Supporting Information

Dependence of Crystallite Formation and Preferential Backbone Orientations on the Side Chain Pattern in PBDTTPD Polymers

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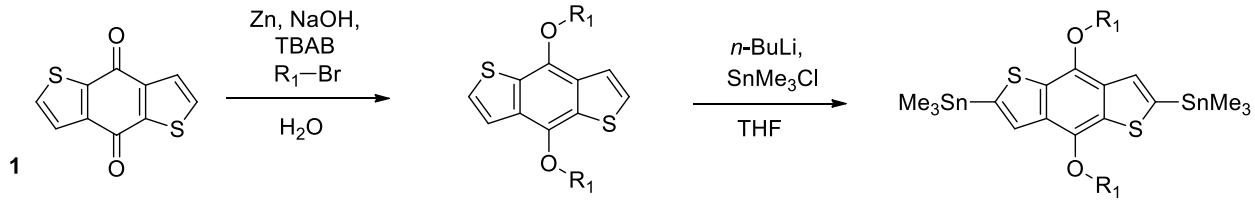
EXPERIMENTAL:

Synthetic Details

Methods and Materials: All reagents from commercial sources were used without further purification. Reactions were carried out under nitrogen atmosphere. Solvents were dried and purified using standard techniques. Flash chromatography was performed with analytical-grade solvents using Silicycle Silica Flash P60 (particle size 40-63 μm, 60 Å, 230 - 400 mesh) silica gel. Flexible plates PE SilG/UV 250 μm from Whatman® were used for TLC. Compounds were detected by UV irradiation or staining with I2, unless otherwise stated. All compounds were characterized by 1H NMR (400 MHz) and 13C NMR (100 MHz) on a Bruker Avance III Ultrashielded 400 Plus instrument and acquired at room temperature. High-resolution mass spectrometry (HRMS) data were recorded using a Thermo Scientific - LTQ Velos Orbitrap MS in positive electro spray ionization (+ESI) or positive atmospheric pressure photoionization (+APPI) mode. Elemental analyses were carried out on a Flash 2000 - Thermo Scientific CHNO Analyzer. Size exclusion chromatography (SEC) was performed with 1,3,5-trichlorobenzene (TCB) at an elution rate of at 1.0 mL/min (injection volume: 200 μL) through a PLgel MIXED-B column (10 μm) (+PLgel guard), at 135^{o}C. The SEC system consisted of an Alliance 2000 separation module equipped with RI detector. The apparent molecular weights and polydispersities (Mw/Mn) were determined with a calibration based on linear polystyrene (PS) standards. Note: Considering the moderate solubility of the PBDTTPD polymers in room-temperature tetrahydrofuran (THF) or chloroform ($CHCl_3$), this system was preferred over more conventional SEC systems equipped with PLgel MIXED-C columns (5 μm) for which THF or $CHCl_3$ are used as eluents.

Synthetic Procedures:



linear side-chain	**2,** R_1= *n*-$C_{14}H_{29}$ **3,** R_1= *n*-$C_{16}H_{33}$ **4,** R_1= *n*-$C_{18}H_{37}$	**linear side-chain**	**BDT(C14),** R_1= *n*-$C_{14}H_{29}$ **BDT(C16),** R_1= *n*-$C_{16}H_{33}$ **BDT(C18),** R_1= *n*-$C_{18}H_{37}$
branched side-chain	**5,** R_1= 2-ethylhexyl **6,** R_1= 2-propylpentyl **7,** R_1= 2-butyloctyl	**branched side-chain**	**BDT(2EH),** R_1= 2-ethylhexyl **BDT(2PP),** R_1= 2-propylpentyl **BDT(2BO),** R_1= 2-butyloctyl

Benzo[1,2-b:4,5-b']dithiophene-4,8-dione (**1**) was synthesized according to previously reported methods.[1,2]

General procedure for the alkylation of Benzo[1,2-b:4,5-b']dithiophene-4,8-dione: Compound (**1**) (2.2 g, 10 mmol) was suspended in 30 mL of water into a 100 mL flask equipped with a condenser. Zinc powder (1.43 g, 22 mmol) was added under vigorous stirring, followed by 6 g of NaOH. As the temperature was raised from room temperature to reflux, the color of the mixture changed from yellow, to dark red, and then to orange. After 1 h, the alkyl bromide (30 mmol) and a catalytic amount of tetrabutylammonium bromide were added to the reaction mixture (Note: an excess amount of zinc powder (0.65 g, 10 mmol) can be added if the color doesn't turn to yellow within two hours). After an additional 4 h, the reaction mixture was poured into iced water, and extracted with diethyl ether (x4). The organic layers were combined, washed with brine, dried over anhydrous $MgSO_4$, and concentrated under vacuum. The crude product was finally purified by column chromatography (hexane, then hexane/chloroform: 9/1) to afford the desired compound.

4,8-bis(tetradecyloxy)benzo[1,2-b:4,5-b']dithiophene (2): (4.98 g, 81%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 7.48 (d, *J* = 5.5 Hz, 2H), 7.37 (d, *J* = 5.5 Hz, 2H), 4.27 (t, *J* = 6.6 Hz, 4H), 1.87 (m, 4H), 1.56 (m, 4H), 1.30 (m, 40H), 0.88 (t, *J* = 6.5 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 144.5, 131.6, 130.1, 125.9, 120.3, 73.9, 31.9, 30.5, 29.7, 29.6, 29.5, 29.4, 26.1, 22.7, 14.1. HRMS (+APPI, m/z): calcd. for $C_{38}H_{62}O_2S_2$ $[M]^{+\cdot}$: 614.4191; found, 614.4163.

4,8-bis(hexadecyloxy)benzo[1,2-b:4,5-b']dithiophene (3): (5.36 g, 80%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 7.47 (d, *J* = 5.6 Hz, 2H), 7.36 (d, *J* = 5.6 Hz, 2H), 4.26 (t, *J* = 6.5 Hz, 4H), 1.86 (m, 4H), 1.56 (m, 4H), 1.42-1.20 (m, 48H), 0.87 (t, *J* = 6.9 Hz, 6H).^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 144.5, 131.7, 130.3, 126.1, 120.5, 74.1, 32.1, 30.7, 29.9, 29.8, 29.6, 29.5, 26.2, 22.8, 14.3. HRMS (+APPI, m/z): calcd. for $C_{42}H_{70}O_2S_2$ $[M]^{+\cdot}$: 670.4817; found, 670.4793.

4,8-bis(octadecyloxy)benzo[1,2-b:4,5-b']dithiophene (4): (5.81 g, 80%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 7.47 (d, *J* = 5.5 Hz, 2H), 7.36 (d, *J* = 5.5 Hz, 2H), 4.27 (t, *J* = 6.6 Hz, 4H), 1.87 (m, 4H), 1.56 (m, 4H), 1.43-1.22 (m, 56H), 0.88 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 144.6, 131.7, 130.3, 126.1, 120.5, 74.1, 32.1, 30.7, 29.9, 29.8, 29.7, 29.6,29.5, 26.2, 22.8, 14.1. HRMS (+APPI, m/z): calcd. for $C_{46}H_{78}O_2S_2$ $[M]^{+\cdot}$: 726.54377; found, 726.54211.

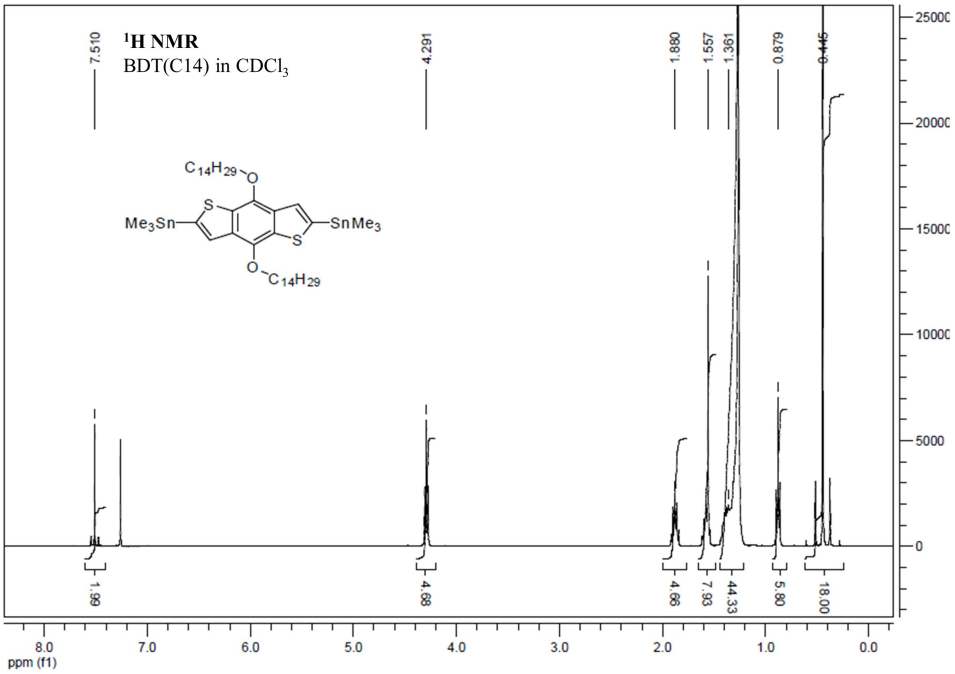
4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene (5): (3.39 g, 76%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 7.49 (d, *J* = 5.5 Hz, 2H), 7.37 (d, *J* = 5.5 Hz, 2H), 4.19 (d, *J* = 5.50 Hz, 4H), 1.86-1.34 (m, 18H), 1.02 (t, *J* = 7.42 Hz, 6H), 0.94 (t, *J* = 7.20 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 144.9, 131.8, 130.2, 126.2, 120.5, 76.3, 40.9, 30.7, 29.5, 24.2, 23.4, 14.5, 11.6. HRMS (+APPI, m/z): calcd. for $C_{26}H_{38}O_2S_2$ $[M]^{+\cdot}$: 446.2313; found, 446.2305.

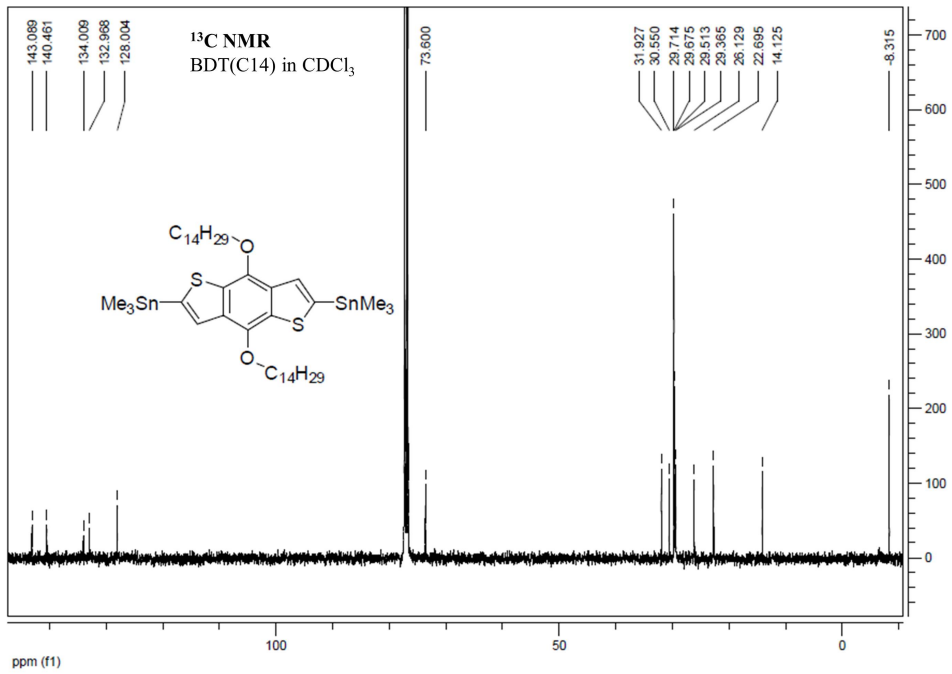
4,8-bis((2-propylpentyl)oxy)benzo[1,2-b:4,5-b']dithiophene (6): (3.44 g, 77%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 7.47 (d, *J* = 5.5 Hz, 2H), 7.36 (d, *J* = 5.5 Hz, 2H), 4.17 (d, *J* = 5.4 Hz, 4H), 1.90 (m, 2H), 1.63 (m, 4H), 1.53-1.40 (m, 12H), 0.97 (t, *J* = 7.0 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 144.8, 131.6, 130.1, 126.1, 120.4, 76.5, 38.9, 33.8, 20.3, 14.7. HRMS (+APPI, m/z): calcd. for $C_{26}H_{38}O_2S_2$ $[M]^{+\cdot}$: 446.23077; found, 446.23024.

4,8-bis((2-butyloctyl)oxy)benzo[1,2-b:4,5-b']dithiophene (7): (4.13 g, 74%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 7.47 (d, *J* = 5.5 Hz, 2H), 7.36 (d, *J* = 5.5 Hz, 2H), 4.17 (d, *J* = 5.4 Hz, 4H), 1.86 (m, 2H), 1.63 (m, 4H), 1.56-1.22 (m, 28H), 0.95 (t, *J* = 6.8 Hz, 6H), 0.89 (t, *J* = 6.9 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 145.0, 131.8, 130.2, 126.2, 120.6, 76.7, 39.5, 32.2, 31.6, 31.3, 30.1, 29.5, 27.3, 23.4, 23.0, 14.5, 14.4. HRMS (+APPI, m/z): calcd. for $C_{34}H_{54}O_2S_2$ $[M]^{+\cdot}$: 558.35597; found, 558.35445.

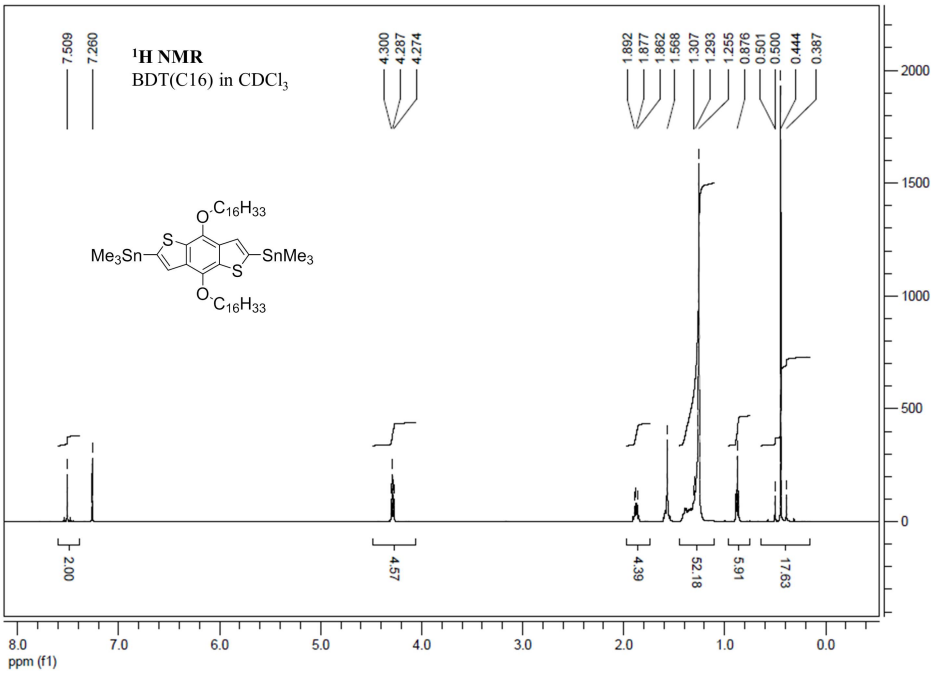
General procedure for the stanyllation of 4,8-bis(alkyloxy)benzo[1,2-b:4,5-b']dithiophene (BDT): Compound **2**, **3**, **4**, **5**, **6** or **7** (4 mmol) was solubilized in 75 mL of dry THF under inert atmosphere. The mixture was cooled down to -78 °C using a dry ice-acetone bath, and 4.55 mL of *n*-butyllithium (8.8 mmol, 2.5 M in n-hexane) was added dropwise. After being stirred at -78 °C for 1 h, the solution was slowly warmed up to room temperature and stirred for 30 min. The cloudy mixture was cooled in the dry ice-acetone bath, and trimethyltin chloride (1.99 g, 10 mmol) was added in one portion (the mixture turned clear). The reaction mixture was stirred overnight at room temperature, was then poured into 200 mL of cool water, and was extracted with diethyl ether (x4). The organic layers were combined, washed with brine (x1), dried over anhydrous $MgSO_4$ and concentrated under vacuum. The residue was recrystallized twice from ethanol to yield the desired compounds as colorless needles.

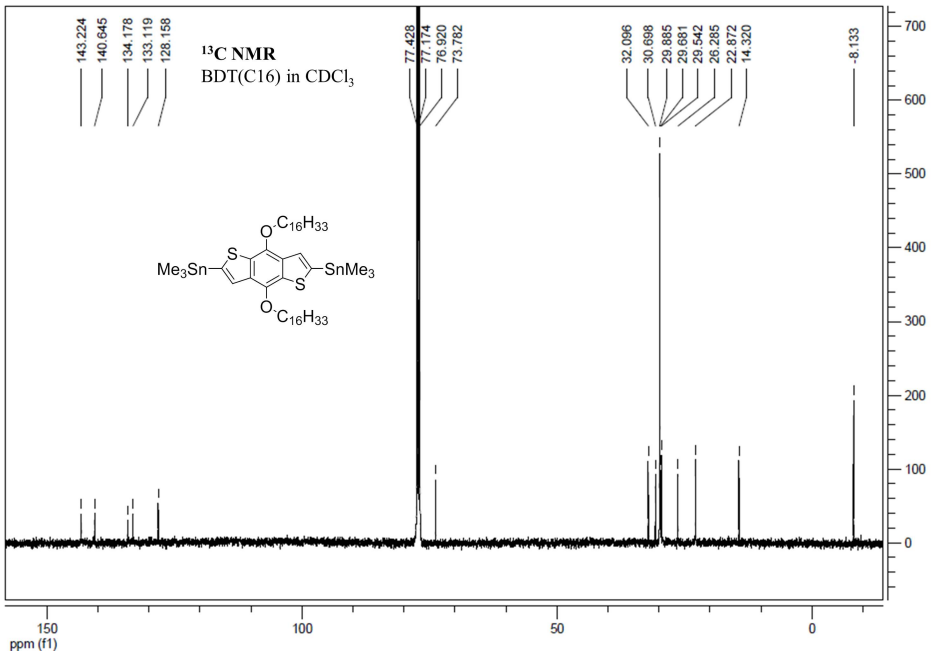
(4,8-bis(tetradecyloxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (BDT(C14)): (2.71 g, 72%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 7.51 (s, 2H), 4.29 (t, *J* = 6.6 Hz, 4H), 1.88 (quintuplet, *J* = 7.2 Hz, 4H), 1.55 (m, 4H), 1.45-1.20 (m, 40H), 0.87 (t, *J* = 6.5 Hz, 6H), 0.44 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 143.1, 140.5, 134.0, 132.9, 128.0, 73.6, 31.9, 30.5, 29.7, 29.6, 29.5, 29.4, 26.1, 22.7, 14.1, -8.3. HRMS (+APPI, m/z): calcd. for $C_{44}H_{78}O_2S_2Sn_2$ $[M]^{+\cdot}$: 942.3487; found, 942.3482.



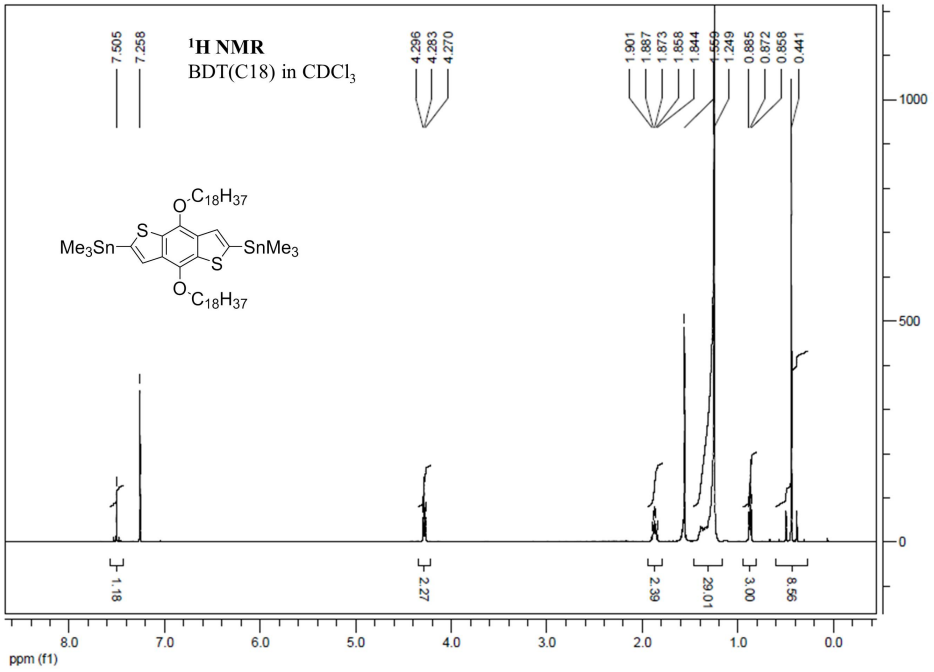


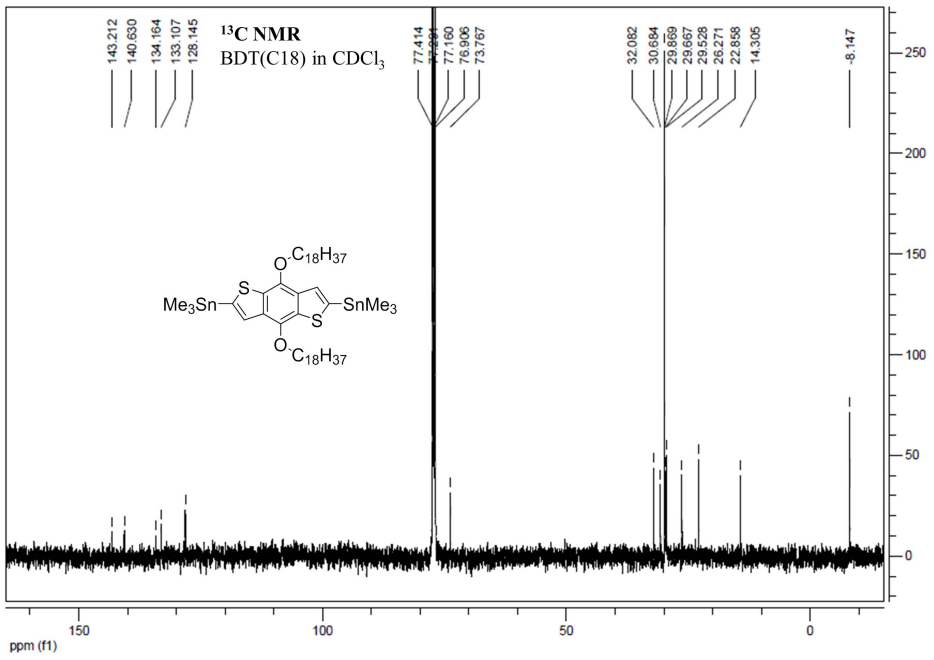
(4,8-bis(hexadecyloxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (BDT(C16)): (2.36 g, 59%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 7.51 (s, 2H), 4.29 (t, *J* = 6.6 Hz, 4H), 1.88 (quintuplet, *J* = 7.2 Hz, 4H), 1.58 (m, 4H), 1.45-1.20 (m, 48H), 0.88 (t, *J* = 6.5 Hz, 6H), 0.45 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 143.2, 140.6, 134.2, 133.1, 128.1, 73.6, 32.1, 30.7, 29.9 (m), 29.8, 29.7, 29.5, 26.3, 22.8, 14.3, -8.2. HRMS (+APPI, m/z): calcd. for $C_{48}H_{86}O_2S_2Sn_2$ $[M]^{+\cdot}$: 998.4113; found, 998.4103.



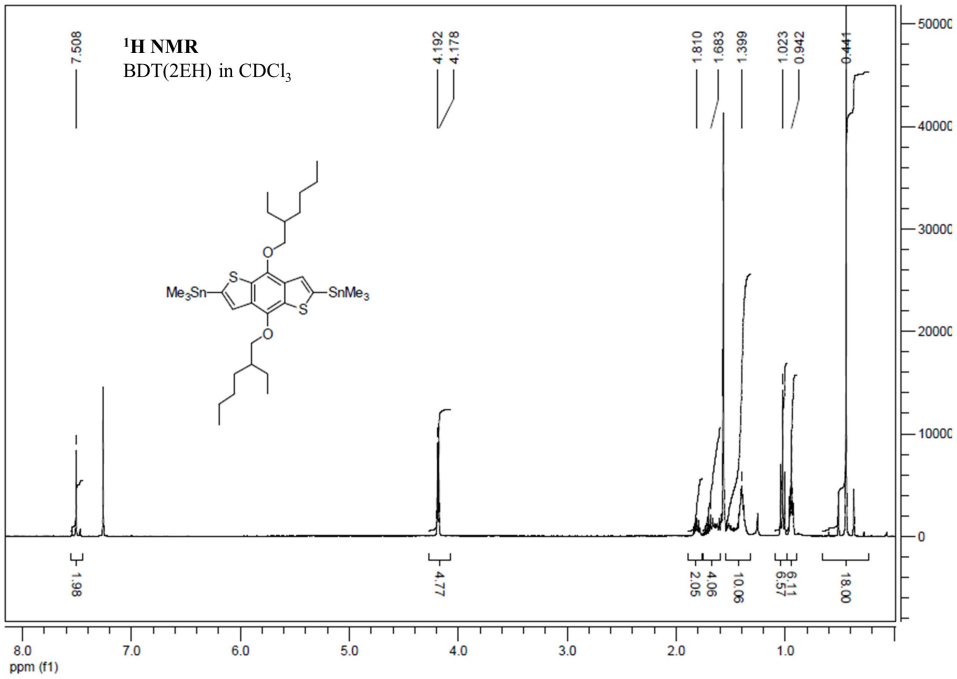


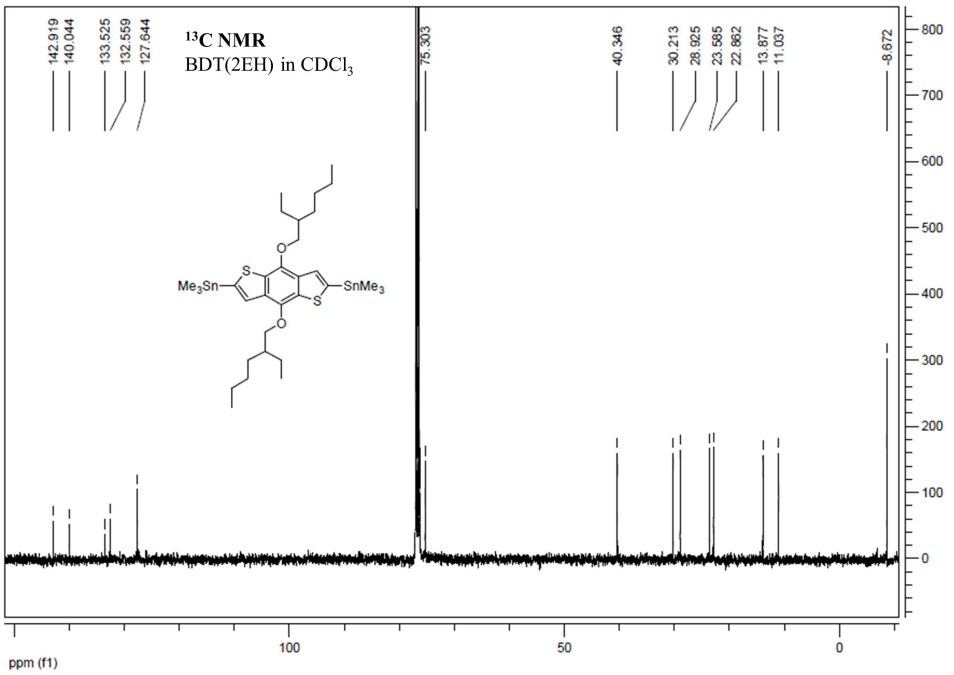
(4,8-bis(octadecyloxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (BDT(C18)): (2.61 g, 62%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 7.51 (s, 2H), 4.29 (t, *J* = 6.6 Hz, 4H), 1.88 (quintuplet, *J* = 7.8 Hz, 4H), 1.57 (m, 4H), 1.43-1.22 (m, 56H), 0.88 (t, *J* = 7.0 Hz, 6H), 0.44 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 143.1, 140.5, 134.1, 133.0, 128.0, 73.7, 32.0, 30.5, 29.8 (m), 29.6, 29.4, , 26.2, 22.7, 14.2, -8.3. HRMS (+APPI, m/z): calcd. for $C_{52}H_{94}O_2S_2Sn_2$ $[M]^{+\cdot}$: 1054.4734; found, 1054.4746.



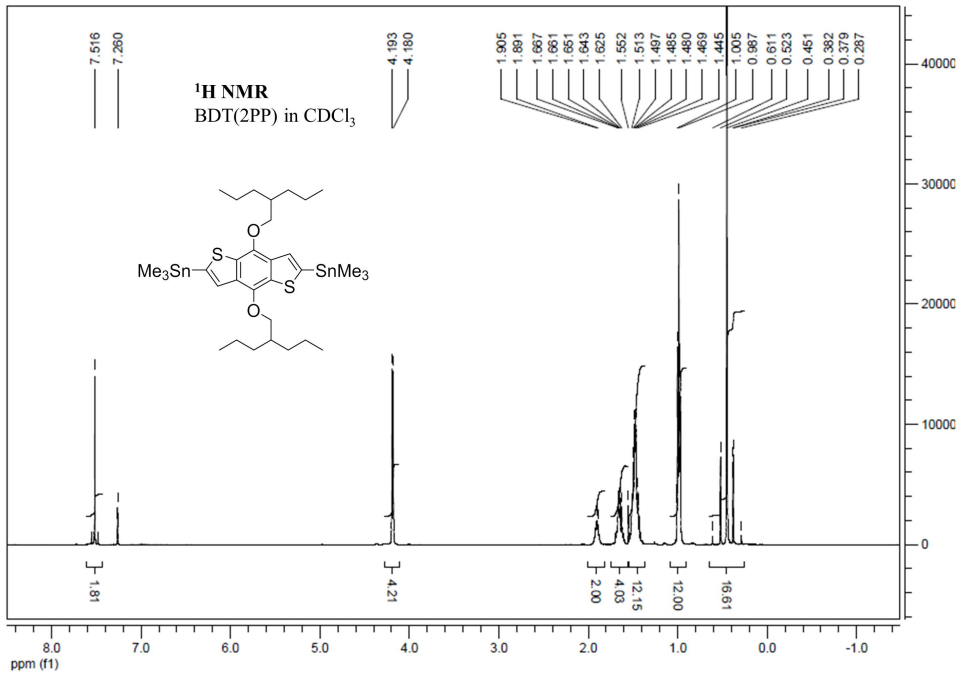


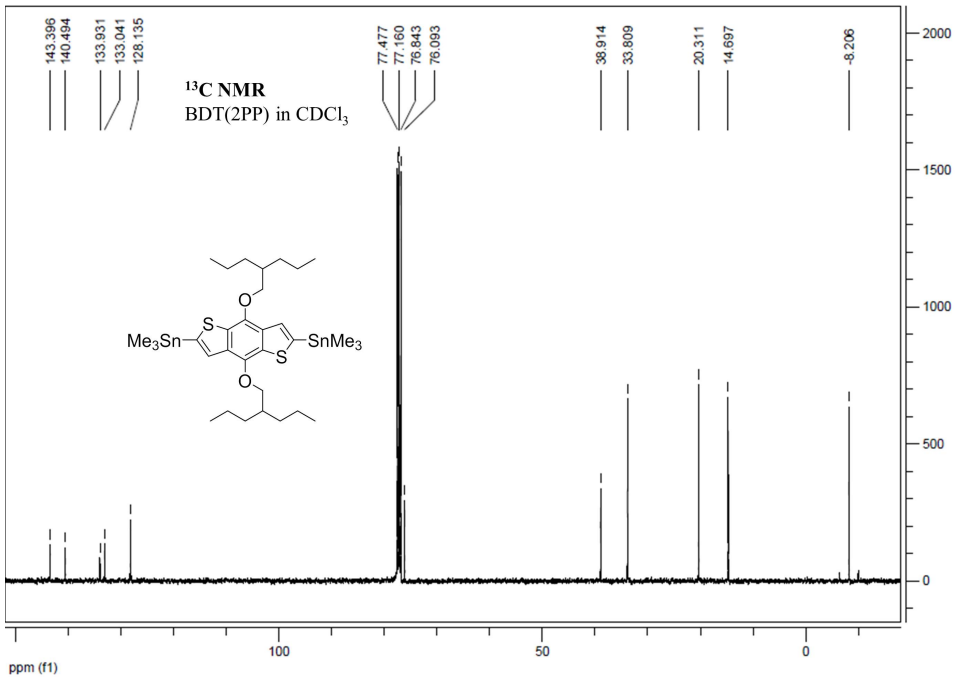
(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (BDT(2EH)): (2.51 g, 81%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 7.51 (s, 2H), 4.19 (d, *J* = 5.41 Hz, 4H), 1.81 (m, 2H), 1.73-1.31 (m, 16H), 1.02 (t, *J* = 7.44 Hz, 6H), 0.94 (t, *J* = 6.77 Hz, 6H), 0.44 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 142.9, 140.0, 133.5, 132.5, 127.6, 75.3, 40.3, 30.2, 28.9, 23.6, 22.8, 13.9, 11.0, -8.7. HRMS (+APPI, m/z): calcd. for $C_{32}H_{54}O_2S_2Sn_2$ $[M]^{+\cdot}$: 774.1609; found, 774.1595.



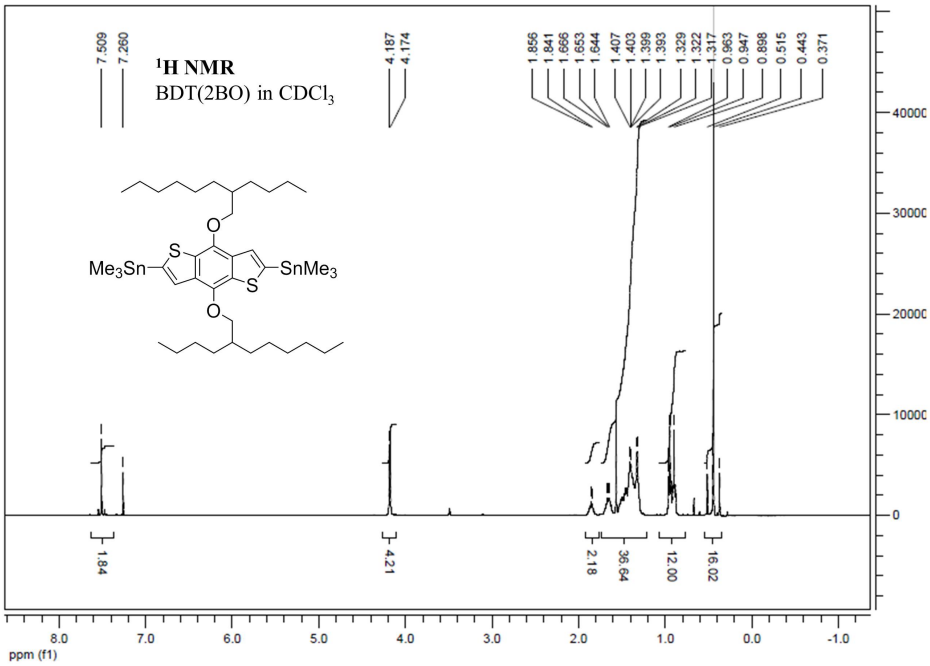


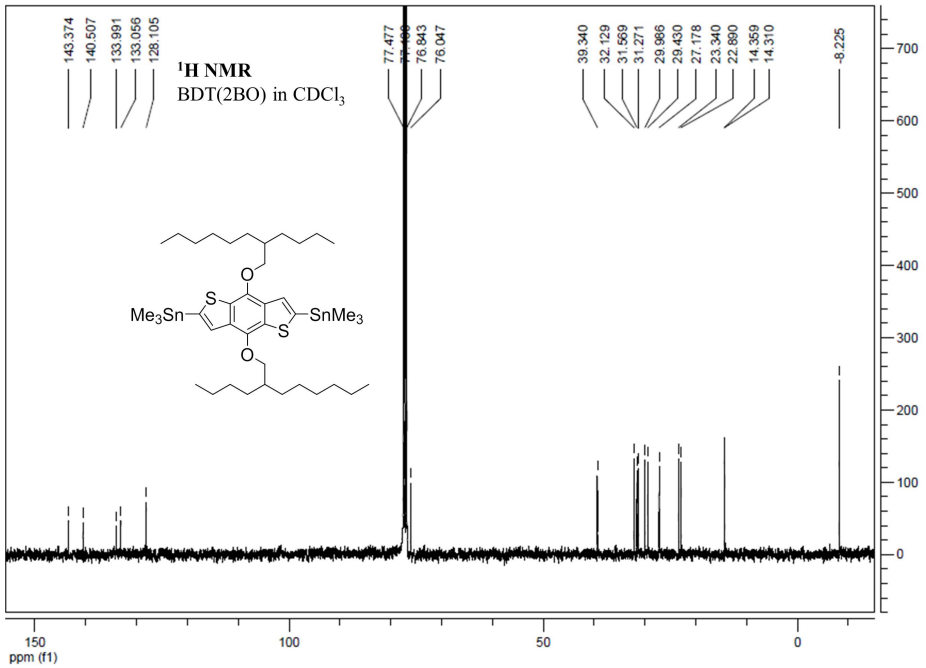
(4,8-bis((2-propylpentyl)oxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (BDT(2PP)): (2.07 g, 67%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 7.51 (s, 2H), 4.18 (d, *J* = 5.4 Hz, 4H), 1.89 (m, 2H), 1.64 (m, 4H), 1.53-1.40 (m, 12H), 0.98 (t, *J* = 7.0 Hz, 12H), 0.44 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 142.9, 140.0, 133.5, 132.5, 127.6, 75.3, 40.3, 30.2, 28.9, 23.6, 22.8, 13.9, 11.0, -8.7. HRMS (+APPI, m/z): calcd. for $C_{32}H_{54}O_2S_2Sn_2$ $[M]^{+\cdot}$: 774.16037; found, 774.16050.

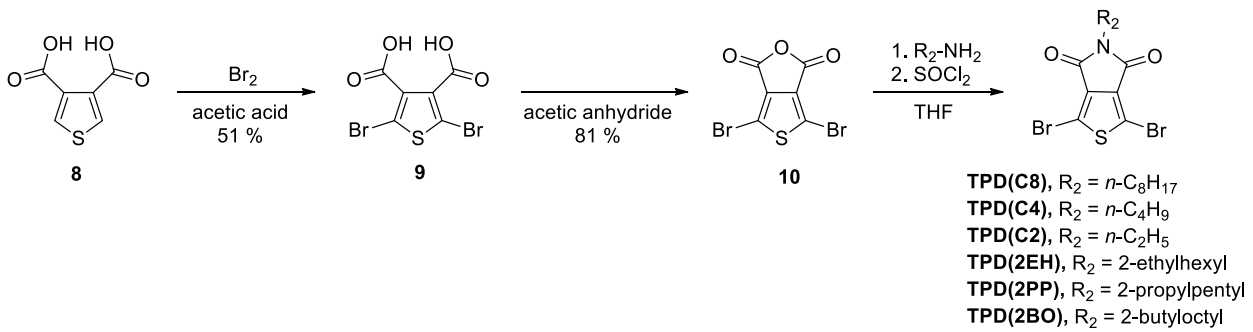




(4,8-bis((2-butyloctyl)oxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (BDT(2BO)): (2.30 g, 65%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 7.51 (s, 2H), 4.17 (d, *J* = 5.3 Hz, 4H), 1.86 (m, 2H), 1.65 (m, 4H), 1.55-1.25 (m, 28H), 0.95 (t, *J* = 6.8 Hz, 6H), 0.90 (t, *J* = 6.8 Hz, 6H), 0.44 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 143.2, 140.3, 133.8, 132.9, 127.9, 75.9, 39.2, 32.0, 31.4, 31.1, 29.8, 29.3, 27.0, 23.2, 22.7, 14.2, 14.1, -8.4. HRMS (+APPI, m/z): calcd. for $C_{40}H_{70}O_2S_2Sn_2$ $[M]^{+\cdot}$: 886.2856; found, 886.2880.



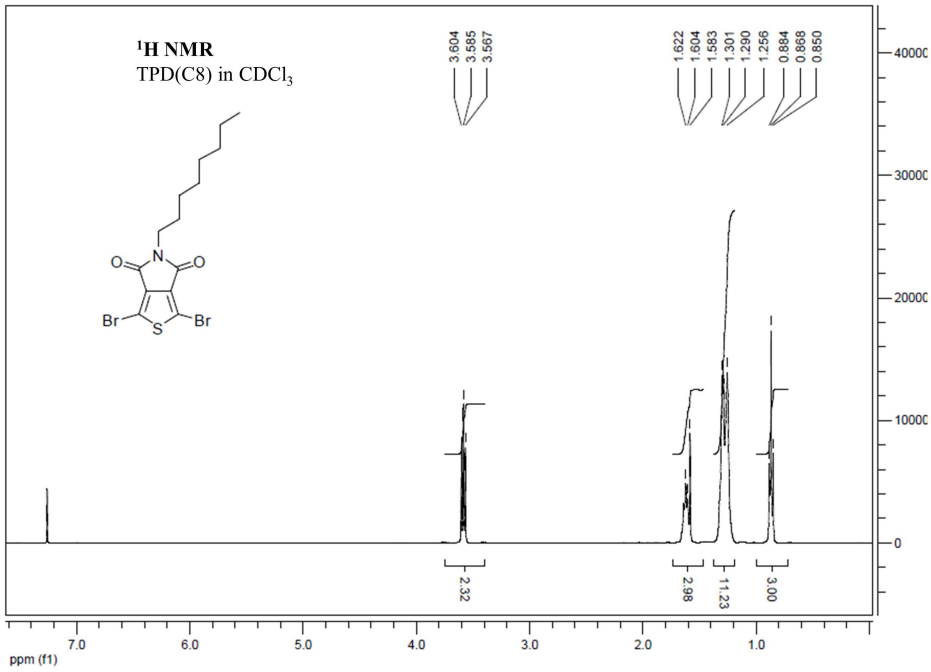


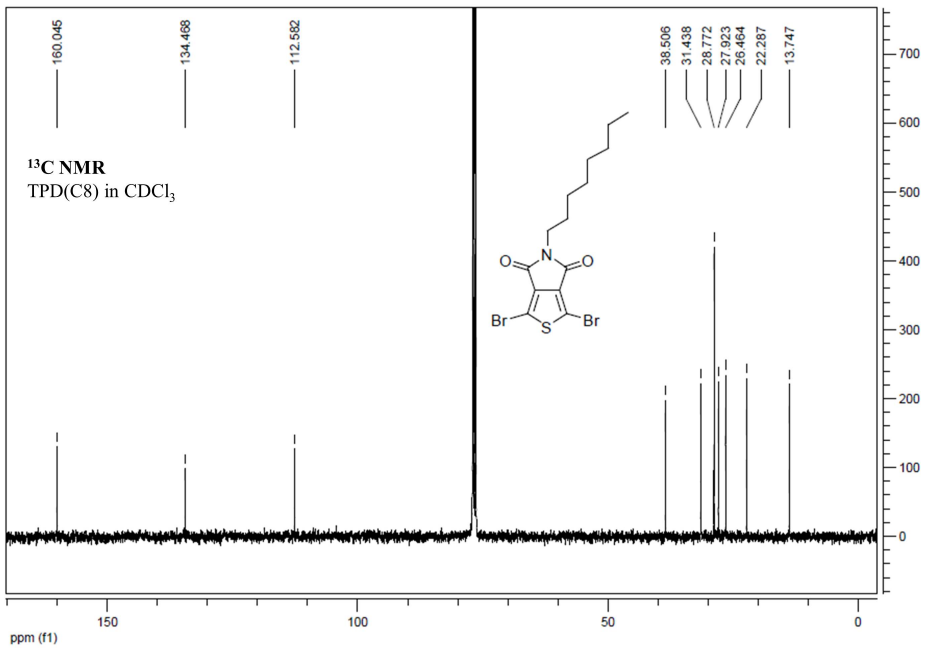


2,5-Dibromothiophene-3,4-dicarboxylic acid (9)[3] and **4,6-Dibromothieno[3,4-*c*]furan-1,3-dione (10)**[4] were synthesized according to previously reported methods.

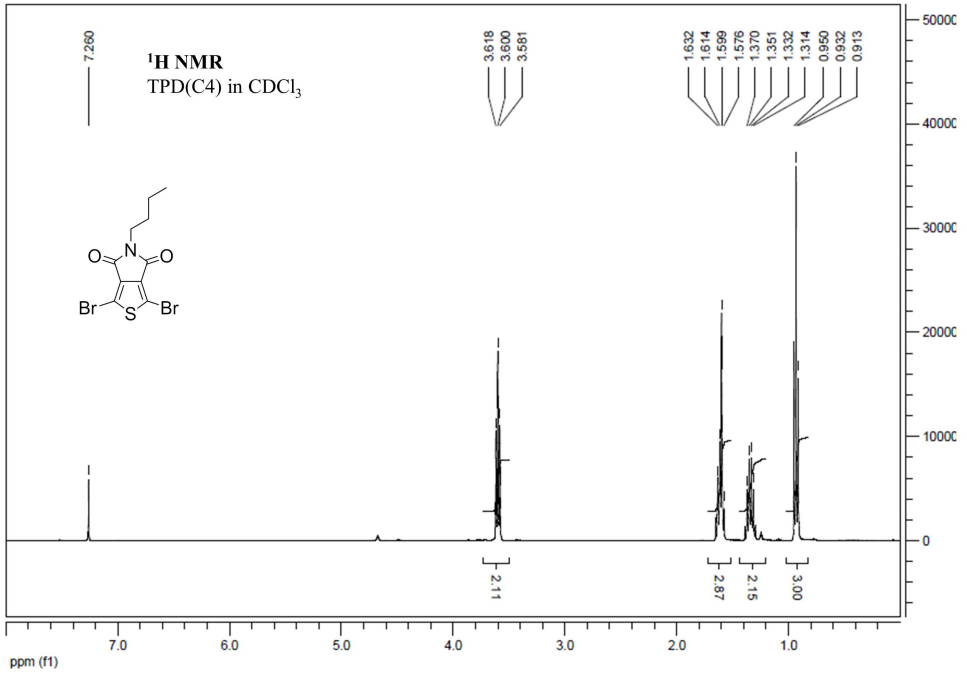
General procedure for the preparation of 1,3-Dibromo-5-(n-alkyl)-4H-thieno[3,4-*c*]pyrrole-4,6(5H)-dione(TPD). Compound **10** (1.46 g, 4.68 mmol) was combined with 12 mL of dry THF in a 50 mL flask, and *n*-alkylamine (4.90 mmol) was added. The reaction mixture was stirred at 50 °C for 3 h. The volatiles were removed in vacuo, thionyl chloride (5 mL) was added to the residue, and the reaction mixture was stirred at 55 °C for 4 h. The reaction contents were added dropwise to a mixture of water (100 mL) and methanol (50 mL). The precipitate was filtered, dried and purified by column chromatography using $CHCl_3$ as the eluent. The $CHCl_3$ solution was concentrated by evaporation, and the solid was finally recrystallized from ethanol to yield the corresponding TPD monomer as white flakes.

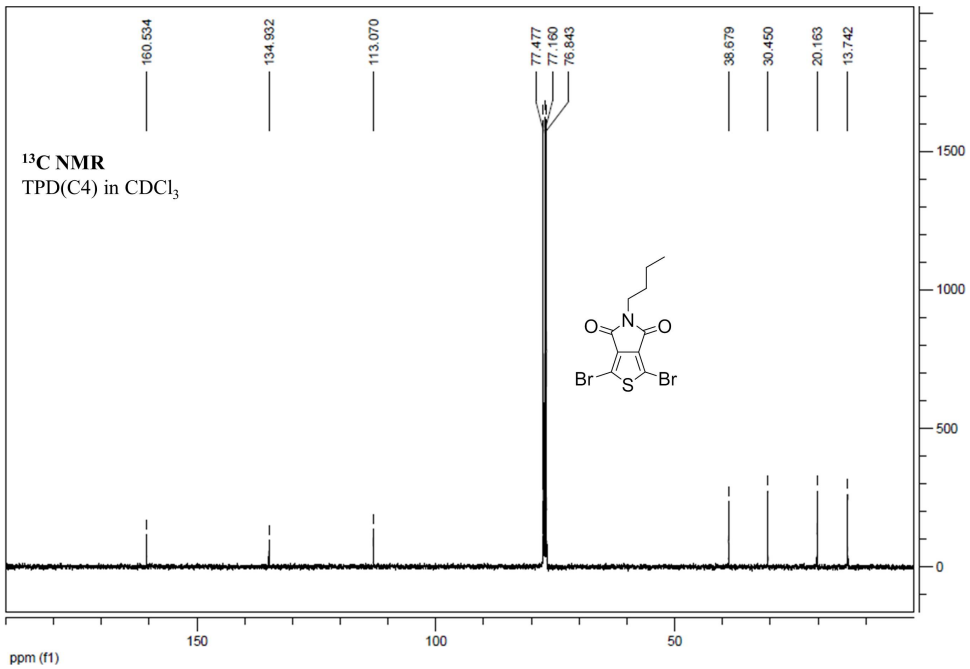
1,3-Dibromo-5-(n-octyl)-4H-thieno[3,4-*c*]pyrrole-4,6(5H)-dione (**TPD(C8)**): (1.66 g, 84%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm)= 3.58 (t, *J* = 7.3 Hz, 2H), 1.60 (m, 2H), 1.29 (m, 10H), 0.86 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm)= 160.0, 134.5, 112.6, 38.5, 31.4, 28.7, 27.9, 26.4, 22.3, 13.7. HRMS (+ESI, *m/z*): calcd. for $C_{14}H_{18}Br_2NO_2S$ $[M+H]^+$: 421.9425; found, 421.9408.



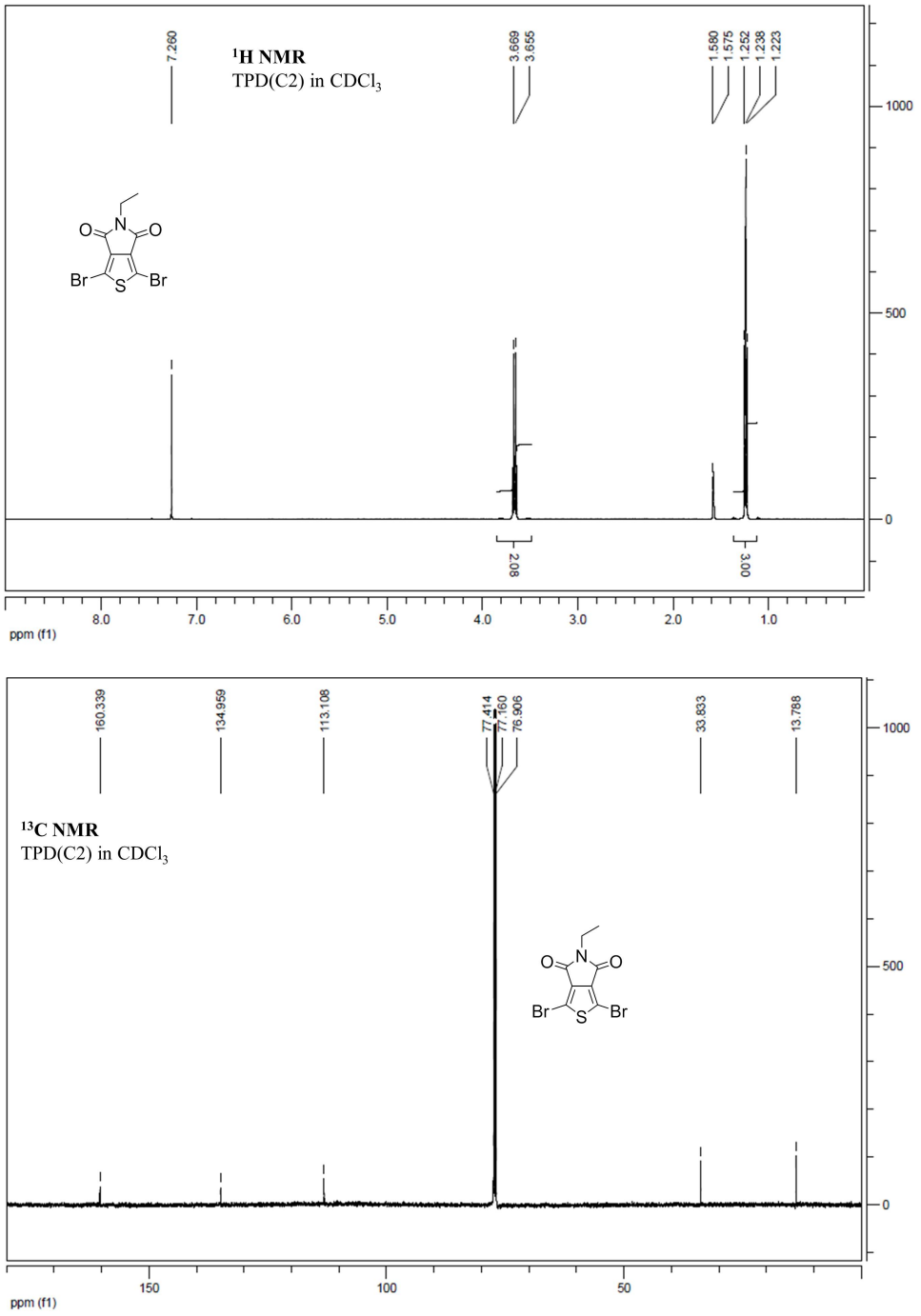


1,3-Dibromo-5-(n-butyl)-4H-thieno[3,4-*c*]pyrrole-4,6(5H)-dione (**TPD(C4)**): (0.97 g, 57%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm)= 3.60 (t, *J* = 7.2 Hz, 2H), 1.60 (dd, 2H), 1.34 (dd, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm)= 160.4, 134.8, 112.9, 38.5, 30.3, 20.0, 13.6. HRMS (+ESI, *m/z*): calcd. for $C_{10}H_{10}Br_2NO_2S$ $[M+H]^+$: 365.87935; found, 365.87888.

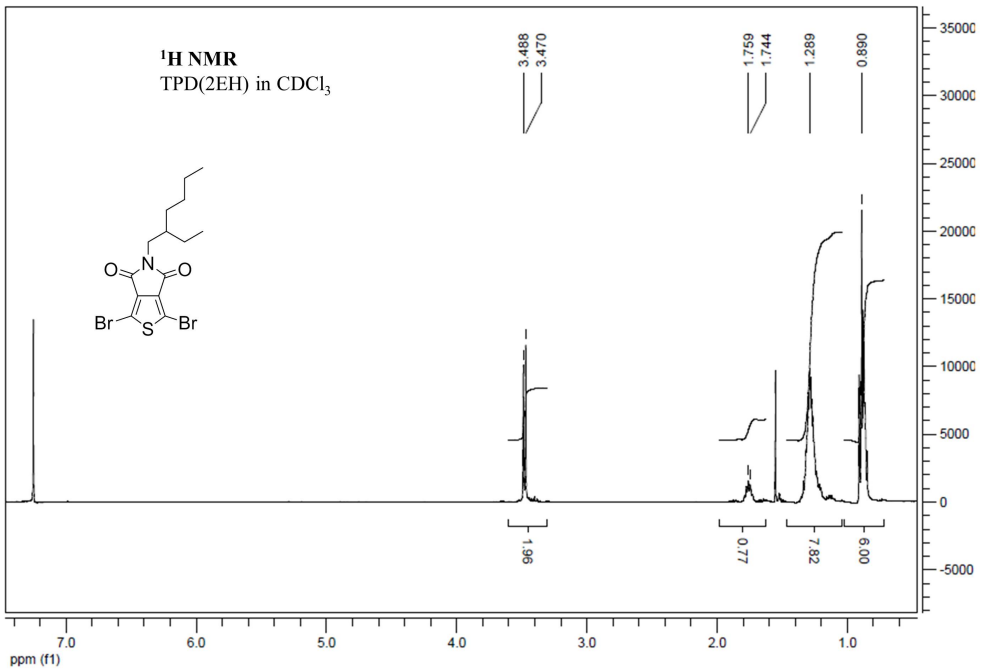


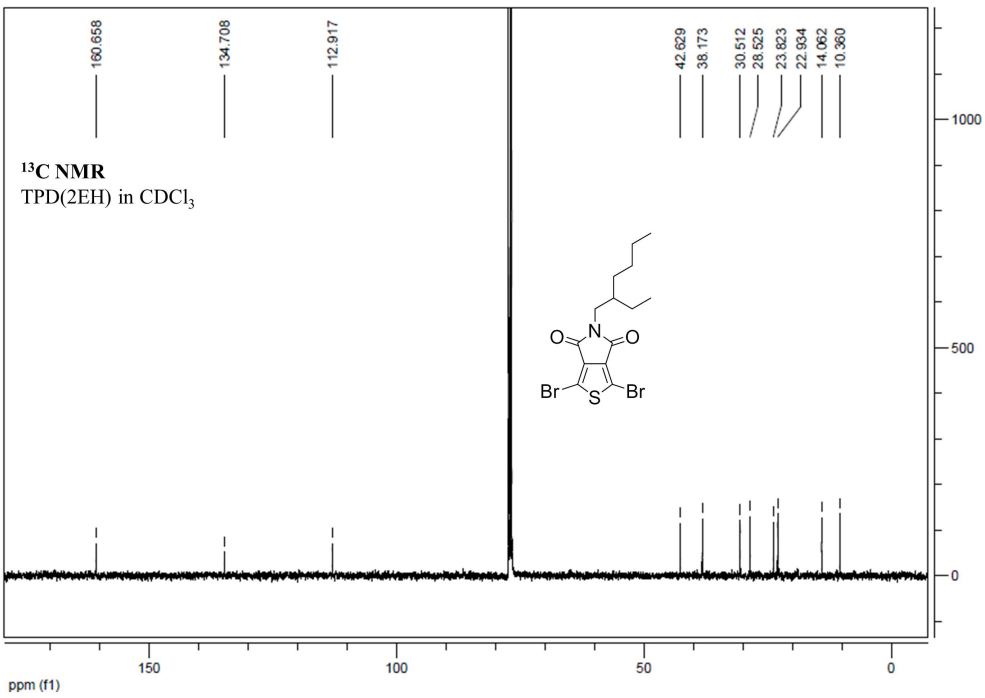


1,3-Dibromo-5-(n-ethyl)-4H-thieno[3,4-*c*]pyrrole-4,6(5H)-dione (**TPD(C2)**): (1.02 g, 65%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm)= 3.66 (q, *J* = 7.2 Hz, 2H), 1.24 (*J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm)= 160.2, 134.9, 113.0, 33.7, 13.7. HRMS (+ESI, *m/z*): calcd. for $C_8H_6Br_2NO_2S$ $[M+H]^+$: 337.84805; found, 337.84644.

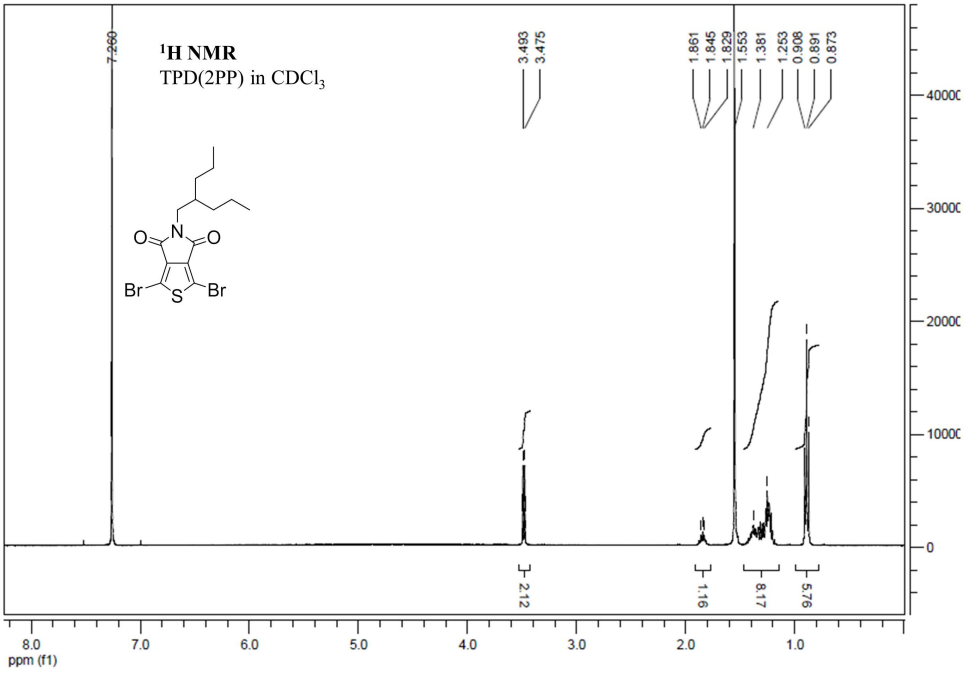


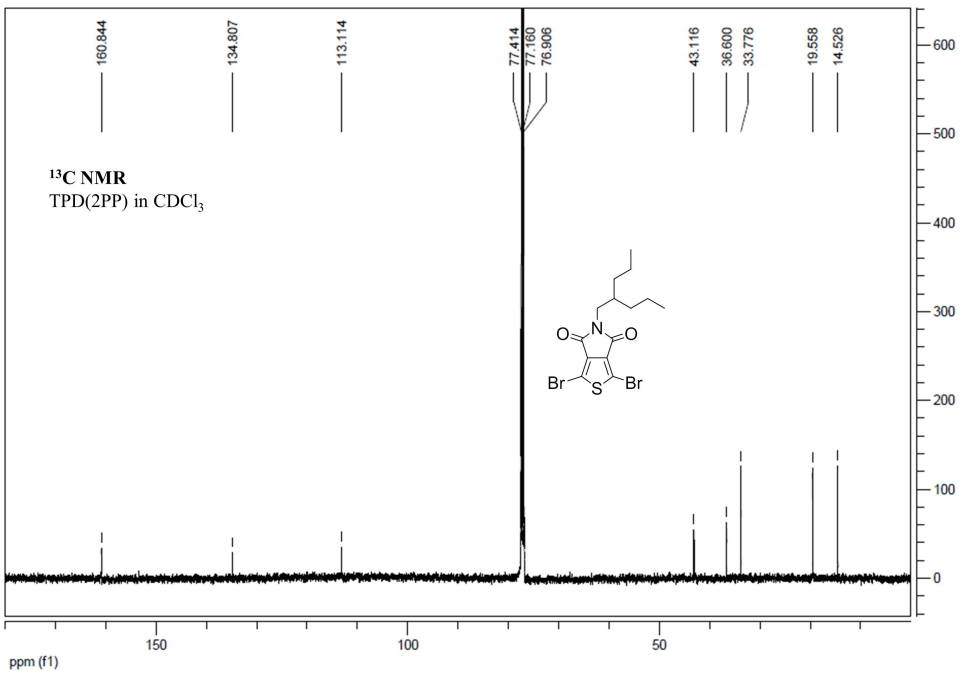
1,3-Dibromo-5-(2-ethylhexyl)-4H-thieno[3,4-*c*]pyrrole-4,6(5H)-dione (**TPD(2EH)**): (1.64 g, 83%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm)= 3.49 (d, *J* = 7.2 Hz, 2H), 1.77 (m, 1H), 1.37-1.22 (m, 8H), 0.89 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm)= 160.7, 134.7, 112.9, 42.7, 38.2, 30.5, 28.5, 23.8, 22.9, 14.1, 10.4 HRMS (+ESI, *m/z*): calcd. for $C_{14}H_{18}Br_2NO_2S$ $[M+H]^+$: 421.9420; found, 421.9402.



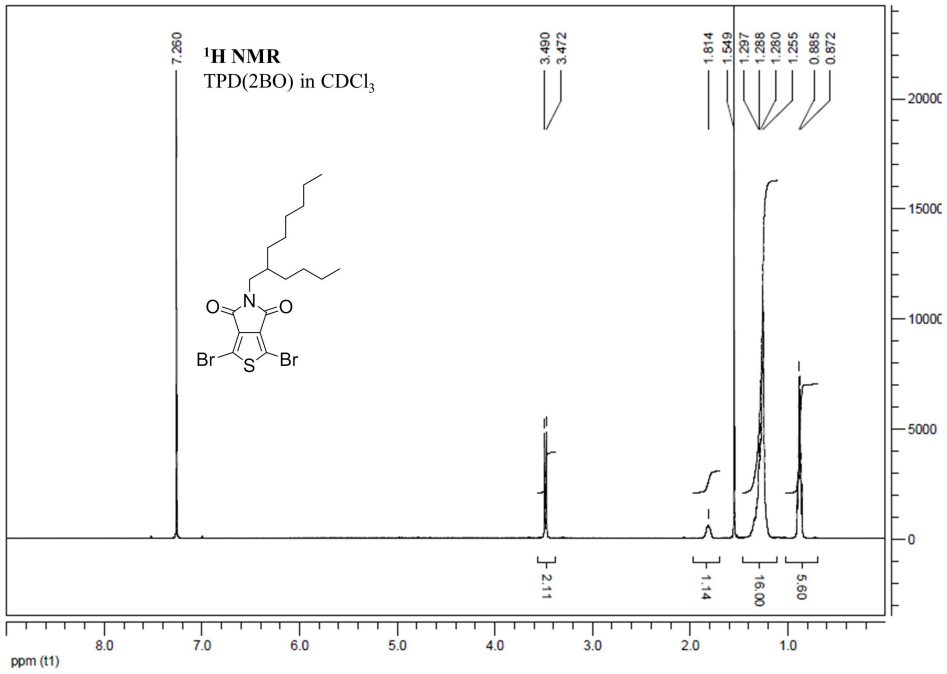


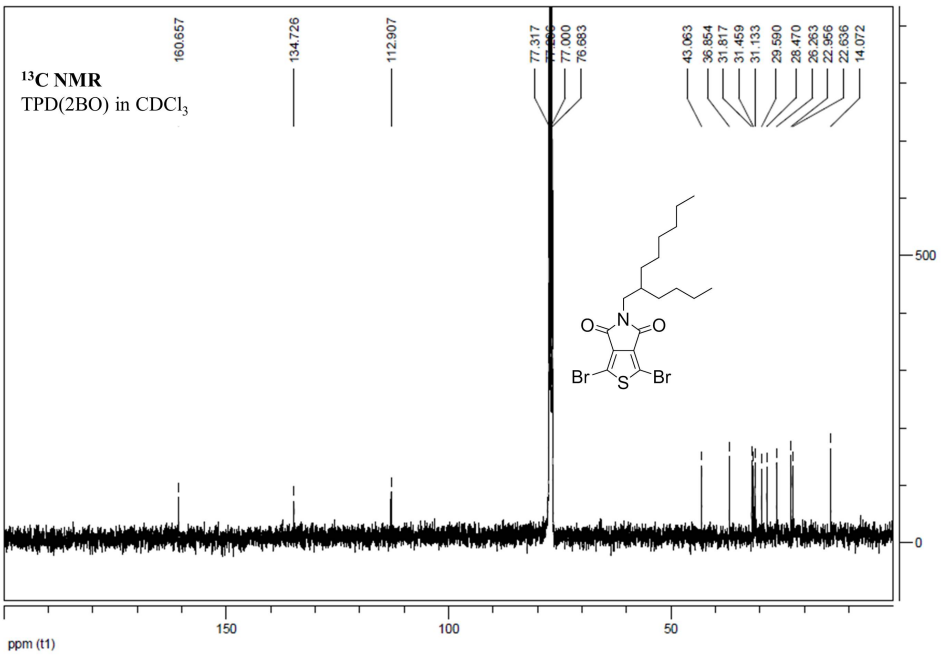
1,3-Dibromo-5-(2-propylpentyl)-4H-thieno[3,4-*c*]pyrrole-4,6(5H)-dione (**TPD(2PP)**): (1.38 g, 70%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm)= 3.48 (t, *J* = 7.2 Hz, 2H), 1.85 (m, 1H), 1.44-1.22 (m, 8H), 0.87 (t, *J* = 6.5 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm)= 160.8, 134.7, 113.0, 43.0, 36.5, 33.7, 19.4, 14.4. HRMS (+ESI, *m/z*): calcd. for $C_{14}H_{18}Br_2NO_2S$ $[M+H]^+$: 421.9420; found, 421.9402.

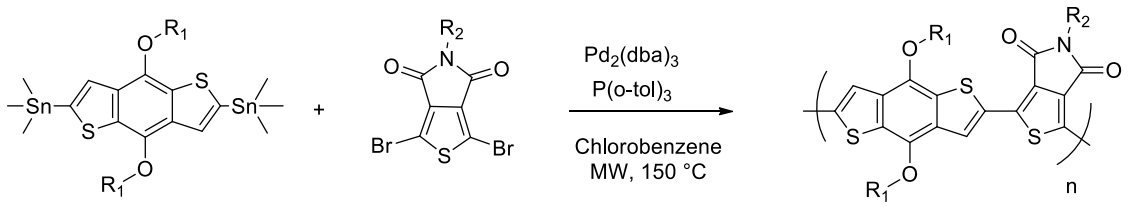




1,3-Dibromo-5-(2-butyloctyl)-4H-thieno[3,4-*c*]pyrrole-4,6(5H)-dione (**TPD(2BO)**): (1.79 g, 80%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm)= 3.48 (d, *J* = 7.2 Hz, 2H), 1.81 (m, 1H), 1.37-1.22 (m, 16H), 0.87 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm)= 160.7, 134.7, 112.9, 43.1, 36.9, 31.8, 31.5, 31.1, 29.6, 28.5, 26.3, 23.0, 22.6, 14.1(d) HRMS (+ESI, *m/z*): calcd. for $C_{18}H_{26}Br_2NO_2S$ $[M+H]^+$: 478.00455; found, 478.00397.







BDT(C14), R_1= *n*-$C_{14}H_{29}$
BDT(C16), R_1= *n*-$C_{16}H_{33}$
BDT(C18), R_1= *n*-$C_{18}H_{37}$
BDT(2EH), R_1= 2-ethylhexyl
BDT(2PP), R_1= 2-propylpentyl
BDT(2BO), R_1= 2-butyloctyl

TPD(C8), R_2 = *n*-C_8H_{17}
TPD(C4), R_2 = *n*-C_4H_9
TPD(C2), R_2 = *n*-C_2H_5
TPD(2EH), R_2 = 2-ethylhexyl
TPD(2PP), R_2 = 2-propylpentyl
TPD(2BO), R_2 = 2-butyloctyl

PBDTTPD(C18/C2)
PBDTTPD(C16/C4)
PBDTTPD(C14/C8)
PBDTTPD(2EH/C8)
PBDTTPD(2PP/C8)
PBDTTPD(2BO/C8)
PBDTTPD(2PP/2PP)
PBDTTPD(2EH/2EH)
PBDTTPD(2EH/2BO)
PBDTTPD(2BO/2BO)

General procedure for the microwave-assisted (MW) polymerization of the PBDTTPD(R_1/R_2) analogs: 1,3-Dibromo-5-(n-alkyl)-4H-thieno[3,4-*c*]pyrrole-4,6(5H)-dione (133 µmol), (4,8-bis(alkyloxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (130 µmol), tris(dibenzylideneacetone)dipalladium (3.5 mg, 3.9 µmol) and tri-*o*-tolylphosphine (4.7 mg, 15.5 µmol) were combined in a 5 mL microwave reactor. Then, 2.5 mL of freshly degassed chlorobenzene (*via* F.P.T cycles) was added to the reaction flask and the reaction mixture was stirred for 1 h at 150 °C. Next, the polymerization mixture was cooled down to 55 °C, and the strong complexing ligand *N,N*-diethyl-2-phenyldiazenecarbothioamide (9 mg, 39 µmol) was added with $CHCl_3$ (2 mL) and the mixture was stirred for 3 h at 55 °C under inert atmosphere. The mixture was then slowly precipitated into methanol (50 mL). The precipitate was filtered through a Soxhlet thimble and purified *via* Soxhlet extraction for 20 h with methanol, 5 h with hexane, and the polymer was finally collected from chloroform. Note concerning the Soxhlet extraction of the (2EH/C8) and (2PP/C8) analogs (systems of lower-solubility): hexane was swapped for dichloromethane and chloroform was swapped for chlorobenzene. The polymer solution was then concentrated by evaporation, precipitated into methanol (50 mL), and the polymer residues were filtered off. The polymerization yields and SEC results are shown in Table S1.

Table S1. Yields & SEC analyses of the PBDTTPD derivatives

PBDTTPD(R_1/R_2)	Yield	M_n (kDa)	M_w (kDa)	PDI
(C18/C2)	100 mg, 85%	18.8	71.0	3.8
(C16/C4)	99 mg, 87%	20.9	96.3	4.6
(C14/C8)	104 mg, 91%	18.3	78.9	4.3
(2EH/C8)	87 mg, 94%	14.7	55.4	3.8
(2PP/C8)	76 mg, 82%	14.8	50.5	3.4
(2BO/C8)	91 mg, 85%	15.8	43.4	2.8
(2PP/2PP)	70 mg, 85%	10.1	20.5	2.0
(2EH/2EH)	82 mg, 89%	17.4	63.6	3.7
(2EH/2BO)	91 mg, 92%	12.0	38.1	3.2
(2BO/2BO)	101 mg, 89%	14.3	48.1	3.3

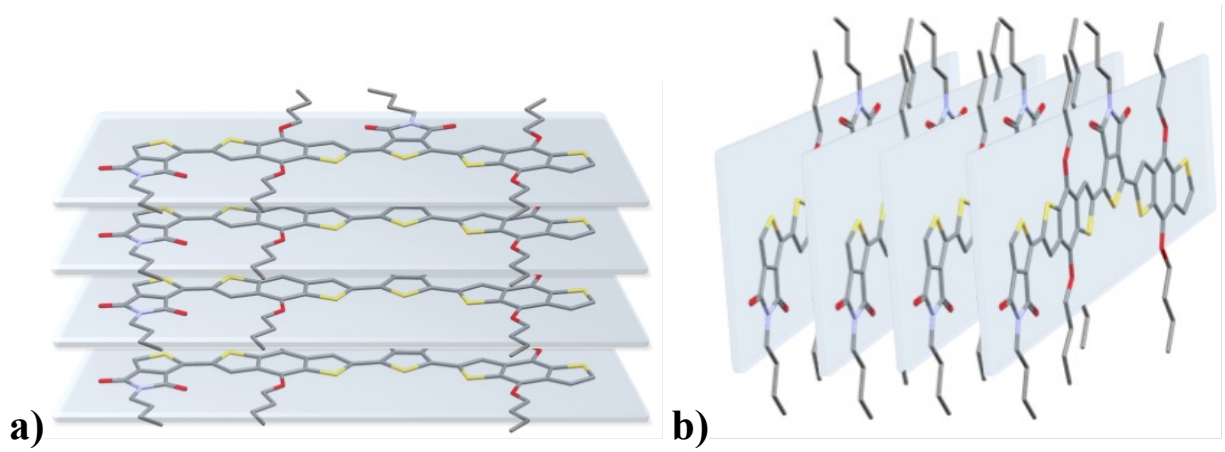


Figure S1. Schematic representation of **a)** preferential "*face-on*" orientations (π–π stacking "out-of-plane"), and **b)** preferential "*edge-on*" orientations (π–π stacking "in-plane"), of ordered polymer crystallites in thin-films.

X-Ray Analyses

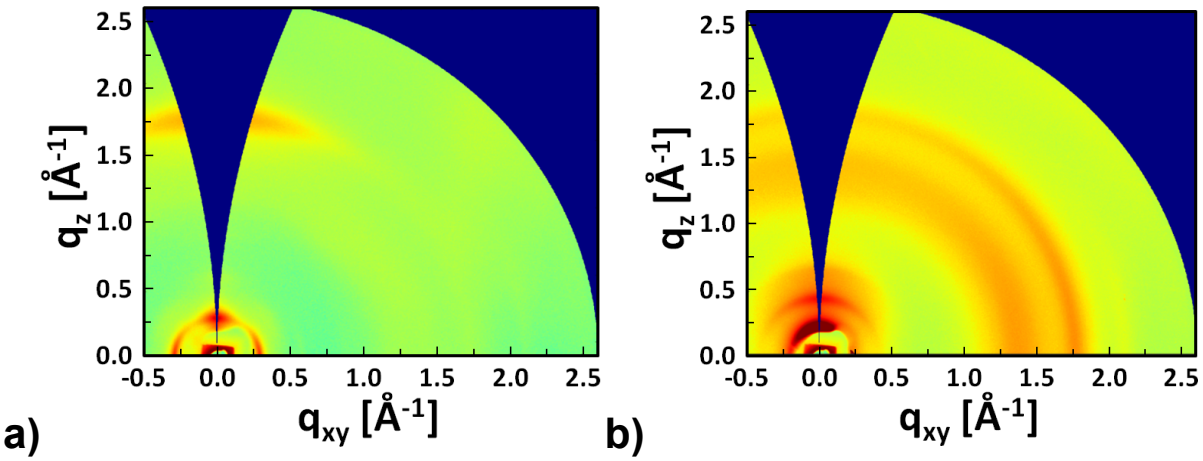
Grazing Incidence X-ray Scattering (GIXS)

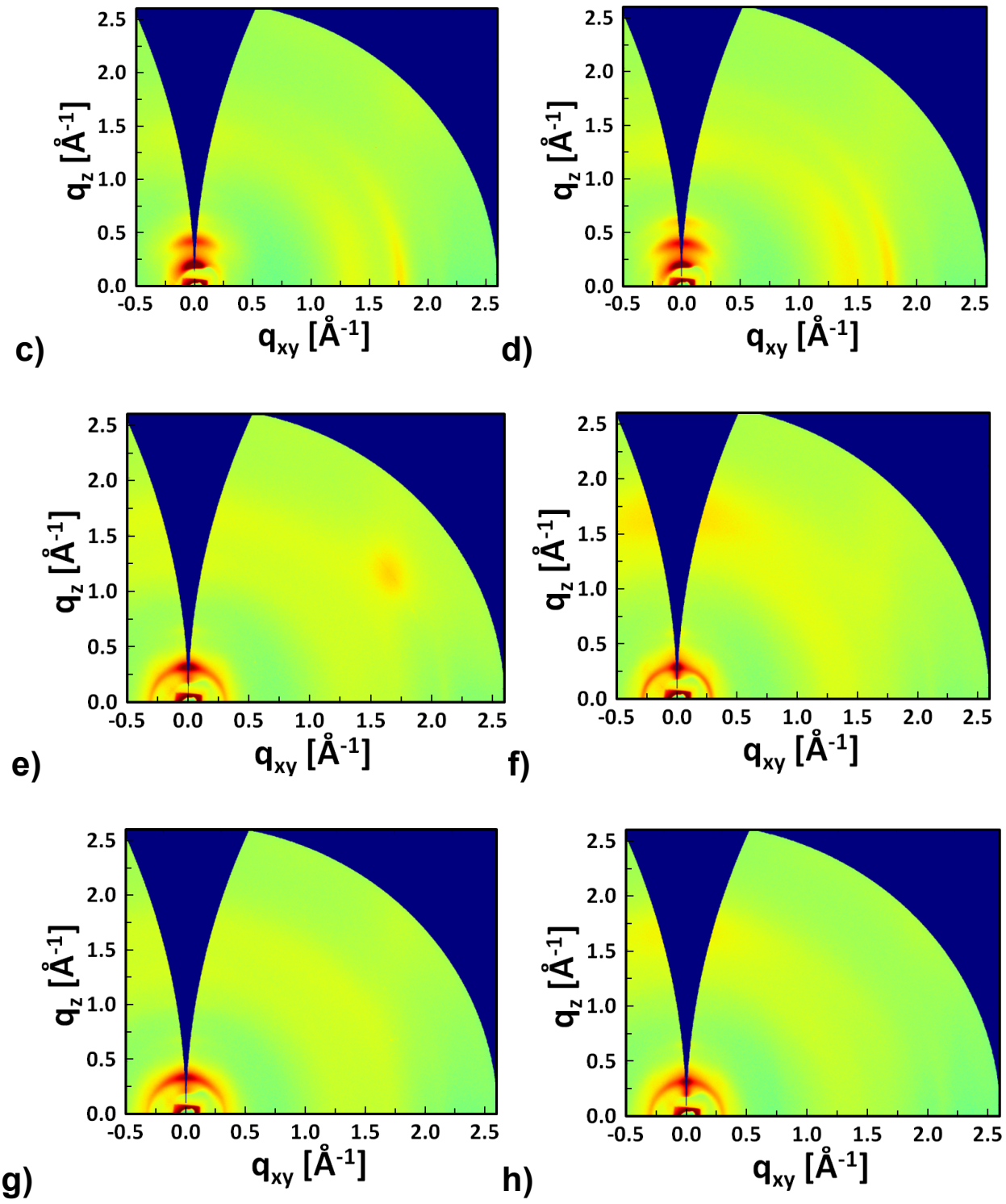
Silicon substrates were sonicated (Branson 5510) for 15 min each in successive baths of acetone and isopropanol. Substrates were then dried with pressurized nitrogen before being exposed to a UV−ozone plasma for 15 min. An aqueous solution of PEDOT:PSS (Clevios P VP AI 4083) was spin-cast at 4,000 rpm onto the substrates and baked at 140 °C for 15 min. The samples were then transferred into a dry nitrogen glovebox (<3 ppm O2) for active layer deposition. All

solutions were prepared in the glovebox using polymers dissolved in chlorobenzene (10 mg mL^{-1}) overnight at 115 °C, with and without 5% 1-chloronaphthalene (CN) additive (v/v). Thin films were spin-cast from the solutions at 95 °C at an optimized speed for 45 seconds using a programmable spin coater from Specialty Coating Systems (Model G3P-8), resulting in thicknesses of 100-120 nm.

GIXS experiments were performed at the Stanford Synchrotron Radiation Lightsource beamline 11-3 using a photon energy of 12.7 keV, a MAR345 image plate area detector, and an incident X-ray beam angle of ~0.12°. During measurement, samples were kept in a helium-filled chamber to prevent beam damage and to minimize X-ray scattering due to air.

All X-ray diffraction data analyses were performed with the WxDiff software package developed by Dr. Stefan Mannsfeld. A background subtraction and normalization with respect to the beam stop were applied to all the pole figures. Furthermore, the geometrical correction of cos (χ) was applied to the intensity of the pole figures to account for differential counting of the scattered x-rays in the in-plane vs. out-of-plane directions [see Baker et al., Langmuir, 2010, 11, 9146, "Quantification of Thin Film Crystallographic Orientation Using X-ray Diffraction with an Area Detector"].




c)
d)
e)
f)
g)
h)
q_z [Å^{-1}]
q_{xy} [Å^{-1}]
0.0
0.5
1.0
1.5
2.0
2.5
-0.5

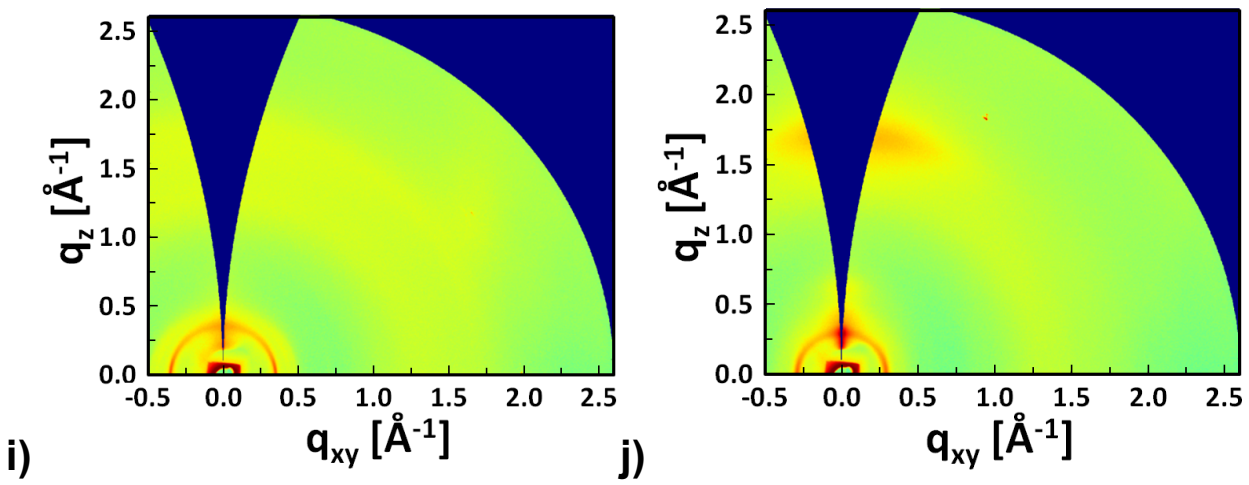


Figure S2. GIXS patterns of (a) PBDTTPD(2EH/C8), (b) PBDTTPD(C14/C8), (c) PBDTTPD(C16/C4), (d) PBDTTPD(C18/C2), (e) PBDTTPD(2PP/C8), (f) PBDTTPD(2BO/C8), (g) PBDTTPD(2EH/2EH), (h) PBDTTPD(2EH/2BO), (i) PBDTTPD(2PP/2PP), (j) PBDTTPD(2BO/2BO) analogs (neat polymers) in thin-films cast from chlorobenzene (no CN additive). The scattering intensity is plotted on a logarithmic scale and normalized in each GIXS pattern.

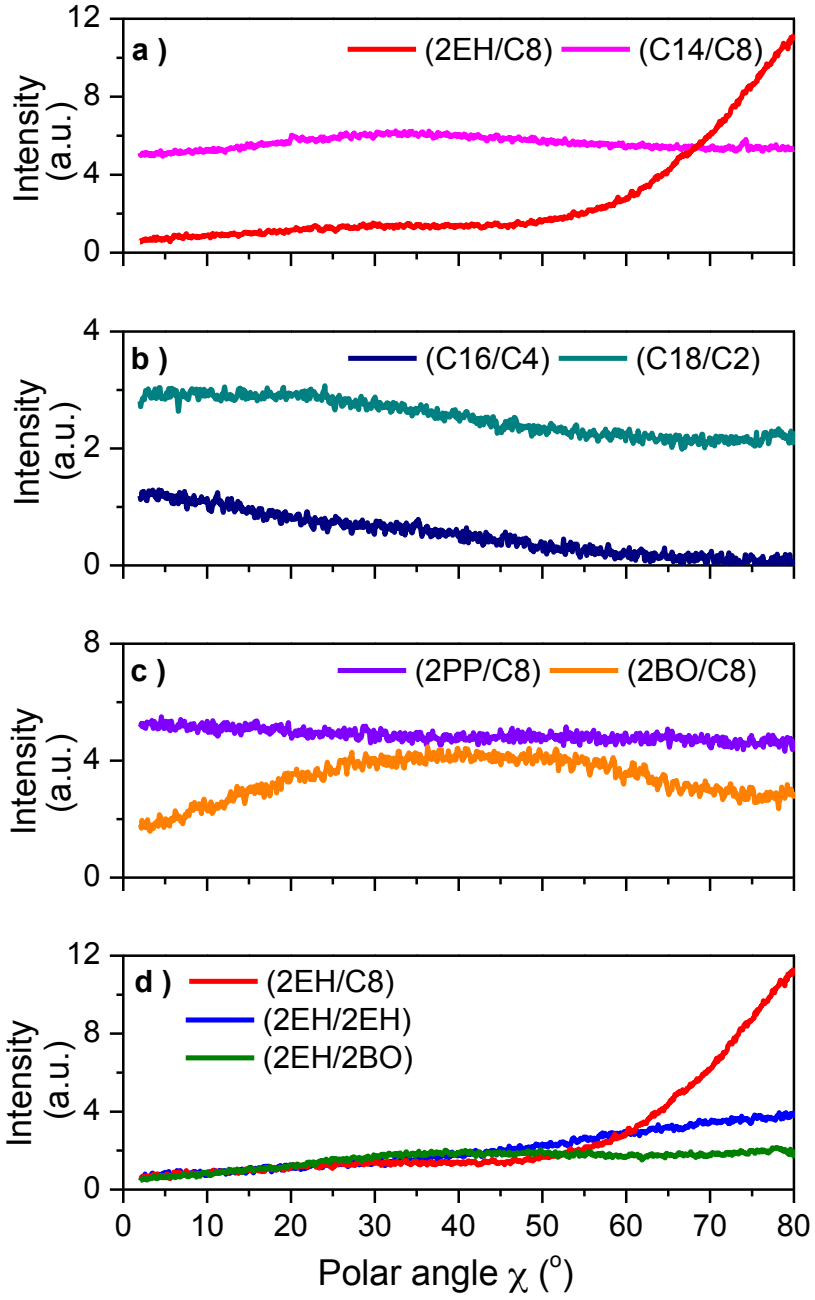


Figure S3. Integrated intensity ($1.65 > q > 1.85$ Å^{-1}) vs. χ angle for **a)** PBDTTPD(2EH/C8) and PBDTTPD(C14/C8), **b)** PBDTTPD(C16/C4) and PBDTTPD(C18/C2), **c)** PBDTTPD(2PP/C8) and PBDTTPD(2BO/C8), **d)** PBDTTPD(2EH/C8), PBDTTPD(2EH/2EH) and PBDTTPD(2EH/2BO). The scattering intensity is plotted for a cake segment ($2° > \chi > 81°$).

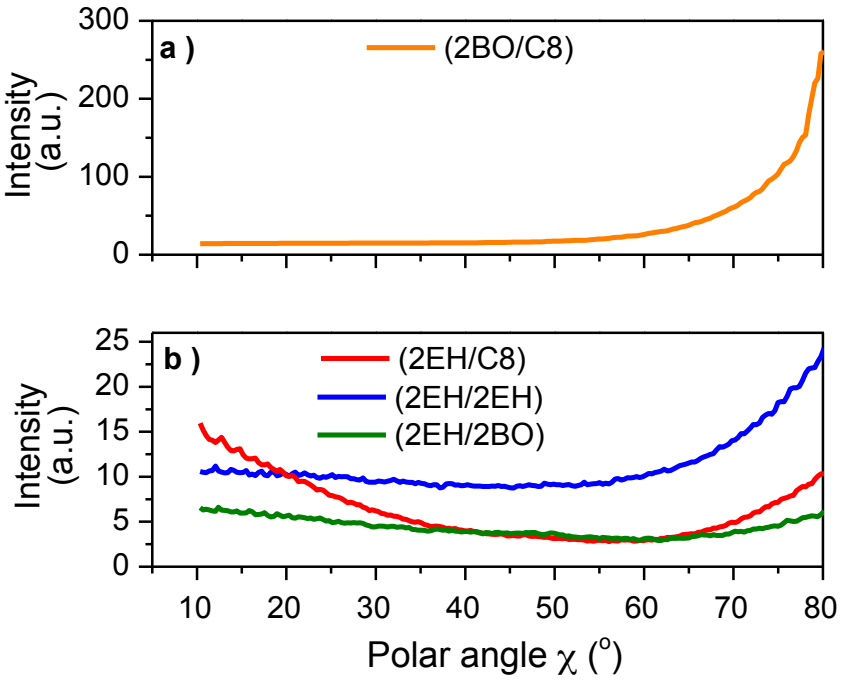


Figure S4. Integrated intensity (0.25 > q > 0.4 Å^{-1}) vs. χ angle of the first-order lamellar reflection arc for **a)** PBDTTPD(2BO/C8), **b)** PBDTTPD(2EH/C8), PBDTTPD(2EH/2EH) and PBDTTPD(2EH/2BO). The scattering intensity is plotted for a cake segment (10°> χ > 80°).

PBDTTPD(R_1/R_2)	Out-of-Plane	In-Plane	Ratio (out/in)	Total integrated intensity
(2EH/C8)	10800	3700	2.92	103000
(2EH/2EH)	4000	3900	1.03	94000
(2EH/2BO)	2100	3200	0.66	80000
(2BO/C8)	3000	9800	0.31	187000
(2BO/2BO)	3400	12300	0.28	201000
(2PP/2PP)	550	2300	0.24	44000
(C14/C8)	5300	25900	0.20	309000
(2PP/C8)	4800	26700	0.18	271000
(C18/C2)	2300	14900	0.15	144000
(C16/C4)	95	6100	0.02	36000

Table S2. Integrated intensity for the PBDTTPD analogs (1.65 > q > 1.85 Å^{-1}, in-plane angle 2° > χ > 7° & out-of-plane angle 76° > χ > 81°), and intensity ratio comparing the distribution of crystal orientation. The total integrated intensity is for 2° > χ > 81°.

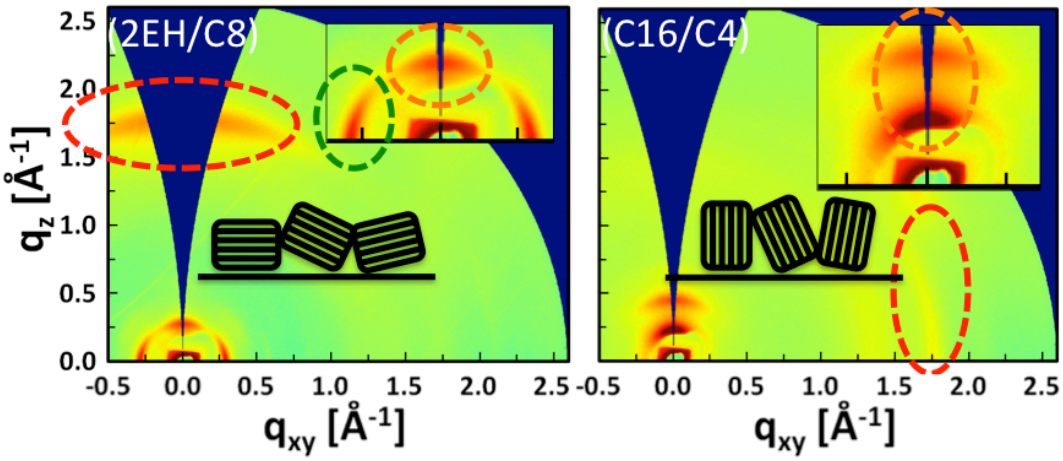


Figure S5. GIXS patterns of PBDTTPD(2EH/C8) (left) with a branched 2-ethylhexyl substituent on the BDT motif and a linear octyl substituent on the TPD motif; and PBDTTPD(C16/C4) (right) with a long linear hexadecyl substituent on the BDT motif and a short linear butyl substituent on the TPD motif. The red dotted circles emphasize the π-stacking reflections; PBDTTPD(2EH/C8) (left) → the partial arc pronounced near the out-of-plane direction indicates that crystallites adopt a preferential "*face-on*" orientation relative to the substrate (π–π stacking "out-of-plane") → represented by  ; PBDTTPD(C16/C4) (right) → the partial arc more pronounced near the in-plane direction indicates that crystallites adopt a preferential "*edge-on*" orientation relative to the substrate (π–π stacking "in-plane") → represented by  .

References

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