

Supporting Information for

**Very Small Bandgap π -Conjugated Polymers with
Extended Thienoquinoids**

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Materials and Methods

All chemicals and solvents are of reagent grade unless otherwise indicated. THF, cyclohexane, DMF, toluene, and ether were purified with a Glass Contour solvent purification system prior to use. 2,6-Bis(trimethylsilyl)-3,7-diiodobenzo[1,2-*b*:4,5-*b'*]dithiophene¹ and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene² were synthesized according to the literature. The synthesis of **T-Sn** and **TTD2T-Br2** is described in Supporting Information. Polymerization was carried out in the microwave reactor Biotage Initiator. NMR spectra were obtained in deuterated chloroform (CDCl₃) or *o*-dichlorobenzene (DCB-*d*₄) with TMS as internal reference using a JEOL JNM-ECS400 spectrometer. High-resolution mass spectrometry was carried out with a JEOL JMS-T100GCV. Elemental analysis was performed with a Yanaco MT-6 CHN CORDER. The molecular weights of the polymers were determined by gel permeation chromatography (GPC) with TOSOH HLC-8121GPC/HT at 140 °C using DCB as the eluent, and were calibrated with polystyrene standards.

Synthesis

4,4'-Dibromo-5,5'-diisopropylsilyl-2,2'-bithiophene (1)

To a freshly prepared solution of lithium diisopropylamide (LDA) (42 mmol) in THF (40 mL) was added a solution of 5,5'-dibromo-2,2'-bithiophene (6.48 g, 20.0 mmol) in THF (80 mL) dropwise over a period of 10 min at −78 °C. The resulting mixture was stirred at −78 °C for 2 h and then at −40 °C for 1 h. To the mixture was added triisopropylsilyl chloride (TIPSCl) (9.2 mL, 43 mmol) dropwise over a period of 5 min, and the mixture was stirred for 4 h while gradually raising the temperature to room temperature. The mixture was extracted with dichloromethane, and the organic layer was washed with brine and dried over magnesium sulfate. After removing the solvent by evaporation, the crude product was recrystallized from chloroform/methanol to give **1** as an off-white solid (9.76 g, 15.3 mmol, yield = 77%). ¹H-NMR (CDCl₃, 400 MHz): δ (ppm) 7.21 (s, 2H), 1.58 (septet, 6H, *J* = 7.6 Hz), 1.15 (d, 36H, *J* = 7.6 Hz). ¹³C-NMR (CDCl₃, 100 MHz): δ (ppm) 140.93, 130.69, 129.51, 118.00, 18.75, 12.38. HRMS (ESI): Calcd for C₂₆H₄₄Si₂S₂Br₂ [M+H]⁺: 635.0868. Found: 635.0861.

4,4'-Bis[4-(4-decylhexadecyl)thiophen-2-yl]-2,2'-bithiophene (2)

A solution of **1** (1.40 g, 2.20 mmol), **T-Sn** (3.06 g, 5.00 mmol), tetrakis(triphenylphosphine)palladium(0) (50 mg, 0.043 mmol), and toluene (10 mL) in a sealed reaction vessel was heated at 160 °C for 1 h in a microwave reactor. After cooling to room temperature, tetrabutylammonium fluoride (TBAF) (1 M in THF, 20 mmol) was added, and the reaction mixture was stirred for 2 h. The reaction mixture was extracted with hexane, and the organic layer was washed with water and dried over magnesium sulfate. After removing the solvent by evaporation, the crude product was purified by silica gel column chromatography (eluent: hexane) to give **2** as a white solid (2.27 g, 2.14 mmol, yield = 97%). ¹H-NMR (CDCl₃, 400 MHz): δ

(ppm) 7.36 (s, 2H), 7.23 (s, 2H), 7.06 (s, 2H), 6.81 (s, 2H), 2.58 (t, 4H, $J = 7.6$ Hz), 1.61 (m, 4H), 1.30-1.23 (m, 86H), 0.88 (t, 12H, $J = 6.2$ Hz). ^{13}C -NMR (CDCl_3 , 100 MHz): δ (ppm) 144.03, 138.27, 137.57, 136.55, 124.80, 122.69, 118.75, 118.24, 37.25, 33.62, 33.28, 31.93, 30.99, 30.15, 29.72, 29.67, 29.38, 27.54, 26.70, 22.70, 14.13. HRMS (ESI): Calcd for $\text{C}_{68}\text{H}_{114}\text{S}_4$ $[\text{M}+\text{H}]^+$: 1059.7882. Found: 1059.7881.

4,4'-Bis[4-(4-decylhexadecyl)thiophen-2-yl]-2,2'-bithiophene-5,5'-dione (BTD2T)

To a solution of *n*-butyllithium (1.6 M in hexane) (2.63 mL, 4.2 mmol) and THF (40 mL) was added 2,2,6,6-tetramethylpiperidine (0.72 mL, 4.2 mmol) dropwise at -78 °C to form lithium tetramethylpiperide (LTMP). After stirring for 15 min, a solution of **2** (2.12 g, 2.0 mmol) in THF (35 mL) was added dropwise over a period of 20 min. After stirring at -78 °C for 1 h and then at -60 °C for 1 h, triisopropyl borate (3.00 mL, 13.1 mmol) was added. The reaction mixture was stirred for 3 h while gradually raising the temperature to room temperature. The reaction was quenched with 1 M HCl aqueous solution, and the organic layer was extracted with ether and washed with water three times. The organic layer was added to a solution of 35% hydrogen peroxide (30 mL) and ether (30 mL), and the reaction mixture was stirred vigorously for 20 min. The reaction mixture was extracted with hexane, and the organic layer was washed with water and dried over magnesium sulfate. After removing the solvent by evaporation, the crude product was purified by silica gel column chromatography (eluent: hexane/dichloromethane = 8/2) in the dark to give **BTD2T** as a red oil (0.85 g, 0.80 mmol, yield = 39%). Note that the compound was obtained as a mixture of (*E*)- and (*Z*)-isomers ($R_f = 0.30$ (*E*), 0.15 (*Z*)), and the assignment of the thin-layer chromatography and the ^1H -NMR spectrum as shown below was carried out on the basis of the results of **BTD2T-Br2**. ^1H -NMR (CDCl_3 , 400 MHz): δ (ppm) 8.03 (s, 2H, (*Z*)), 7.71 (d, 2H, $J = 0.8$ Hz, (*Z*)), 7.69 (s, 2H, (*E*)), 7.68 (d, 2H, $J = 0.8$ Hz, (*E*)), 7.11 (s, 2H, (*E*)), 7.09 (s, 2H, (*Z*)), 2.59 (m, 4H), 1.60 (m, 4H), 1.29-1.22 (m, 86H), 0.87 (t, 12H, $J = 6.8$ Hz). ^{13}C -NMR (CDCl_3 , 100 MHz): δ (ppm) 189.43, 189.32, 144.92, 144.90, 137.02, 136.84, 135.24, 134.06, 133.71, 132.60, 130.77, 130.66, 130.59, 125.34, 124.38, 37.22, 33.57, 33.21, 31.93, 30.14, 29.72, 29.67, 29.38, 27.53, 26.69, 22.70, 14.14. HRMS (ESI): Calcd for $\text{C}_{68}\text{H}_{112}\text{O}_2\text{S}_4$ $[\text{M}+\text{H}]^+$: 1089.7623. Found: 1089.7627.

4,4'-Bis[5-bromo-4-(4-decylhexadecyl)thiophen-2-yl]-2,2'-bithiophene-5,5'-dione (BTD2T-Br2)

To a solution of **3** (730 mg, 0.67 mmol) in THF (25 mL) was added *N*-bromosuccinimide (NBS) (262 mg, 1.47 mmol) at 0 °C. The reaction mixture was gradually warmed to room temperature over a period of 30 min, and then stirred at 45 °C for 20 h. The reaction mixture was extracted with hexane, and the organic layer was washed with water and dried over magnesium sulfate. After removing the solvent by evaporation, the crude product was purified by silica gel column chromatography (eluent: hexane/dichloromethane = 8/2) in the dark to give **BTD2T-Br2** as a red solid (680 mg, 0.55 mmol, yield = 81%). Note that the compound was obtained as a mixture of (*E*)- and (*Z*)-isomers ($R_f = 0.38$ (*E*) and 0.21 (*Z*)). Analytical amounts (~20 mg) of (*E*)- and (*Z*)-isomers were isolated by silica gel column chromatography and used for NMR measurement without exposure to light. ^1H -NMR (CDCl_3 , 400 MHz): δ (ppm) for (*E*)-isomer: 7.62 (s, 2H), 7.48

(s, 2H), 2.55 (m, 4H), 1.60-1.54 (m, 4H), 1.31-1.23 (m, 86H), 0.87 (t, 12H, $J = 7.0$ Hz). δ (ppm) for (*Z*)-isomer: 7.95 (s, 2H), 7.53 (s, 2H), 2.55 (m, 4H), 1.60-1.54 (m, 4H), 1.31-1.23 (m, 86H), 0.87 (t, 12H, $J = 7.0$ Hz). ^{13}C -NMR (CDCl_3 , 100 MHz): δ (ppm) for (*E*)-isomer: 189.23, 143.67, 136.23, 134.43, 132.92, 132.18, 130.03, 116.49, 37.13, 33.53, 31.94, 30.14, 29.85, 29.73, 29.69, 29.38, 26.72, 26.67, 22.70, 14.15. δ (ppm) for (*Z*)-isomer: 189.15, 143.69, 137.16, 134.43, 132.22, 129.97, 129.92, 115.28, 37.13, 33.52, 33.13, 31.93, 30.14, 29.73, 29.68, 29.38, 26.71, 26.67, 22.70, 14.14). MS (ESI) $m/z = 1245.6$ $[\text{M}+\text{H}]^+$. HRMS (ESI): Calcd for $\text{C}_{68}\text{H}_{110}\text{O}_2\text{S}_4\text{Br}_2$ $[\text{M}+\text{H}]^+$: 1245.5834. Found: 1245.5837.

3,7-Bis[4-(4-decylhexadecyl)thiophen-2-yl]benzo[1,2-b:4,5-b']dithiophene (3)

A solution of 2,6-bistrimethylsilyl-3,7-diiodobenzo[1,2-b:4,5-b']dithiophene (2.35 g, 4.0 mmol), **T-Sn** (5.51 g, 9.0 mmol), tetrakis(triphenylphosphine)palladium(0) (185 mg, 0.16 mmol), and toluene (13 mL) in a sealed reaction vessel was heated at 160 °C for 1 h in a microwave reactor. After cooling to room temperature, TBAF (1 M in THF, 30 mmol) was added, and the reaction mixture was stirred for 2 h. After the mixture was extracted with hexane, the organic layer was washed with water and dried over magnesium sulfate. After removing the solvent by evaporation, the crude product was purified by silica gel column chromatography (eluent: hexane) to give **3** as a colorless oil (4.29 g, 3.96 mmol, yield = 99%). ^1H -NMR (CDCl_3 , 400 MHz): δ (ppm) 8.61 (s, 2H), 7.54 (s, 2H), 7.23 (d, 2H, $J = 0.8$ Hz), 6.98 (s, 2H), 2.68 (t, 4H, $J = 7.4$ Hz), 1.68 (m, 4H), 1.38-1.25 (m, 86H), 0.87 (t, 12H, $J = 6.6$ Hz). ^{13}C -NMR (CDCl_3 , 100 MHz): δ (ppm) 144.01, 138.21, 136.78, 135.50, 129.88, 126.71, 124.82, 119.57, 116.85, 37.31, 33.68, 33.42, 31.92, 31.08, 30.15, 29.71, 29.66, 29.36, 27.67, 26.73, 22.69, 14.11. HRMS (ESI): Calcd for $\text{C}_{70}\text{H}_{114}\text{S}_4$ $[\text{M}]^+$: 1082.7803. Found: 1082.7806.

3,7-Bis[4-(4-decylhexadecyl)thiophen-2-yl]benzo[1,2-b:4,5-b']dithiophene-2,6-dione (BDTD2T)

To freshly prepared LTMP (3.55 mmol) as described above was added a solution of **3** (1.60 g, 1.48 mmol) in THF (23 mL) dropwise over a period of 20 min. After stirring at -78 °C for 3 h, triisopropyl borate (1.60 mL, 7.00 mmol) was added. The reaction mixture was stirred for 5 h while gradually raising the temperature to room temperature. The reaction was quenched with 1 M HCl aqueous solution, and the organic layer was extracted with ether and washed with water three times. The organic layer (~20 mL) was added to a solution of 35% hydrogen peroxide (40 mL) and ether (40 mL), and stirred vigorously for 20 min. After the reaction mixture was extracted with hexane, the organic layer was washed with water and dried over magnesium sulfate. After removing the solvent by evaporation, the crude product was purified by silica gel column chromatography (eluent: hexane/dichloromethane = 85/15) to give **BDTD2T** as a dark purple solid (778 mg, 0.70 mmol, yield = 47%). ^1H -NMR (CDCl_3 , 400 MHz): δ (ppm) 7.69 (d, 2H, $J = 0.8$ Hz), 7.66 (s, 2H), 7.28 (d, 2H, $J = 0.8$ Hz), 2.64 (t, 4H, 7.6 Hz), 1.62 (m, 4H), 1.31-1.23 (m, 86H), 0.87 (t, 12H, $J = 6.6$ Hz). ^{13}C -NMR (CDCl_3 , 100 MHz): δ (ppm) 191.07, 145.19, 139.60, 139.05, 133.45, 132.39, 130.11, 127.23, 119.77, 37.25, 33.60, 33.28, 31.92, 30.68, 30.13, 29.71, 29.66, 29.37, 26.70, 22.69, 14.12. HRMS (ESI): Calcd for $\text{C}_{70}\text{H}_{112}\text{O}_2\text{S}_4$ $[\text{M}+\text{H}]^+$: 1113.7623. Found: 1113.7616.

3,7-Bis[5-bromo-4-(4-decylohexadecyl)thiophen-2-yl]benzo[1,2-b:4,5-b']dithiophene-2,6-dione
(BDTD2T-Br2)

To a solution of **7** (667 mg, 0.60 mmol) in THF (20 mL) was added NBS (235 mg, 1.32 mmol) at 0 °C, and the reaction mixture was gradually warmed to room temperature over a period of 30 min, and then stirred at 45 °C for 6 h. After the reaction mixture was extracted with hexane, the organic layer was washed with water and dried over magnesium sulfate. After removing the solvent by evaporation, the crude product was purified by silica gel column chromatography (eluent: hexane/dichloromethane = 9/1) to give **BDTD2T-Br2** as a dark purple solid (718 mg, 0.57 mmol, yield = 94%). ¹H-NMR (CDCl₃, 400 MHz): δ (ppm) 7.55 (s, 2H), 7.54 (s, 2H), 2.60 (t, 4H, J = 7.4 Hz), 1.59 (m, 4H), 1.31-1.23 (m, 86H), 0.87 (t, 12H, J = 6.6 Hz). ¹³C-NMR (CDCl₃, 100 MHz): δ (ppm) 190.81, 144.18, 139.81, 138.53, 132.83, 132.59, 129.30, 119.47, 118.65, 37.15, 33.56, 33.19, 31.92, 30.12, 29.83, 29.71, 29.67, 29.37, 26.67, 22.69, 14.12. HRMS (ESI): Calcd for C₇₀H₁₁₀O₂S₄Br₂ [M+H]⁺: 1269.5834. Found: 1269.5854.

General procedure for polymerization

To a reaction vessel, dibrominated thienoquinoid monomers (1 eq), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (1 eq), tetrakis(triphenylphosphine)palladium(0) (2 mol%), and toluene (20 mM) were added. The reaction vessel was filled with argon, sealed, and heated at 180 °C for 1 h in a microwave reactor. After cooling to room temperature, the reaction mixture was poured into methanol containing 12 N hydrochloric acid (4 vol%), and the resulting suspension was stirred for 5 h. The precipitate was collected by filtration and subjected to sequential Soxhlet extraction with methanol, hexane, and chloroform (additionally with chlorobenzene (CB) and DCB as necessary). The extracted solution was concentrated and poured into methanol. The precipitated polymer was collected by filtration and dried in vacuo.

PTTD4T

Collected as a CB fraction: dark green solid (27.1 mg, yield = 74%, M_n = 48 kDa, M_w = 1883 kDa, PDI = 39.3). ¹H-NMR (DCB-*d*₄, 400 MHz, 120 °C): δ (ppm) 7.71 (bs, 2 H), 2.90 (bs, 4H), 1.82 (bs, 4H), 1.48-1.29 (m, 86H), 0.86 (bs, 12H). Two protons at the β -positions of the unsubstituted thiophene may be obscured by DCB signals. Elemental analysis: Calcd for C₇₄H₁₁₂O₂S₆: C, 72.49; H, 9.21. Found: C, 72.19; H, 9.23.

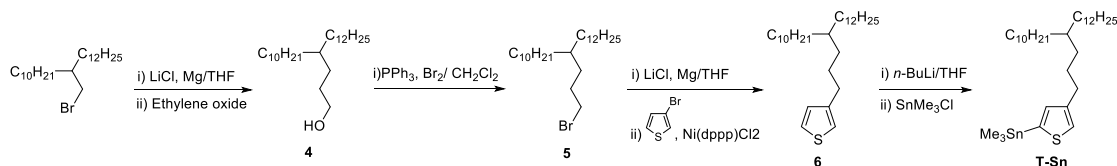
PBTD4T

Collected as a chloroform fraction: dark green solid (95.0 mg, yield = 79%, M_n = 37 kDa, M_w = 126 kDa, PDI = 3.4). ¹H-NMR (DCB-*d*₄, 400 MHz, 120 °C): δ (ppm) 7.95 (bs, 0.7 H), 7.76 (bs, 0.7H), 7.73 (bs, 1.3H), 7.63 (bs, 1.3H), 7.14 (bs, 4H), 2.87 (bs, 4H), 1.80 (bs, 4H), 1.47-1.27 (m, 86H), 0.85 (bs, 12H). EA: Calcd for C₇₆H₁₁₄O₂S₆: C, 72.90; H, 9.18. Found: C, 72.65; H, 9.23.

PBDTD4T

Collected as a DCB fraction: dark brown solid (22.0 mg, yield = 57%, M_n = 58 kDa, M_w = 182 kDa, PDI = 3.1). ^1H -NMR (DCB- d_4 , 400 MHz, 120 °C): δ (ppm) 7.91 (bs, 2 H), 7.65 (bs, 2H), 7.16 (m, 4H), 2.92 (bs, 4H), 1.84 (bs, 4H), 1.49-1.28 (m, 86H), 0.85 (bs, 12H). EA: Calcd for $\text{C}_{78}\text{H}_{114}\text{O}_2\text{S}_6$: C, 73.41; H, 9.00. Found: C, 72.93; H, 8.92.

Scheme S1. Synthesis of 2-trimethylstannyl-4-(4-decylhexadecyl)thiophene



4-Decylhexadecan-1-ol (4)

Magnesium turnings (24.22 g, 996 mmol) and lithium chloride (42.32 g, 998 mmol) in a Schlenk flask was heated at 180 °C for 10 min in vacuo. To the flask were added THF (220 mL) and 1,2-dibromoethane (0.75 mL, 8.7 mmol), and then the mixture was refluxed for 15 sec by using a heat gun. After cooling to 15 °C, a solution of 11-(bromomethyl)tricosane (123.7 g, 296 mmol) in THF (80 mL) was added dropwise to the mixture over 2 h. The mixture was then warmed to room temperature and stirred for 2 h. 1 mL of the mixture was taken and titrated with iodine to estimate the concentration of the Grignard reagent (0.40 M). The Grignard reagent (330 mL, 132 mmol) was transferred to a three neck flask and diluted with THF (100 mL). To the solution was added dropwise a solution of ethylene oxide (1.2 M in THF) (100 mL, 120 mmol) at 0 °C over 30 min. After the reaction mixture was stirred at 50 °C for 6 h, the reaction was quenched with 1 M hydrochloric acid. The reaction mixture was extracted with hexane, and the organic layer was washed with water and dried over magnesium sulfate. After removing the solvent by evaporation, the crude product was purified by silica gel column chromatography (eluent: dichloromethane) to give **4** as colorless liquid (29.47 g, 77.0 mmol, yield = 64% vs ethylene oxide). ^1H NMR (CDCl_3 , 400 MHz): δ (ppm) 3.62 (t, 2H, J = 6.6 Hz), 1.54 (quintet, 2H, J = 7.0 Hz), 1.41-1.24 (m, 43H), 0.88 (t, 6H, J = 6.6 Hz). ^{13}C NMR (CDCl_3 , 100 MHz): δ (ppm) 63.60, 37.20, 33.57, 31.92, 30.12, 29.96, 29.71, 29.66, 29.52, 29.37, 26.64, 22.69, 14.12. HRMS (ESI): Calcd for $\text{C}_{26}\text{H}_{54}\text{O}$ [MNa^+]: 405.4072. Found: 405.4070.

11-(3-Bromopropyl)tricosane (5)

To a solution of triphenylphosphine (24.66 g, 94.0 mmol) in dichloromethane (130 mL) was added bromine (15.0 g, 93.9 mmol) at 0 °C over 10 min. After the reaction mixture was stirred at 0 °C for 20 min, **4** (29.40 g, 76.8 mmol) was added dropwise over 20 min at 0 °C. After the reaction mixture was stirred at room temperature for 20 h, the solvent was removed by evaporation. The

crude product was purified by silica gel column chromatography (eluent: hexane) to give **5** as colorless liquid (34.06 g, 76.4 mmol, yield = 99%). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 3.39 (t, 2H, *J* = 7.2 Hz), 1.83 (quintet, 2H, *J* = 7.4 Hz), 1.37-1.24 (m, 43H), 0.88 (t, 6H, *J* = 6.8 Hz). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 36.84, 34.53, 33.51, 32.16, 31.92, 30.17, 30.07, 29.69, 29.37, 26.60, 22.69, 14.13. HRMS (ESI): Calcd for C₂₆H₅₃Br [M⁺]: 444.3331. Found: 444.3319.

3-(4-Decylhexadecyl)thiophene (**6**)

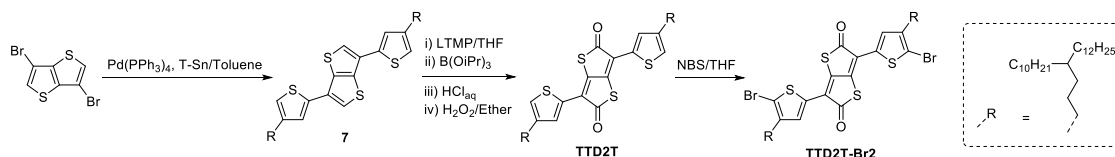
Magnesium turnings (7.29 g, 300 mmol) and lithium chloride (12.72 g, 300 mmol) in a Schlenk flask was heated at 180 °C for 10 min in vacuo. To the flask were added THF (50 mL) and 1,2-dibromoethane (0.25 mL, 2.9 mmol), and then the mixture was refluxed for 15 sec by using a heat gun. After cooling to 15 °C, a solution of **5** (33.9 g, 76.0 mmol) in THF (35 mL) was added dropwise to the mixture over 30 min, and then the mixture was stirred at room temperature for 90 min. The supernatant solution was then added dropwise to a solution of 3-bromothiophene (12.4 g, 76.0 mmol) and dichloro(1,3-bis(diphenylphosphino)propane)nickel(II) (0.41 mg, 0.76 mmol) in THF (50 mL) at 0 °C over the period of 10 min. After the reaction mixture was stirred at 50 °C for 16 h, the reaction was quenched with 1 M hydrochloric acid (150 mL). The reaction mixture was extracted with hexane, and the organic layer was washed with water and dried over magnesium sulfate. After removing the solvent by evaporation, the crude product was purified by silica gel column chromatography (eluent: hexane) to give **6** as colorless liquid (23.2 g, 51.6 mmol, yield = 68%). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.23 (dd, 1H, *J* = 3.0, 5.0 Hz), 6.94 (dd, 1H, *J* = 1.0, 4.8 Hz), 6.92 (dd, 1H, *J* = 1.0, 2.8 Hz), 2.60 (t, 2H, *J* = 7.8 Hz), 1.59 (quintet, 2H, *J* = 7.8 Hz), 1.32-1.22 (m, 43H), 0.88 (t, 6H, *J* = 6.8 Hz). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 143.31, 128.25, 125.02, 119.73, 37.25, 33.62, 33.34, 31.93, 30.72, 30.13, 29.71, 29.67, 29.38, 27.67, 26.68, 22.70, 14.13. HRMS (ESI): Calcd for C₃₀H₅₇S₁ [MH⁺]: 449.4181. Found: 449.4174.

2-Trimethylstannyl-4-(4-decylhexadecyl)thiophene (**T-Sn**)

To a solution of *n*-butyllithium (1.6 M in hexane, 6.65 mL, 10.5 mmol) and THF (20 mL) was added 2,2,6,6-tetramethylpiperidine (1.48 g, 10.5 mmol) dropwise at -78 °C to form lithium tetramethylpiperide (LTMP). After stirring for 15 min, to the mixture was added dropwise a solution of **6** (4.49 g, 10.0 mmol) in THF (12 mL) over the period of 10 min at -78 °C. After stirring at -78 °C for 90 min, to the mixture was added dropwise trimethylstannylchloride (2.19 g, 11.0 mmol) over the period of 5 min. The mixture was stirred for 5 h, during which time the temperature was raised to room temperature. The reaction mixture was extracted with hexane, and the resulting organic layer was washed with water and then dried over magnesium sulfate. Evaporation of the solvent gave **T-Sn** as colorless liquid (5.96 g, 9.75 mmol, yield = 98 %). This

compound was subjected to the next reaction without further purification. ^1H NMR (CDCl_3 , 400 MHz): δ (ppm) 7.20 (d, 1H, $J = 0.8$ Hz), 7.01 (d, 2H, $J = 0.8$ Hz), 2.62 (t, 2H, $J = 7.6$ Hz), 1.60 (m, 2H), 1.26 (m, 43H), 0.88 (t, 6H, $J = 6.8$ Hz), 0.35 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz): δ (ppm) 144.66, 137.24, 136.60, 125.63, 37.26, 33.61, 33.48, 31.93, 30.41, 30.15, 29.72, 29.67, 29.38, 27.85, 26.69, 22.70, 14.14, -8.30 . HRMS (ESI): Calcd for $\text{C}_{33}\text{H}_{64}\text{NaSSn} [\text{MNa}^+]$: 635.3668. Found: 635.3548.

Scheme S2. Synthesis of the TTD-based monomer (**TTD2T-Br**)



3,6-Bis(4-(4-decylohexadecyl)thiophen-2-yl)thieno[3,2-b]thiophene (**7**)

A solution of 3,6-dibromothieno[3,2-*b*]thiophene (0.72 g, 2.4 mmol), **T-Sn** (4.15 g, 6.79 mmol), tetrakis(triphenylphosphine)palladium(0) (57 mg, 0.048 mmol), and toluene (10 mL) in a sealed reaction vessel was heated at 160 °C for 1 h in a microwave reactor. After cooled to room temperature, the mixture was extracted with hexane, and the resulting organic layer was washed with water and dried over magnesium sulfate. After evaporation of the solvent, the residue was purified by silica gel column chromatography (eluent: hexane) to give **7** as white solid (1.91 g, 1.84 mmol, yield = 77 %). ^1H -NMR (CDCl_3 , 400 MHz): δ (ppm) 7.50 (s, 2 H), 7.23 (s, 2H), 6.89 (s, 2H), 2.63 (d, 4H, $J = 7.6$ Hz), 1.64 (m, 4H), 1.29 (m, 86H), 0.87 (t, 12H, $J = 6.6$ Hz). ^{13}C -NMR (CDCl_3 , 100 MHz): δ (ppm) 144.13, 137.36, 128.74, 125.35, 121.34, 119.12, 37.27, 33.65, 33.29, 31.93, 30.98, 30.16, 29.73, 29.67, 29.38, 27.52, 26.72, 22.69, 14.12. HRMS (ESI): Calcd for $\text{C}_{66}\text{H}_{112}\text{S}_4$ $[\text{M}+\text{H}]^+$: 1033.7725. Found: 1033.7734.

3,6-Bis(4-(4-decylohexadecyl)thiophen-2-yl)thieno[3,2-*b*]thiophene-2,5-dione (**TTD2T**)

To a solution of *n*-butyllithium (1.6 M in hexane, 3.16 mL, 5.0 mmol) and THF (5 mL) was added diisopropylamine (0.70 mL, 5.0 mmol) dropwise at -78 °C. After stirring for 15 min, to the mixture was added dropwise a solution of **7** (1.77 g, 1.71 mmol) in THF (20 mL) over 10 min. After stirring at -78 °C for 90 min, to the mixture was added triisopropyl borate (2.29 mL, 10.0 mmol), and the mixture was gradually warmed to room temperature. The reaction was quenched with 1 M HCl aqueous solution, and the organic layer was extracted with ether and washed with water twice. The organic layer was then added to a solution of 35% hydrogen peroxide (15 mL) and ether (15 mL), and the resulting mixture was stirred vigorously at room temperature for 1 h. The organic

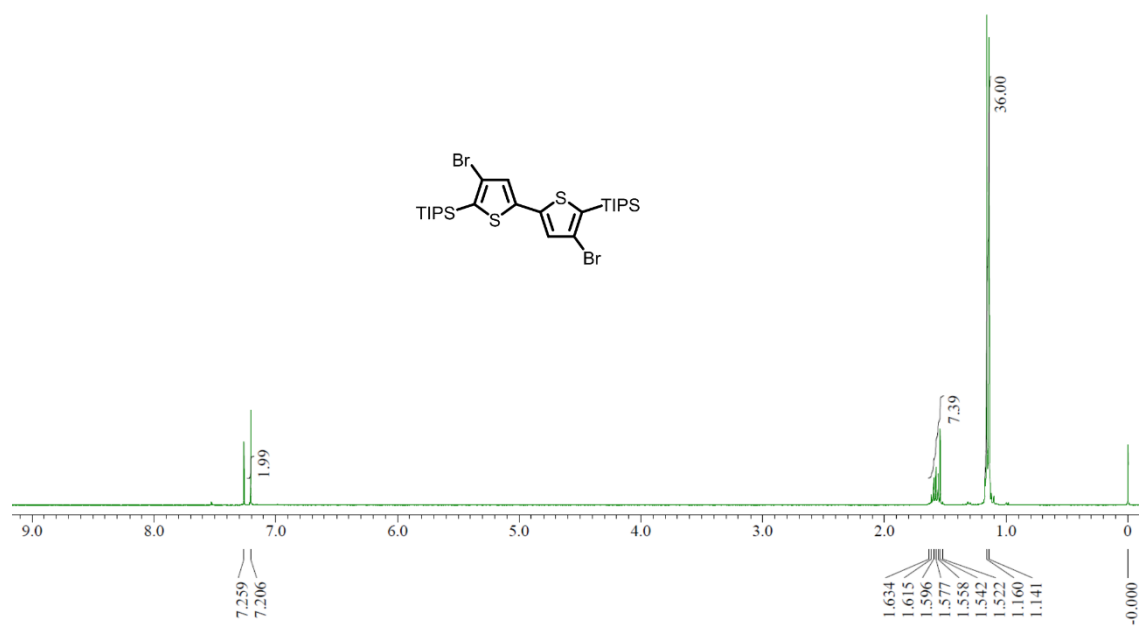
layer was extracted with hexane and washed with water, and dried over magnesium sulfate. After evaporation of the solvent, the residue was purified by silica gel column chromatography (eluent: hexane/dichloromethane = 9/1) to give **TTD2T** as red solid (368 mg, 0.35 mmol, yield = 20%). ¹H-NMR (CDCl₃, 400 MHz): δ (ppm) 7.62 (s, 2 H), 7.20 (s, 2H), 2.62 (d, 4H, *J* = 7.6 Hz), 1.59 (m, 4H), 1.29 (m, 86H), 0.88 (t, 12H, *J* = 6.4 Hz). ¹³C-NMR (CDCl₃, 100 MHz): δ (ppm) 187.28, 147.03, 144.93, 131.67, 131.56, 126.62, 126.16, 37.22, 33.60, 33.19, 30.69, 30.13, 29.72, 29.67, 29.37, 27.50, 26.69, 22.69, 14.12. HRMS (ESI): Calcd for C₆₆H₁₁₀O₂S₄ [M+H]⁺: 1063.7468. Found: 1063.7467.

3,6-Bis(4-(4-decylhexadecyl)thiophen-2-yl)thieno[3,2-b]thiophene-2,5-dione (TTD2T-Br2)

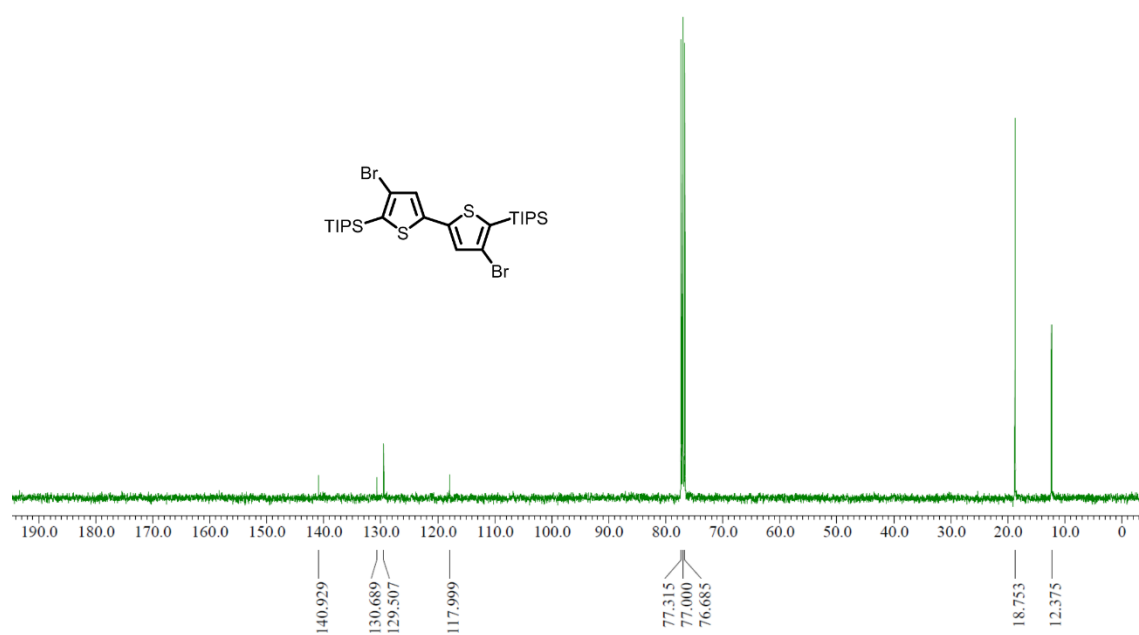
To a solution of **TTD2T** (0.34 g, 0.32 mmol) in THF (20 mL) was added NBS (0.28 g, 1.6 mmol) at room temperature. The reaction mixture was stirred at 50 °C for 14 h. After cooling to room temperature, the mixture was extracted with hexane and the organic layer was washed with water and dried over magnesium sulfate. After evaporation of the solvent, the crude product was purified by silica gel column chromatography (eluent: hexane/dichloromethane = 19/1) to give **TTD2T-Br2** as red purple solid (375 mg, 0.32 mmol, yield = 96%). ¹H-NMR (CDCl₃, 400 MHz): δ (ppm) 7.38 (s, 2 H), 2.56 (d, 4H, *J* = 7.6 Hz), 1.54 (m, 4H), 1.25 (m, 86H), 0.88 (m, 12H); ¹³C-NMR (CDCl₃, 100 MHz): δ (ppm) 186.80, 146.56, 143.82, 131.38, 131.08, 125.76, 117.29, 37.126, 33.55, 33.07, 31.93, 30.13, 29.79, 29.73, 29.68, 29.38, 26.67, 22.69, 14.12. HRMS (ESI): Calcd for C₆₆H₁₀₈O₂Br₂S₄ [M+H]⁺: 1219.5663. Found: 1219.5677.

References

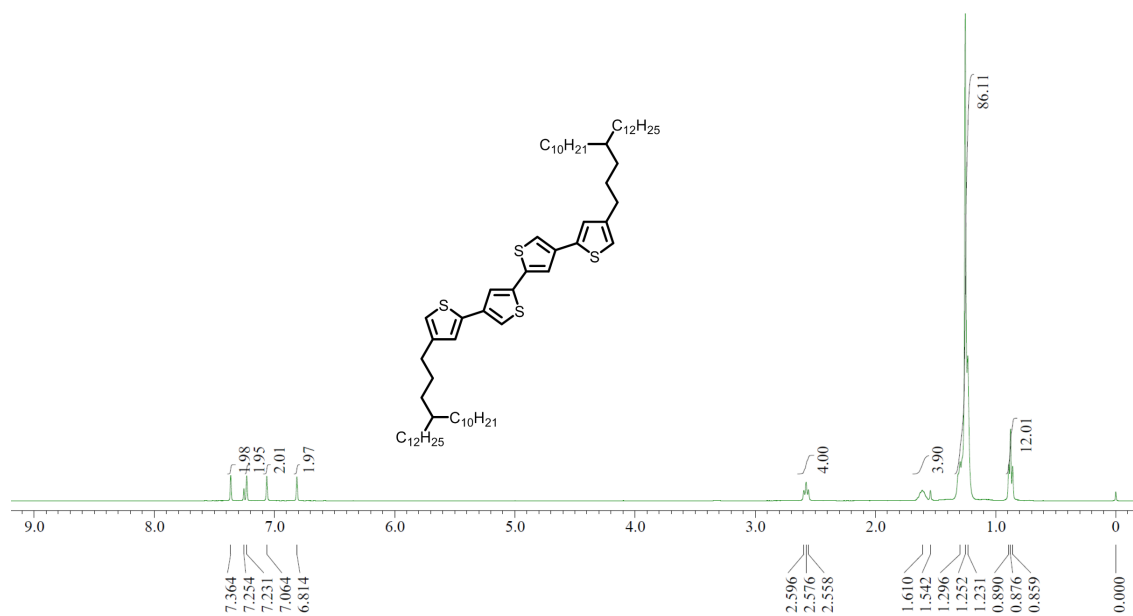
- (S1) Ebata, H.; Miyazaki, E.; Yamamoto, T.; Takimiya, K. *Org. Lett.* **2007**, *9*, 4499.
- (S2) Chung, D. S.; Park, J. W.; Kim, S.-O.; Heo, K.; Park, C. E.; Ree, M.; Kim, Y.-H.; Kwon, S.-K. *Chem. Mater.* **2009**, *21*, 5499.



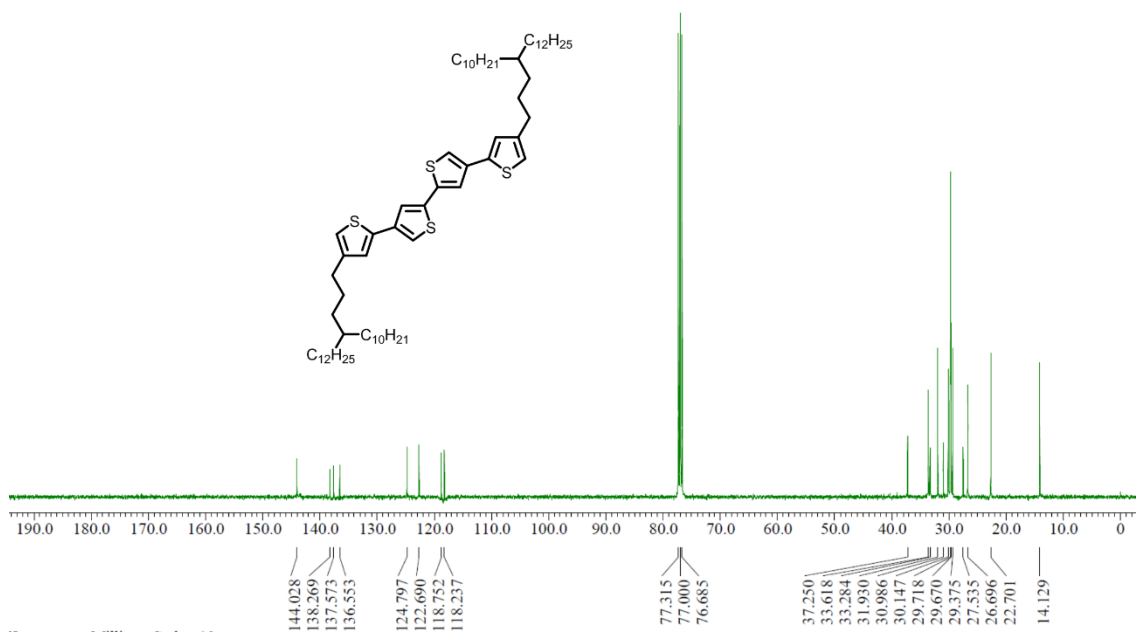
^1H NMR spectrum of **1** in CDCl_3 .



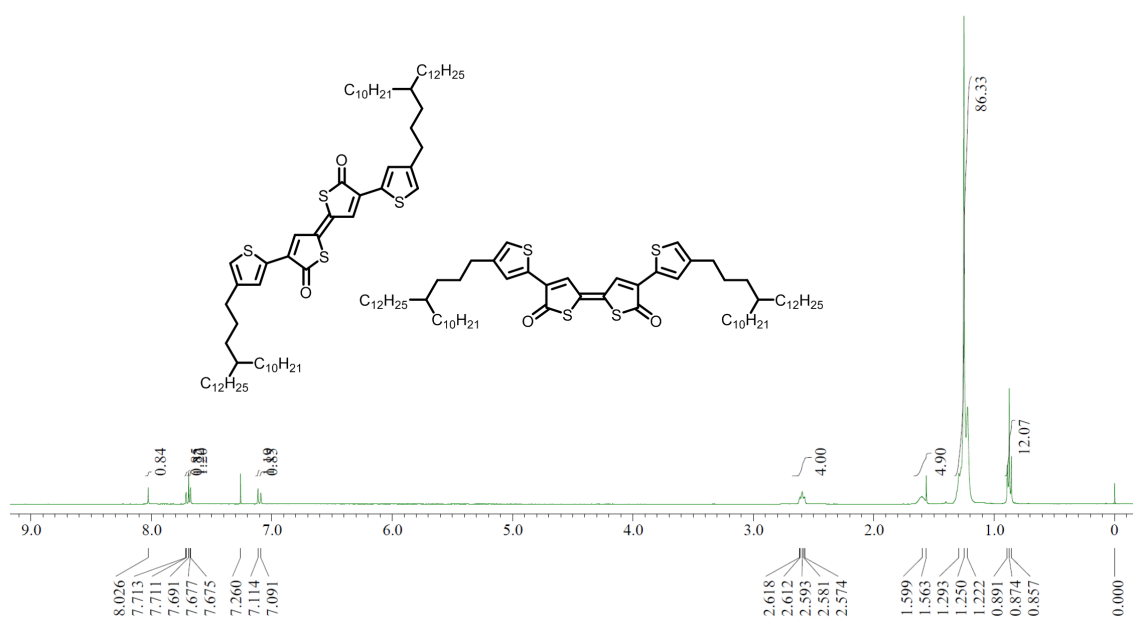
^{13}C NMR spectrum of **1** in CDCl_3 .



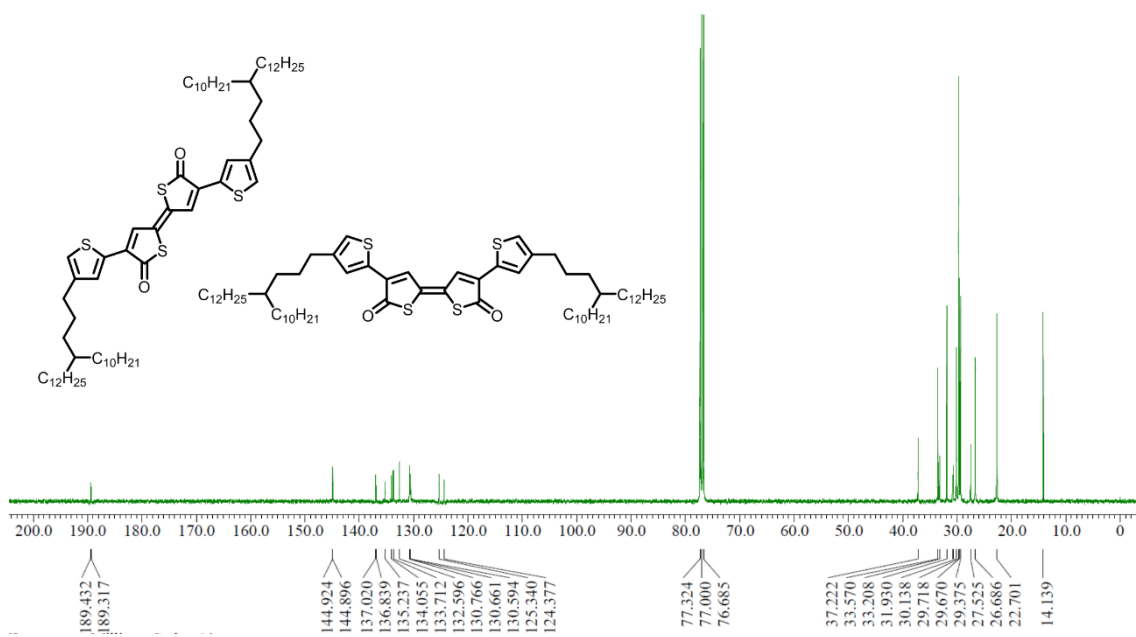
¹H NMR spectrum of **2** in CDCl₃.



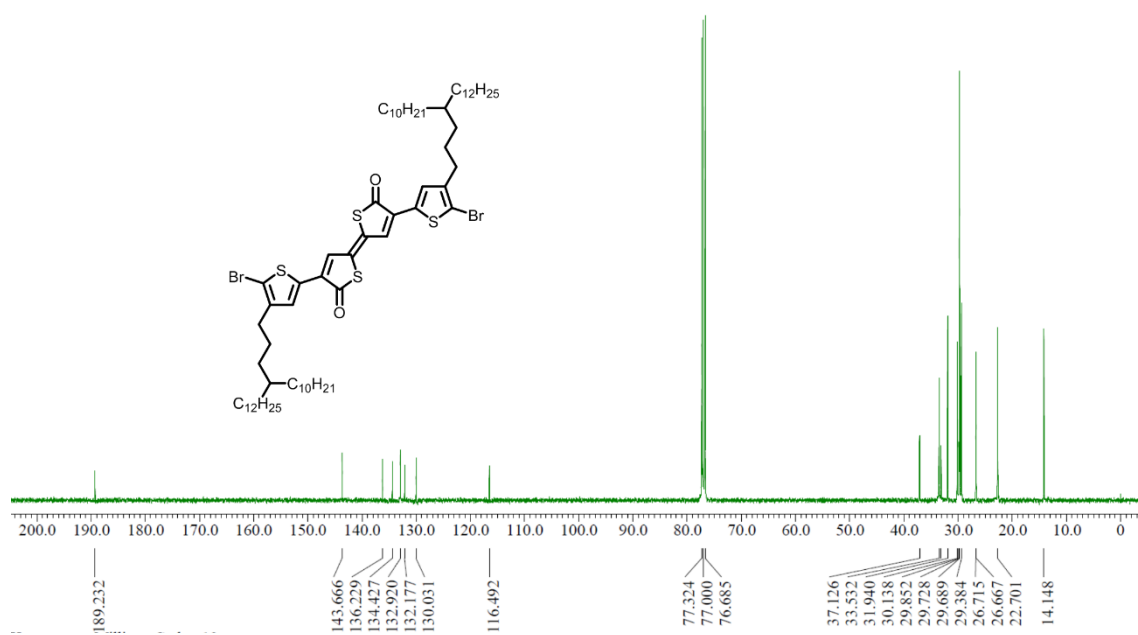
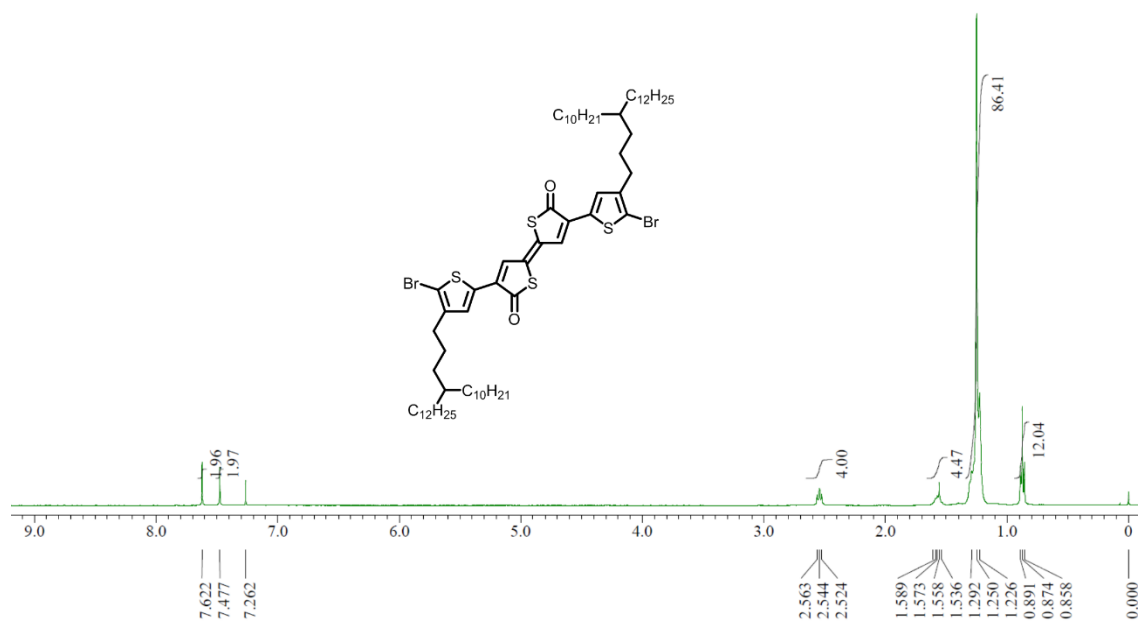
¹³C NMR spectrum of **2** in CDCl₃.

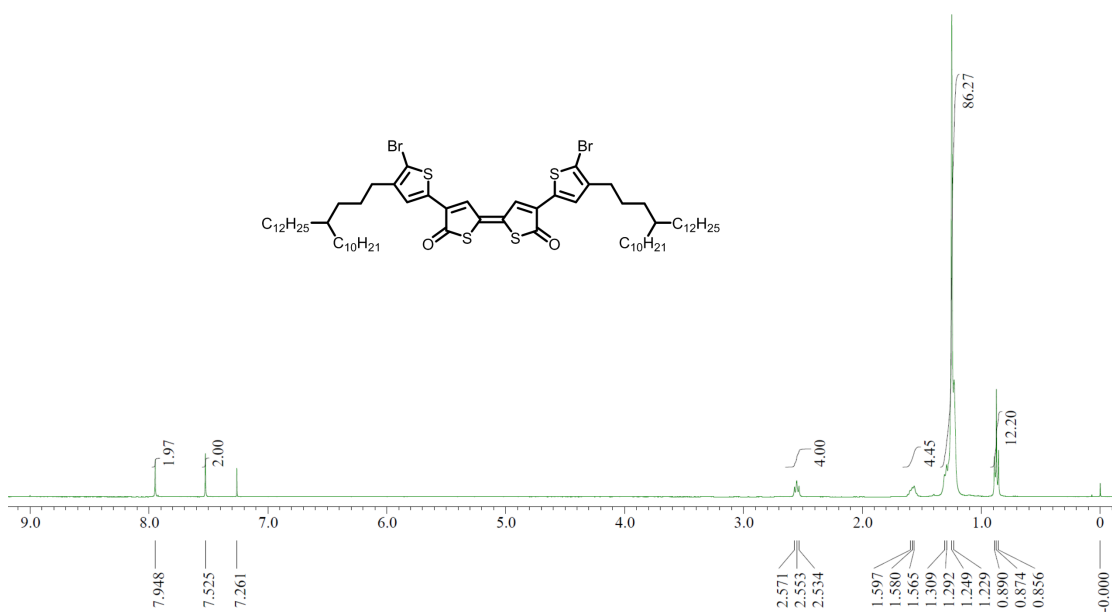


^1H NMR spectrum of **BTD2T** in CDCl_3 : mixture of (*E*) and (*Z*) isomers.

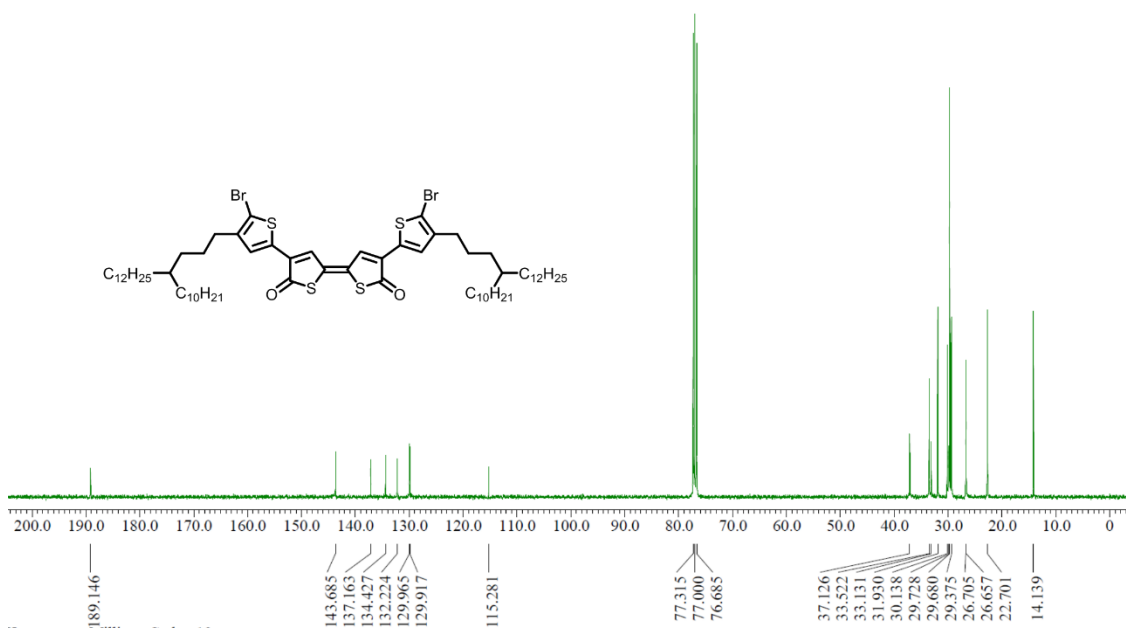


^{13}C NMR spectrum of **BTD2T** in CDCl_3 : mixture of (*E*) and (*Z*) isomers.

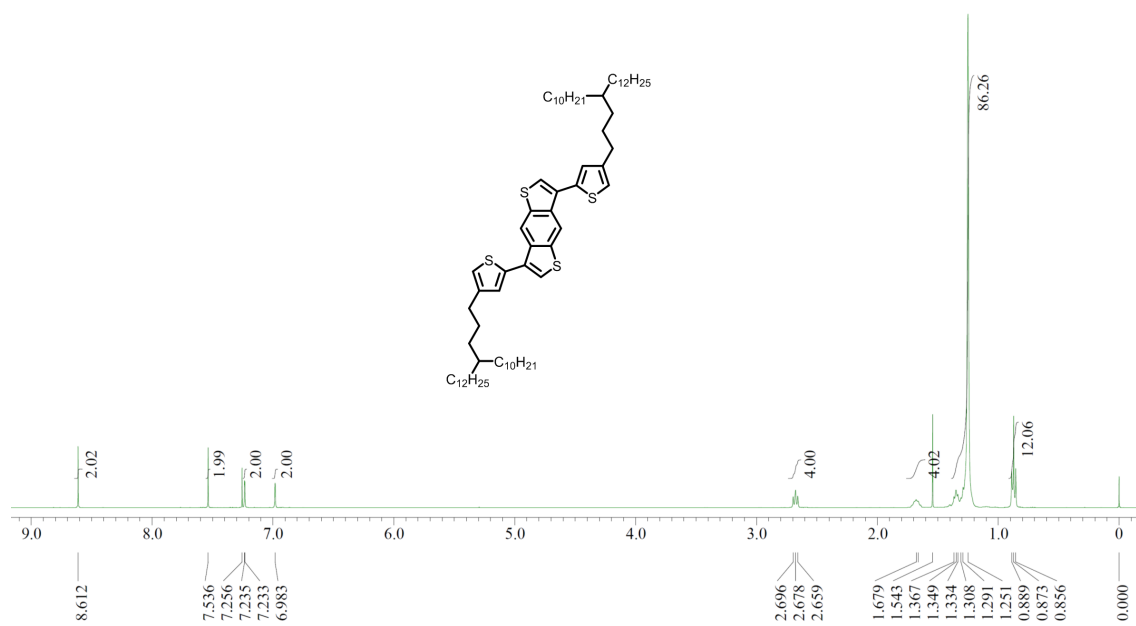




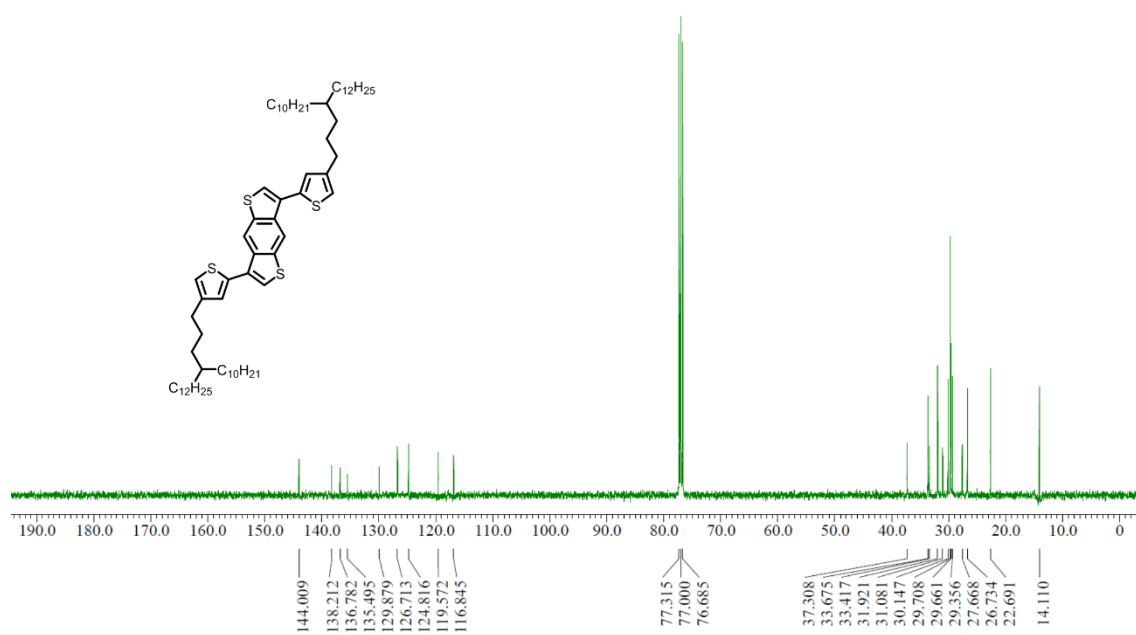
¹H NMR spectrum of **BTD2T-Br2** in CDCl₃: (Z)-isomer.



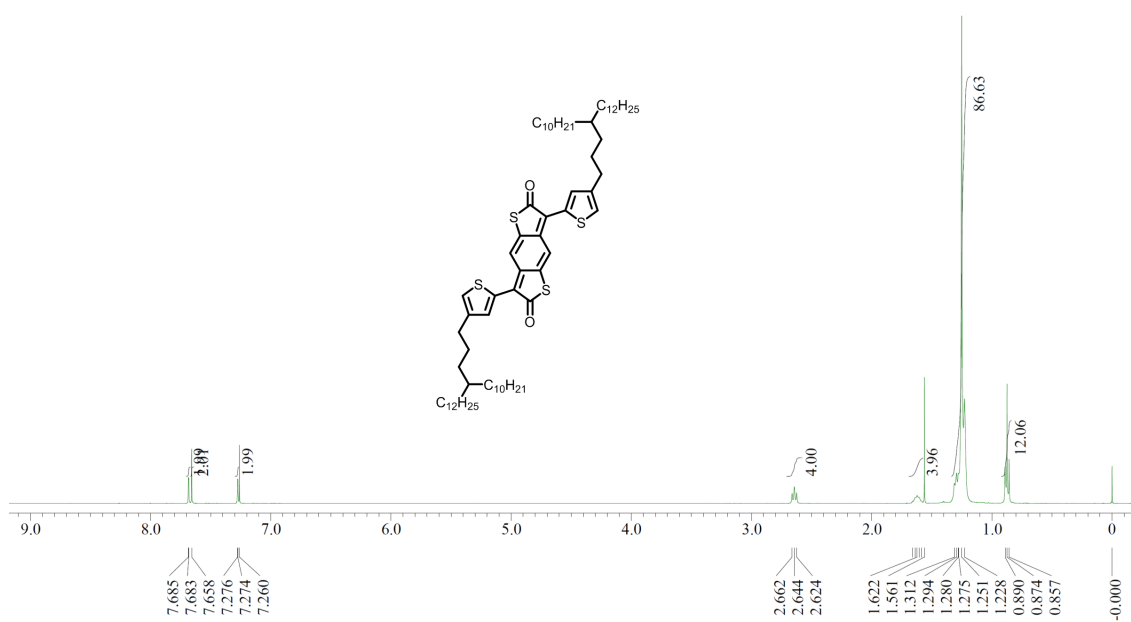
¹³C NMR spectrum of **BTD2T-Br2** in CDCl₃: (Z)-isomer.



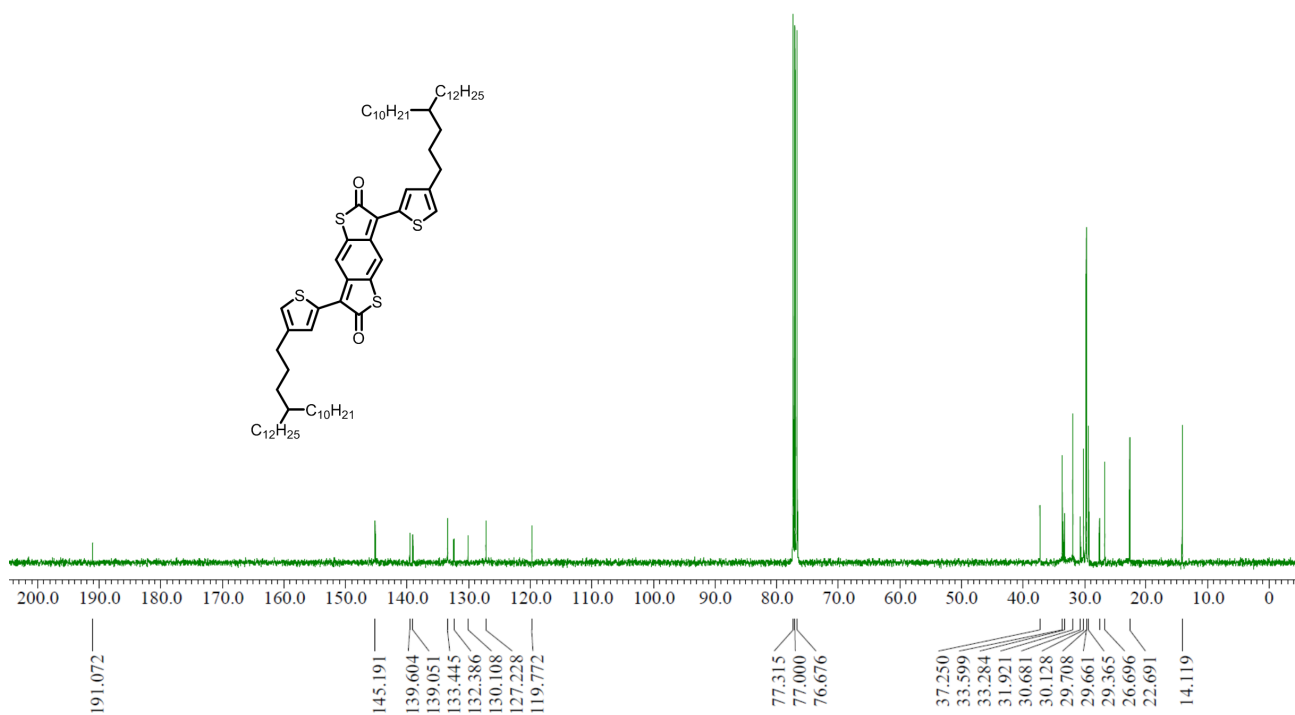
¹H NMR spectrum of **3** in CDCl₃



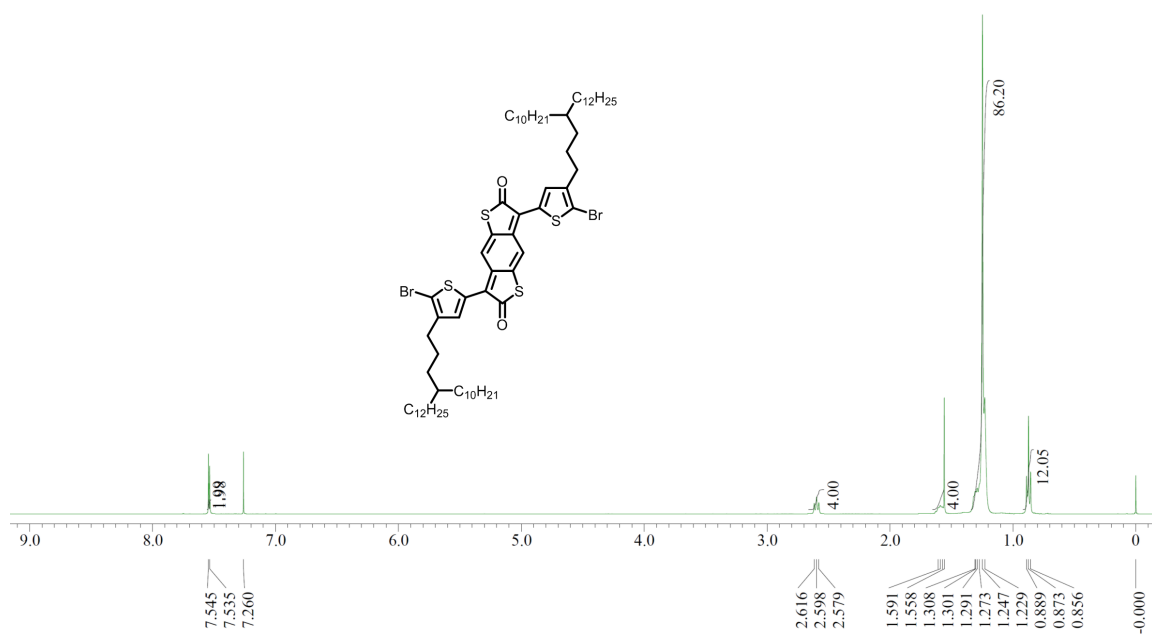
¹³C NMR spectrum of **3** in CDCl₃.



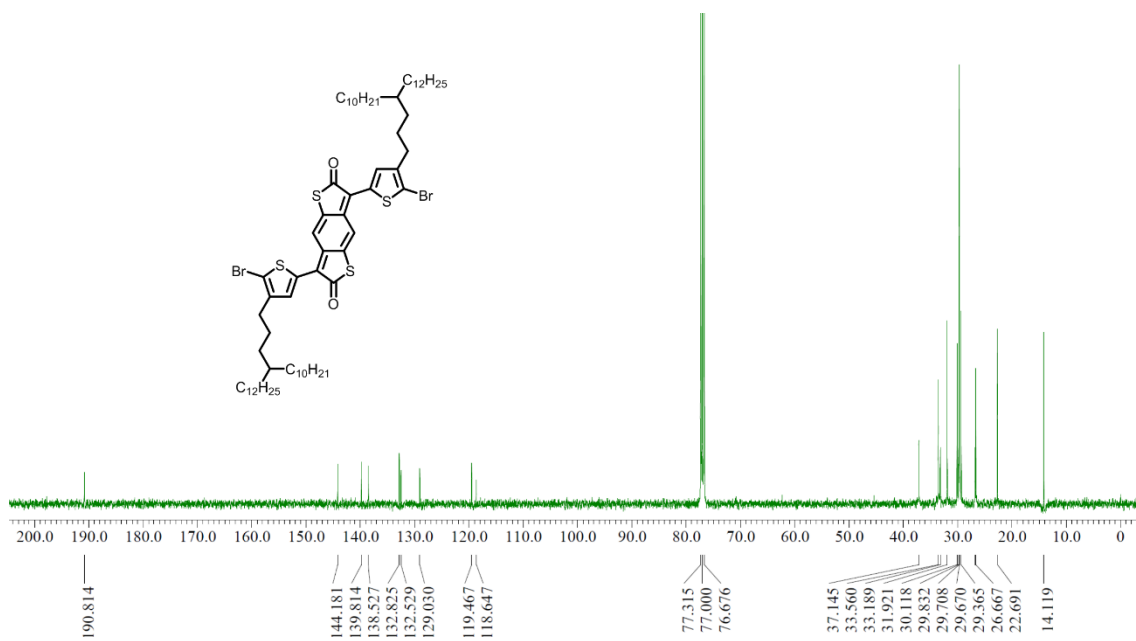
¹H NMR spectrum of **BDTD2T** in CDCl₃



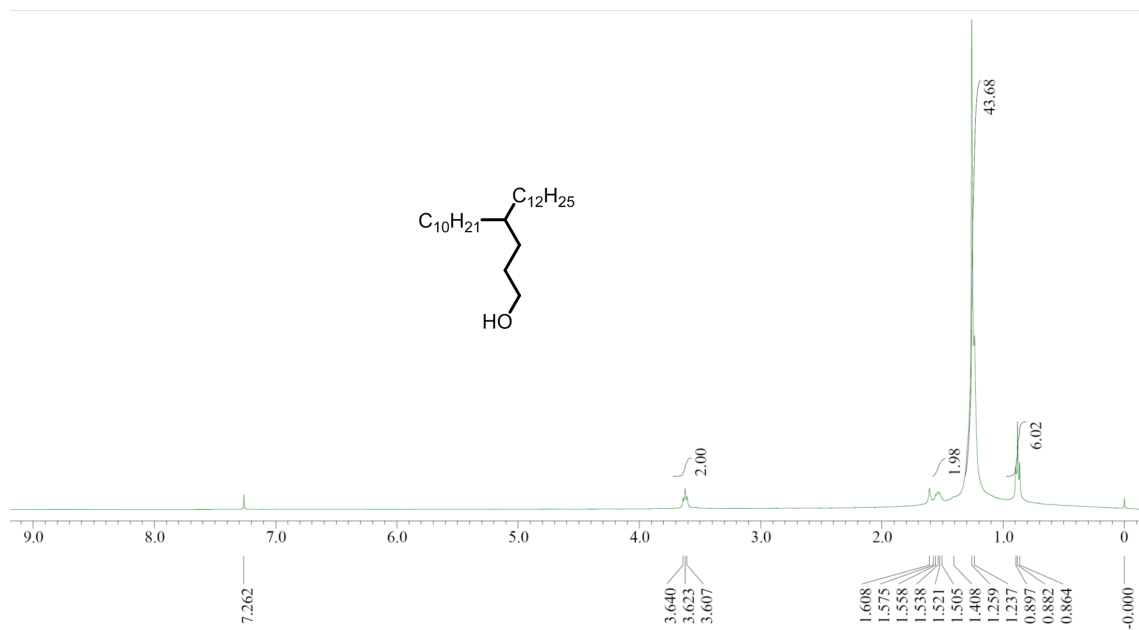
¹³C NMR spectrum of **BDTD2T** in CDCl₃.



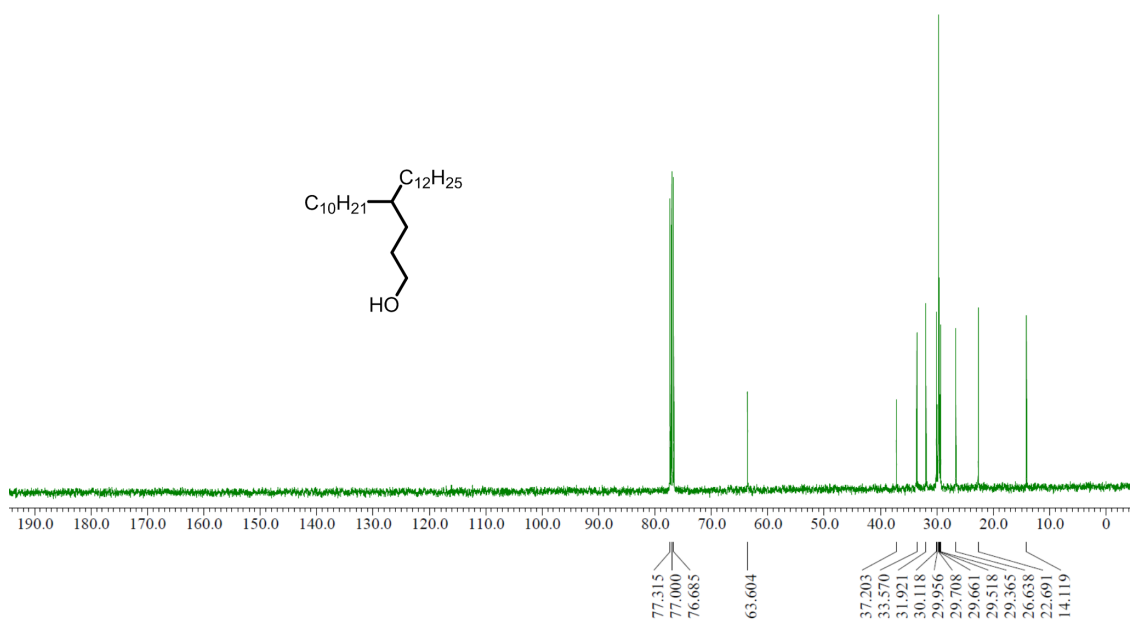
¹H NMR spectrum of **BDTD2T-Br2** in CDCl₃



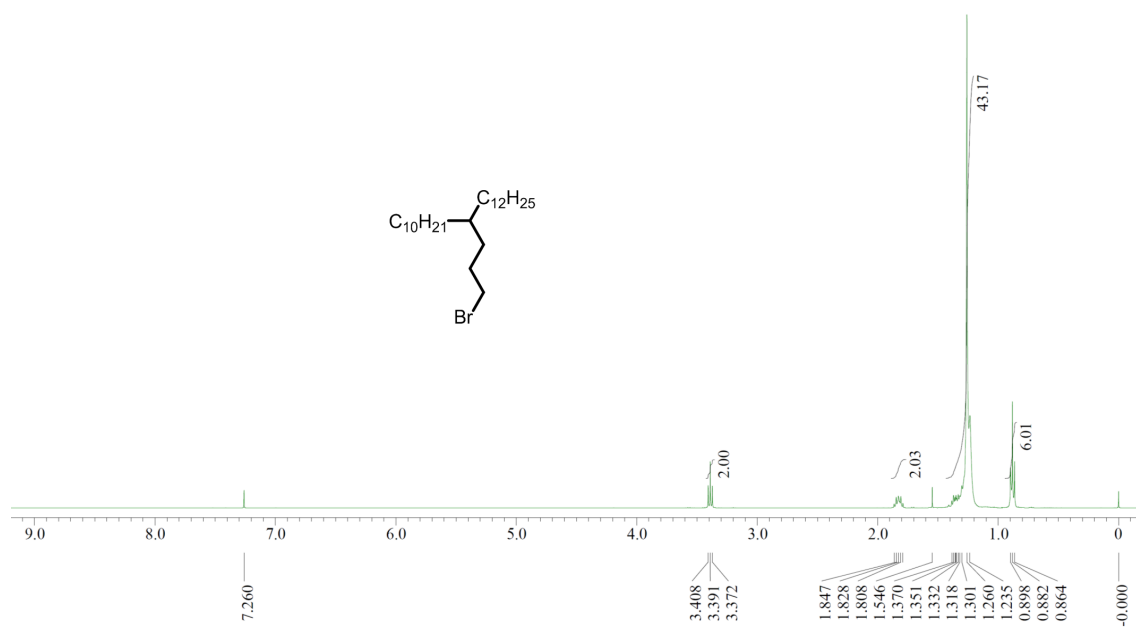
¹³C NMR spectrum of **BDTD2T-Br2** in CDCl₃.



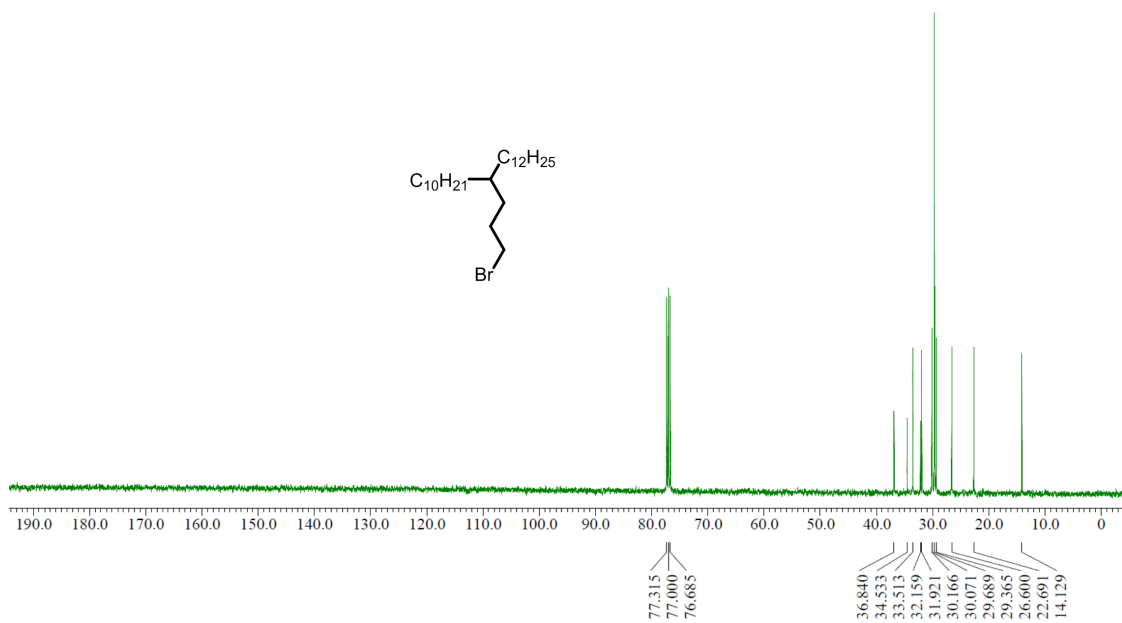
^1H NMR spectrum of **4** in CDCl_3



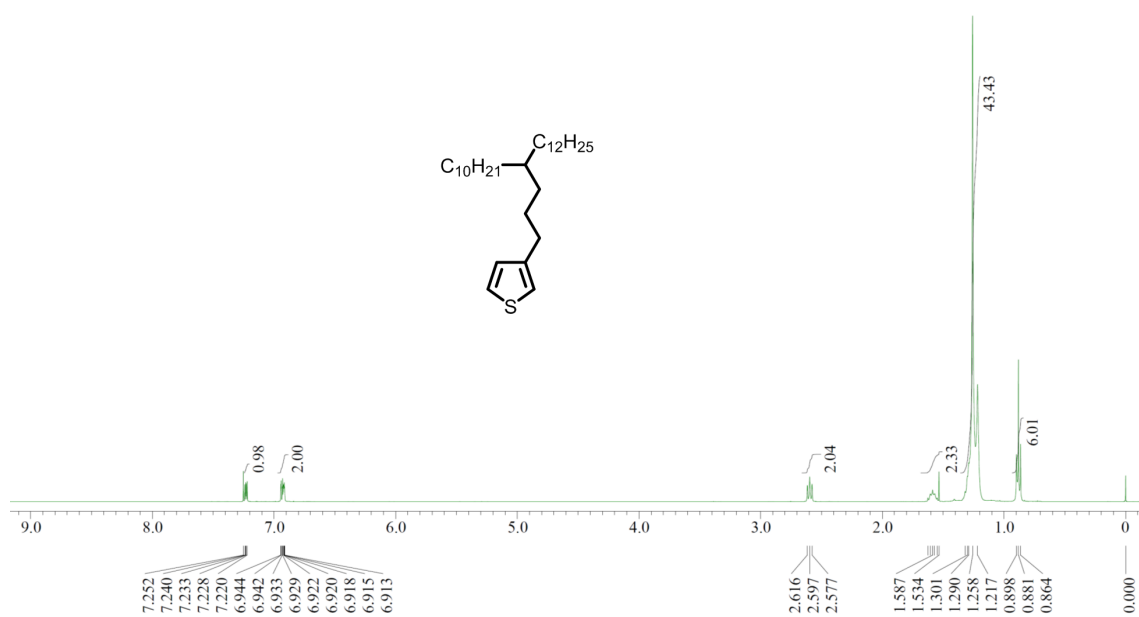
^{13}C NMR spectrum of **4** in CDCl_3



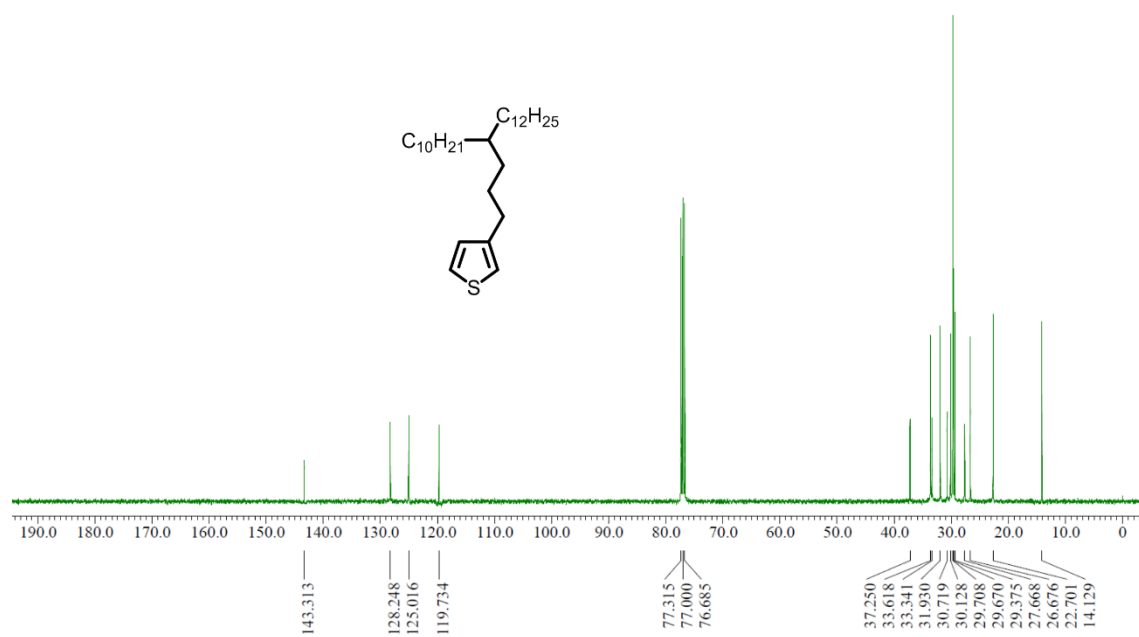
^1H NMR spectrum of **5** in CDCl_3



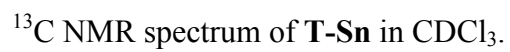
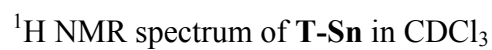
^{13}C NMR spectrum of **5** in CDCl_3

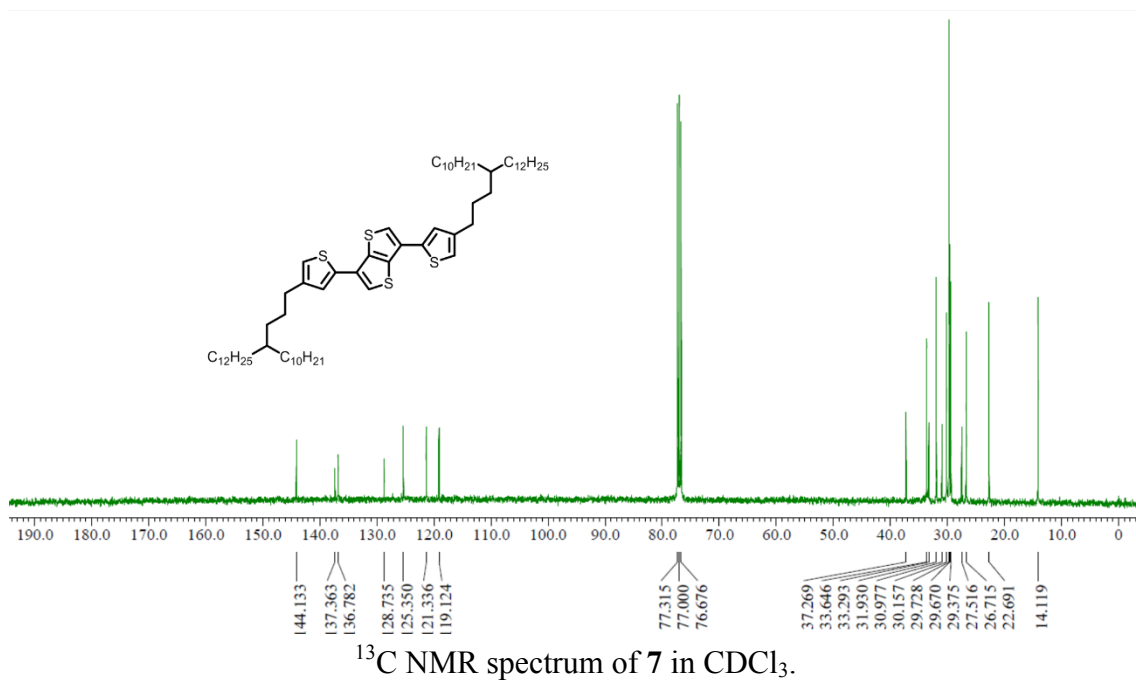
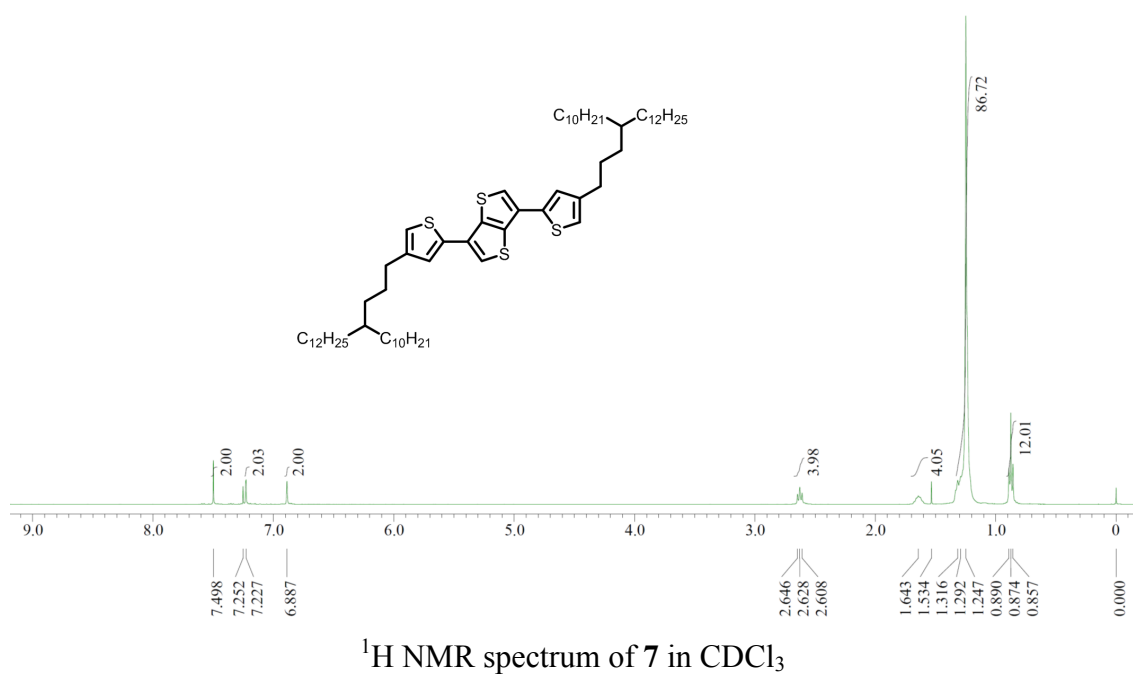


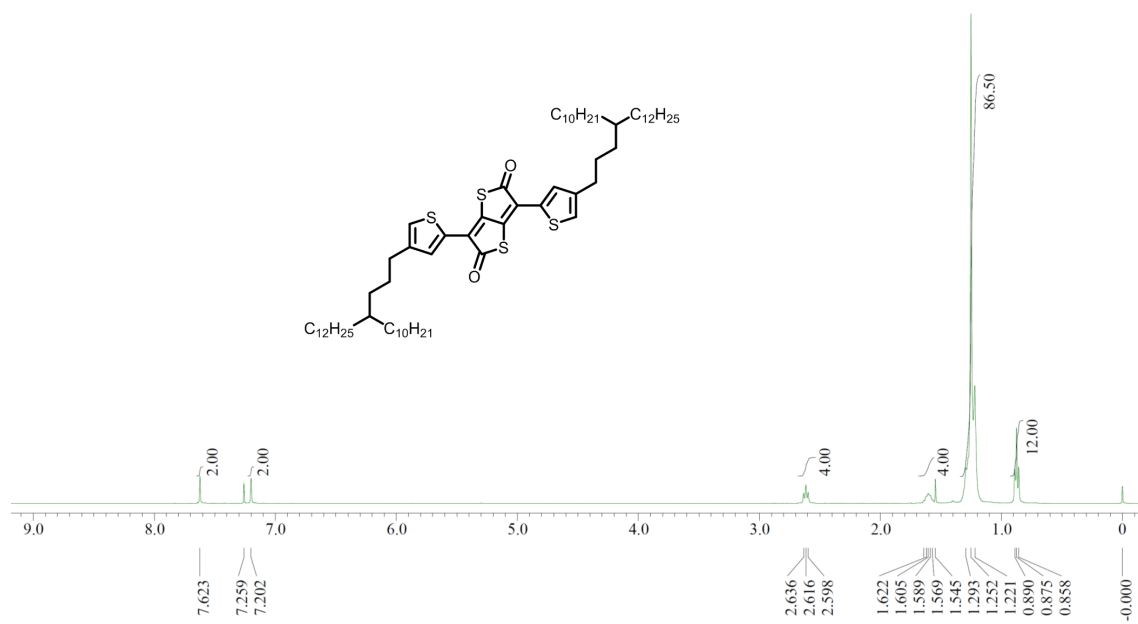
^1H NMR spectrum of **6** in CDCl_3



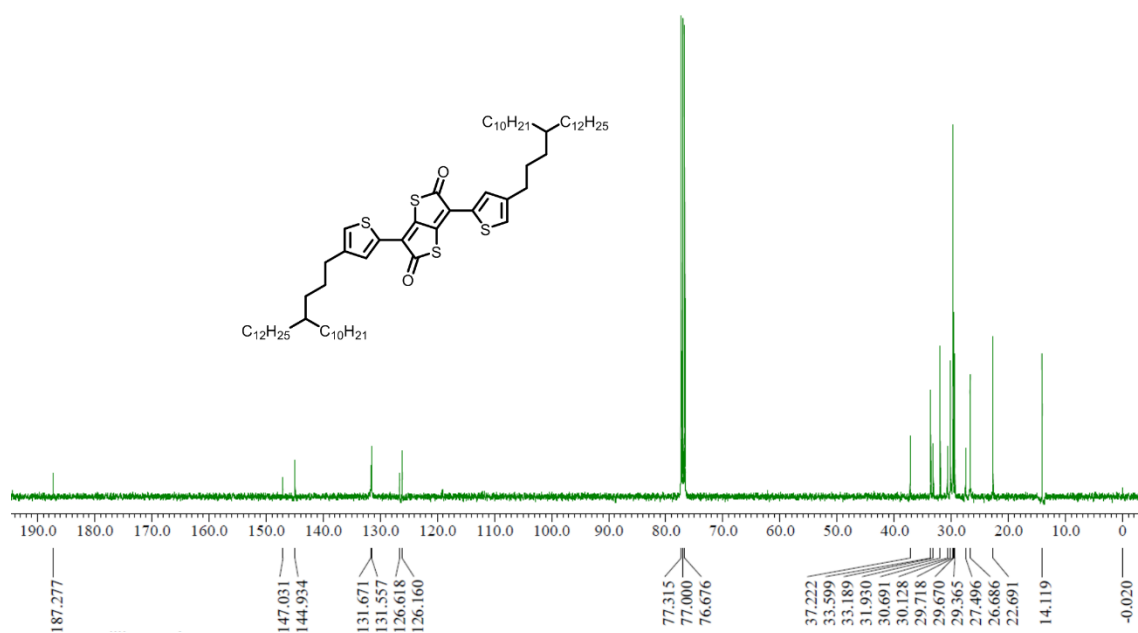
^{13}C NMR spectrum of **6** in CDCl_3



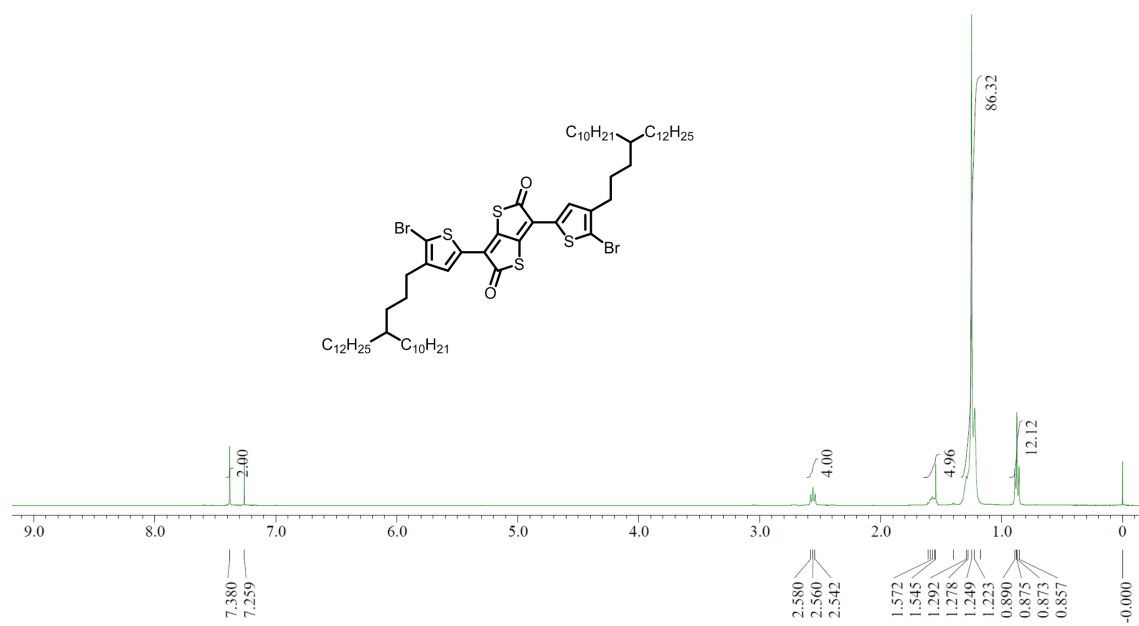




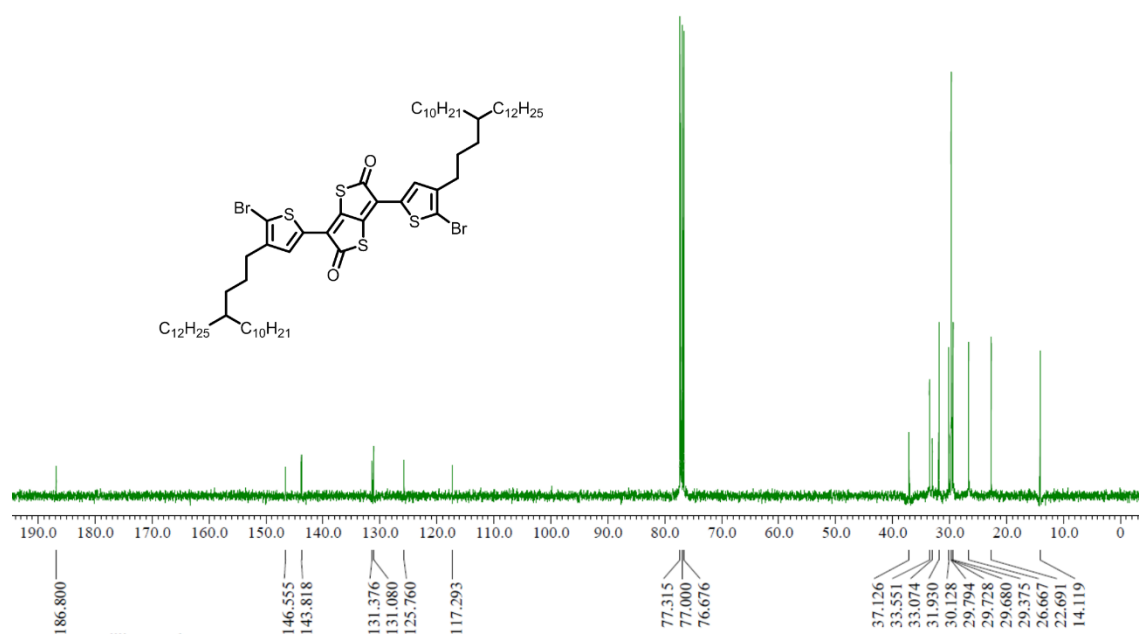
¹H NMR spectrum of TTD2T in CDCl₃



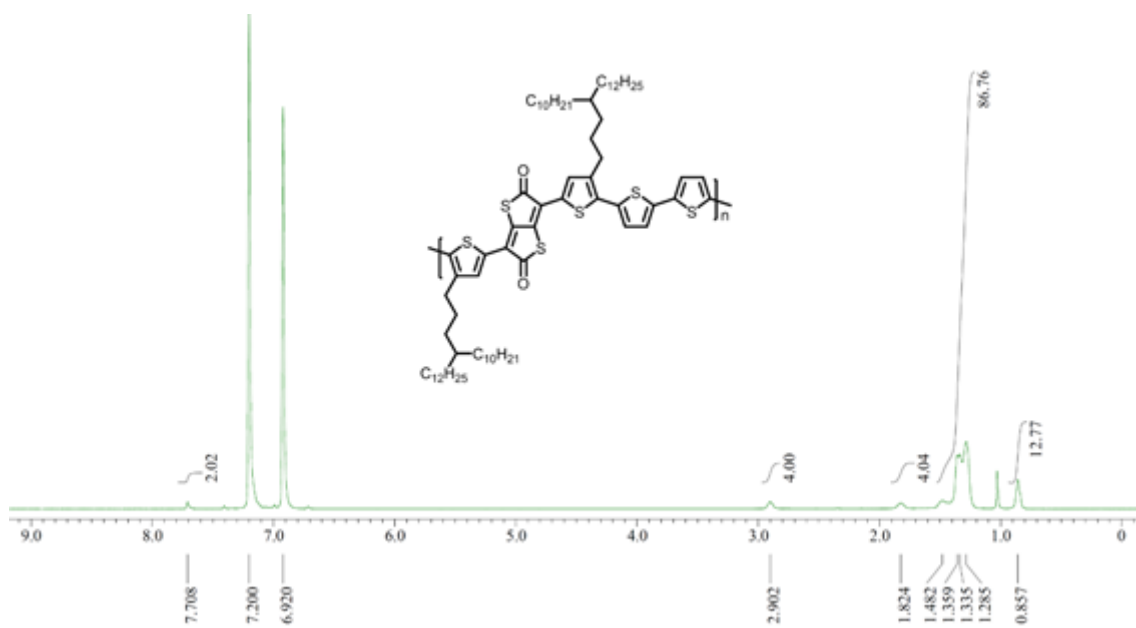
¹³C NMR spectrum of TTD2T in CDCl₃.



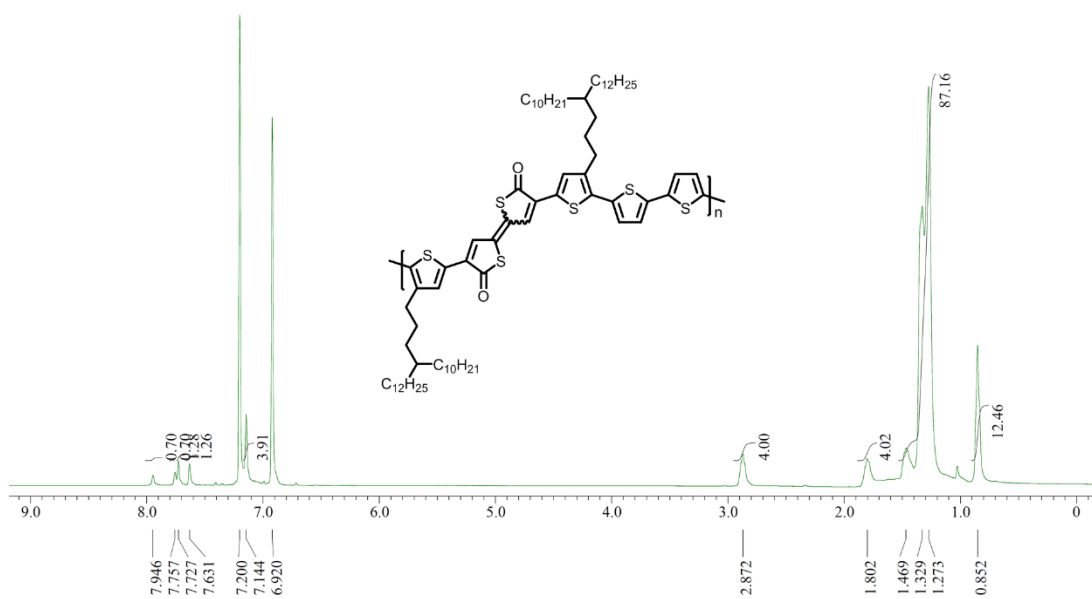
¹H NMR spectrum of TTD2T-Br2 in CDCl₃



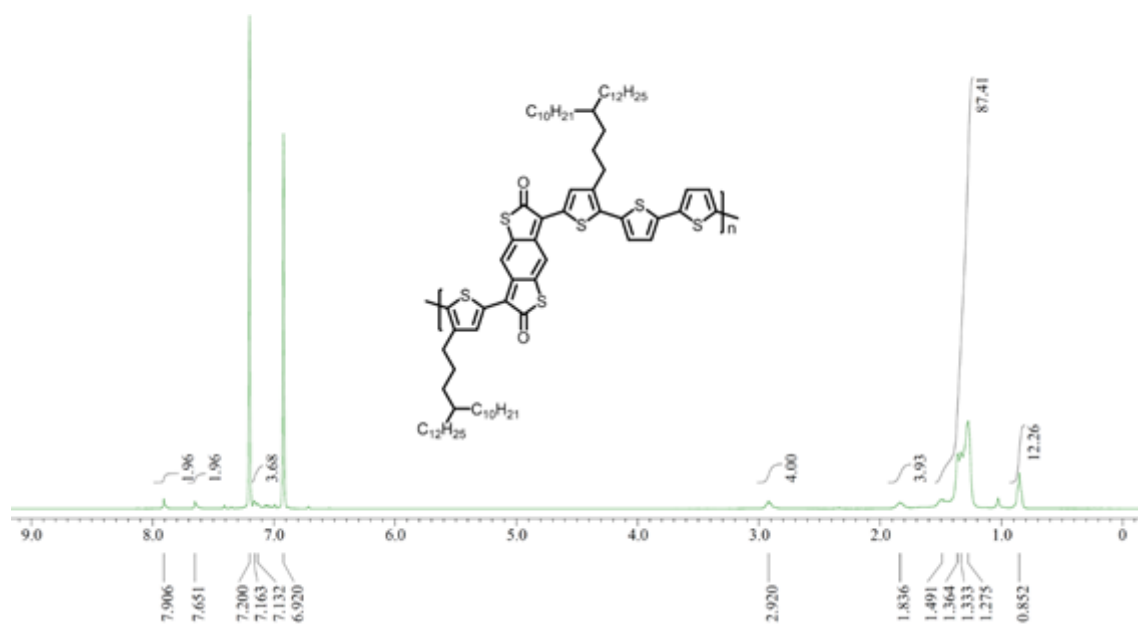
¹³C NMR spectrum of TTD2T-Br2 in CDCl₃.



¹H NMR spectrum of **PTTD4T** in DCB-*d*₄ at 120 °C.



¹H NMR spectrum of **PBTD4T** in DCB-*d*₄ at 120 °C.



¹H NMR spectrum of **PBDTD4T** in DCB-*d*₄ at 120 °C.

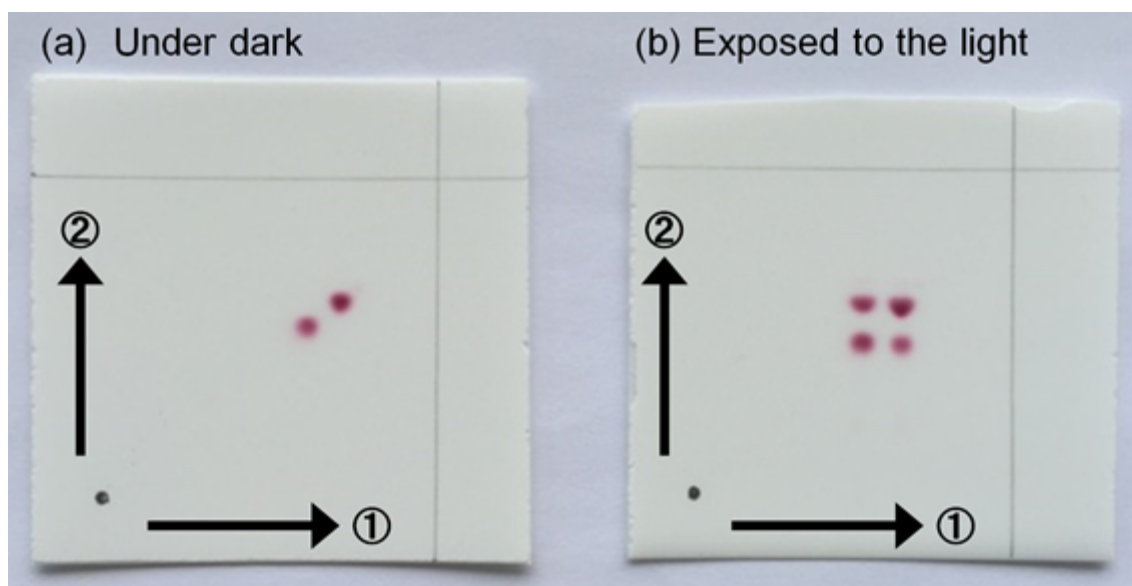


Figure S1. Photos of two-dimensional thin layer chromatography (2D-TLC) analysis for **BTD2T** (*E-Z* mixture), in which **BTD2T** was eluted with dichloromethane/hexane (= 4/6) in the dark (a) and with exposure to ambient light (b). The bottom-left black dots indicate the position of the spotted analyte before the elution. The arrows and numbers denote the direction and the order of elution. Under the dark condition, (*E*) and (*Z*) isomers could not isomerize into each other to be clearly separated into two spots on the TLC plate through the elution (a). With exposure to ambient light just before the second elution, (*E*) and (*Z*) isomers that were separated after the first elution were photo-isomerized, and then were eluted again to give four spots on the plate (b).

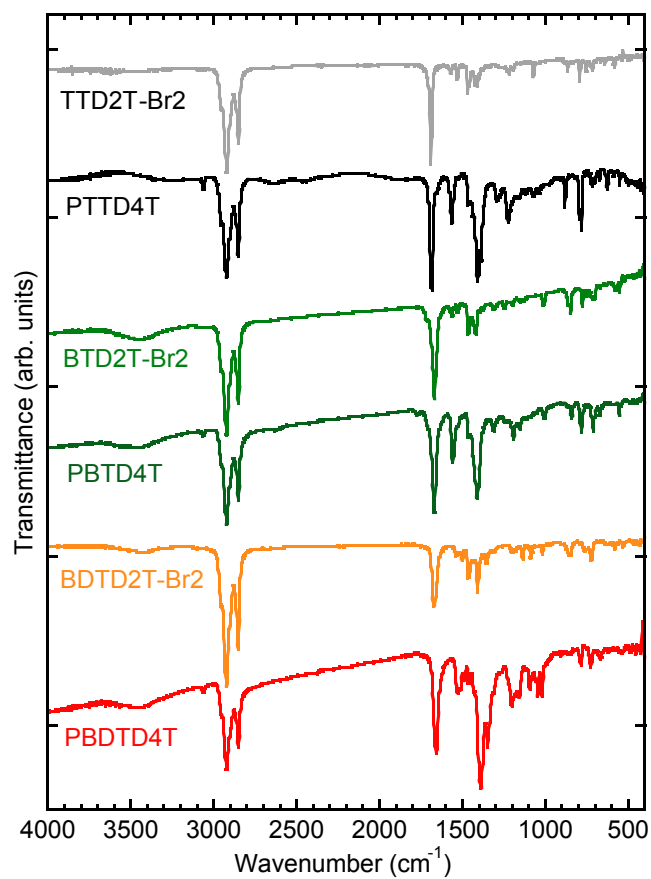


Figure S2. IR spectra of the monomers and polymers.

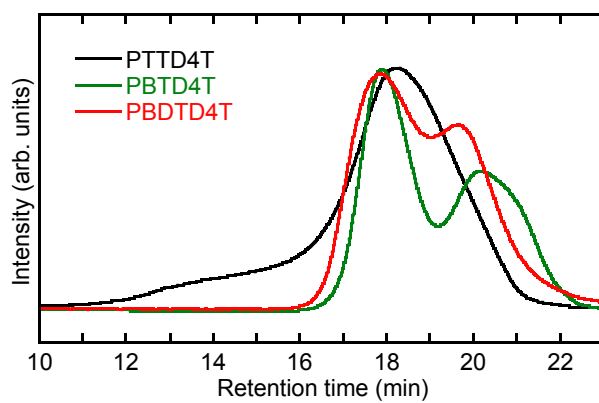


Figure S3. GPC chromatograms of the polymers

Instrumentation

UV-vis absorption spectra were recorded on a Shimadzu UV-3600 spectrometer. Cyclic voltammograms were recorded on a ALS Electrochemical Analyzer Model 612D with the three electrode system consisting of a platinum disc working electrode ($\phi = 3$ mm), a platinum wire counter electrode, and an Ag/AgCl reference electrode in a benzonitrile solution containing tetrabutylammonium hexafluorophosphate (0.1 M) at a scan rate of 100 mVs^{-1} . Polymer thin films were cast from DCB solutions on the platinum disc working electrode. All the potentials were calibrated with the half-wave potential of the ferrocene/ferrocenium redox couple measured under identical condition. Differential scanning calorimetry (DSC) analysis was carried out with an EXSTAR DSC7020 (SII Nanotechnology, Inc.) at a cooling and heating rate of $10 \text{ }^{\circ}\text{Cmin}^{-1}$. 2D-GIXD experiments were conducted at SPring-8 on beamline BL46XU. The samples were irradiated with an X-ray energy of 12.39 keV ($\lambda = 1 \text{ \AA}$) at a fixed incident angle of 0.12° through a Huber diffractometer, and the GIXD patterns were recorded on a 2-D image detector (Pilatus 300K). Polymer thin films for the X-ray measurements were prepared under the same condition used for the OFET fabrication. Photoemission yield spectra were taken with a photoemission yield spectrometer, model AC-2, in air (Riken Keiki, Tokyo, Japan) using polymer thin films spun on the indium-tin-oxide coated glass substrates.

The density functional theory (DFT) calculations were performed by using a Gaussian 09 program package.¹ The calculations of the optimized geometry of monomer units and trimers and their molecular orbitals were carried out at the B3LYP/6-31G(d) level. Time-dependent DFT (TD-DFT) calculations at the optimized structure of monomer units were also carried out at the B3LYP/6-31G(d) level.

OFET devices were fabricated in a bottom-gate-top-contact configuration on a heavily doped n^{+} -Si(100) wafer with 200-nm-thickness thermally grown SiO_2 ($C_i = 17.3 \text{ nFcm}^{-2}$). The Si/ SiO_2 substrates were ultrasonicated with water for three min thrice, and acetone and isopropanol for 10 min, respectively, and rinsed in boiled isopropanol for 10 min, and then were subjected to UV-ozone treatment for 30 min. Onto the cleaned substrate, a solution of octadecyltriethoxysilane in trichloroethylene (3 mM) was spincoated at a rate of 3000 rpm for 15 sec followed by hydrolysis in a closed container in the presence of ammonia hydroxide solution for 24 h. After the hydrolysis, the substrates were rinsed with water and boiling isopropanol. In a glove box under nitrogen atmosphere, polymer thin films were spin-coated from hot 1,2,4-trichlorobenzene solutions (5 gL^{-1}) at the spin-rate of 3000 rpm for 80 sec. The polymer films were annealed at 300°C for **PTTD4T** and **PBTD4T**, and 200°C for **PBDTD4T** for 30 min. On top of the polymer thin films, gold drain and source contact electrodes (thickness: 80 nm) with the channel length and width of $40 \text{ }\mu\text{m}$ and $1500 \text{ }\mu\text{m}$, respectively, were deposited in vacuum through shadow masks.

Current-voltage characteristics of the OFET devices were measured at room temperature under ambient conditions (relative humidity: approximately 30%) with a Keithley 4200-SCS

semiconductor parameter analyzer. Threshold voltages of the devices were estimated from the transfer plots by extrapolating the square root of the drain current to the horizontal axis. Hole and electron field-effect mobilities were extracted from the square root of the drain current in the saturation regime by using the following equation,

$$\mu = \frac{2L}{WC_i} \left(\frac{d\sqrt{|I_d|}}{dV_g} \right)^2$$

where, L and W are channel length and width, respectively, and C_i is capacitance of the gate insulator. The average hole and electron mobilities and threshold voltages were obtained over more than eight devices.

Reference

1. Gaussian 09, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

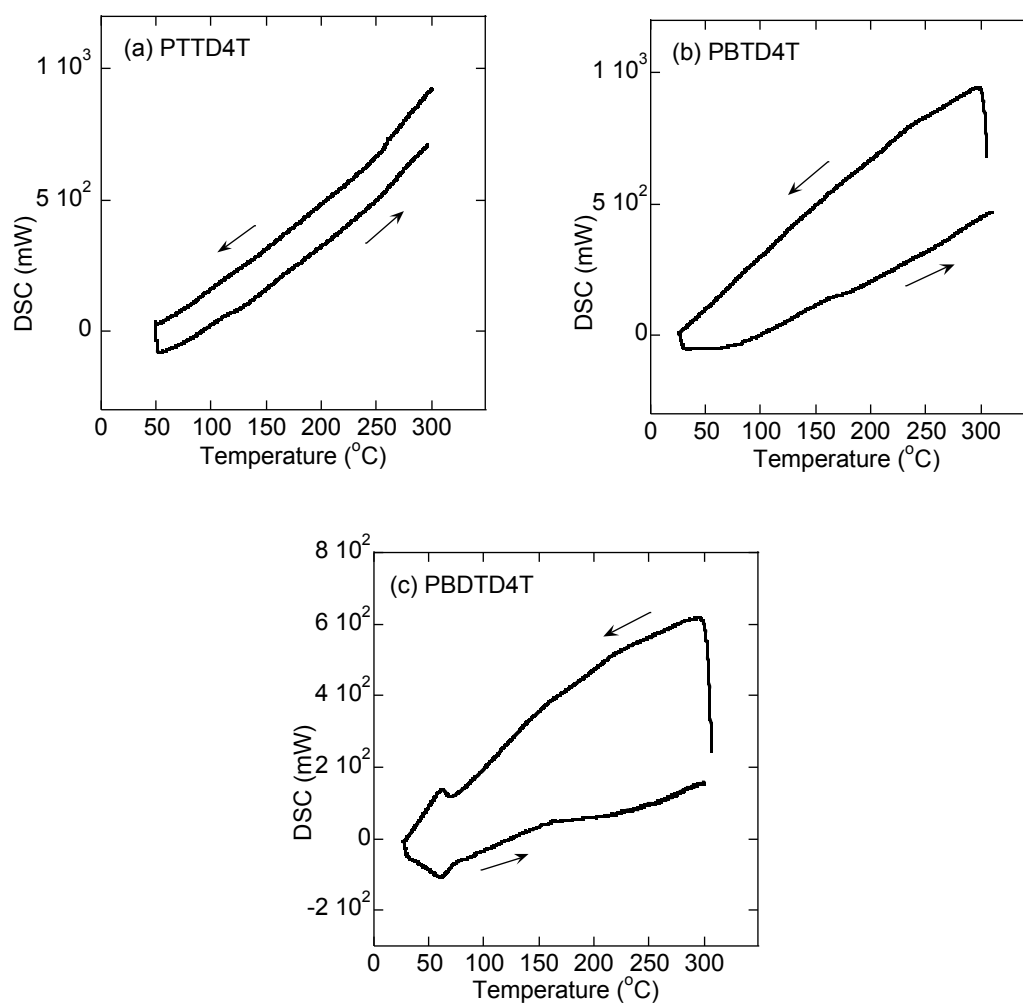


Figure S4. DSC curves of **PTTD4T** (a), **PBTD4T** (b), and **PBDTD4T** (c).

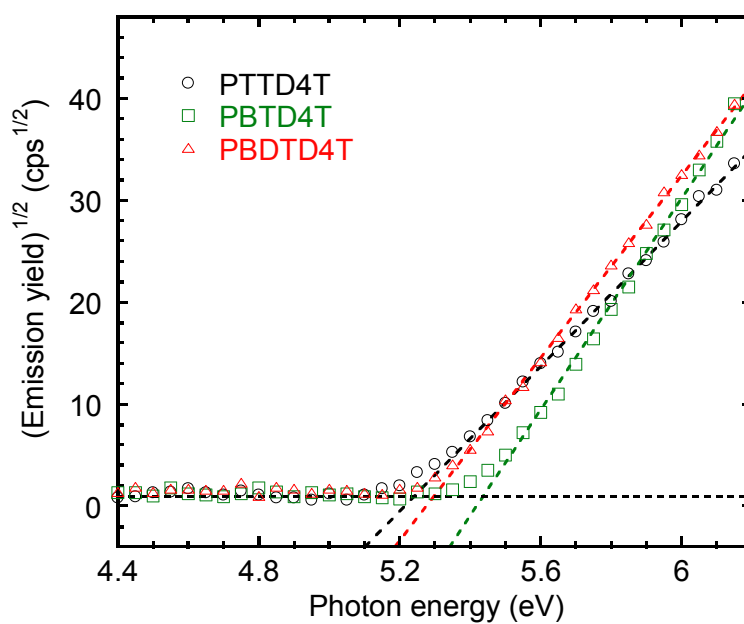


Figure S5. Photoemission yield spectra of the polymer thin films.

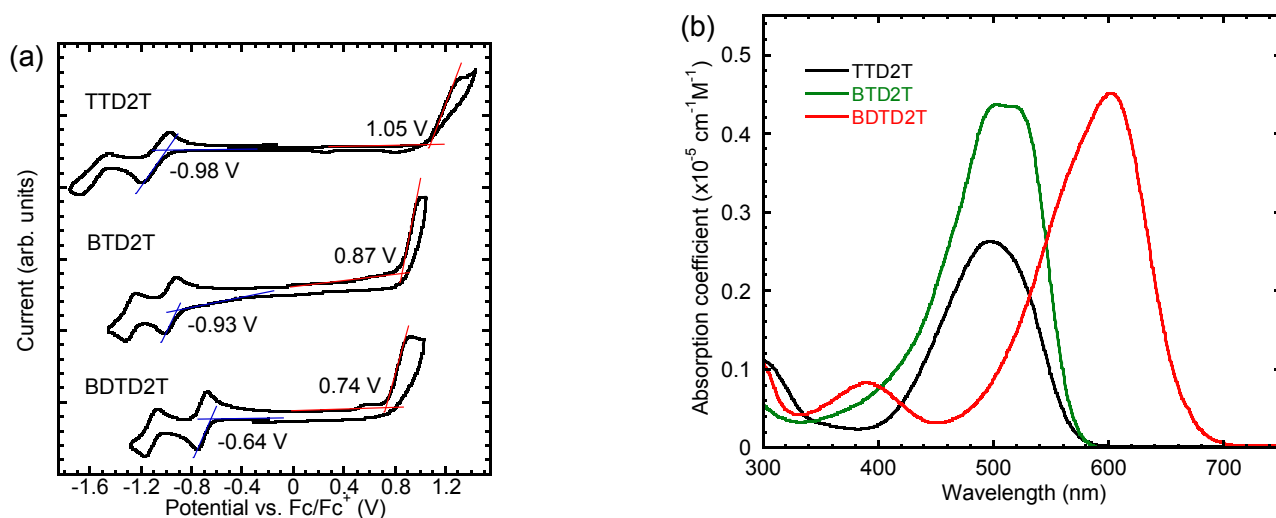


Figure S6. Cyclic voltammograms (a) and absorption spectra (b) of **TTD2T**, **BTD2T**, and **BDTD2T**. Onset redox potentials are shown in Figure S4a.

Table S1. Results of cyclic voltammetry^a and UV-vis absorption spectroscopy^b for TTD2T, BTD2T, and BDTD2T.

Triad	E_{LUMO} (eV) ^c	E_{HOMO} (eV) ^c	E_{g}^{EC} (eV) ^d	λ_{max} (nm) ^e	λ_{edge} (nm) ^f	$E_{\text{g}}^{\text{opt}}$ (eV) ^g
TTD2T	-3.83	-5.85	2.02	497	567	2.19
BTD2T	-3.87	-5.67	1.80	502, 517	569	2.18
BDTD2T	-4.16	-5.54	1.38	602	667	1.86

^aCarried out in benzonitrile solution. ^bCarried out in CB solution. ^cEvaluated by cyclic voltammetry.

^dHOMO–LUMO gap determined by cyclic voltammetry ($E_{\text{LUMO}} - E_{\text{HOMO}}$). ^eAbsorption maximum.

^fAbsorption edge. ^gOptical bandgap estimated from the absorption edge.

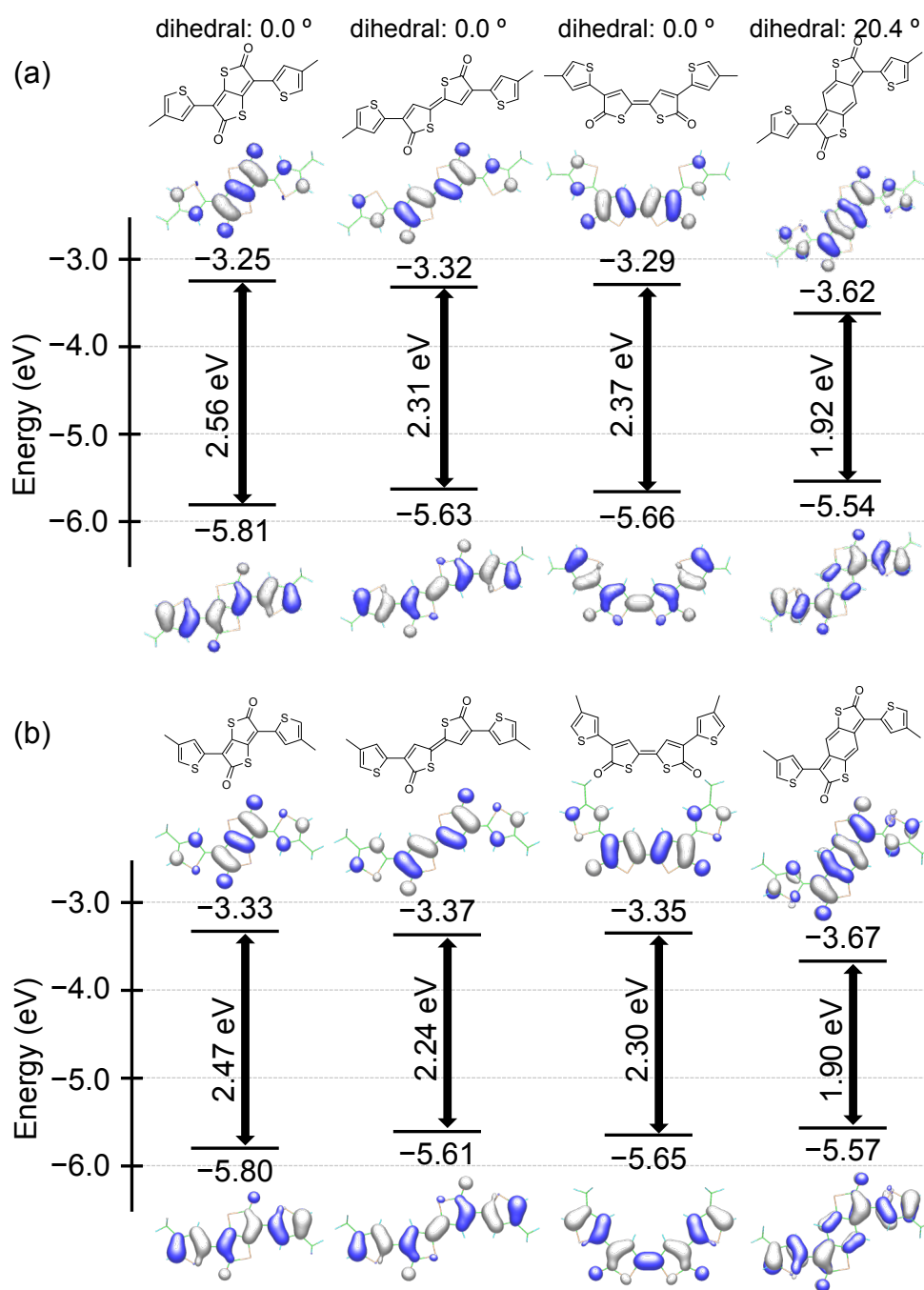


Figure S7. HOMO and LUMO geometry and energy levels of TTD2T, BTD2T, and BDTD2T calculated by the DFT method at the B3LYP/6-31G(d) level. The 4-decylhexadecyl groups were replaced with the methyl groups in order to simplify the calculation.

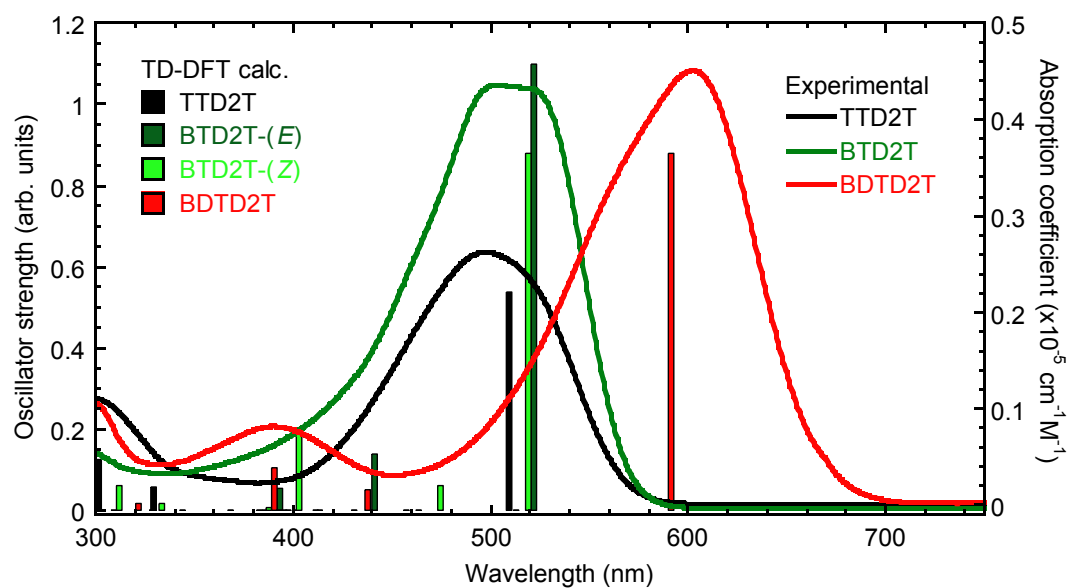


Figure S8. Oscillator strength of TTD2T, BTD2T, and BDTD2T (with the methyl groups) calculated by the TD-DFT method in comparison with the absorption spectra of TTD2T, BTD2T, and BDTD2T in chlorobenzene solution.

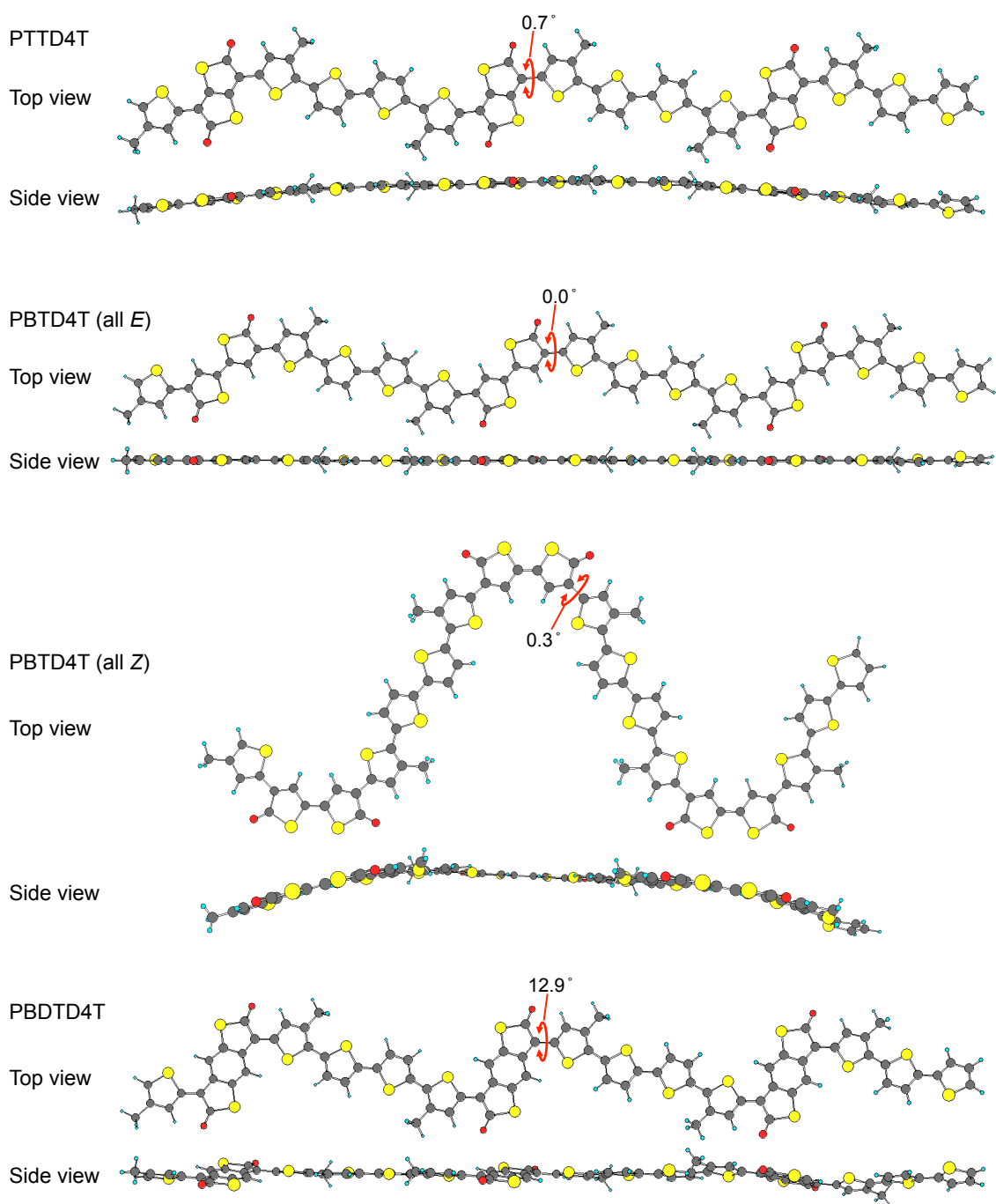


Figure S9. Optimized geometries of the model trimers that have anti-configuration at between thienoquinoidal units and the adjacent alkylthiophenes calculated by DFT method at the B3LYP/6-31G(d) level. The values indicated with red arrows are the dihedral angles between central thienoquinoids and methyl thiophene.

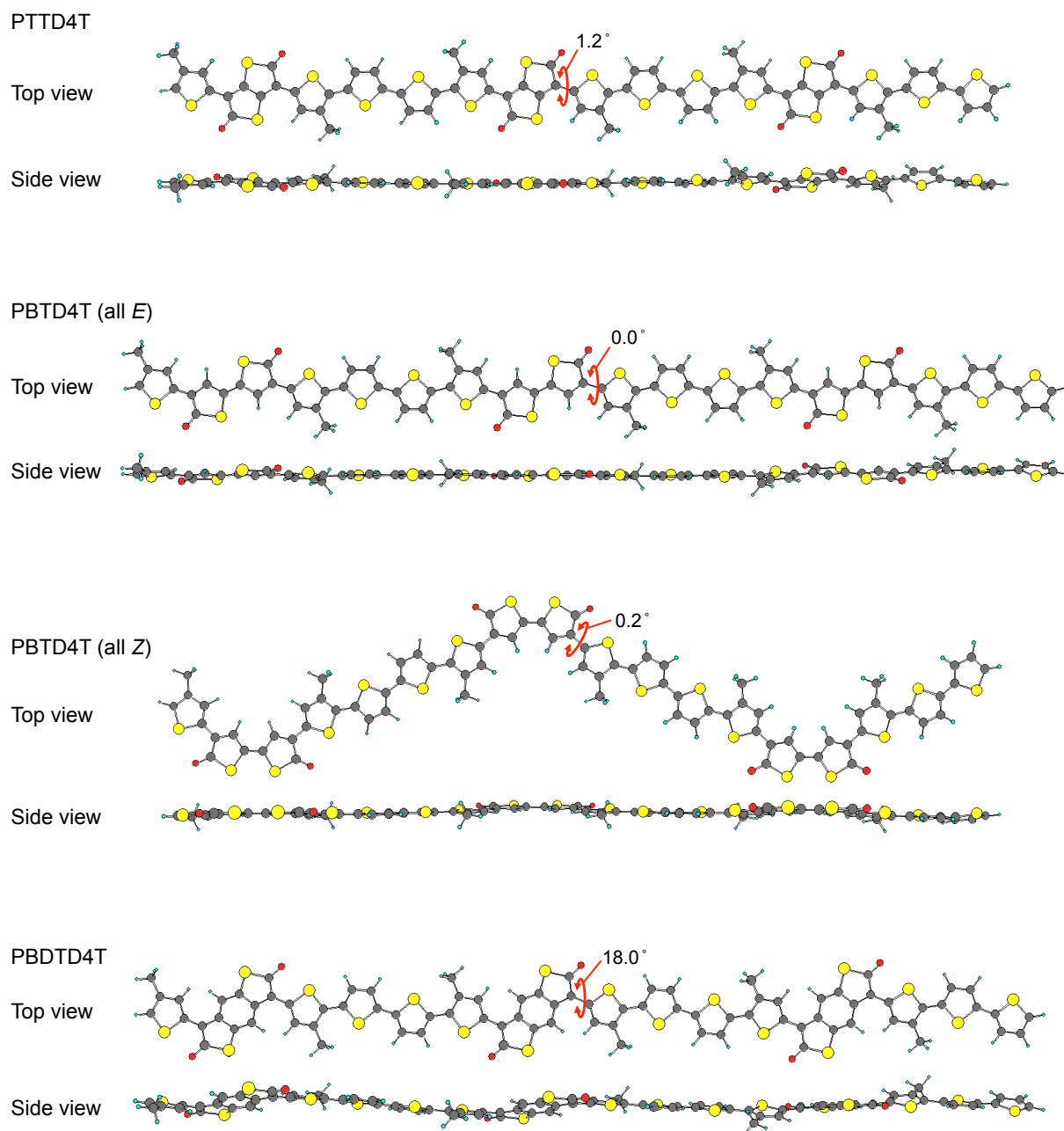


Figure S10. Optimized geometries of the model trimers that have syn-configuration at between thienoquinoidal units and the adjacent alkylthiophenes calculated by DFT method at the B3LYP/6-31G(d) level. The values indicated with red arrows are the dihedral angles between central thienoquinoids and methyl thiophene.

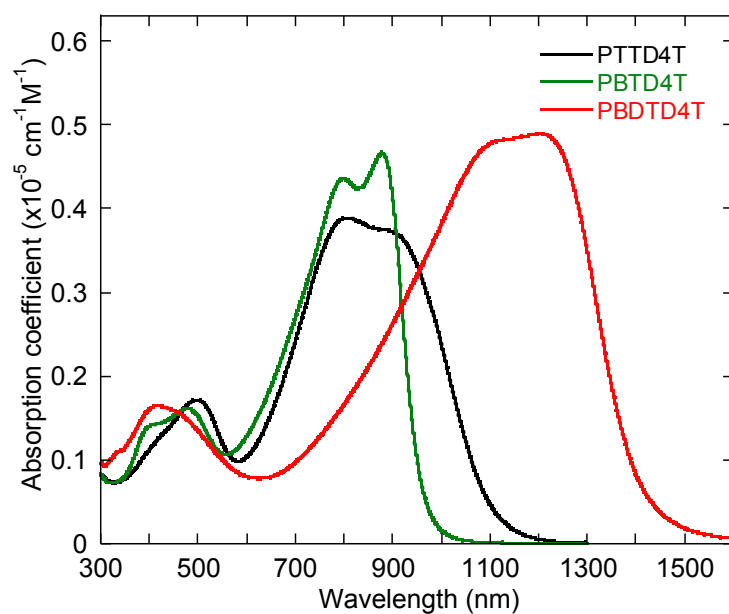


Figure S11. Absorption spectra of the polymers in chlorobenzene solution.

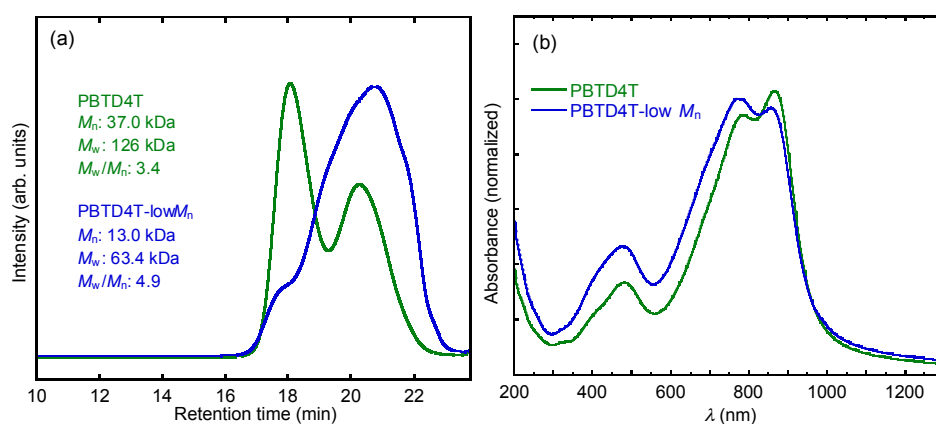


Figure S12. GPC chromatographs of **PBTD4T** from chloroform (green) and hexane (blue) Soxhlet fractions (a) and their absorption spectra in thin film (b).

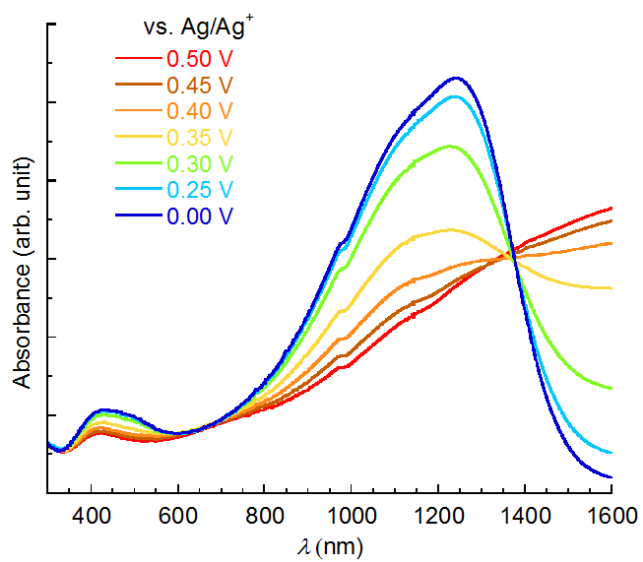


Figure S13. Absorption spectra of **PBDTD4T** film spin-coated on ITO glass at various applied potentials (vs. Ag/Ag⁺) during oxidation process.

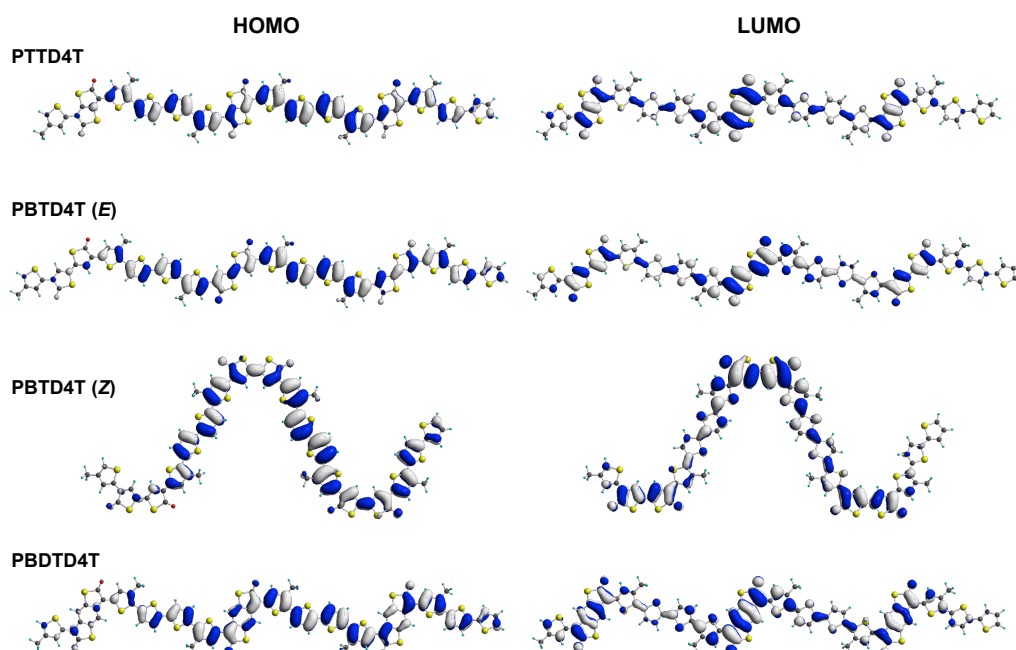


Figure S14. HOMO and LUMO geometry of the model trimers that have anti-configuration at between thienoquinoidal units and the adjacent alkylthiophenes calculated by DFT method at the B3LYP/6-31G(d) level.

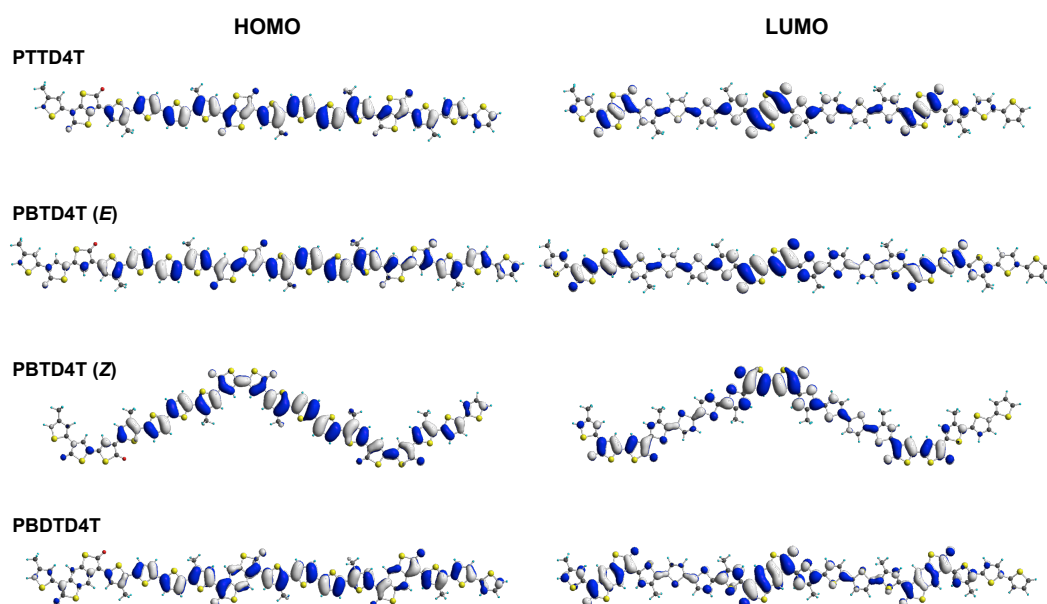


Figure S15. HOMO and LUMO geometry of the model trimers that have syn-configuration at between thienoquinoidal units and the adjacent alkylthiophenes calculated by DFT method at the B3LYP/6-31G(d) level.

Table S2. Heat of formation of model trimers optimized by DFT method at the B3LYP/6-31G(d) level, and difference in the heat of formation between the trimers with different conformation.

Polymer		Heat of formation (kcal/mol)	Difference in heat of formation (kcal/mol)
PTTD4T	anti-	−6516868.612	0.837
	syn-	−6516869.449	(most stable)
PBTD4T	(E)	anti-	−6662599.403
		syn-	−6662596.546
	(Z)	anti-	−6662596.164
		syn-	−6662591.914
PBDTD4T	anti-	−6806086.244	(most stable)
	syn-	−6806085.602	0.642

Table S3. HOMO-LUMO energy gaps of the model trimers optimized by DFT method at the B3LYP/6-31G(d) level.

Polymer		E_{HOMO} (eV)	E_{LUMO} (eV)	$E_{\text{g, HOMO-LUMO}}$ (eV)
PTTD4T	anti-	−4.98	−3.45	1.53
	syn-	−4.93	−3.51	1.42
PBTD4T	(E)	anti-	−4.96	1.45
		syn-	−4.88	1.34
	(Z)	anti-	−5.05	1.53
		syn-	−4.94	1.40
PBDTD4T	anti-	−4.87	−3.82	1.05
	syn-	−4.85	−3.83	1.02

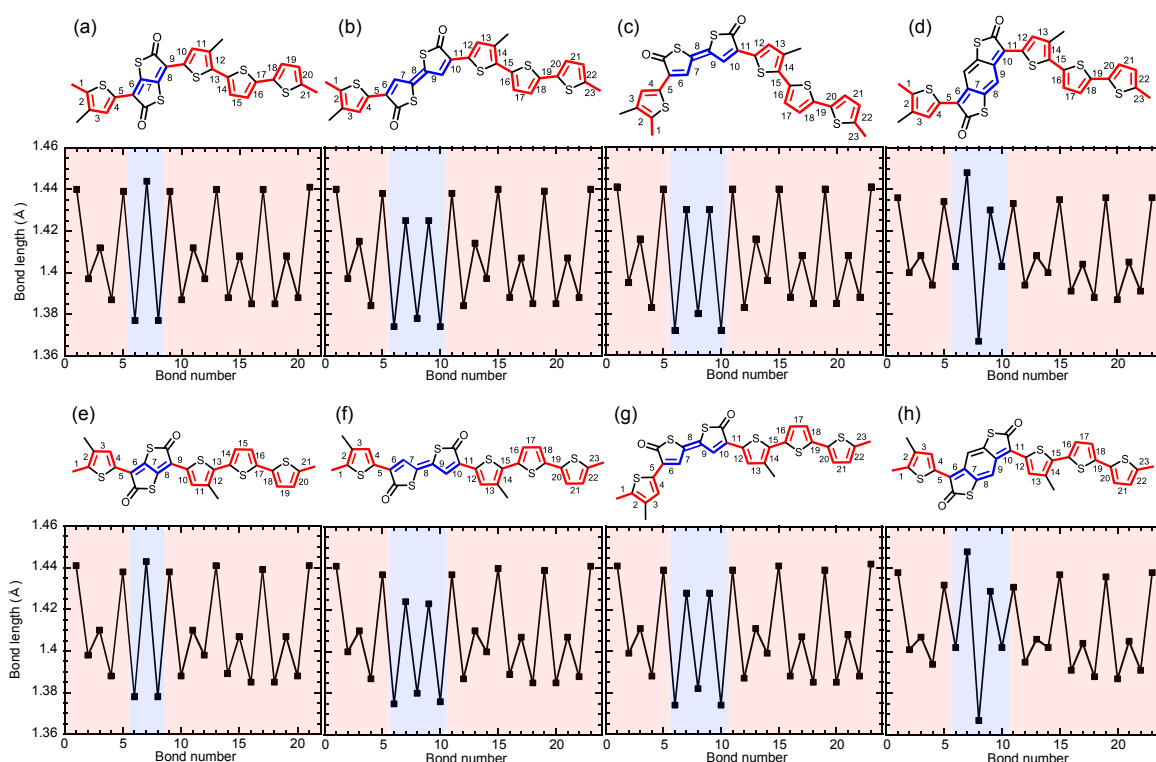


Figure S16. Chemical structures of polymer repeat units with carbon–carbon bond numbers and plots of carbon–carbon bond length at the respective bond number for **PTTD4T** (a), **PBTD4T** having (*E*)-configuration (b), **PBTD4T** having (*Z*)-configuration (c) and **PBDTD4T** (d) with the anti conformation between thienoquinoidal units and the adjacent alkylthiophene, and **PTTD4T** (e), **PBTD4T** having (*E*)-configuration (f), **PBTD4T** having (*Z*)-configuration (g) and **PBDTD4T** (h) with the syn conformation. The bond lengths were extracted from the central repeat unit of the trimer model optimized by the DFT method at the B3LYP/6-31G(d) level.

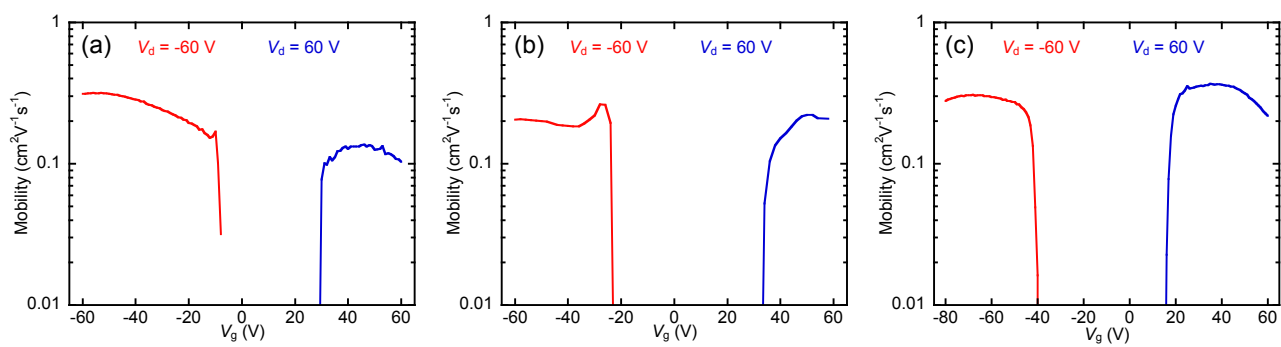


Figure S17. Typical gate-voltage-dependent mobilities of the OFET devices based on **PTTD4T** (a), **PBTD4T** (b), and **PBDTD4T** (c), respectively. Red and blue lines correspond to the data measured under p- and n-channel operation, respectively.