Supporting Information

Buta-1,3-diyne Based π-Conjugated Polymers for Organic Transistors and Solar Cells

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Materials Synthesis

The synthesis of 3-alkylthiophene compounds **1b-1d**[1-3] by Kumada coupling of 3-bromothiophene with the corresponding alkylmagnesium bromides and synthesis of 3-alkyl-2-bromothiophene compounds **2b-d**[4-6] by electrophilic bromination of **1b-d** with N-bromosuccinimide were carried out according to the literature procedures cited. The reagent 3-bromothiophene was purchased from Sigma-Aldrich and was used without further purification. All other commercially available reagents were used without further purification unless otherwise stated. Anhydrous THF was distilled from Na/benzophenone. Reactions were carried out under N_2 atmosphere using standard Schlenk technique unless otherwise noted.

General Procedure for the Sonogashira Coupling between 3-Alkyl-2-Bromothiophenes 2b-d and (Trimethylsilyl)acetylene. Compounds **2b-d** (1 equiv), $Pd(PPh_3)_2Cl_2$ (10 mol%), and CuI (10 mol%) were loaded into an oven-dried two-neck round bottom flask with stir bar and mounted with a condenser. Anhydrous toluene (0.3 M) and anhydrous piperidine (1.0M) were added, and the reaction solution was bubbled with N_2 for 15 min. (Trimethylsilyl)acetylene (1.50 equiv) was then added through a side neck, and the reaction was heated to 70 ^{o}C and stirred for 18 h. The crude product was next concentrated under reduced pressure, and the solids were filtered off and washed with hexanes. The hexane fractions were then concentrated under reduced pressure and purified by column chromatography on silica gel using hexanes as the eluent.

((3-Hexylthiophen-2-yl)ethynyl)trimethylsilane (**3b**). Yield = 3.34 g (12.6 mmol; 77.9 %) of the title compound as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 (d, *J* = 5.1 Hz, 1H), 6.83 (d, *J* = 5.2 Hz, 1H), 2.69 (d, *J* = 7.5 Hz, 2H), 1.62 (p, *J* = 7.4 Hz, 2H), 1.31 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H), 0.25 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.97, 128.20, 126.00, 118.36, 100.81, 97.69, 31.73, 30.22, 29.58, 29.04, 22.75, 14.24, 0.14. HRMS (ESI-TOF-MS): *m/z* calcd for $C_{15}H_{24}SSi$ $[M+H]^+$ 265.1441, found 265.1441.

((3-Dodecylthiophen-2-yl)ethynyl)trimethylsilane (**3c**). Yield = 3.75 g (10.8 mmol; 88.6 %) of the title compound as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 (d, J = 5.2 Hz, 1H), 6.82 (d, J = 5.2 Hz, 1H), 2.68 (t, J = 7.5 Hz, 2H), 1.61 (p, J = 7.5 Hz, 2H), 1.26 (m, 18H), 0.89 (t, J = 7.0 Hz, 3H), 0.25 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.98, 128.20, 125.99, 118.35, 100.81, 97.69, 32.08, 30.27, 29.85, 29.82, 29.81, 29.77, 29.61, 29.55, 29.52, 29.41, 22.85, 14.28, 0.14. HRMS (ESI-TOF-MS): *m/z* calcd for $C_{21}H_{36}SSi$ $[M+H]^+$ 349.2380, found 349.2373.

((3-(2-Ethylhexyl)thiophen-2-yl)ethynyl)trimethylsilane (**3d**). Yield = 1.54 g (5.3 mmol; 66.8 %) of the title compound as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 (d, *J* = 5.1 Hz, 1H), 6.80 (d, *J* = 5.1 Hz, 1H), 2.63 (d, *J* = 7.1 Hz, 2H), 1.64 (m, 1H), 1.28 (m, 8H), 0.89 (m, 6H), 0.24 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.08, 128.89, 125.78, 118.92, 100.73, 97.92, 40.63, 33.76, 32.74, 28.97, 25.80, 23.22, 14.27, 10.89, 0.12. HRMS (ESI-TOF-MS): *m*/*z* calcd for $C_{17}H_{28}SSi$ $[M+H]^+$ 293.1754, found 293.1756.

General Procedure for the Deprotection of 3b-d with K_2CO_3. Compounds **3b-d** (1 equiv) and K_2CO_3 (5 equiv) were loaded into a single-neck round bottom flask with stir bar. Dichloromethane (0.33 M) and methanol (0.33 M) were added, and the reaction was stirred for 18 h at room temperature. Solids were removed by filtration and the organic phase was then washed with water and dried over $MgSO_4$. The organic phase was then collected by filtration, concentrated under reduced pressure, and purified by column chromatography on silica gel with hexanes as the eluent.

2-Ethynyl-3-hexylthiophene (**4b**). Yield = 1.63 g (8.5 mmol; 94.2%) of the title compound as a yellow-brown oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (d, *J* = 5.2 Hz, 1H), 6.85 (d, *J* = 5.1 Hz, 1H), 3.43 (s, 1H), 2.71 (t, *J* = 7.5 Hz, 2H), 1.62 (p, *J* = 7.5 Hz, 2H), 1.32 (m, 6H), 0.89 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.20, 128.17, 126.29, 117.13, 83.26, 31.76, 30.31, 29.53, 29.06, 22.74, 14.23. HRMS (ESI-TOF-MS): *m*/*z* calcd for $C_{12}H_{16}S$ $[M+H]^+$ 193.1045, found 193.1058.

3-Dodecyl-2-ethynylthiophene (**4c**). Yield = 1.47 g (5.3 mmol; 93.6%) of the title compound as a yellow-brown oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (d, *J* = 5.1 Hz, 1H), 6.85 (d, *J* = 5.2 Hz, 1H), 3.43 (s, 1H), 2.70 (t, *J* = 7.5 Hz, 2H), 1.61 (p, *J* = 7.4 Hz, 2H), 1.28 (m, 18H), 0.88 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.04, 128.00, 126.11, 116.94, 83.08, 76.98, 31.90, 30.17, 29.65, 29.63, 29.62, 29.55, 29.38, 29.35, 29.33, 29.22, 22.67, 14.10. HRMS (ESI-TOF-MS): *m*/*z* calcd for $C_{18}H_{28}S$ $[M+H]^+$ 277.1984, found 277.1964.

3-(2-Ethylhexyl)-2-ethynylthiophene (**4d**). Yield = 1.01 g (4.6 mmol; 91.0%) of the title compound as a yellow-brown oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (d, *J* = 5.1 Hz, 1H), 6.82 (d, *J* = 5.2 Hz, 1H), 3.42 (s, 1H), 2.64 (d, *J* = 7.1 Hz, 2H), 1.63 (m, 1H), 1.29 (m, 8H), 0.88 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.38, 128.73, 126.11, 117.73, 83.24, 77.12, 40.58, 33.74, 32.69, 28.94, 25.87, 23.18, 14.27, 10.96. HRMS (ESI-TOF-MS): *m*/*z* calcd for $C_{14}H_{20}S$ $[M+H]^+$ 221.1028, found 221.1056.

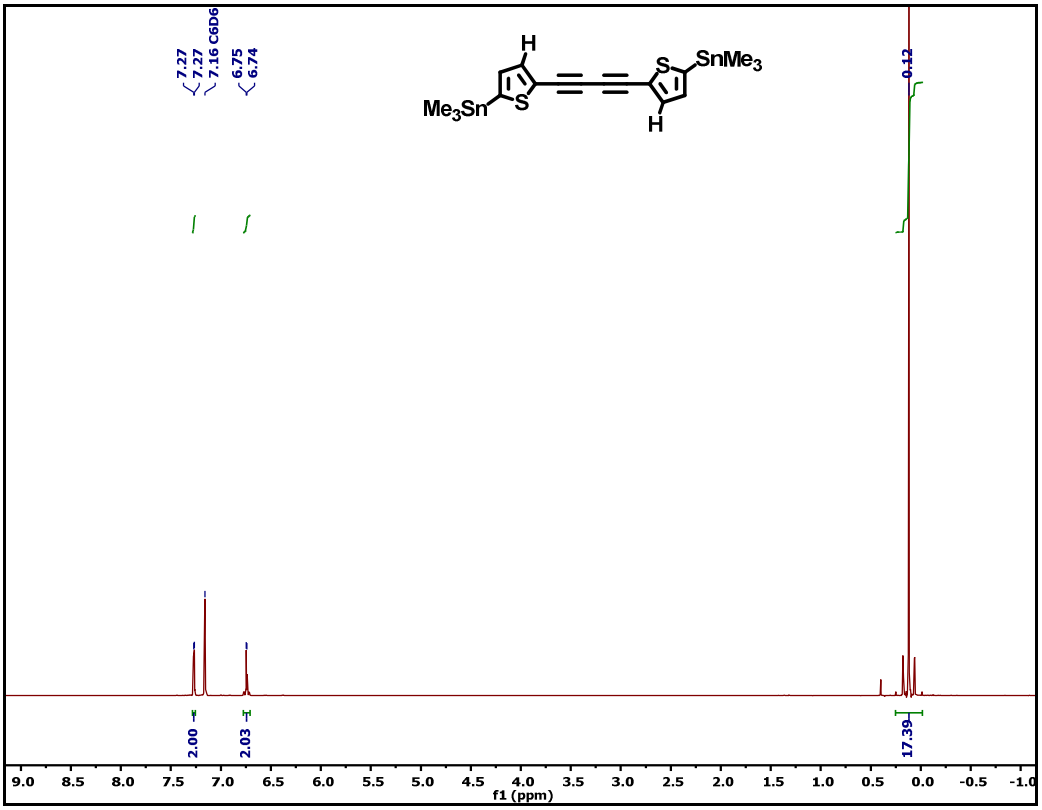

Figure S1. ^{1}H NMR spectrum of compound **6a**

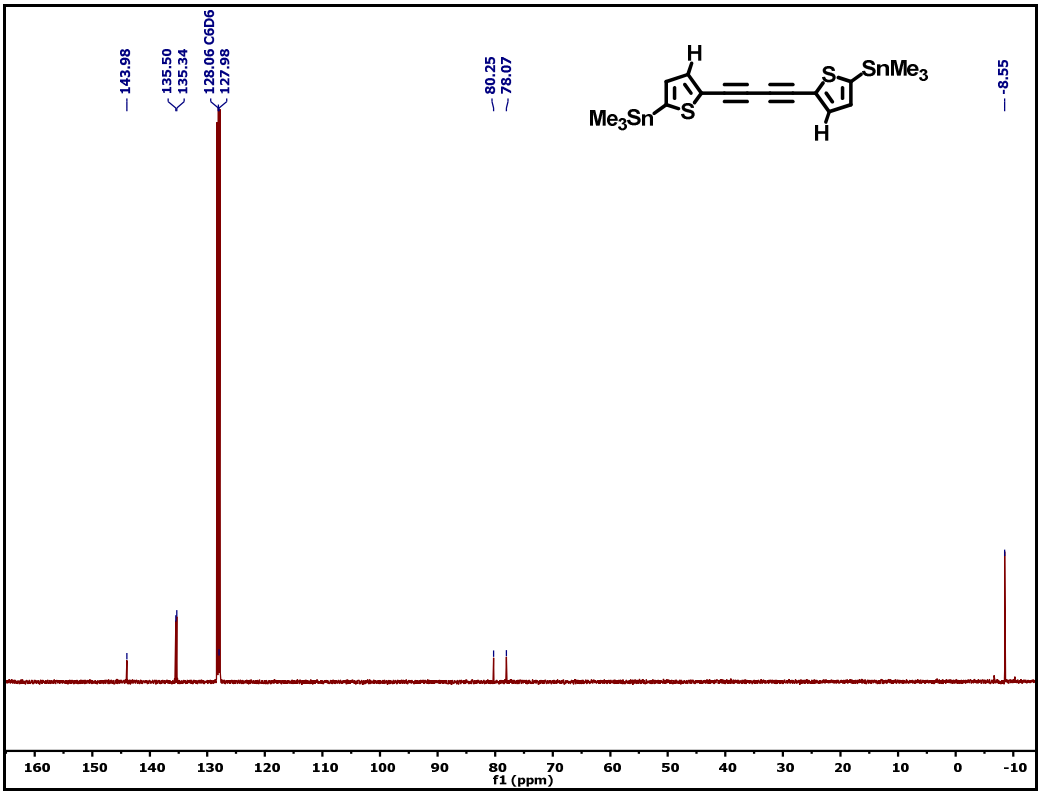

Figure S2. ^{13}C NMR spectrum of compound **6a**

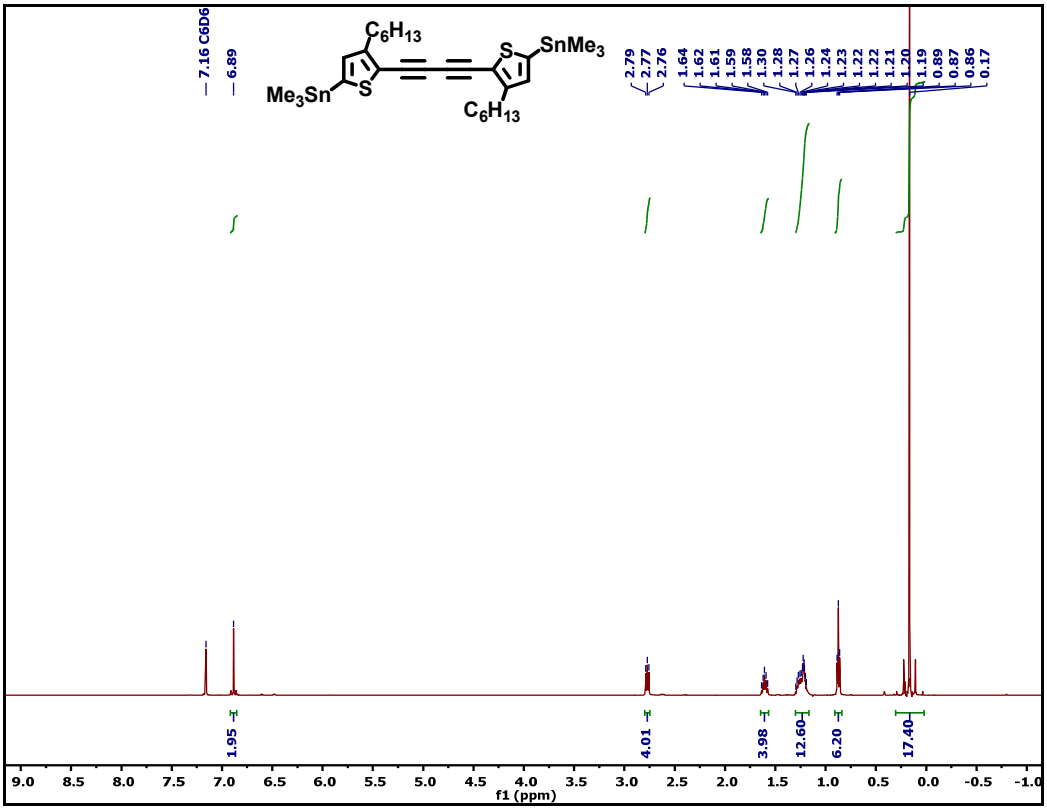

Figure S3. ^{1}H NMR spectrum of compound **6b**

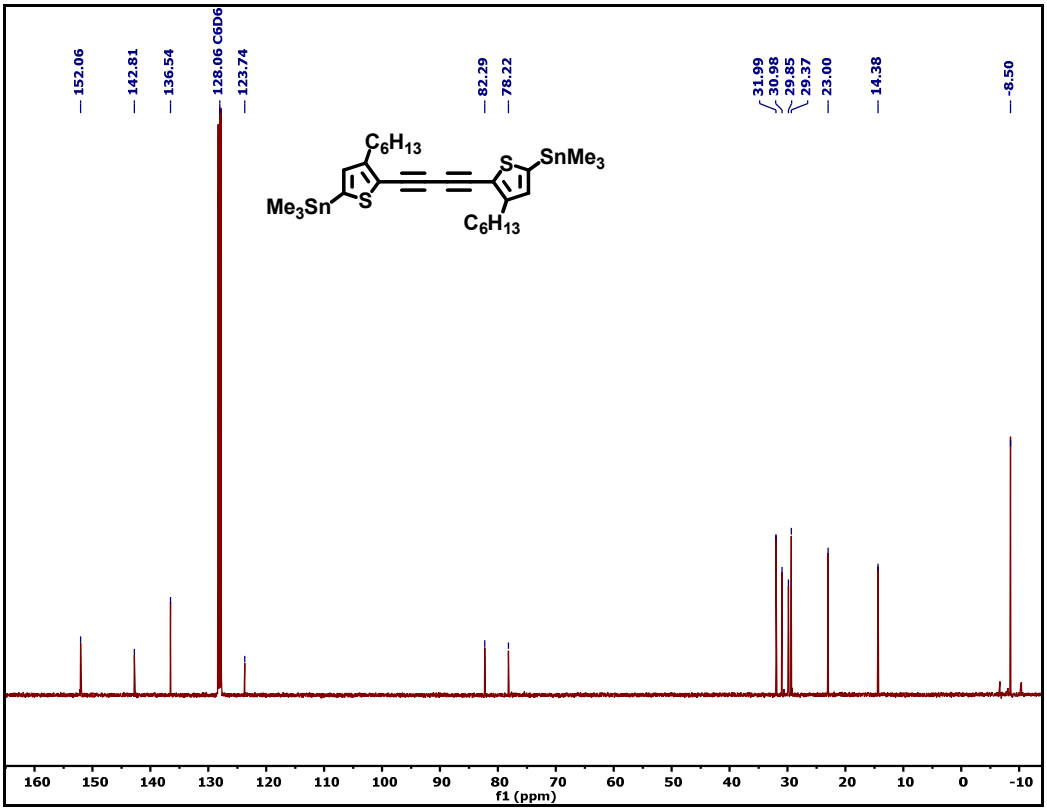

Figure S4. ^{13}C NMR spectrum of compound **6b**

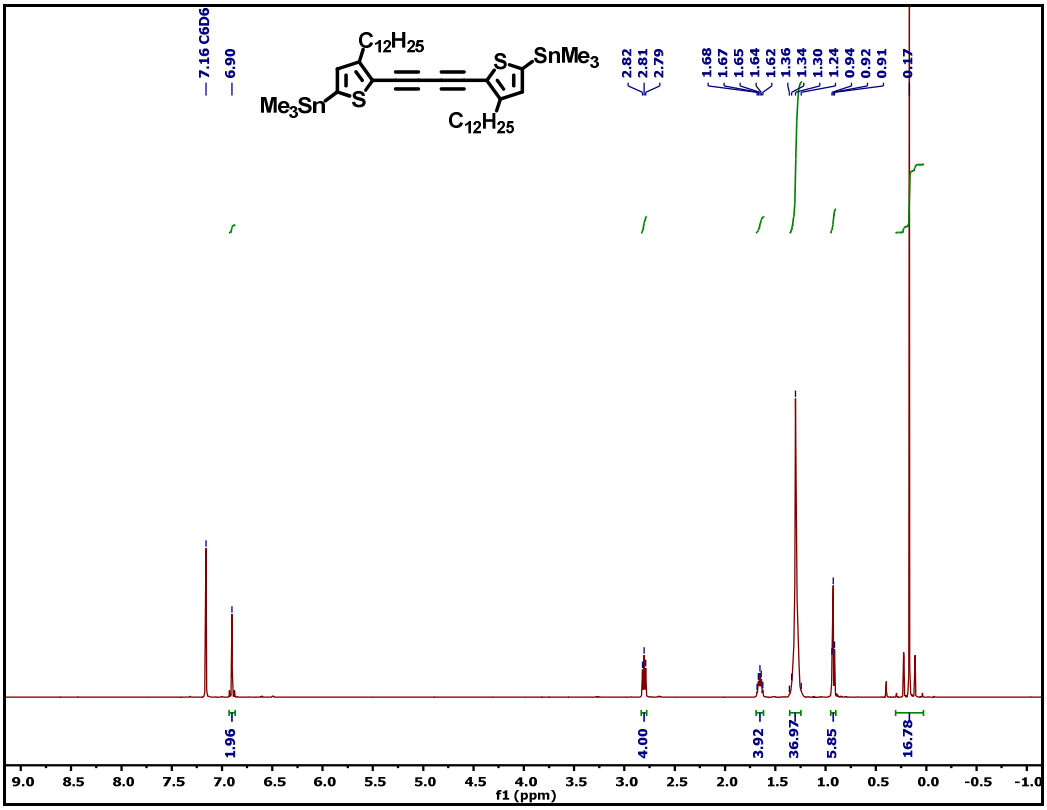

Figure S5. ^{1}H NMR spectrum of compound **6c**

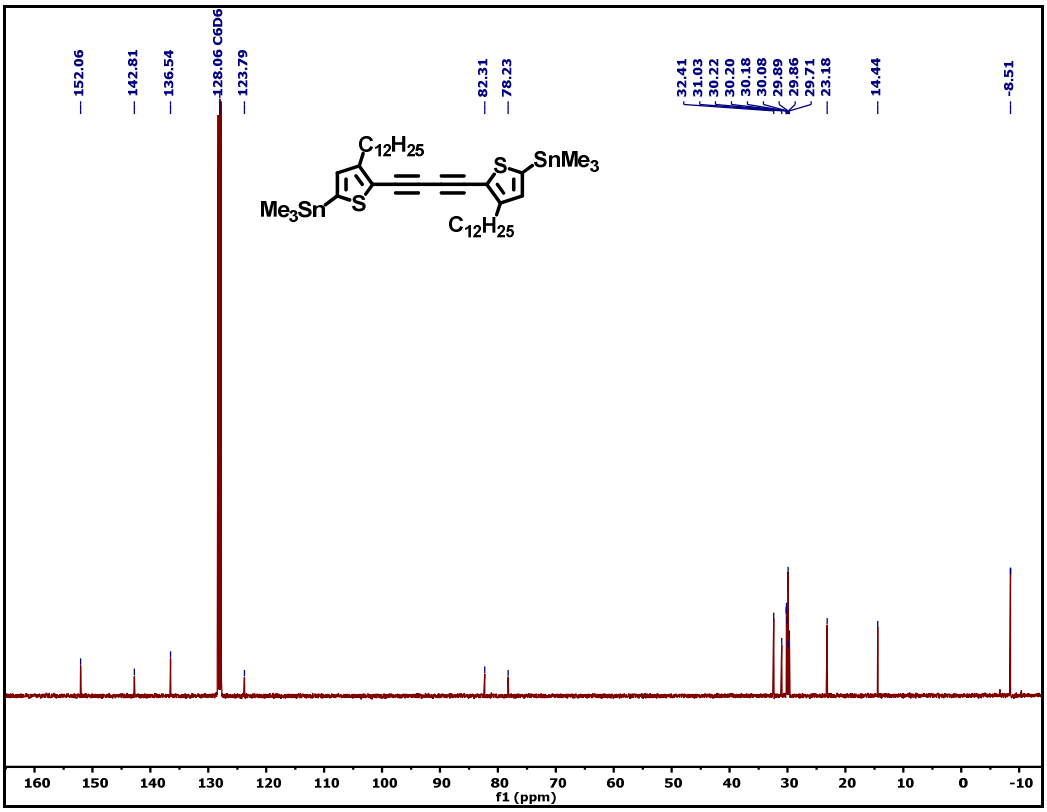

Figure S6. ^{13}C NMR spectrum of compound **6c**

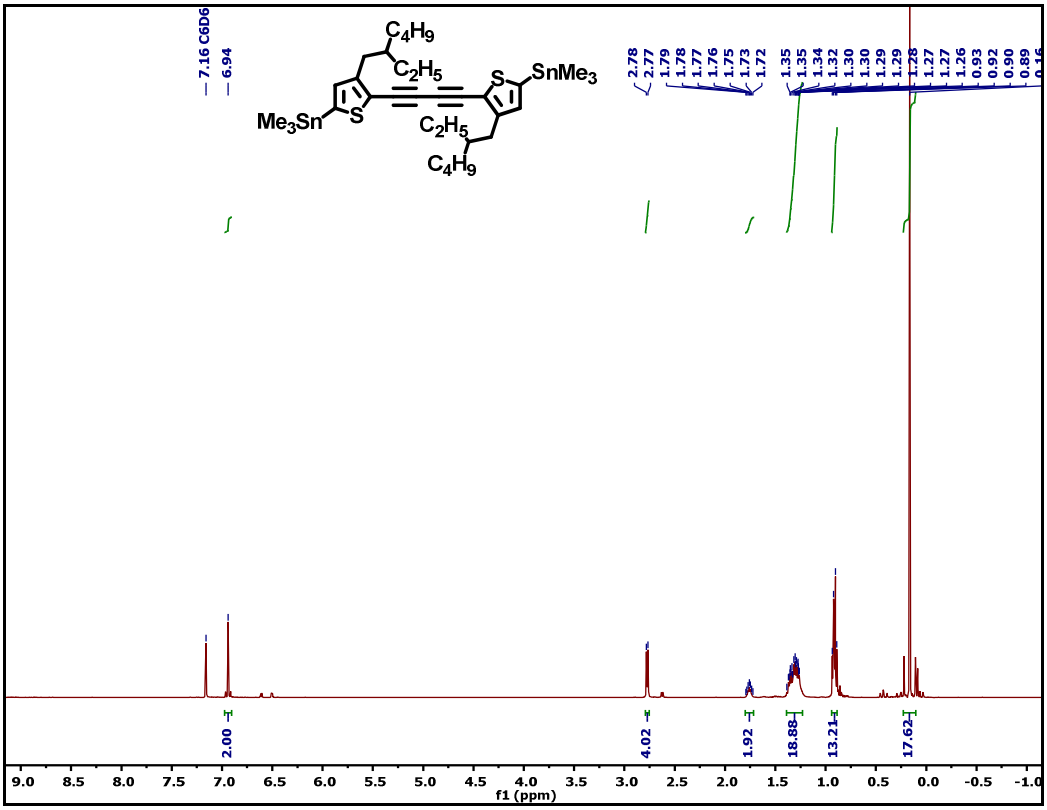

Figure S7. ^{1}H NMR spectrum of compound **6d**

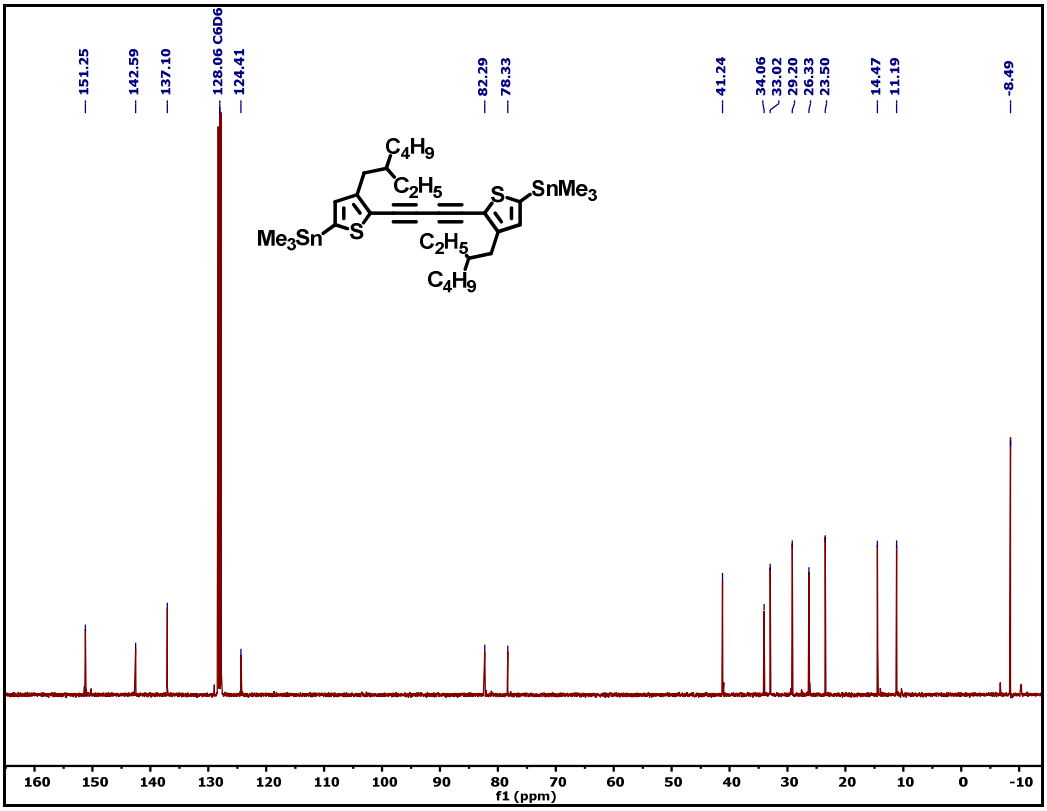

Figure S8. ^{13}C NMR spectrum of compound **6d**

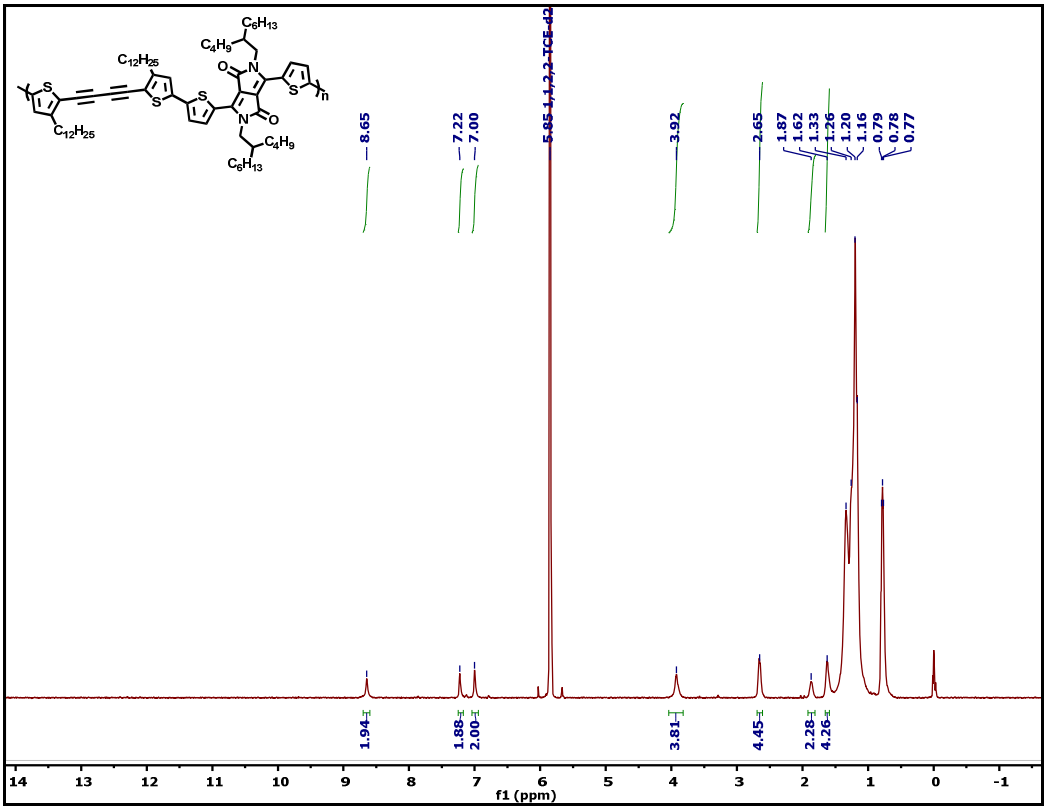

Figure S9. ^{1}H NMR spectrum of polymer **P3** (100 ^{o}C in 1,1,2,2-tetrachloroethane-d_2)

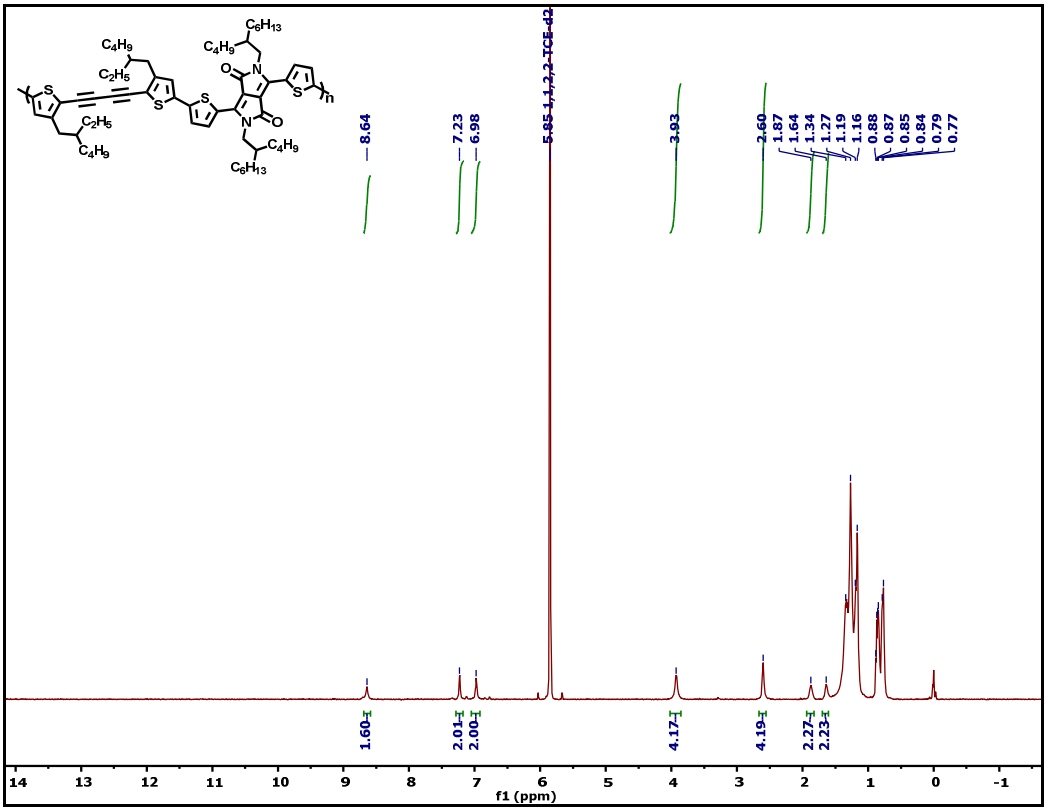

Figure S10. ^{1}H NMR spectrum of **P4** (100 ^{o}C in 1,1,2,2-tetrachloroethane-d_2)

DFT Computation

Geometry and electronic structure optimization of DTB monomer analogues were performed at the B3LYP/6-31G** level of theory using Q-Chem 4.2.

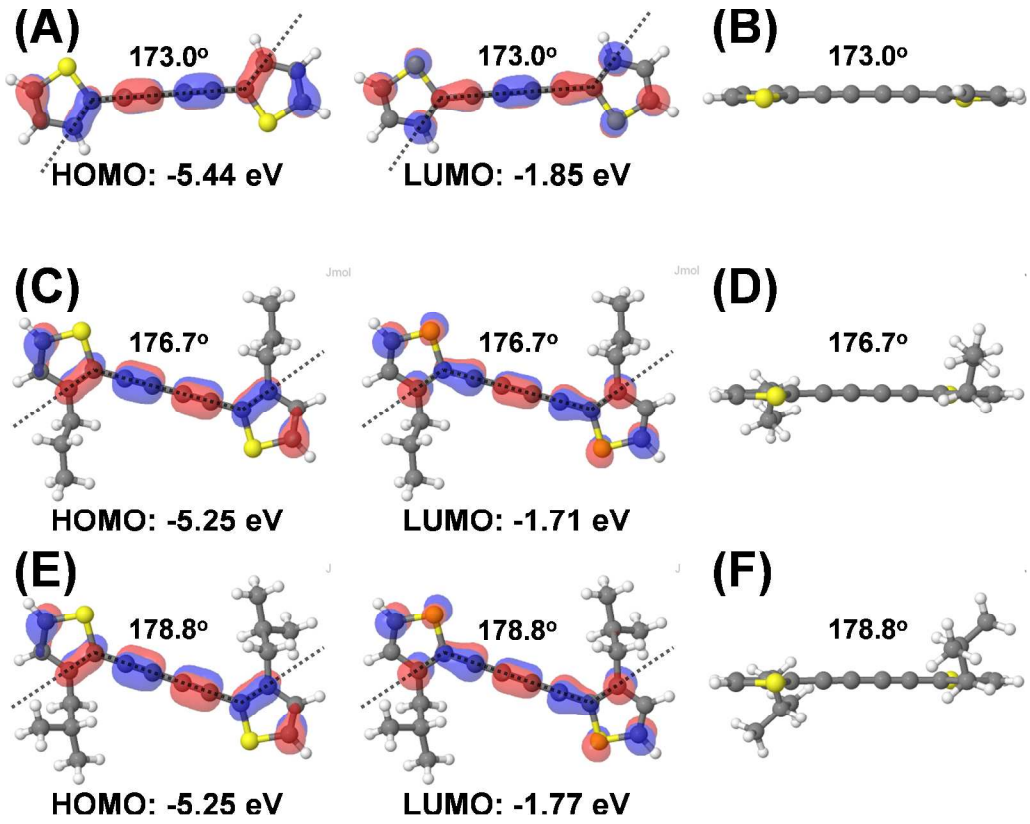

Figure S11. The HOMO/LUMO surfaces and pi-plane profile are shown (A) and (B) for the DTB core with no side-chains, (C) and (D) for the DTB core with propyl (linear) side-chains, and (E) and (F) for the DTB core with 2-methylpropyl (branched) side-chains, respectively. The torsional angles between thiophene planes are also indicated.

Cyclic Voltammetry

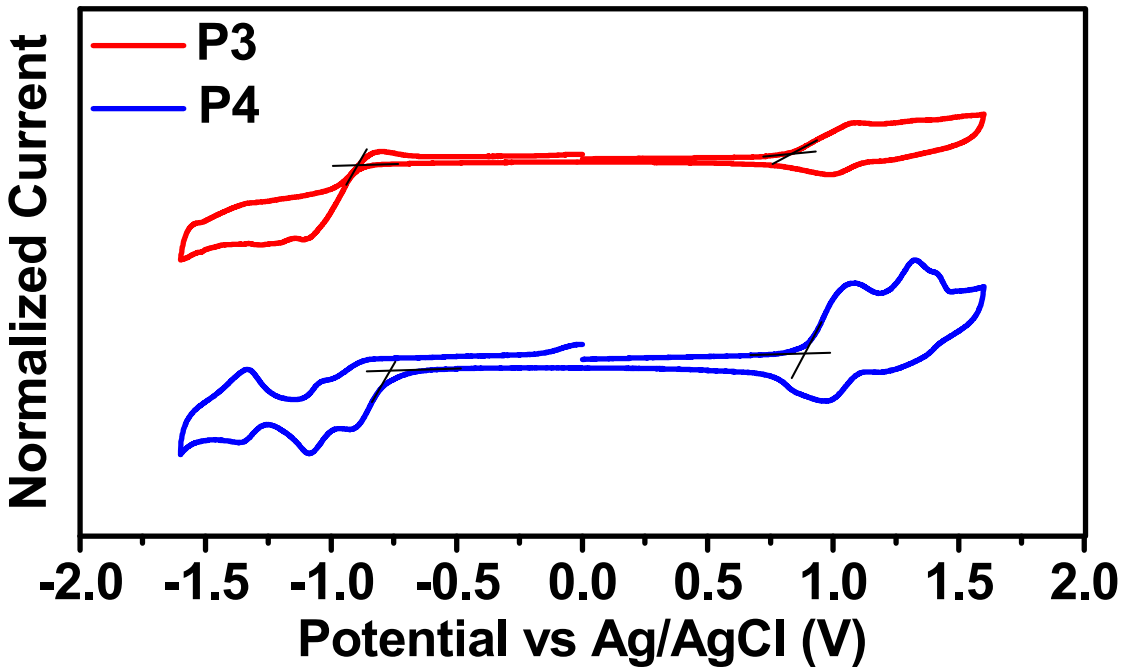

Figure S12. Cyclic voltammograms of **P3** and **P4** films on a glassy carbon electrodes. The measurements were performed in 0.1 M TBA-PF6 in acetonitrile at a scanning rate of 100 mV/sec. Linear extrapolation used to estimate onset potentials included.

Thermal Characterization

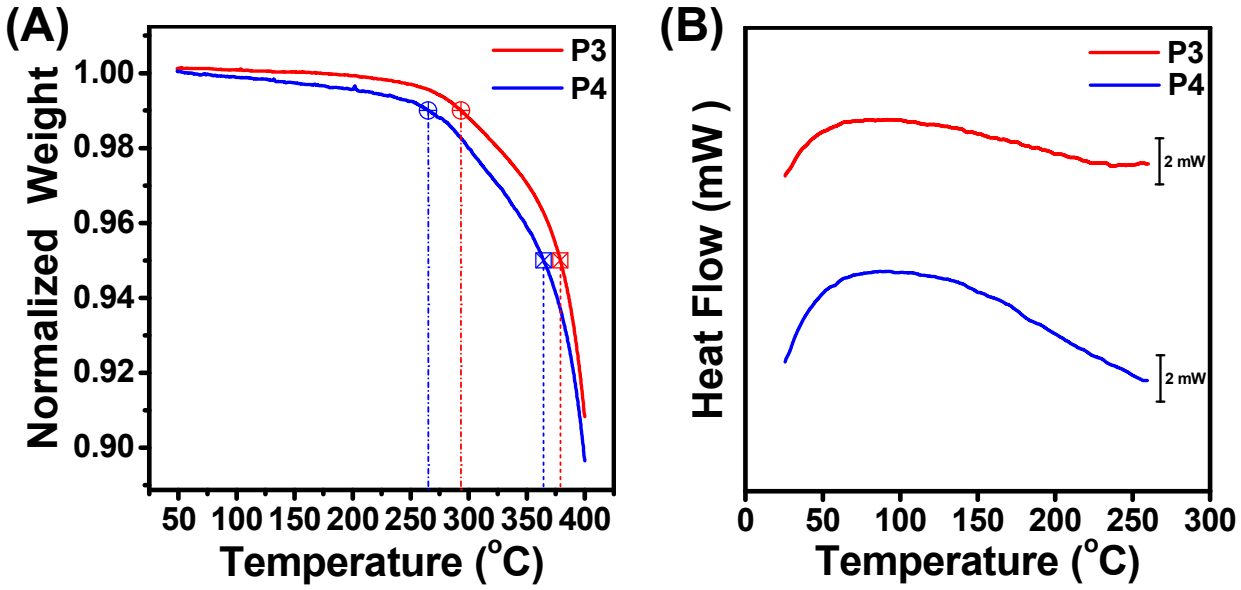

Figure S13. Thermal characterization of **P3** and **P4**. (A) Thermogravimetric analysis (TGA) scanned at 10 °C per minute. The circle and square crosshairs indicate 1 % and 5 % mass loss, respectively. (B) Differential scanning calorimetry (DSC) spectrum showing the second heating scans, scanned at 10 °C per min.

OFET Characteristics

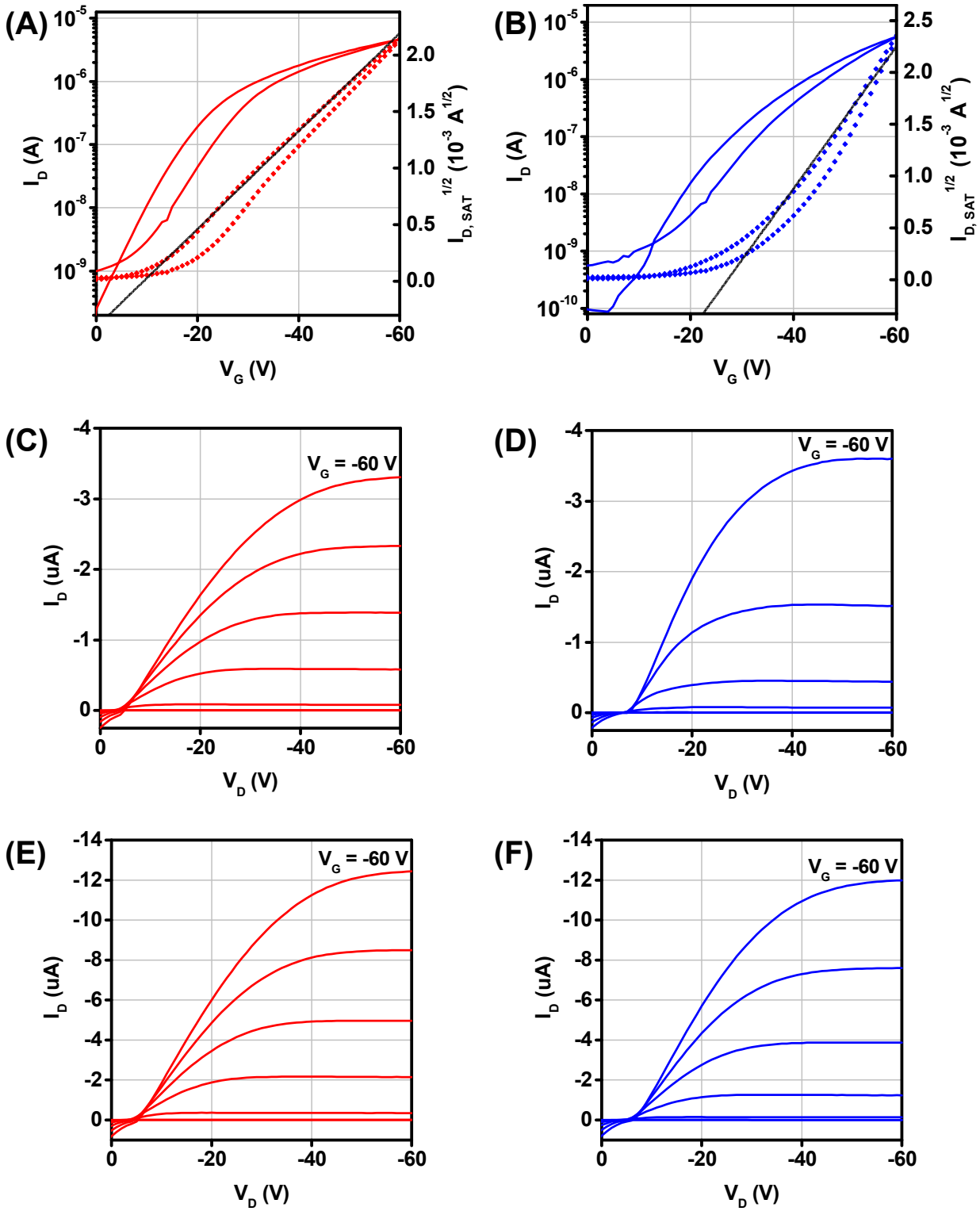

Figure S14. Representative transfer plots of unannealed OFETs of (A) **P3** and (B) **P4**, output plots with V_G = 0 to -60 V in 10 V increments of unannealed OFETs of (C) **P3** and (D) **P4**, and output plots with V_G = 0 to -60 V in 10 V increments of 180 °C annealed OFETs of (E) **P3** and (F) **P4**.

OFET Films AFM

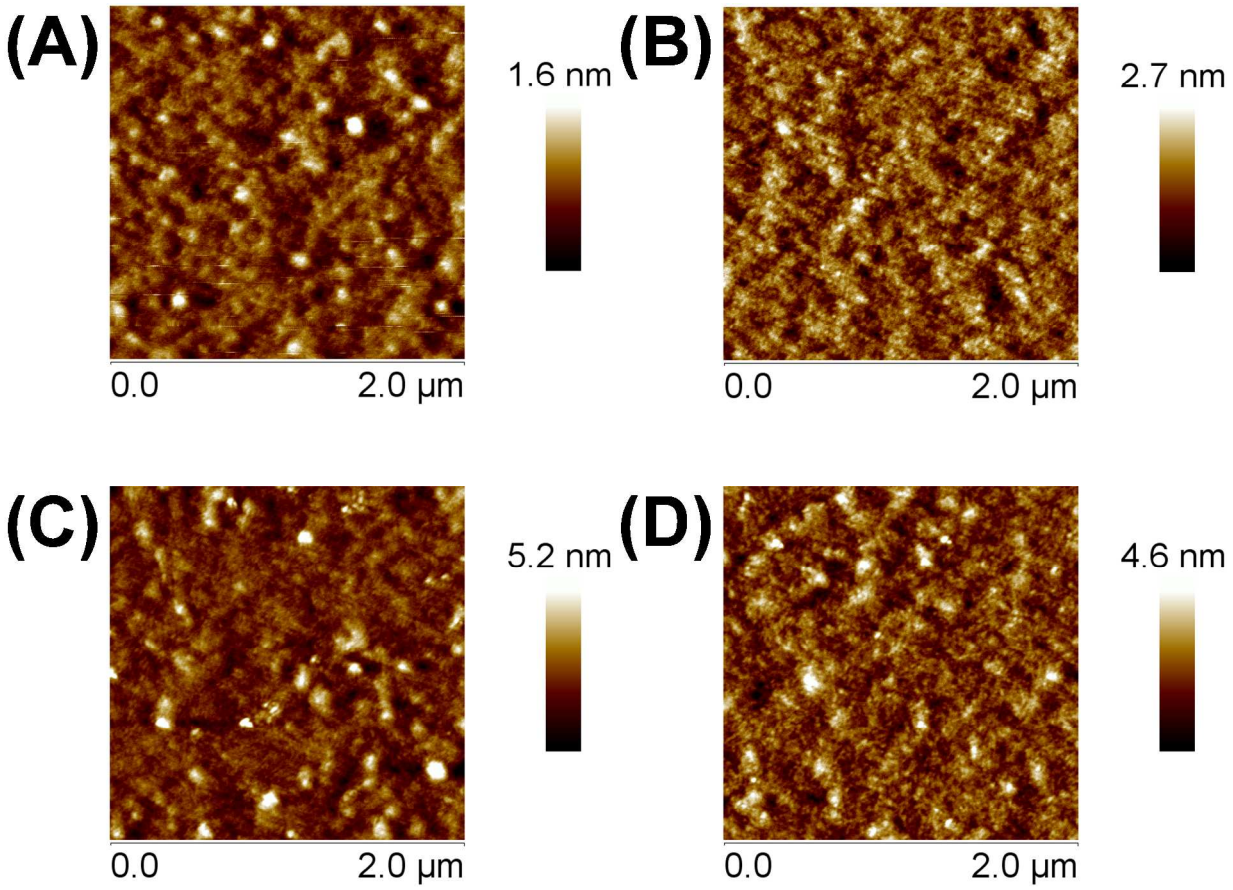

Figure S15. AFM images of films processed according to OFET fabrication. (A) **P3** unannealed, (B) **P3** annealed at 180 °C, (C) **P4** unannealed, and (D) **P4** annealed at 180 °C.

2D GIWAXS

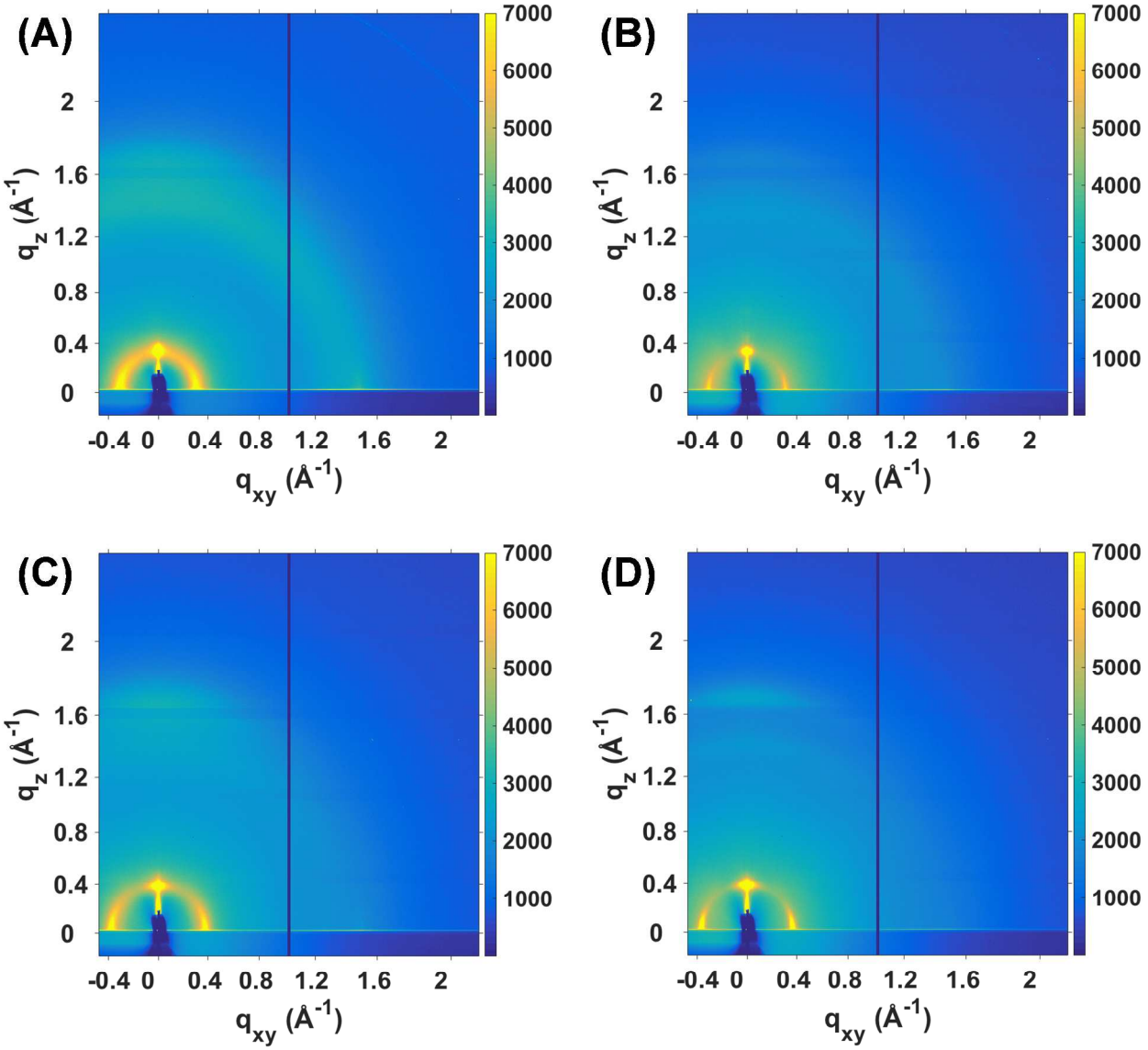

Figure S16. Two-dimensional (2D) GIWAXS images of (A) **P3** unannealed, (B) **P4** unannealed, (C) **P3** annealed at 180 °C, and **P4** annealed at 180 °C. Films were deposited on OTS treated *p*-doped Si/SiO_2 substrates and annealed according to OFET fabrication procedure.

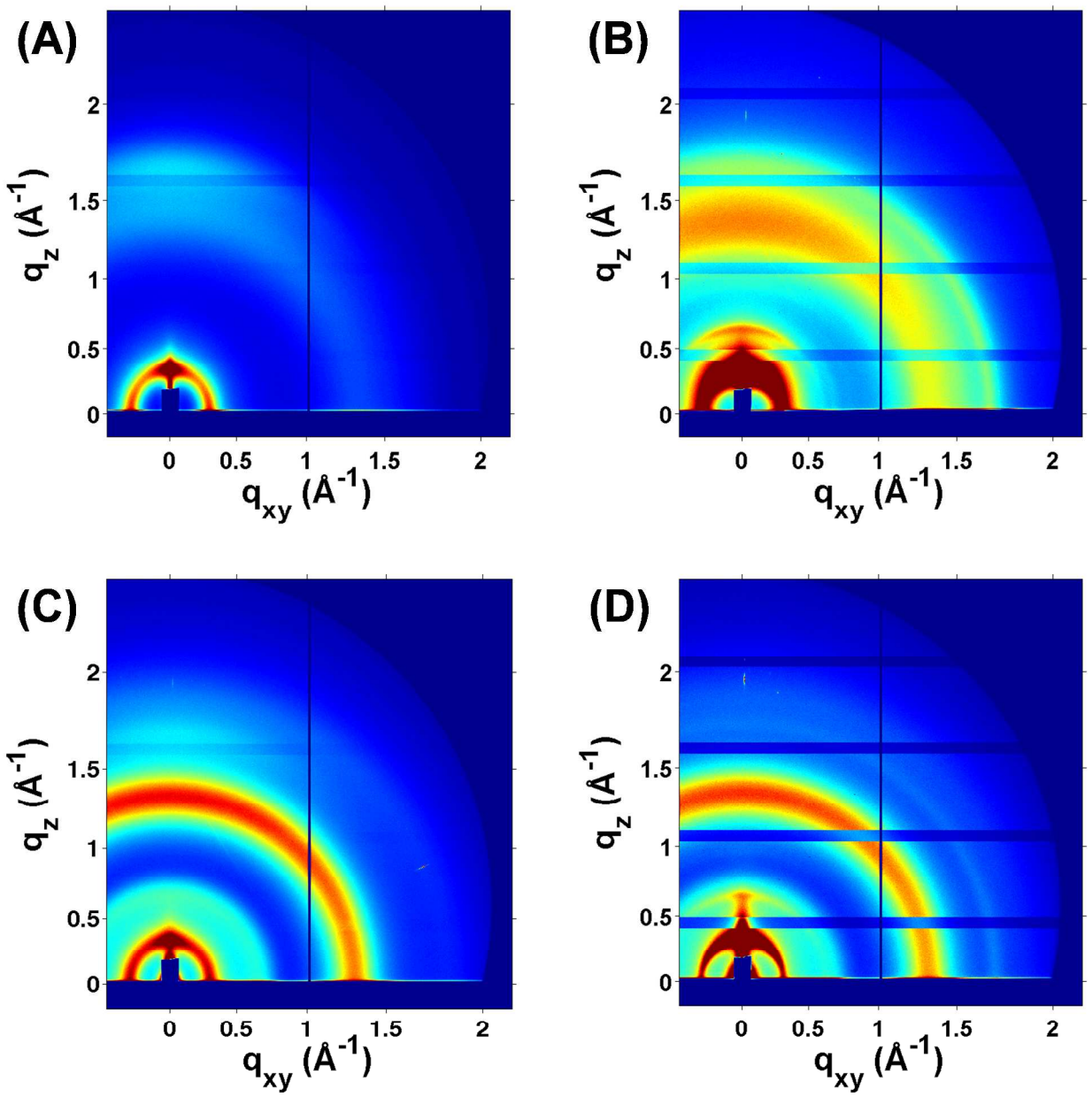

Figure S17. 2D GIWAXS images of (A) neat **P3** film processed from CF, (B) neat **P3** film processed from CF/CN = 95:5 (v/v), (C) Blend **P3**:$PC_{71}BM$ = 1:2 (w/w) film processed from CF, and (D) blend **P3**:$PC_{71}BM$ = 1:2 (w/w) film processed from CF:CN = 95:5 (v/v). The films were deposited on Si substrates following the OSC fabrication procedure.

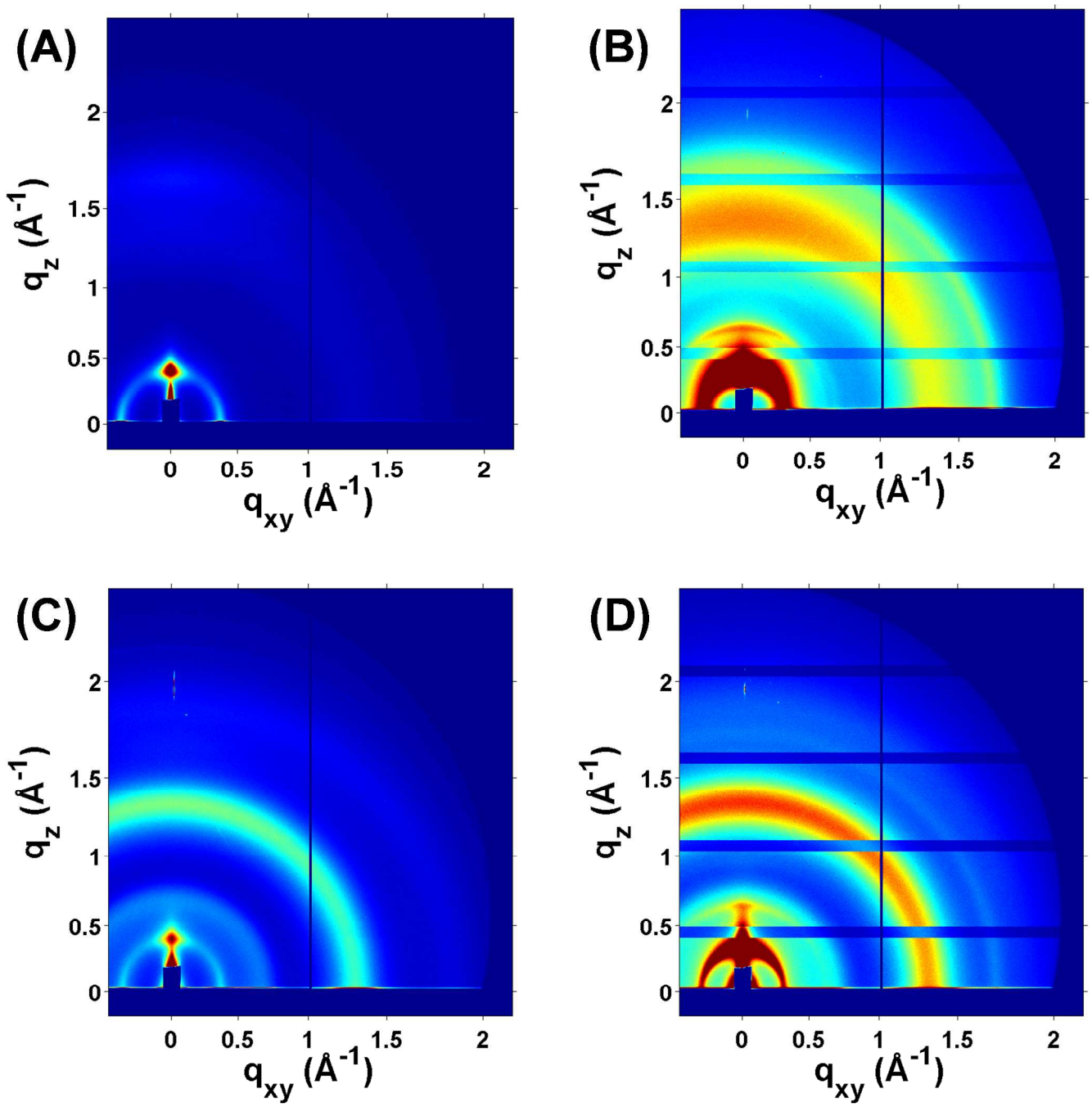

Figure S18. 2D GIWAXS images of (A) neat **P4** film processed from CF, (B) neat **P4** film processed from CF/CN = 95:5 (v/v), (C) Blend **P4**:$PC_{71}BM$ = 1:2 (w/w) film processed from CF, and (D) blend **P4**:$PC_{71}BM$ = 1:2 (w/w) film processed from CF:CN = 95:5 (v/v). The films were deposited on Si substrates following the OSC fabrication procedure.

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