Supporting Information for

Synthesis and Crystallinity of All-Conjugated Poly(3-hexylthiophene) Block Copolymers

Yen-Hao Lin[1], Kendall A. Smith[1], Chloe N. Kempf[1], and Rafael Verduzco*[1]

[1]Department of Chemical and Biomolecular Engineering, MS 362, Rice University, 6100 Main Street,

Houston, Texas 77005

Experimental Methods

Materials. 2,5-dibromo-3-hexylthiophene[1] and 4,7-di-2′-(5′-bromo)-thienyl-2′,1′,3′,- benzothiadiazole)[2] were synthesized as previously described. All other reagents were purchased from Sigma-Aldrich and used as received.

Poly(3-hexylthiophene) (P3HT-Br). The synthetic procedure is a slightly modified from a previous report.[3] In a 50 mL flask purged with nitrogen gas, 2,5-dibromo-3-hexylthiophene (1.9 g, 5.82 mmol) was dissolved in anhydrous THF (5 mL), and the solution was stirred under nitrogen at 0 °C for 15 minutes. A solution of isopropyl magnesium chloride and LiCl (1.3 M) in THF (4.48 mL, 5.82 mmol) was added, and the mixture was stirred for 2 hours. 25 mL of THF was then added before adding Ni(dppp)Cl_2 (105.15 mg, 0.194 mmol), and the mixture was stirred for 15 minutes. The reaction was quenched by adding 5 M HCl (2 mL, 10 mmol), and the solution was stirred for another 15 minutes. The final mixture was collected by precipitation in cold methanol and washed with hexanes and dried under vacuum. Yield: 92%. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 6.95 (1H, Aryl—$\underline{H}$), 2.82 (2H, C—$\underline{CH_2}$—C_5H_{11}), 1.70 (2H, CH_2—$\underline{CH_2}$—C_4H_9), 1.35 (6H, CH_2—$\underline{C_3H_6}$—CH_3), 0.92 (3H, CH_2—$\underline{CH_3}$). Molecular weight and PDI are provided in Table 1.

Poly(3-hexylthiophene)-*b*-poly(9′,9′-dioctylfluorene) (P3HT-*b*-PF) (P3HT36-*b*-PF100 and P3HT81-*b*-PF105). In a representative procedure, P3HT-Br (124 mg, 0.031 mmol), 9′,9′-dioctylfluorene-2′,7′-diboronic acid ester (781 mg, 1.4 mmol), 2′,7′-dibromo-9′,9′-dioctylfluorene (706 mg, 1.288 mmol), tetrakis-(triphenylphosphine) -palladium(0) (75 mg, 0.065 mmol), and aliquat 336

(3 drops) were added to a Schlenk tube loaded with nitrogen-purged toluene (25 mL) and an aqueous solution of Na_2CO_3 (2M, 10 mL). The reaction was stirred at 90 °C for 1 day. The final mixture was collected by precipitation in cold methanol, and the crude product was further purified by washing in a Soxhlet extractor with acetone and then hexanes. The undissolved residue was collected and dried under vacuum. Yield: 80%. ^{1}H NMR (500 MHz, $CDCl_3$) (see Figure S1), δ (ppm): 7.5-7.8 (6H; Aryl—$\underline{H}$), 6.95 (1H, Aryl—$\underline{H}$), 2.82 (2H, C—$\underline{CH_2}$—C_5H_{11}), 2.1 (4H; $\underline{CH_2}$—C_7H_{15}), 1.70 (2H, CH_2—$\underline{CH_2}$—C_4H_9), 1.35 (6H, CH_2—$\underline{C_3H_6}$—CH_3), 1.13 (20H; CH_2—$\underline{C_5H_{10}}$—CH_3), 0.92 (3H, CH_2—$\underline{CH_3}$), 0.80 (6H; C_7H_{14}—$\underline{CH_3}$). Molecular weight and PDI are provided in Table 1.

Poly(3-hexylthiophene)-*b*-poly[(9′,9′-dioctylfluorene)-alt-(2′,3′,5′-benzothiadiazole)] (P3HT-*b*-PFBT) (P3HT51-*b*-PFBT66 and P3HT81-*b*-PFBT90). In a representative procedure, P3HT-Br (74.4 mg, 0.0062 mmol), 9′,9′-dioctylfluorene-2′,7′-diboronic acid ester (346 mg, 0.62 mmol), 4,7-dibromobenzo[1,2,5] thiadiazole (181 mg, 0.61 mmol), tetrakis-(triphenylphosphine)-palladium(0) (75 mg, 0.065 mmol), and aliquat 336 (3 drops) were added to a Schlenk tube loaded with nitrogen-purged toluene (25 mL) and an aqueous solution of Na_2CO_3 (2M, 10 mL). The reaction was stirred at 90 °C for 1 day. The final mixture was collected by precipitation in cold methanol, and the crude product was further purified by washing in a Soxhlet extractor with acetone and then hexanes. The undissolved residue was collected and dried under vacuum. Yield: 83%. ^{1}H NMR (500 MHz, $CDCl_3$) (see Figure S2), δ (ppm): 7.3-8.2 (8H; Aryl—$\underline{H}$), 6.95 (1H, Aryl—$\underline{H}$), 2.82 (2H, C—$\underline{CH_2}$—C_5H_{11}), 2.1 (4H; $\underline{CH_2}$—C_7H_{15}), 1.70 (2H, CH_2—$\underline{CH_2}$—C_4H_9), 1.35 (6H, CH_2—$\underline{C_3H_6}$—CH_3), 1.13 (20H; CH_2—$\underline{C_5H_{10}}$—CH_3), 0.92 (3H, CH_2—$\underline{CH_3}$), 0.80 (6H; C_7H_{14}—$\underline{CH_3}$). Molecular weight and PDI are provided in Table 1.

Poly(3-hexylthiophene)-*b*-poly(2,7-(9′,9′-dioctyl-fluorene)-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′,-benzothiadiazole) (P3HT-*b*-PFTBT) (P3HT51-*b*-PFTBT17 and P3HT81-*b*-PFTBT12). In a representative procedure, P3HT-Br (139 mg, 0.0116 mmol), 9′,9′-dioctylfluorene-2′,7′-diboronic acid ester (506 mg, 0.9 mmol), 4,7-di-2′-(5′-bromo)-thienyl-2′,1′,3′,-benzothiadiazole) (407 mg, 0.89 mmol), Tetrakis-(triphenylphosphine)-palladium(0) (75 mg, 0.065 mmol), and aliquat 336 (3 drops) were added to a Schlenk tube loaded with nitrogen-purged toluene (25 mL) and an aqueous solution of Na_2CO_3 (2M, 10 mL). The reaction was stirred at 90 °C for 1 day. The final mixture was collected by precipitation in cold methanol and the crude product was further purified by washing in a Soxhlet extractor with acetone and then hexanes. The undissolved residue was collected and dried under vacuum. Yield: 70%. ^{1}H NMR

(500 MHz, $CDCl_3$) (see Figure S3), δ (ppm): 8.18 (2H), 7.94 (2H), 7.6-7.8 (6H; Aryl—$\underline{H}$), 7.49 (2H) , 6.95 (1H, Aryl—$\underline{H}$ (P3HT)), 2.82 (2H, C—$\underline{CH_2}$—C_5H_{11}), 2.1 (4H; $\underline{CH_2}$—C_7H_{15}), 1.70 (2H, CH_2—$\underline{CH_2}$—C_4H_9), 1.35 (6H, CH_2—$\underline{C_3H_6}$—CH_3), 1.13 (20H; CH_2—$\underline{C_5H_{10}}$—CH_3), 0.92 (3H, CH_2—$\underline{CH_3}$), 0.80 (6H; C_7H_{14}—$\underline{CH_3}$). Molecular weight and PDI are provided in Table 1.

Instrumentation

Size Exclusion Chromatography (SEC). Molecular weights and polydispersities were obtained by SEC using an Agilent 1200 module equipped with three PSS SDV columns in series (100, 1000, and 10 000 Å pore sizes), an Agilent variable wavelength UV/visible detector, and a Wyatt Technology Optilab reX RI detector. This system enables SEC with simultaneous refractive index (SEC-RI) and UV-VIS detection. THF was used as the mobile phase at a flow rate of 1mL/min at 40 °C. Polystyrene relative molecular weights are calculated using Astra Software Version 5.3.4.

The molecular weight distributions for each polymer block and corresponding homopolymer impurities can be obtained by SEC-UVVIS analysis at two distinct wavelengths. By using a wavelength specific to one polymer block, we first obtain the molecular weight distribution for one block. 450 nm (specific to P3HT), 500 nm (specific to P3HT), and 550 nm (specific to PFDTBT) were used for P3HT-*b*-PF, P3HT-*b*-PFBT, and P3HT-*b*-PFDTBT, respectively. PF and PFBT exhibit no measureable absorbance at 450 and 500 nm, respectively, while P3HT exhibits no measureable absorbance at 550 nm. Next, SEC-UVVIS analysis a second wavelength sensitive to both polymer blocks can be corrected to obtain the molecular weight distribution of the second block. In the case of P3HT-*b*-PF, analysis at 380 nm is sensitive to both blocks, but the contribution of P3HT to the signal is subtracted using the 450 nm SEC-UVVIS trace and the absorbance ratio for P3HT at 450nm relative to 380 nm, measured independently to be 1.82. The 380 nm absorbance trace presented in Figure S5 is the result of this subtraction and reflects the molecular weight distribution of the PF block only. Similar analysis was carried out for P3HT-*b*-PFBT and P3HT-*b*-PFDTBT. 300 nm and 500 nm were used for analysis of P3HT-*b*-PF, with a measured absorbance ratio of 0.12 for P3HT at 500nm relative to 300 nm. 550 nm and 450 nm were used for P3HT-*b*-PFDTBT, with a measured absorbance ratio of 3.2 for PFODTBT at 550 nm relative to 450 nm

Nuclear Magnetic Resonance Spectroscopy (NMR). ^1H NMR spectroscopy was performed on

Varian 500 MHz. Samples were placed in 5 mm o.d. tubes with sample concentrations of about 5 mg/mL. Solvents contain 0.05% TMS as an internal standard. Spectra were processed using 1D NMR Processor in ACDLABS 12.0.

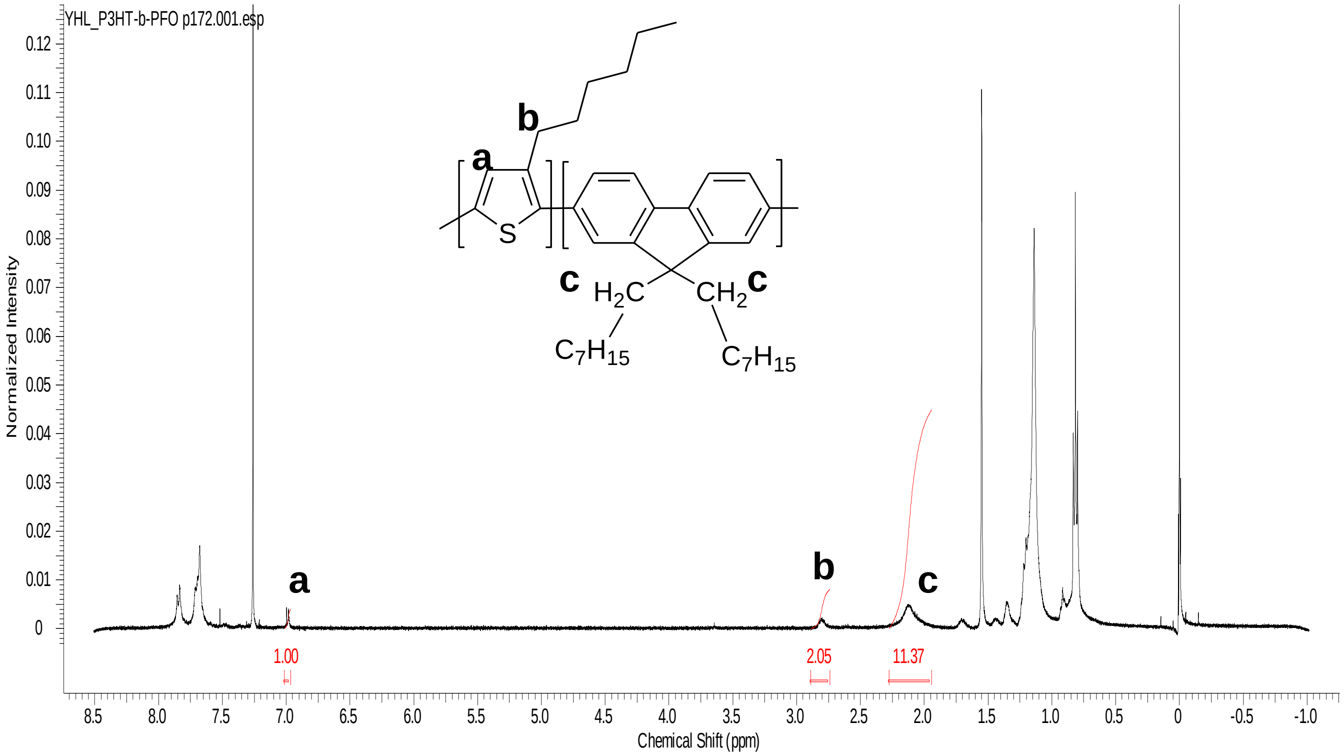
Ultraviolet-Visible Absorbance Spectroscopy (UV-VIS). UV-VIS measurements were carried out with a Varian Cary 50 spectrophotometer with scan range of 190 nm – 1100 nm at the Center for Functional Nanomaterials at Argonne National Laboratory. Samples were prepared by stirring 1 mg/mL solutions in $CHCl_3$ and diluted to a concentration of approximately 1 μg/mL immediately before measurement.

Differential Scanning Calorimetry (DSC). Differential scanning calorimetry measurements were performed using a TA Instrument DSC Q10 with a ramp rate of 5 °C/min under N_2 flow. Samples about 3 mg were placed in hermetic pans from Thermal Support Inc.

Wide-angle X-ray diffraction (XRD). X-ray diffraction was performed with Rigaku D/Max Ultima II with Cu Kα radiation source. Samples were prepared by drop casting 6 mg/mL polymer $CHCl_3$ solution on glass slide and dried under a stream of air. Then, samples were annealed to 220 °C and cooled to room temperature twice before measurement.

Grazing-Incidence Wide Angle X-ray scattering (GIWAXS). Grazing incidence wide angle X-ray scattering measurements were carried out on Sector 8-ID-E at the Advanced Photon Source, Argonne National Laboratory.[4] Beamline 8-ID-E operates at an energy of 7.35 keV and images were collected from a Pilatus 1MF camera (Dectris), with two exposures for different vertical position of the detector. After flatfield correction for detector nonuniformity, the images are combined to fill in the gaps for rows at the borders between modules, leaving dark only the columns of inactive pixels at the center. Using the GIXSGUI package[5] for Matlab (Mathworks), data are corrected for X-ray polarization, detector sensitivity and geometrical solid-angle. The beam size is 200 μm (h) x 20 μm (v). Sample detector distance is 204 mm. Sample measurement and thermal annealing were carried out under vacuum which is in the range of $2{\sim}3 \times 10^{-6}$ bar, with the sample stage interfaced with a Lakeshore 340 unit.

Couple samples (P3HT81-*b*-PFBT90 and P3HT51-*b*-PFTBT17) were carried out on X9 at National Synchrotron Light Source, Brookhaven National Laboratory. Beamline X9 operates at an energy of 14 keV and images were collected from a Pilatus 1MF camera (Dectris). Using the GIXSGUI package[5] for Matlab (Mathworks), data are corrected for x-ray polarization, detector sensitivity and geometrical solid-angle. Sample detector distance is 370 mm for wide-angle detector and 3091 mm for small-angle detector. Sample measurement and thermal annealing were carried out under vacuum which is in the range of 2~3 × 10^{-6} bar.



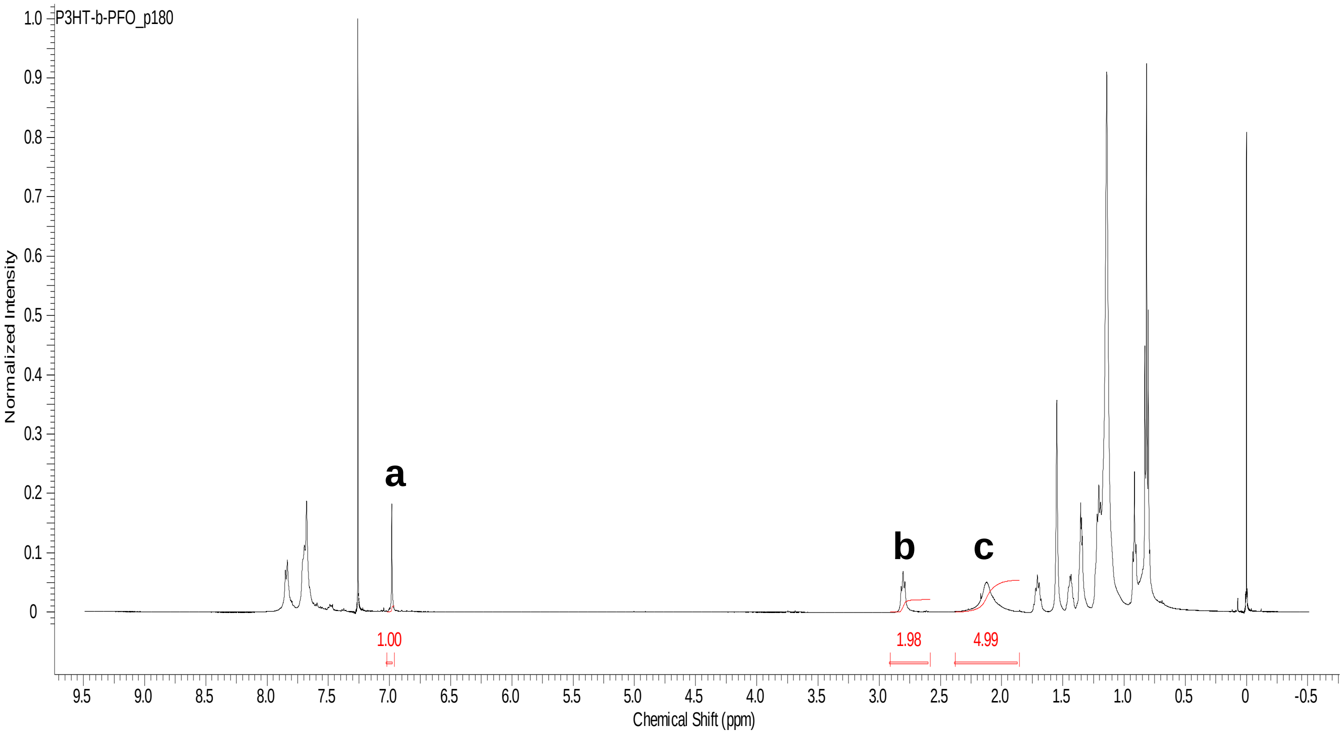


Figure S1. ^{1}H NMR spectrum of P3HT36-*b*-PF100 (top) and P3HT81-*b*-PF105 (bottom).

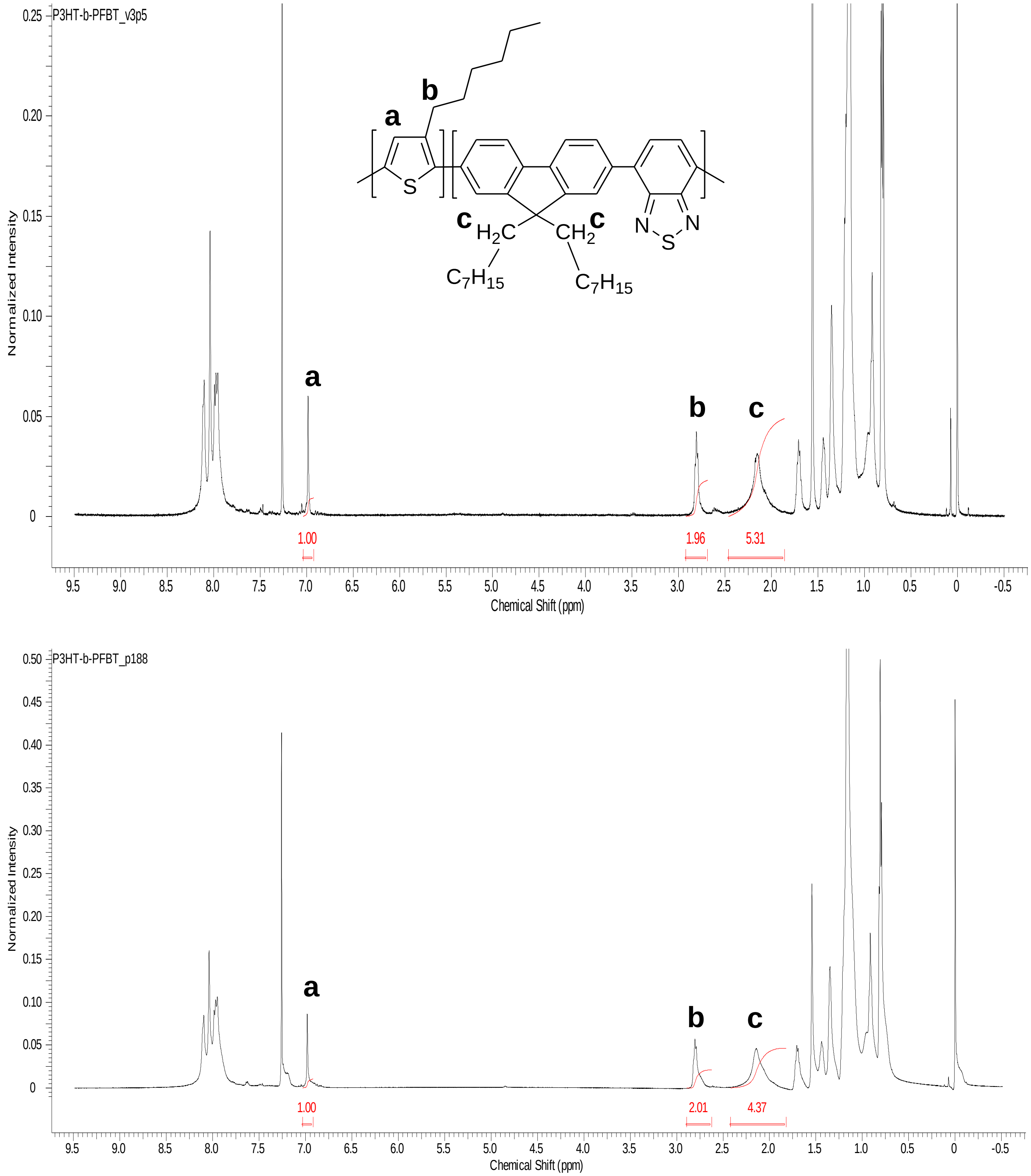


Figure S2. ^{1}H NMR spectrum of P3HT51-*b*-PFBT 66 (top) and P3HT81-*b*-PFBT90 (bottom).

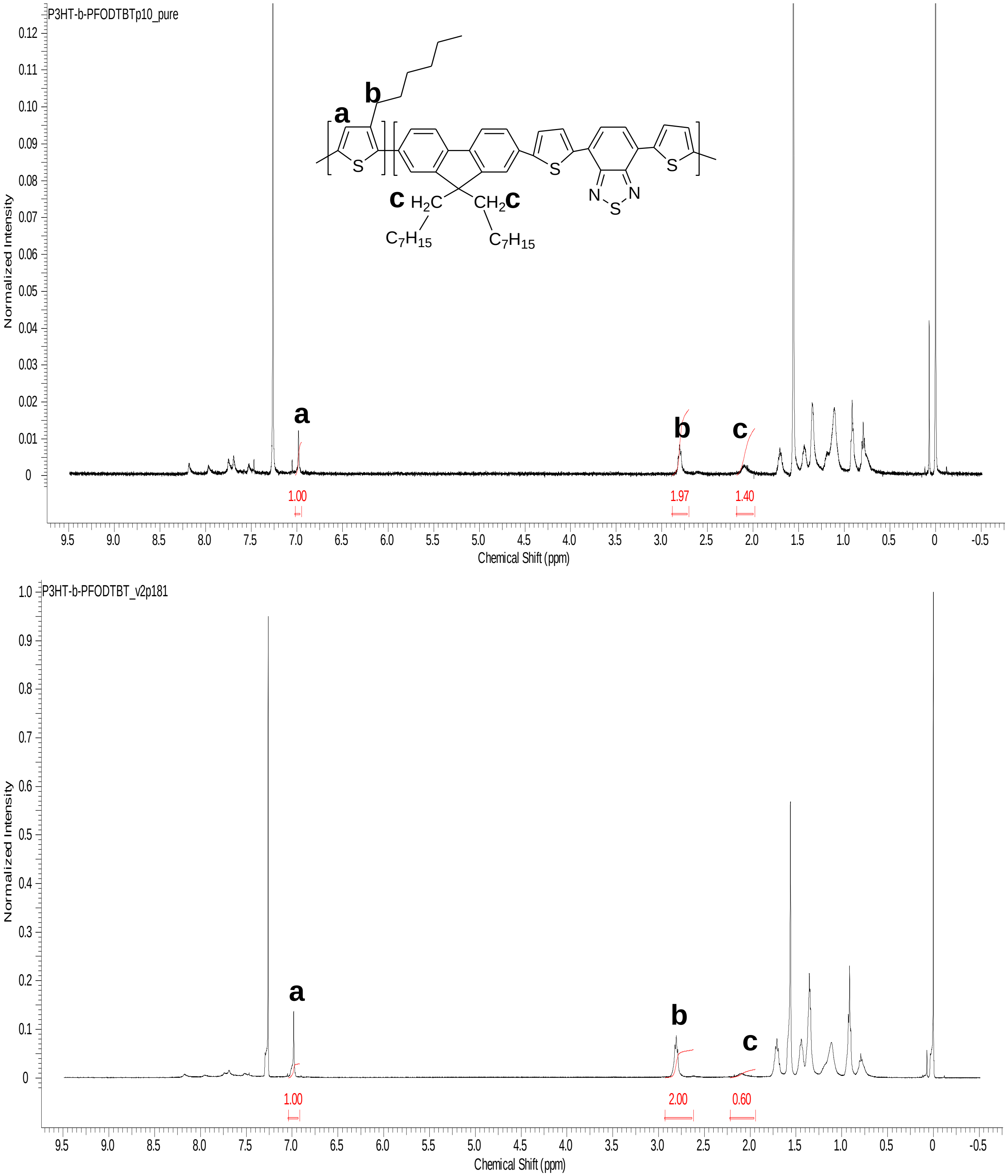


Figure S3. ^{1}H NMR spectrum of P3HT51-*b*-PFTBT17 (top) and P3HT81-*b*-PFTBT12 (bottom).

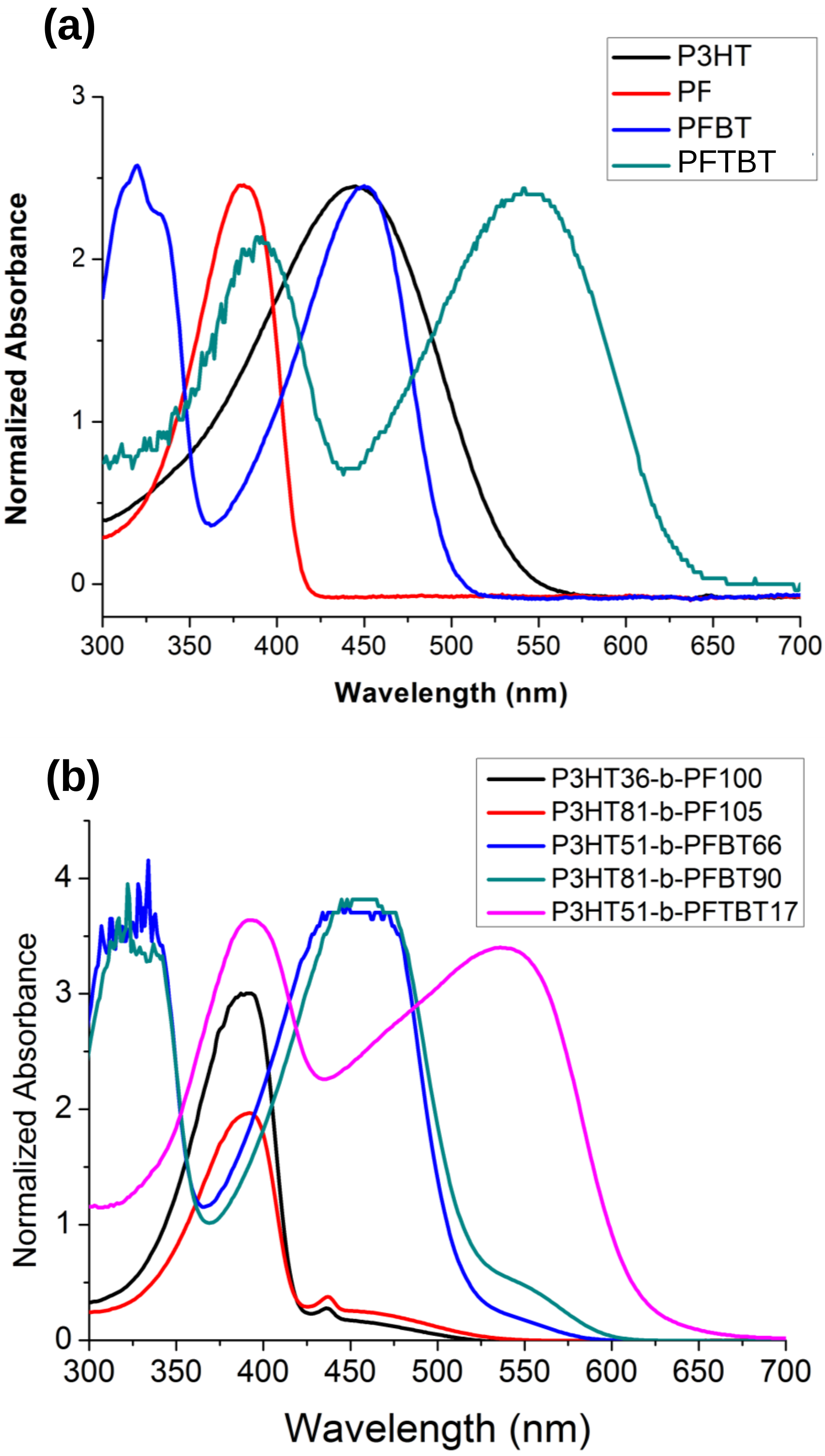
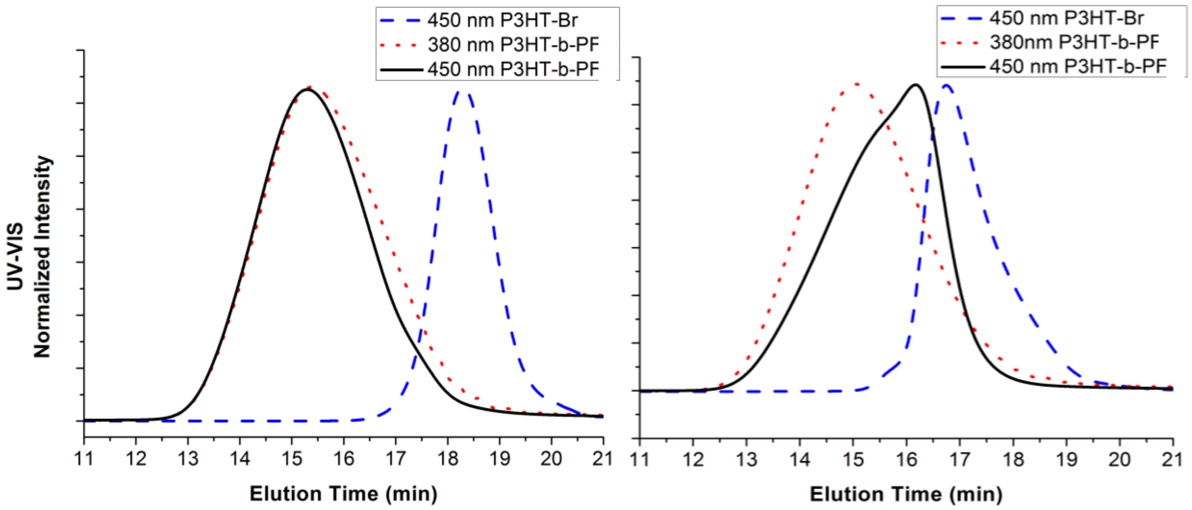
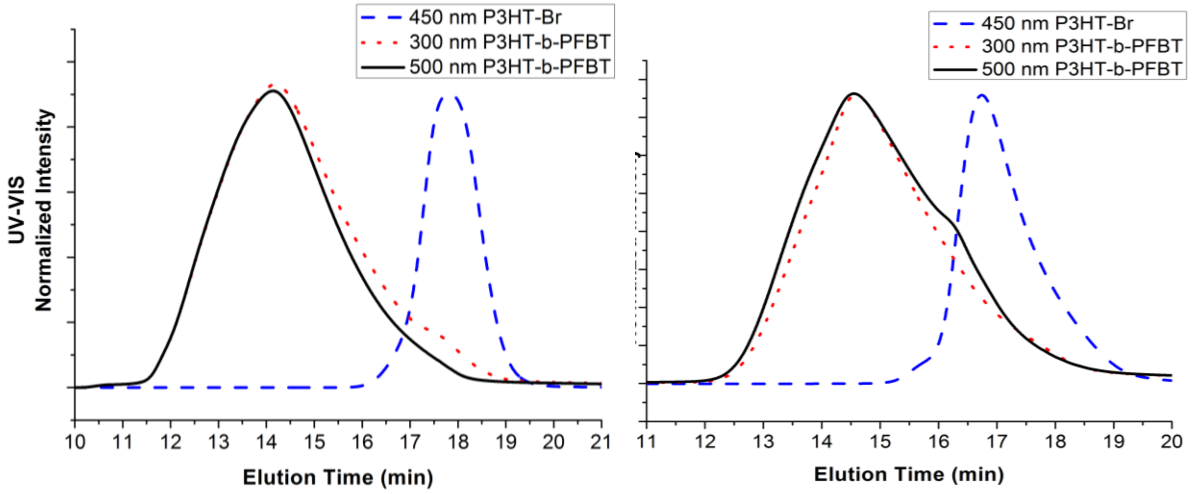

(a)
P3HT
PF
PFBT
PFTBT
Normalized Absorbance
0
1
2
3
300
350
400
450
500
550
600
650
700
Wavelength (nm)
(b)
P3HT36-b-PF100
P3HT81-b-PF105
P3HT51-b-PFBT66
P3HT81-b-PFBT90
P3HT51-b-PFTBT17
Normalized Absorbance
0
1
2
3
4
300
350
400
450
500
550
600
650
700
Wavelength (nm)

Figure S4. (a) UV-VIS absorbance spectra for P3HT, PF, PFBT, and PFTBT homopolymers and (b) UV-VIS absorbance spectra for block copolymers.

(a) P3HT36-*b*-PF100 (b) P3HT81-*b*-PF105



(c) P3HT51-*b*-PFBT66 (d) P3HT81-*b*-PFBT90



(e) P3HT51-*b*-PFTBT17 (f) P3HT81-*b*-PFTBT12

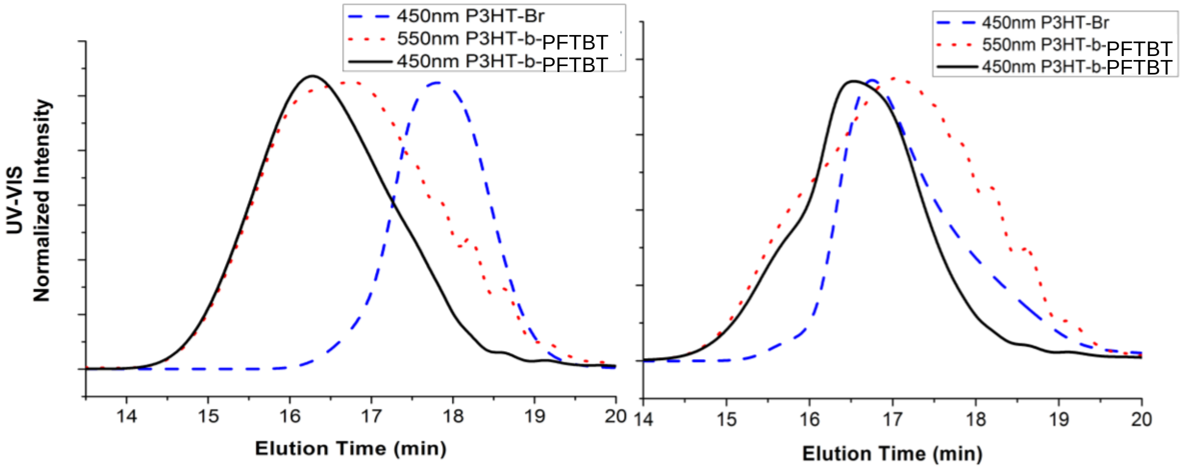


Figure S5. SEC-UVVIS traces for block copolymers and P3HT macroreagents. All traces are normalized for clarity. SEC-UVVIS traces at 380 nm for P3HT-*b*-PF, 300 nm for P3HT-*b*-PFBT, and 450 nm for P3HT-*b*-PFTBT were corrected as described in Experimental Methods. SEC-UVVIS traces for block copolymers reflect the molecular weight distribution of one polymer block only.

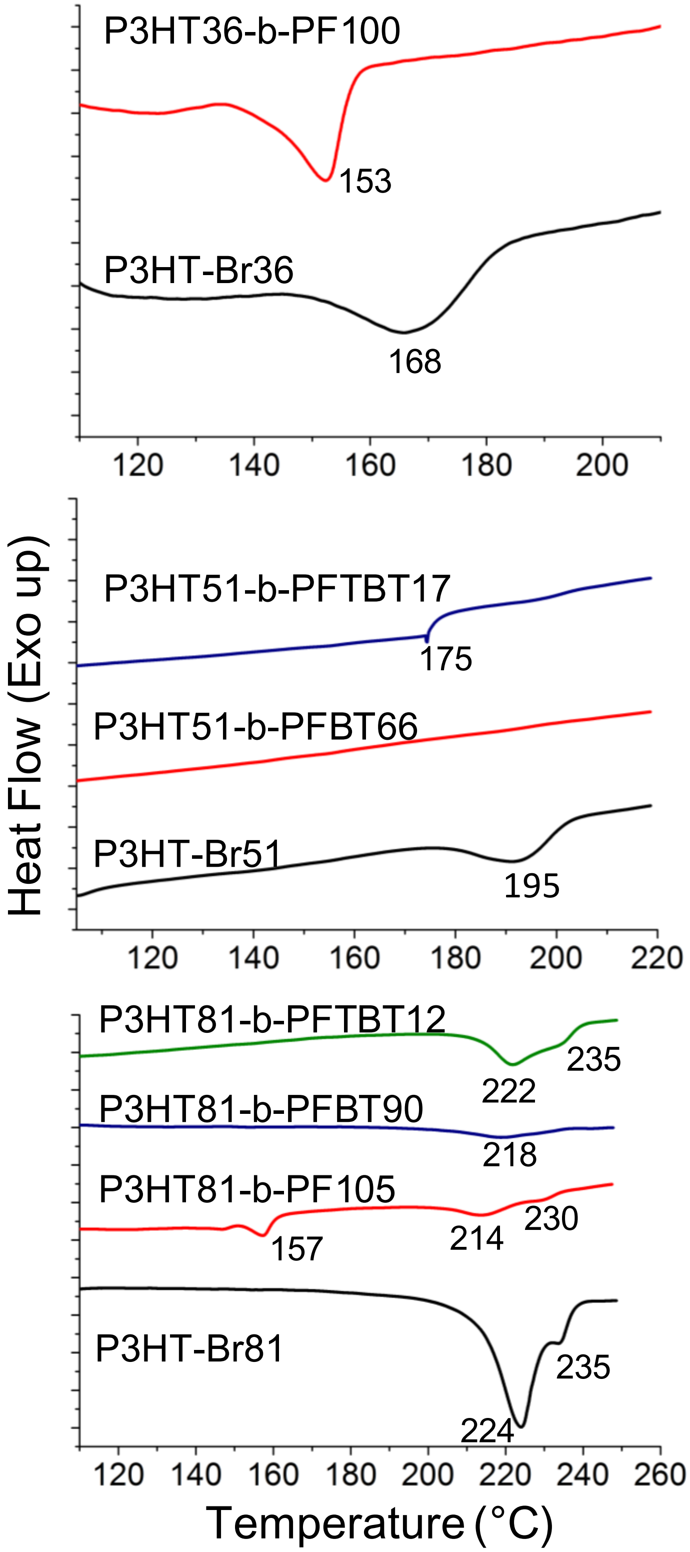


Figure S6. DSC data for all-conjugated block copolymers and P3HT-Br macroreagents. Third heating cycles are shown for all samples, and a heating rate of 5 °C/min is used for all samples.

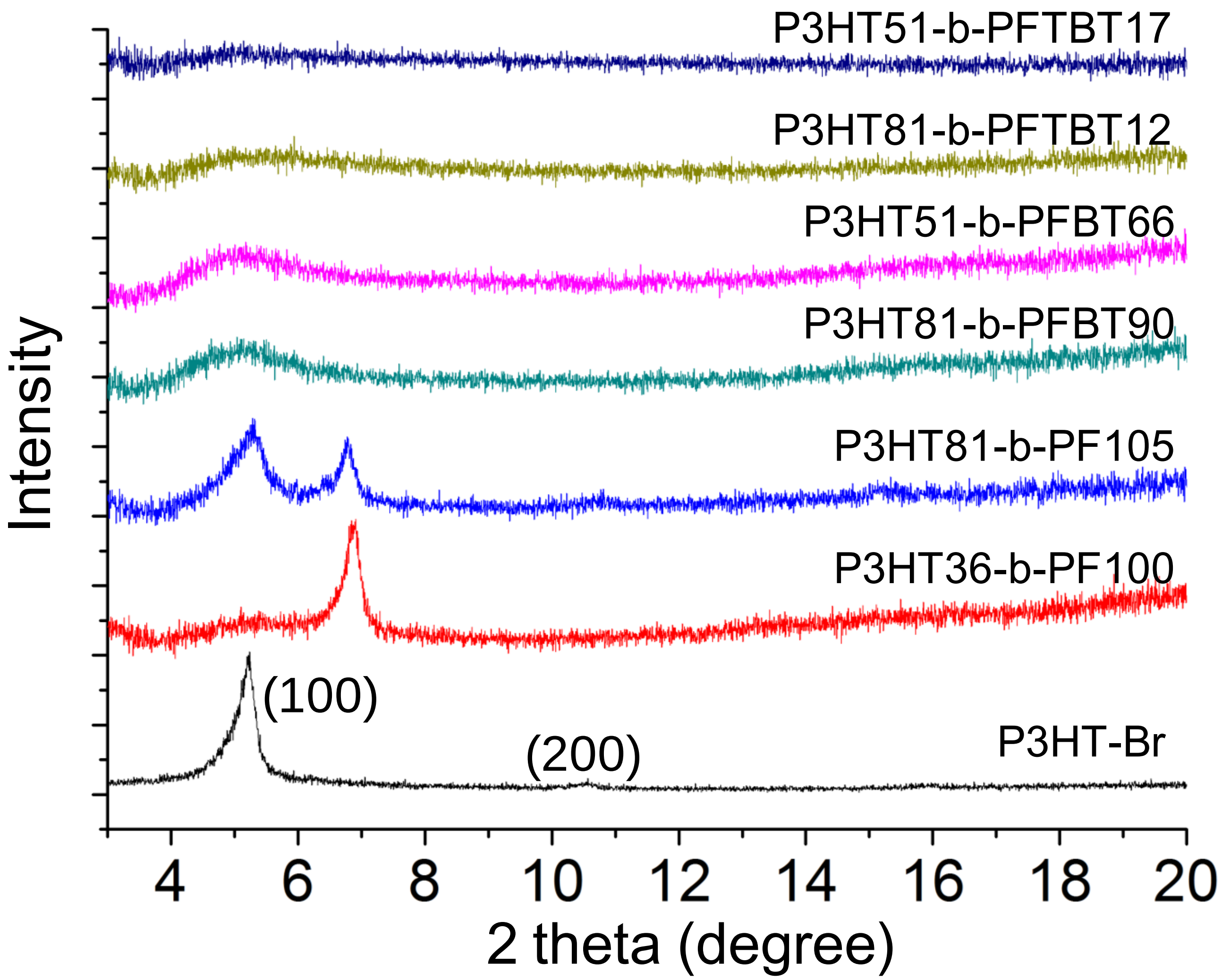
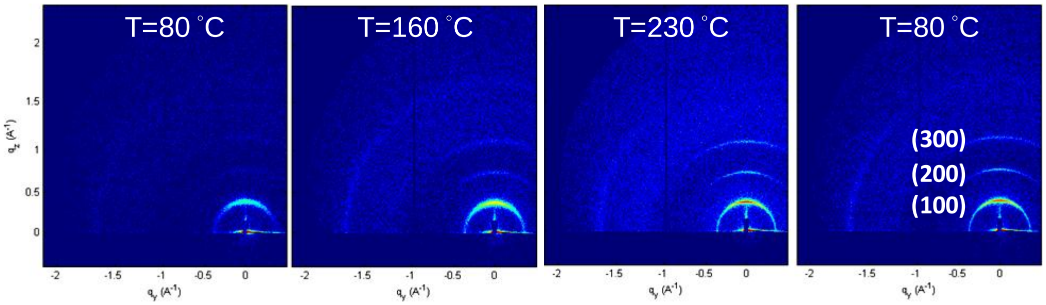
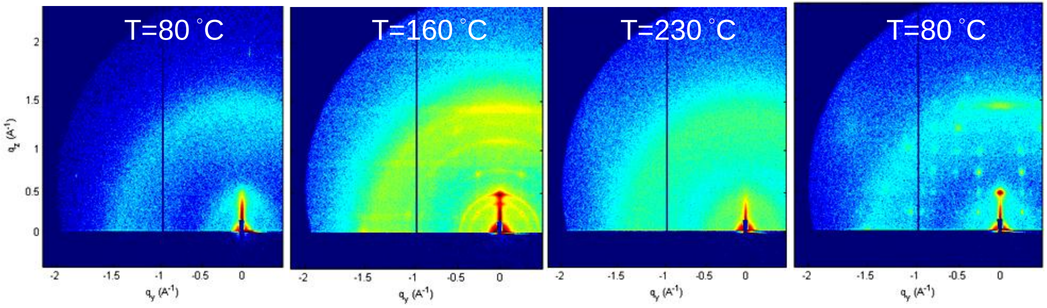


Figure S7. XRD analysis of all-conjugated block copolymer thin films and representative P3HT-Br thin films.

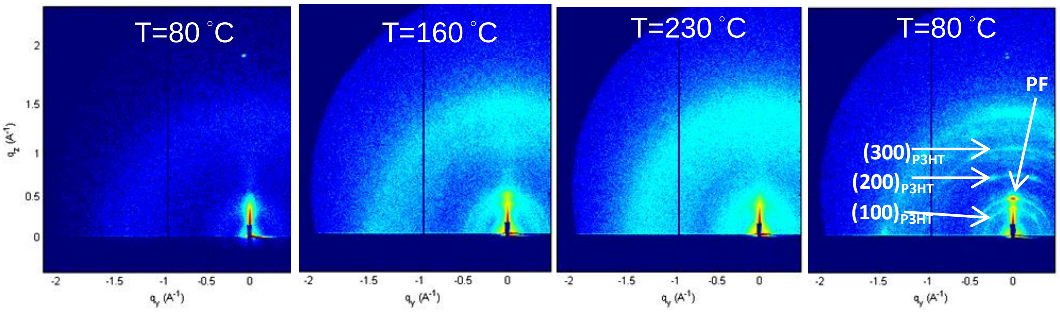
(a) P3HT-Br81



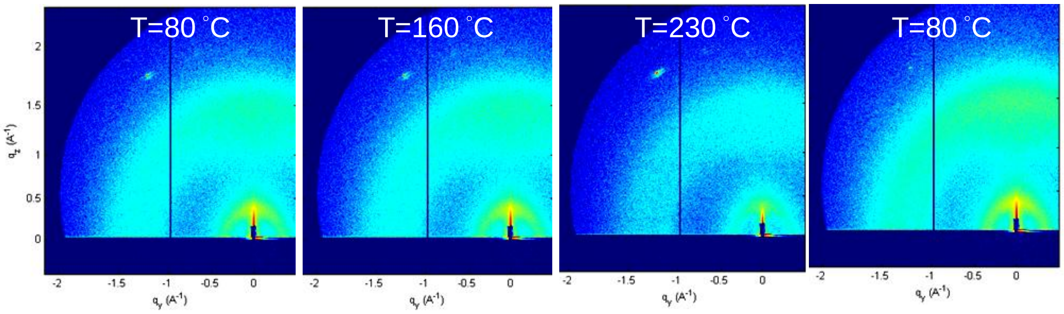
(b) P3HT36-b-PF100



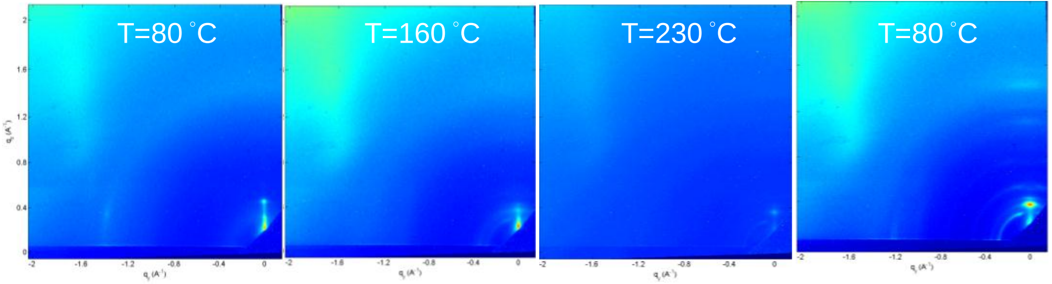
(c) P3HT81-b-PF105



(d) P3HT51-*b*-PFBT66



(e) P3HT81-*b*-PFBT90



(f)P3HT51-*b*-PFTBT17

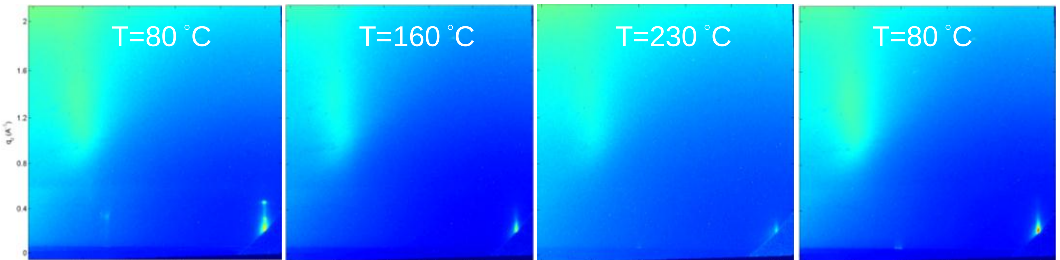


Figure S8. Temperature-dependent GIWAXS measurements for block copolymer polymer thin films. (a) P3HT-Br81, (b) P3HT36-*b*-PF100, (c) P3HT81-*b*-PF105, (d) P3HT51-*b*-PFBT66, (e) P3HT81-*b*-PFBT90, (f) P3HT51-*b*-PFTBT17. Samples were heated from room temperature and measured at 80 °C, 160 °C and 230 °C before cooling and measuring again at 80 °C, as indicated for each sample from left to right. All samples were measured at an incident angle of 0.25° and 20 second exposure time. In frame a, the (100), (200), and (300) P3HT reflections are identified. These appear at q_z = 0.38, 0.75, and 1.12 $Å^{-1}$, respectively. In frame c, scattering peaks corresponding to P3HT crystallites (at at q_z = 0.38, 0.75, and 1.12 $Å^{-1}$) and PF crystallites are identified. The specific PF crystallite peak identified appears at q_z = 0.50 $Å^{-1}$.

References

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3. R. H. Lohwasser and M. Thelakkat, *Macromolecules*, 2011, **44**, 3388-3397.

4. Z. Jiang, X. F. Li, J. Strzalka, M. Sprung, T. Sun, A. R. Sandy, S. Narayanan, D. R. Lee and J. Wang, *J. Synchrot. Radiat.*, 2012, **19**, 627-636.

5. Z. Jiang, *GIXSGUI is available for download:* *http://www.aps.anl.gov/Sectors/Sector8/Operations/GIXSGUI.html*.