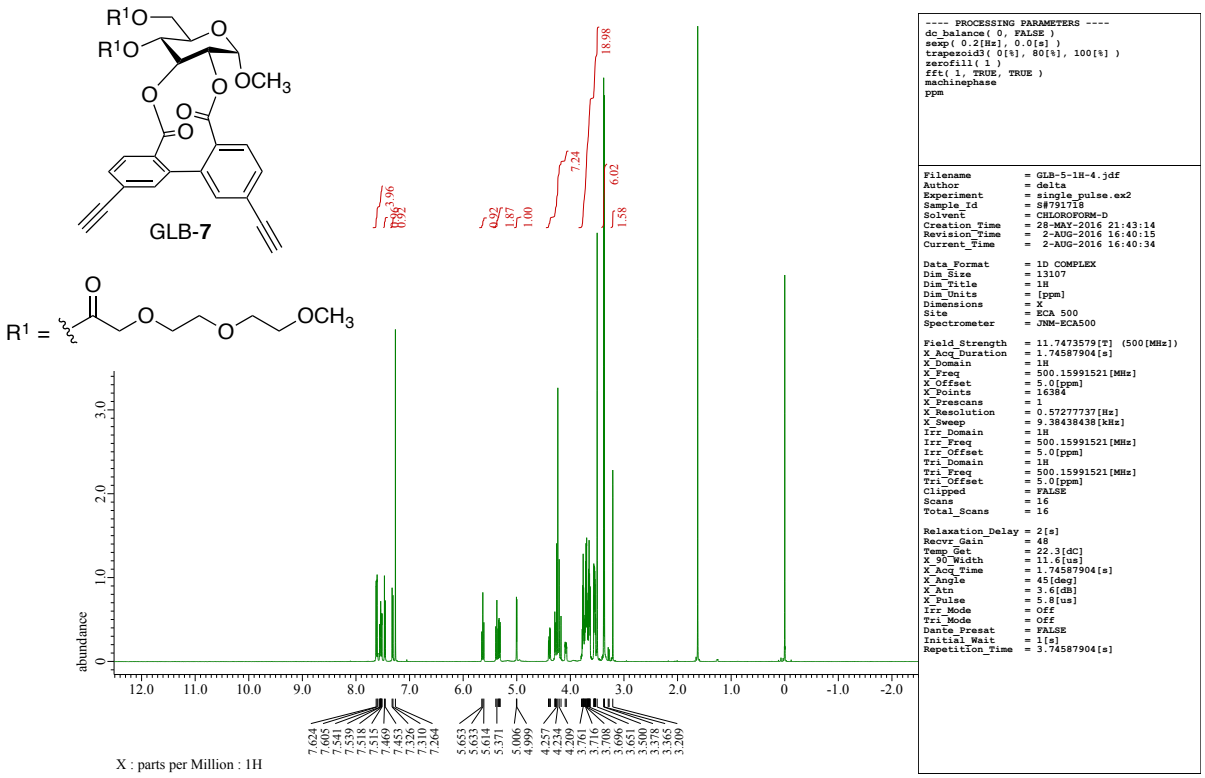


Fig. S22 ^{1}H NMR ($CDCl_3$, 500 MHz, rt) spectrum of GLB-**7**.

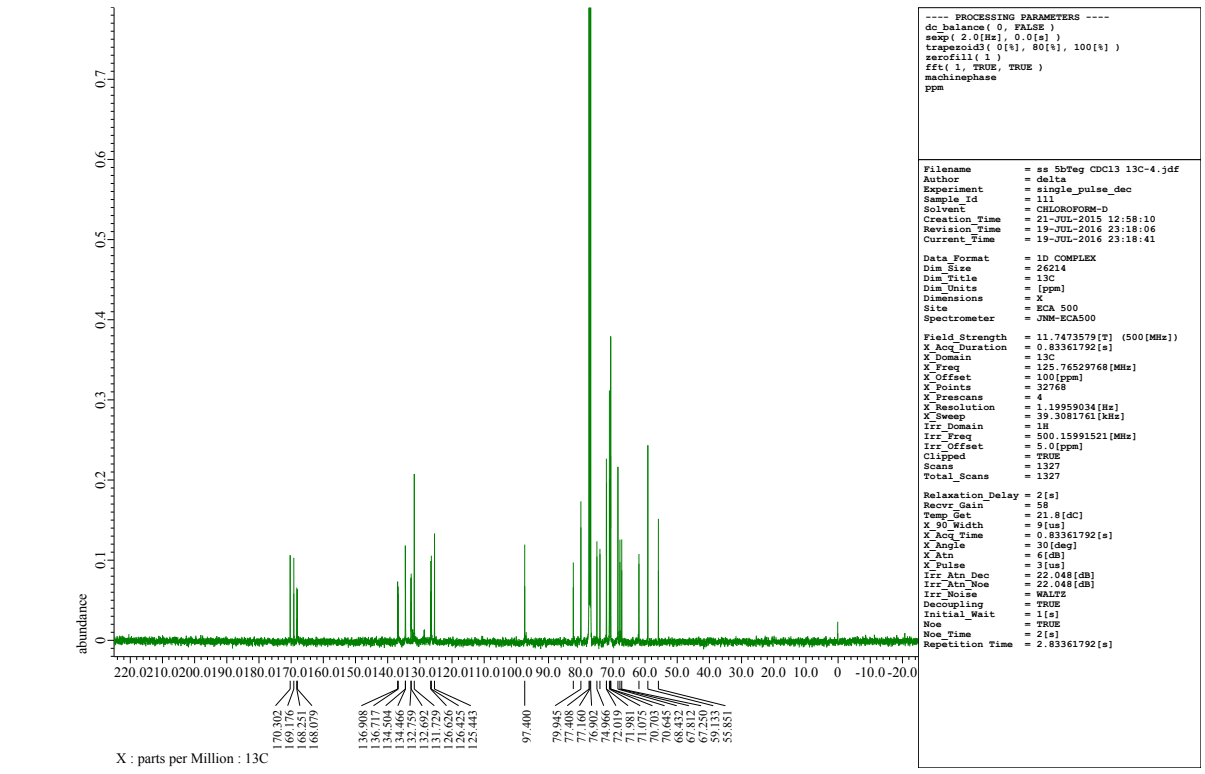


Fig. S23 ^{13}C NMR ($CDCl_3$, 125 MHz, rt) spectrum of GLB-**7**.

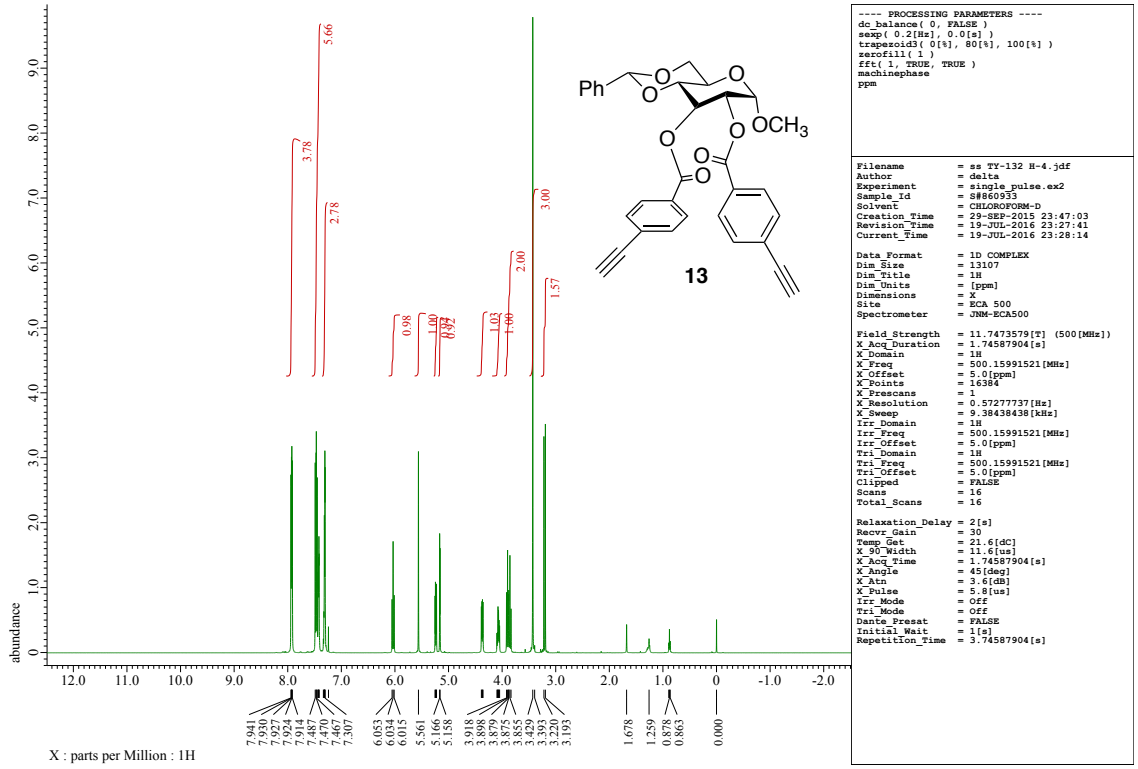


Fig. S24 ^{1}H NMR ($CDCl_3$, 500 MHz, rt) spectrum of **13**.

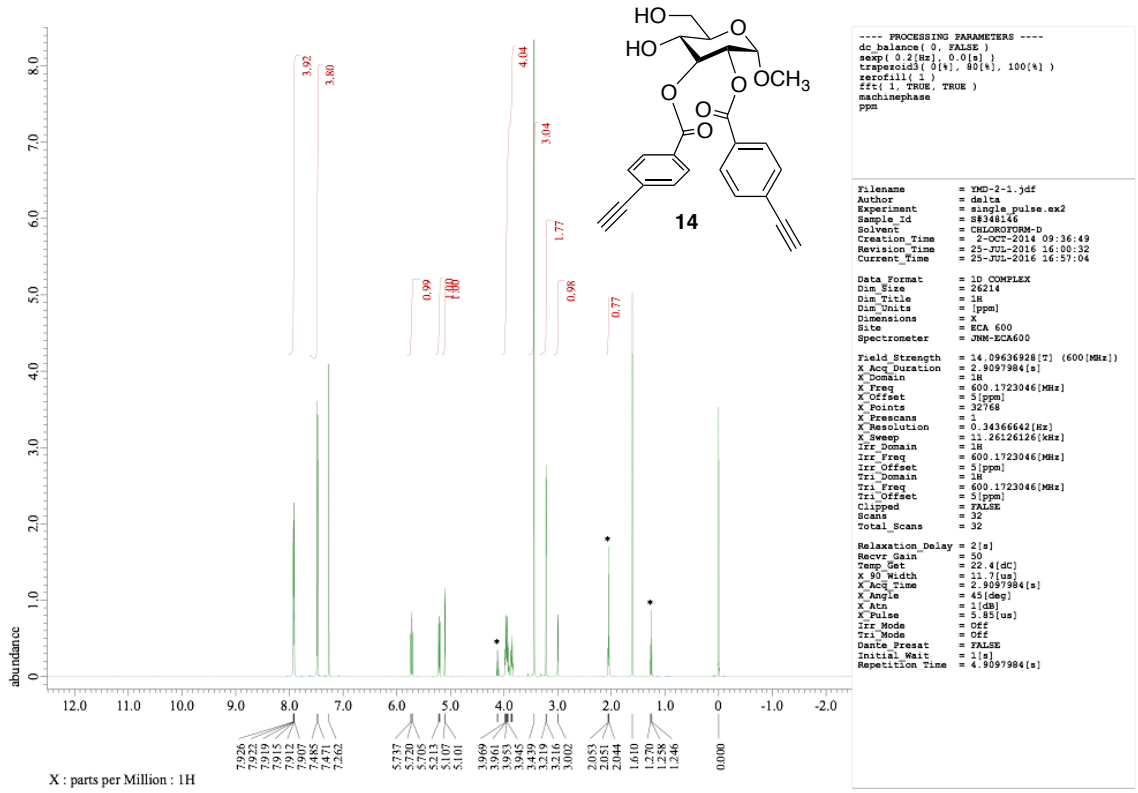


Fig. S25 ^{1}H NMR ($CDCl_3$, 600 MHz, rt) spectrum of **14**. Asterisks denote residual solvent peaks.

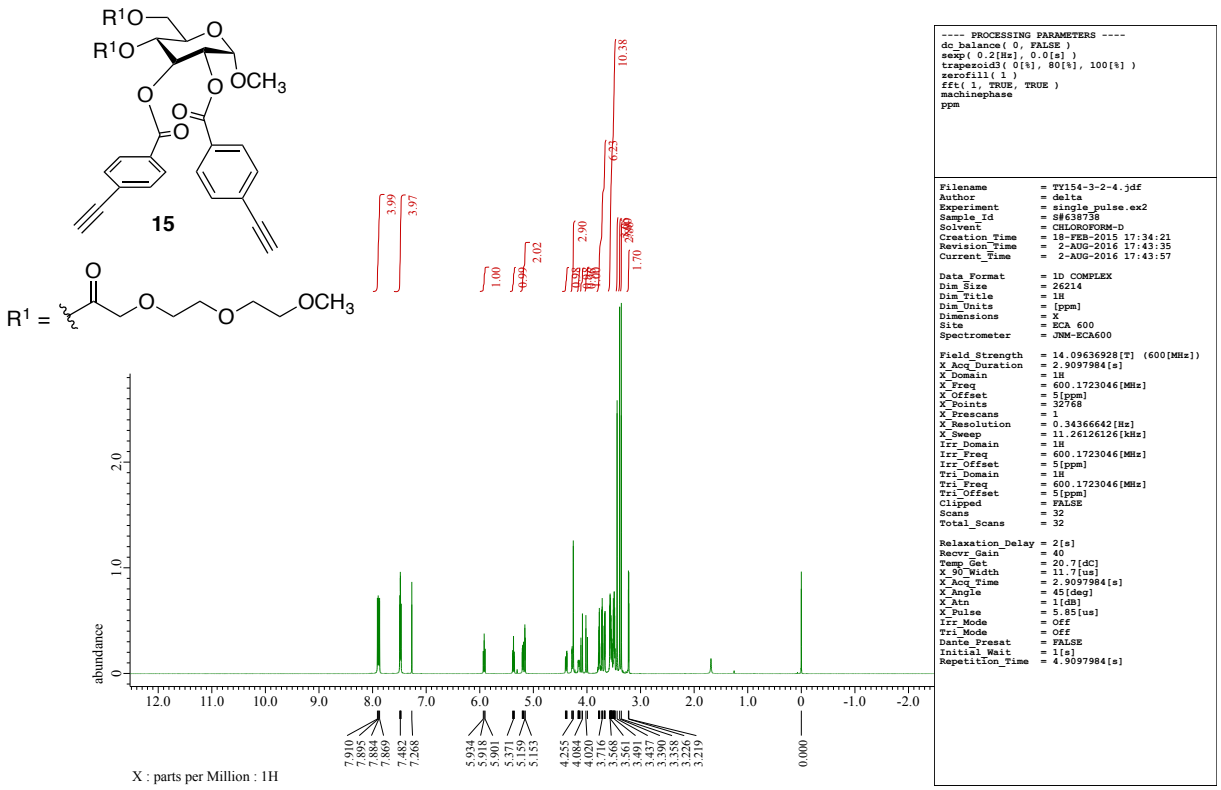


Fig. S26 ^{1}H NMR ($CDCl_3$, 600 MHz, rt) spectrum of **15**.

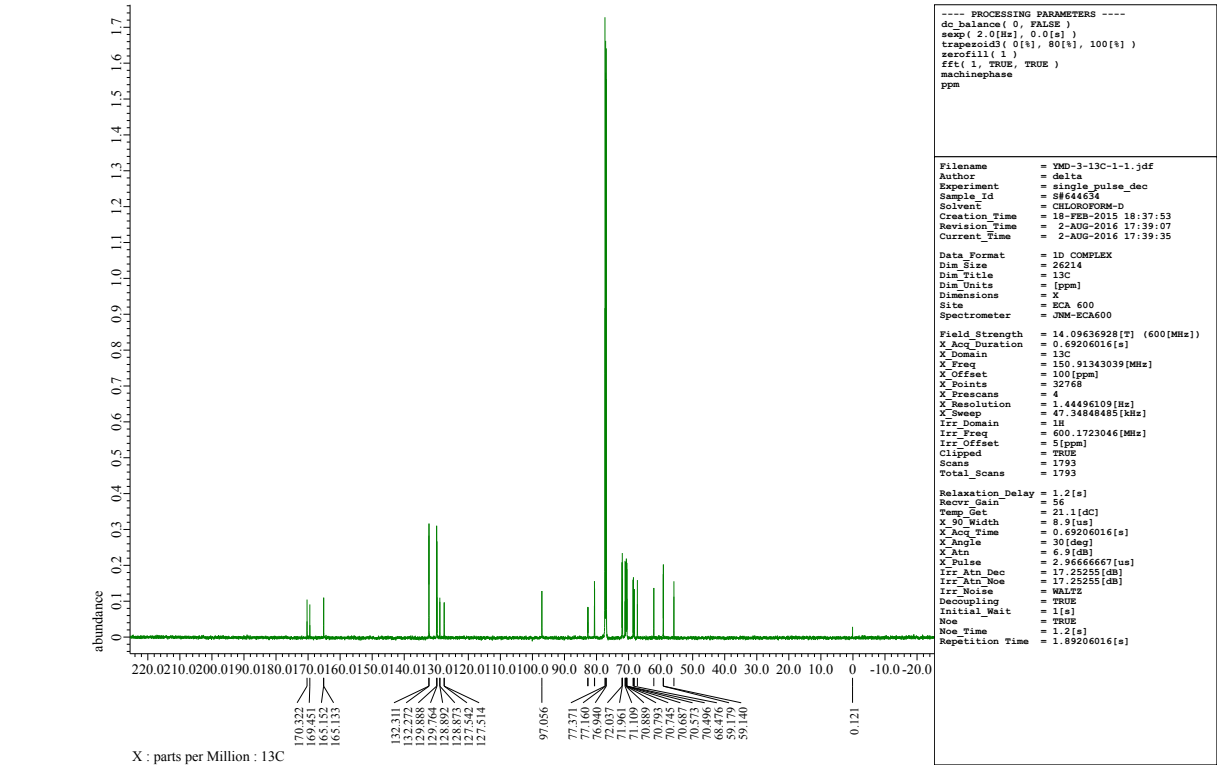


Fig. S27 ^{13}C NMR ($CDCl_3$, 150 MHz, rt) spectrum of **15**.

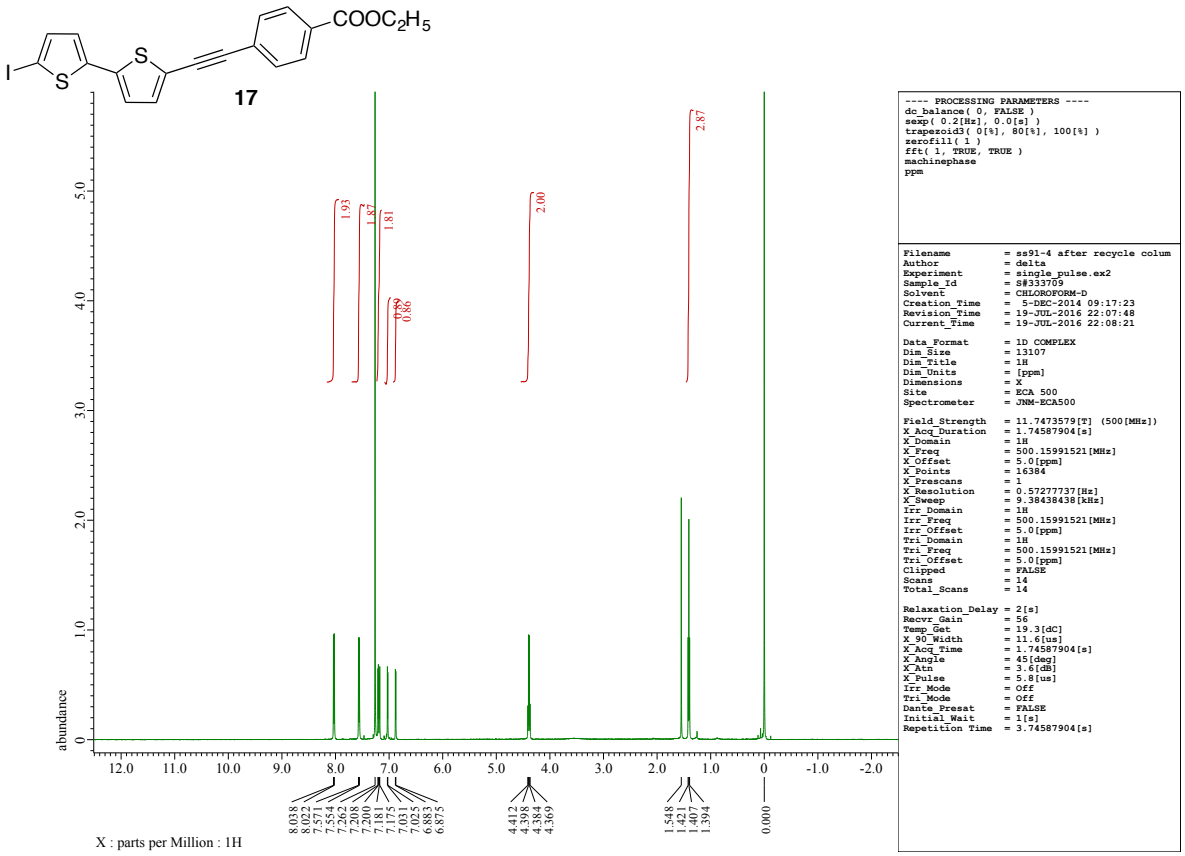


Fig. S28 ^{1}H NMR ($CDCl_3$, 500 MHz, rt) spectrum of **17**.

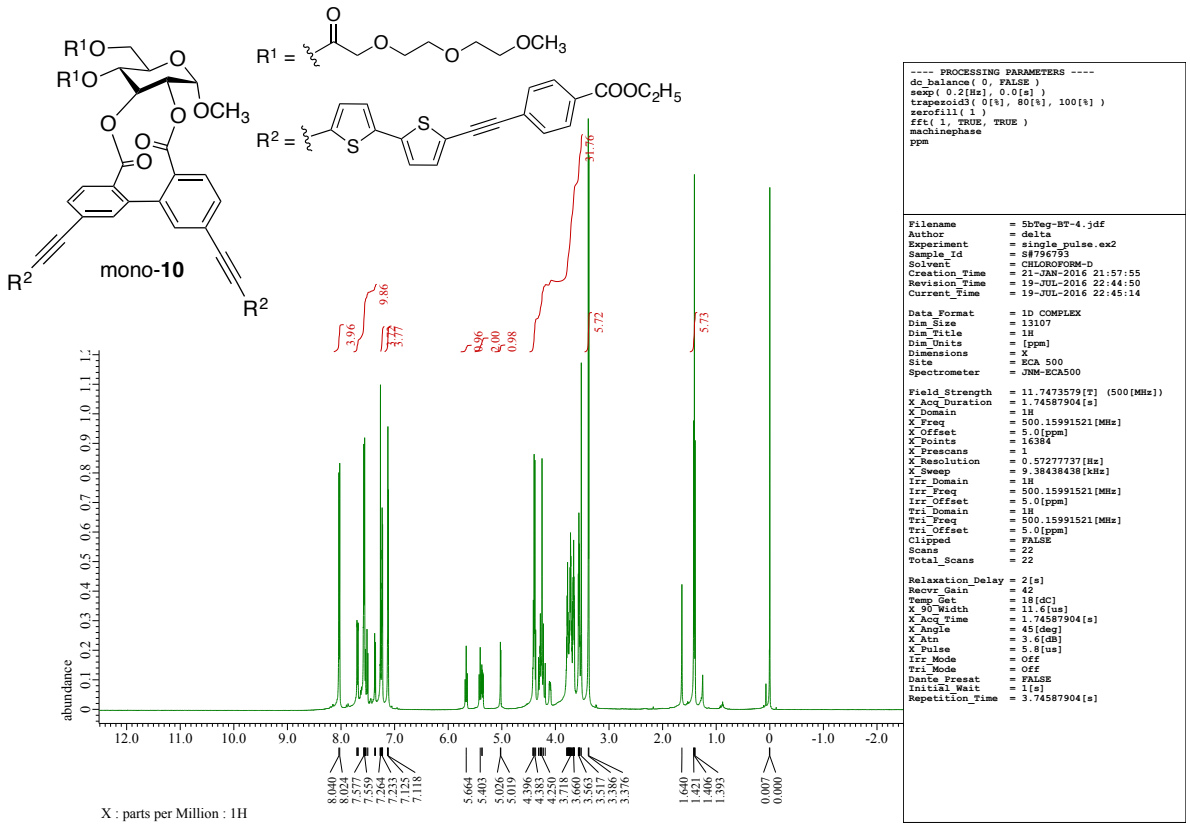


Fig. S29 ^{1}H NMR ($CDCl_3$, 500 MHz, rt) spectrum of mono-**10**.

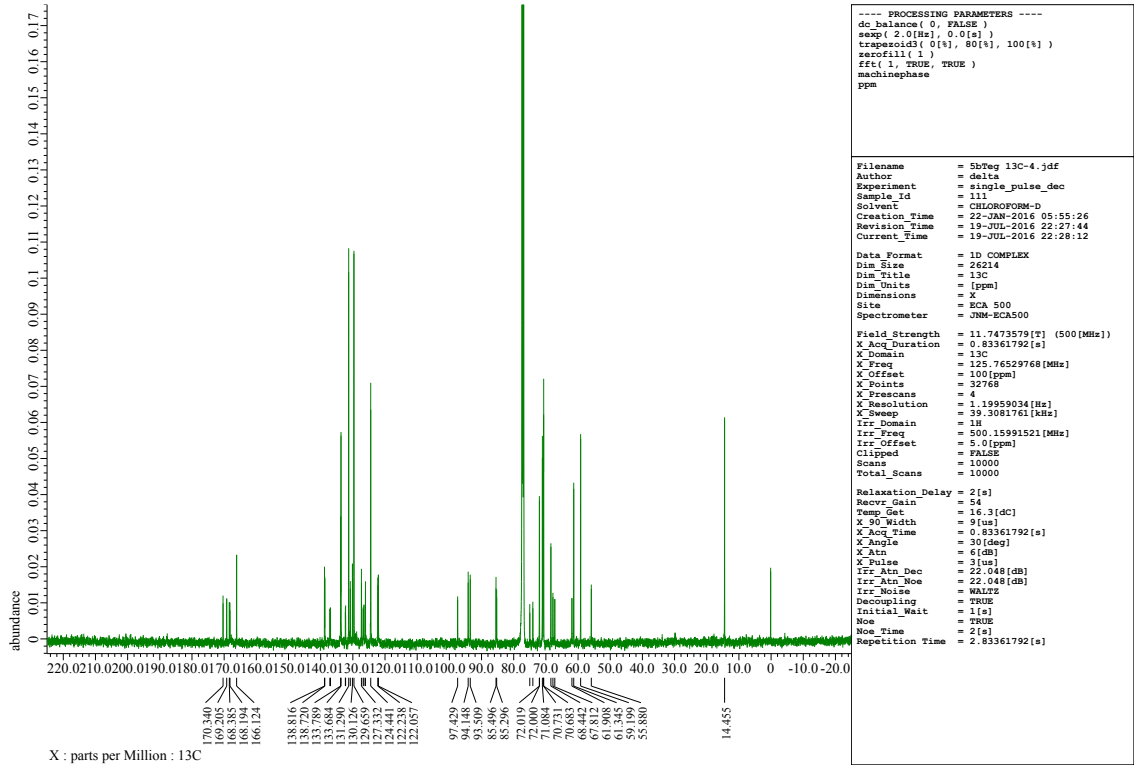


Fig. S30 ^{13}C NMR ($CDCl_3$, 125 MHz, rt) spectrum of mono-**10**.

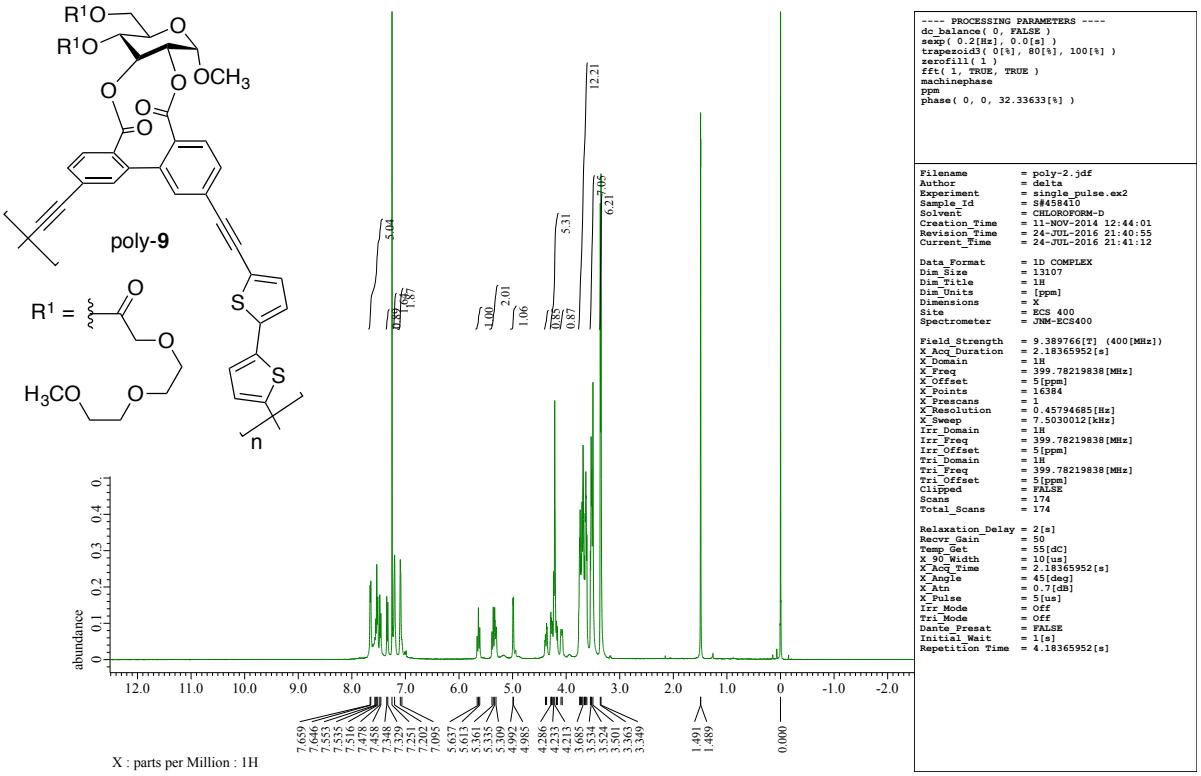


Fig. S31 ^{1}H NMR ($CDCl_3$, 400 MHz, 55 °C) spectrum of poly-**9**.

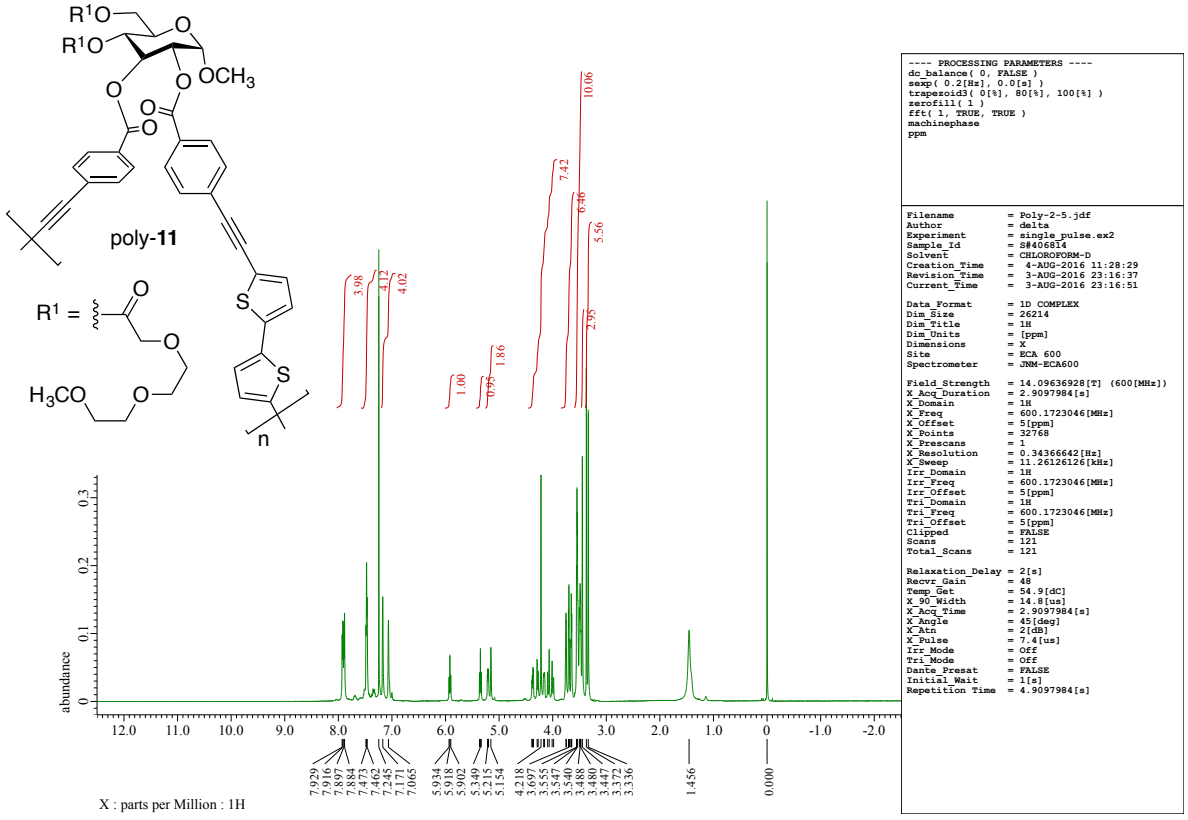


Fig. S32 ^{1}H NMR ($CDCl_3$, 600 MHz, 55 °C) spectrum of poly-**11**.

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