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Supplementary Information

Evaluating Structure-Function Relationships Toward Three-Component Conjugated Polymers via Direct Arylation Polymerization (DArP) for Stille-Convergent Solar Cell Performance

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1. Materials & Methods

Unless otherwise noted, all reagents were purchased and used as received from commercial sources. Solvents were purchased from VWR and used without purification except for tetrahydrofuran (THF), which was dried over sodium/benzophenone before distillation, and anhydrous 2-methyltetrahydrofuran (MeTHF) which was distilled onto molecular sieves to remove the inhibitor. All reactions were performed under dry N_2 in glassware that was pre-dried in an oven, unless otherwise noted. Flash chromatography was performed on a Teledyne CombiFlash Rf instrument with RediSep Rf normal phase disposable columns. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Varian Mercury 400 NMR Spectrometer (small molecules) or a Varian Mercury 600 NMR spectrometer (polymers).

N,N-dimethylacetamide (anhydrous DMA, 99.9%), neodecanoic acid (NDA), thiophene, 3,4-ethylenedioxythiophene (EDOT), cesium carbonate (Cs_2CO_3), potassium carbonate (K_2CO_3), 2,2'-bithiophene (BT) were purchased from Alfa Aesar. Palladium acetate ($Pd(OAc)_2$ was purchased from TCI (USA). Tris(dibenzylideneacetone)dipalladium(0) (Pd_2dba_3) and Tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$ were purchased from Strem Chemicals Inc. The monomers 2-bromo-3-hexylthiophene, 2-bromo-5-trimethyltin-3-hexylthiophene, 2,5-bis(trimethyltin)thiophene, 2,5-diethylhexyl-3,6-dithiophene-2-yl-pyrrolo[3,4-c]pyrrole-1,4-dione, and 2,5-diethylhexyl-3,6-bis(5-bromothiophene-2-yl)pyrrolo[3,4-c]-pyrrole-1,4-dione were synthesized following published procedures.[1,2] The synthesis of (E)-2-(2-(thiophen-2-yl)vinyl)thiophene (TvT),[3] 4,4'-dimethyl-2,2'-bithiazole (BTz),[4] 2,8-dibromo-4,10-bis(2-ethylhexyl)thieno[2',3':5,6]pyrido[3,4-g]thieno[3,2-c]isoquinoline-5,11(4H,10H)-dione (Br-TPTI),[5] 5,8-dibromo-2,3-bis(3-(octyloxy)phenyl)quinoxaline (Br-QX),[6] 4,7-bis(5-bromo-4-

hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (Br-BTD),[7] 1,3-dibromo-5-octyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (Br-TPD),[8] were executed without modification as reported in literature. The synthesis of Stille P3HT and Stille P3HTT-DPP was synthesized without modification as reported in the literature:[1,2]

Number average molecular weight (M_n) and polydispersity (Đ) were determined by size exclusion chromatography (SEC) using a Viscotek GPC Max VE 2001 separation module and a Viscotek Model 2501 UV detector, with 70 °C HPLC grade 1,2-dichlorobenzene (*o*-DCB) as eluent at a flow rate of 0.6 mL/min on one 300 × 7.8 mm TSK-Gel GMHHR-H column (Tosoh Corp). The instrument was calibrated vs. polystyrene standards (1050−3,800,000 g/mol), and data were analyzed using OmniSec 4.6.0 software. Polymer samples for SEC measurements were prepared by dissolving a polymer in hot HPLC grade *o*-DCB at a concentration of 0.5 mg/mL and allowed to cool to room temperature prior to filtering through a 0.2 μm PTFE filter.

Cyclic voltammetry (CV) was performed on Princeton Applied Research VersaStat3 potentiostat under the control of VersaStudio Software. A standard three-electrode cell based on a Pt wire working electrode, a silver wire pseudo reference electrode (calibrated vs Fc/Fc^+ which is taken as 5.1 eV vs vacuum),[9,10] and a Pt wire counter electrode was purged with nitrogen and maintained under a nitrogen atmosphere during all measurements. Polymer films were made by drop-casting an *o*-DCB solution of polymer (10 mg/mL) and tetrabutylammonium hexafluorophosphate ($TBAPF_6$) (30 mg/mL) directly onto the Pt wire and dried under nitrogen prior to measurement. Acetonitrile was distilled over CaH_2 prior to use, and $TBAPF_6$ (0.1 M) was used as the supporting electrolyte.

For polymer thin-film measurements, solutions were spin-coated onto pre-cleaned glass slides from *o*-dichlorobenzene (*o*-DCB) solutions at 7 mg/mL. UV−vis absorption spectra were obtained on a Perkin-Elmer Lambda 950 spectrophotometer. Thicknesses of the samples and grazing incidence X-ray diffraction (GIXRD) measurements were obtained using Rigaku diffractometer Ultima IV using a Cu Kα radiation source ($\lambda = 1.54$ Å) in the reflectivity and grazing incidence X-ray diffraction mode, respectively. A GIXRD sampling step of 0.05 was utilized for the acquisition of diffraction data, thus 2θ peak positions (± 0.05) will result in variability of the d_{100} spacing parameters of ± 0.2 Å.

DSC profiles were recorded on a PerkinElmer DSC 8000 under N_2 with a scan rate of 10 °C/min. Sample size was about 3 mg, and polymers were used as obtained after Soxhlet extraction. The second cycle is provided in the Supporting Information below.

General Procedure for Polymerization via Stille.

All monomers were dissolved in dry DMF to give a 0.04 M solution. The solution was then degassed for 20 min. 4 mol% $Pd(PPh_3)_4$ was added in one portion, the solution was degassed for 15 additional minutes and then heated for 48 hours at 95°C. Then the reaction mixture was cooled to r.t. and precipitated in MeOH. Purification was achieved via Soxhlet extraction using MeOH, hexanes and chloroform for all polymers.

Stille P3HT (A1): Used conditions as reported above with 2-bromo-5-trimethyltin-3-hexylthiopehene (1 mmol). Yield (after Soxhlet extraction): 68%, Mn = 17.9 kDa, PDI = 2.40. ^{1}H

NMR (600 MHz, $CDCl_3$) δ6.98 (s, 1H), 2.81-2.57 (2H), 1.71 (m, 2H), 1.44 (m, 2H), 1.36 (m, 4H), 0.92 (m, 3H).

Stille P3HTT-DPP (B1): Used conditions as reported above with 2-bromo-5-trimethyltin-3-hexylthiopehene (263 mg, 0.64 mmol), 2,5-bis(trimethyltin)thiophene (33 mg, 0.08 mmol), 2,5-diethylhexyl-3,6-bis(5-bromothiophene-2-yl)pyrrolo[3,4-c]-pyrrole-1,4-dione (55 mg, 0.08 mmol). Yield (after Soxhlet extraction): 60 %, Mn = 13.8 kDa, PDI = 2.89. ^{1}H NMR (600 MHz, $CDCl_3$) δ8.93 (s, 0.23H), 7.13-6.97 (m, 1.29H), 4.05 (s br, 0.45H), 2.80-2.56 (2H), 1.94 (s, 0.22H), 1.71 (m, 1.98H), 1.44, 1.36 (m, 8.76H), 0.92 (s, 5.03H).

General Procedure for Polymerization via Fagnou DArP.

Monomers were dissolved in dry DMA to yield a predetermined monomer concentration (outlined in the main text) in an oven-dried and cooled under N_2 three-neck flask. Then neodecanoic acid (or PivOH) and 150 mol% K_2CO_3 were added to the reaction mixture. The solution was degassed with nitrogen flow for 10 minutes before $Pd(OAc)_2$ was added and the reaction mixture was further degassed for 20 minutes. Then the reaction was immersed into a pre-heated oil bath at the appropriate temperature and stirred rigorously to disperse the insoluble base under nitrogen for 48 hours. Then the reaction was cooled, a small about of chlorobenzene was added to the reaction mixture and it was precipitated into methanol, filtered, and purified by Soxhlet extraction with methanol, hexanes, and finally chloroform. The final chloroform fraction was concentrated *in vacuo* and precipitated into methanol. The polymers were filtered and dried overnight under high vacuum.

DArP P3HT (A2): Used conditions as reported above with 2-bromo-3-hexylthiophene (247.1 mg, 1.0 mmol) and PivOH (30.6 mg, 0.3 mmol) at 70°C in DMA (25 mL). Yield (after Soxhlet extraction): 55%, M_n = 17.1 kDa, PDI = 3.11. ^{1}H NMR (600 MHz, $CDCl_3$) δ6.98 (s, 1H), 2.81-2.57 (2H), 1.71 (m, 2H), 1.44 (m, 2H), 1.36 (m, 4H), 0.92 (m, 3H).

DArP P3HT (A3): Used conditions as reported above with 2-bromo-3-hexylthiophene (247 mg, 1.0 mmol) and NDA (0.3 mmol) at 70°C in DMA (25 mL). Yield (after Soxhlet extraction): 60%, M_n = 18.2 kDa, PDI = 2.77. ^{1}H NMR (600 MHz, $CDCl_3$) δ6.98 (s, 1H), 2.81-2.57 (2H), 1.70 (m, 2H), 1.44 (m, 2H), 1.34 (m, 4H), 0.92 (m, 3H).

DArP P3HT (A4): Used conditions as reported above with 2-bromo-3-hexylthiophene (247 mg, 1.0 mmol) and NDA (0.038 mmol) at 160°C in 3.125 mL DMA. Yield (after Soxhlet extraction): 88%, M_n = 21.6 kDa, PDI = 3.47. ^{1}H NMR (600 MHz, $CDCl_3$) δ6.98 (s, 1H), 2.81-2.57 (2H), 1.70 (m, 2H), 1.44 (m, 2H), 1.34 (m, 4H), 0.92 (m, 3H).

DArP P3HTT-DPP (B2): Used conditions as reported above with 2-bromo-3-hexylthiophene (247 mg, 1.0 mmol), 2,5-diethyl-hexyl-3,6-bis(5-bromothiophene-2-yl)pyrrole[3,4-c]-pyrrole-1,4-dione (85.3 mg, 0.125 mmol), and thiophene (10 μL, 10.5 mg, 0.125 mmol), which was added via a microliter syringe. Yield (after Soxhlet extraction): 41%, M_n = 9.1 kDa, PDI = 3.43. ^{1}H NMR (600 MHz, $CDCl_3$) δ9.06 -8.93 (0.23H), 7.13-6.97 (m, 1.29H), 4.05 (s br, 0.48H), 2.80-2.57 (2H), 1.94 (s, 0.28H), 1.71 (m, 1.36H), 1.44, 1.36 (m, 8.46H), 0.92 (s, 4.95H).

DArP P3HTT-DPP (B3): Used conditions as reported above with 2-bromo-3-hexylthiophene (247 mg, 1.0 mmol), 2,5-diethylhexyl-3,6-dithiophene-2-yl-pyrrolo[3,4-c]pyrrole-1,4-dione (65.6 mg, 0.125 mmol), and 2,5-dibromothiophene (14.1 μL, 30.2 mg, 0.125 mmol), which was added via a microliter syringe. Yield (after Soxhlet extraction): 18%, M_n = 4.4 kDa, PDI = 1.45. ^{1}H NMR (600 MHz, $CDCl_3$) δ9.05-8.85 (0.11H), 7.13-6.97 (m, 1.39H), 4.05 (s br, 0.25H), 2.80-2.56 (2H), 1.94 (s, 0.19H), 1.71 (m, 2.62H), 1.44, 1.36 (m, 10.29H), 0.92 (s, 5.50H).

General Procedure for Polymerization via Ozawa DArP.

Monomers, neodecanoic acid, Cs_2CO_3, were dissolved in dry THF or MeTHF to yield a monomer concentration of 0.4M in a 15 mL high pressure vessel with a Teflon screw cap. This was degassed with nitrogen for 5 minutes before Cs_2CO_3, P(*o*-anisyl)$_3$, and Pd_2dba_3 were added and the vessel was further degassed for 5 minutes before the reaction was heated to 120°C for 12h. Then the reaction was cooled, a small about of chlorobenzene was added to the reaction mixture and it was precipitated into methanol, filtered, and purified by Soxhlet extraction with methanol, hexanes, and finally chloroform. The final chloroform fraction was concentrated *in vacuo* and precipitated into methanol. The polymers were filtered and dried overnight under high vacuum.

DArP P3HT (A5): Used conditions as reported above with 2-bromo-3-hexylthiophene (247 mg, 1.0 mmol) and NDA (1 mmol) at 120°C in THF (2.5 mL). Yield (after Soxhlet extraction): 81%, M_n = 14.5 kDa, PDI = 2.03. ^{1}H NMR (600 MHz, $CDCl_3$) δ6.98 (s, 1H), 2.81-2.57 (2H), 1.71 (m, 2H), 1.44 (m, 2H), 1.36 (m, 4H), 0.92 (m, 3H).

DArP P3HT (A6): Used conditions as reported above with 2-bromo-3-hexylthiophene (247 mg, 1.0 mmol) and NDA (1 mmol) at 120°C in THF (2.5 mL). Yield (after Soxhlet extraction): 74%, M_n = 19.7 kDa, PDI = 2.11. ^{1}H NMR (600 MHz, $CDCl_3$) δ6.98 (s, 1H), 2.81-2.57 (2H), 1.71 (m, 2H), 1.44 (m, 2H), 1.36 (m, 4H), 0.93 (m, 3H).

DArP P3HTT-DPP (B4): Used conditions as reported above with 2-bromo-3-hexylthiophene (247 mg, 1.0 mmol), 2,5-diethyl-hexyl-3,6-bis(5-bromothiophene-2-yl)pyrrole[3,4-c]-pyrrole-1,4-dione (85.3 mg, 0.125 mmol), and thiophene (10 µL, 10.5 mg, 0.125 mmol), which was added via a microliter syringe. Solvent was 3.1 mL of THF. Yield (after Soxhlet extraction): 62%, M_n = 9.7

kDa, PDI = 2.26. ^{1}H NMR (600 MHz, $CDCl_3$) δ8.94 (0.19H), 7.14-6.98 (m, 1.27H), 4.05 (s br, 0.38H), 2.80-2.57 (2H), 1.94 (s, 0.14H), 1.71 (m, 2.22H), 1.44, 1.36 (m, 8.22H), 0.92 (s, 4.63H).

DArP P3HTT-DPP (B5): Used conditions as reported above with 2-bromo-3-hexylthiophene (247 mg, 1.0 mmol), 2,5-diethylhexyl-3,6-dithiophene-2-yl-pyrrolo[3,4-c]pyrrole-1,4-dione (65.6 mg, 0.125 mmol), and 2,5-dibromothiophene (14.1 µL, 30.2 mg, 0.125 mmol), which was added via a microliter syringe. Solvent was 3.1 mL of THF. Yield (after Soxhlet extraction): 68%, M_n = 9.8 kDa, PDI = 1.97. ^{1}H NMR (600 MHz, $CDCl_3$) δ9.06 -8.96 (0.22H), 7.14-6.98 (m, 1.38H), 4.07 (s br, 0.42H), 2.80-2.57 (2H), 1.97 (s, 0.27H), 1.71 (m, 2.17H), 1.44, 1.36 (m, 8.69H), 0.92 (s, 4.98H).

DArP P3HTT-DPP (B6): Used conditions as reported above with 2-bromo-3-hexylthiophene (247 mg, 1.0 mmol), 2,5-diethyl-hexyl-3,6-bis(5-bromothiophene-2-yl)pyrrole[3,4-c]-pyrrole-1,4-dione (85.3 mg, 0.125 mmol), and thiophene (10 µL, 10.5 mg, 0.125 mmol), which was added via a microliter syringe. Solvent was 3.1 mL of MeTHF. Yield (after Soxhlet extraction): 77%, M_n = 15.8 kDa, PDI = 2.51. ^{1}H NMR (600 MHz, $CDCl_3$) δ8.93 (s, 0.20H), 7.13-6.97 (m, 1.26H), 4.06 (s br, 0.43H), 2.80-2.57 (2H), 1.94 (s, 0.13H), 1.71 (m, 2.05H), 1.44, 1.35 (m, 8.92H), 0.91 (s, 4.92H).

DArP P3HTT-DPP (B7): Used conditions as reported above with 2-bromo-3-hexylthiophene (247 mg, 1.0 mmol), 2,5-diethylhexyl-3,6-dithiophene-2-yl-pyrrolo[3,4-c]pyrrole-1,4-dione (65.6 mg, 0.125 mmol), and 2,5-dibromothiophene (14.1 µL, 30.2 mg, 0.125 mmol), which was added via a microliter syringe. Solvent was 3.1 mL of MeTHF. Yield (after Soxhlet extraction): 71%, M_n = 16.7 kDa, PDI = 2.44. ^{1}H NMR (600 MHz, $CDCl_3$) δ9.07-8.85 (0.21H), 7.13-6.97 (m, 1.56H), 4.05 (s br, 0.44H), 2.80-2.56 (2H), 1.98 (s, 0.21H), 1.71 (m, 2.20H), 1.44, 1.36 (m, 8.72H), 0.92 (s, 4.96H).

General Procedure for Semi-Random Analogs Polymerization via B6 conditions.

An oven-dried 15 mL high pressure vessel with a Teflon screw cap was cooled under nitrogen prior to being charged with 2-bromo-3-hexylthiophene (247 mg, 1.0 mmol), Cs_2CO_3 (978 mg, 3 mmol), NDA (172 mg, 1 mmol) and two other monomers as detailed in the table below:

P1	2,2'-bithiophene (BT) (20.8 mg, 0.125 mmol)	2,5-diethyl-hexyl-3,6-bis(5-bromothiophene-2-yl)pyrrole[3,4-c]-pyrrole-1,4-dione (85 mg, 0.125 mmol)
P2	(E)-2-(2-(thiophen-2-yl)vinyl)thiophene (TvT) (24.0 mg, 0.125 mmol)	2,5-diethyl-hexyl-3,6-bis(5-bromothiophene-2-yl)pyrrole[3,4-c]-pyrrole-1,4-dione (85 mg, 0.125 mmol)
P3	4,4'-dimethyl-2,2'-bithiazole (BTz) (24.5 mg, 0.125 mmol)	2,5-diethyl-hexyl-3,6-bis(5-bromothiophene-2-yl)pyrrole[3,4-c]-pyrrole-1,4-dione (85 mg, 0.125 mmol)
P4	3,4-ethylenedioxythiophene (EDOT) (via microliter syringe) (13.4 µL, 17.8 mg, 0.125 mmol)	2,5-diethyl-hexyl-3,6-bis(5-bromothiophene-2-yl)pyrrole[3,4-c]-pyrrole-1,4-dione (85 mg, 0.125 mmol)
P5	thiophene (via microliter syringe) (10 µL, 10.5 mg, 0.125 mmol)	2,8-Dibromo-4,10-bis(2-ethylhexyl)thieno[2',3':5,6]pyrido[3,4-g]thieno[3,2-c]isoquinoline-5,11(4H,10H)-dione (Br-TPTI) (88.4 mg, 0.125 mmol)
P6	thiophene (via microliter syringe) (10 µL, 10.5 mg, 0.125 mmol)	5,8-dibromo-2,3-bis(3-(octyloxy)phenyl)quinoxaline (Br-QX) (87.1 mg, 0.125 mmol)
P7	thiophene (via microliter syringe) (10 µL, 10.5 mg, 0.125 mmol)	4,7-bis(5-bromo-4-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (Br-BTD) (78.3 mg, 0.125 mmol)
P8	thiophene (via microliter syringe) (10 µL, 10.5 mg, 0.125 mmol)	1,3-dibromo-5-octyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (Br-TPD) (52.9 mg, 0.125 mmol)

After the addition of these monomers, some via microliter syringe, 3.1 mL of MeTHF was added via syringe. The mixture was degassed for 5 minutes before Pd_2dba_3 (11.4 mg, 0.0125 mmol) and P(*o*-anisyl)$_3$ (35.2 mg, 0.1 mmol) were added. This mixture was degassed for 5 more minutes before the Teflon screw cap with o-ring was tightened. The vessel was heated via oil bath at 120°C for 12h. The vessel was allowed to cool to RT, and the contents precipitated into cold MeOH and allowed to stir for several minutes before being filtered into a Soxhlet thimble and extracted with

MeOH, hexanes, and then chloroform. This chloroform fraction was concentrated and precipitated into methanol, filtered through nylon membrane, and dried under vacuum.

P1: Yield (after Soxhlet extraction): 76%, M_n = 16.3 kDa, PDI = 2.33. ^{1}H NMR (600 MHz, $CDCl_3$) δ8.94 (s, 0.21H), 7.13-6.97 (m, 1.78H), 4.06 (s br, 0.41H), 2.80-2.56 (2H), 1.98 (s, 0.68H), 1.71 (m, 3.02H), 1.44, 1.36 (m, 7.99H), 0.92 (s, 4.01H).

P2: Yield (after Soxhlet extraction): 63%, M_n = 14.2 kDa, PDI = 2.27. ^{1}H NMR (600 MHz, $CDCl_3$) δ8.93 (s, 0.22H), 7.13-6.97 (m, 1.97H), 4.06 (s br, 0.41H), 2.80-2.56 (2H), 1.98 (s, 0.55H), 1.71 (m, 2.17H), 1.43, 1.35 (m, 10.58H), 0.92 (s, 5.30H).

P3: Yield (after Soxhlet extraction): 73%, M_n = 15.8 kDa, PDI = 2.56. ^{1}H NMR (600 MHz, $CDCl_3$) δ8.93 (0.22H), 7.13-6.97 (m, 1.36H), 4.07 (s br, 0.47H), 2.80-2.55 (2H), 2.50 (m, 1.07), 1.94 (s, 0.29H), 1.71 (m, 2.38H), 1.43, 1.35 (m, 10.32H), 0.90 (s, 5.83H).

P4: Yield (after Soxhlet extraction): 71%, M_n = 17.7 kDa, PDI = 3.10. ^{1}H NMR (600 MHz, $CDCl_3$) δ9.11-8.93 (0.15H), 7.13-6.97 (m, 1.18H), 4.36 (m br, 0.34H), 4.07 (s br, 0.27), 2.80-2.56 (2H), 1.98 (s, 0.33H), 1.71 (m, 2.53H), 1.43, 1.35 (m, 10.13H), 0.92 (s, 5.16H).

P5: Yield (after Soxhlet extraction): 49%, M_n = 10.0 kDa, PDI = 2.05. ^{1}H NMR (600 MHz, $CDCl_3$) δ8.68-8.48 (0.23H), 7.13-6.97 (m, 1.31H), 4.28-4.15 (d, 0.42H), 2.79-2.57 (2H), 1.97 (s, 0.36H), 1.71 (m, 2.27H), 1.44, 1.36 (m, 8.16H), 0.92 (s, 4.62H).

P6: Yield (after Soxhlet extraction): 36%, M_n = 9.1 kDa, PDI = 1.88. ^{1}H NMR (600 MHz, $CDCl_3$) δ8.13 (s, 0.11H), 7.75 (s, 0.12), 7.48 (s, 0.10), 7.29 (m, 0.12), 7.13-6.97 (m, 1.14H), 3.90 (s, 0.33H), 2.81-2.57 (2H), 1.71 (s, 2.47H), 1.44, 1.35 (m, 8.48H), 0.92 (s, 3.87H).

P7: Yield (after Soxhlet extraction): 52%, M_n = 8.6 kDa, PDI = 2.14. ^{1}H NMR (600 MHz, $CDCl_3$) δ7.99 (s, 0.23H), 7.84 (s, 0.24), 7.13-6.97 (m, 1.21H), 2.90 (s, 0.55H), 2.81-2.57 (2H), 1.71 (m, 2.83H), 1.44, 1.35 (m, 7.39H), 0.92 (s, 3.42H).

P8: Yield (after Soxhlet extraction): 46%, M_n = 7.6 kDa, PDI = 1.97. ^{1}H NMR (600 MHz, $CDCl_3$) δ7.85 (s, 0.19H), 7.13-6.97 (m, 0.98H), 3.68 (s, 0.21H), 2.80-2.57 (2H), 1.71 (m, 2.38H), 1.44, 1.35 (m, 8.12H), 0.92 (s, 3.64H).

Device Fabrication and Characterization

All steps of device fabrication and testing were performed at ambient temperatures and humidity in air. ITO-coated glass substrates (10 Ω/sq, Thin Film Devices Inc.) were sequentially cleaned by sonication in detergent solution, deionized water, tetrachloroethylene, acetone, and isopropyl alcohol, and dried under a nitrogen stream. PEDOT:PSS (Clevios™ PH 1000, filtered with a 0.45 µm poly(vinylidene fluoride) (PVDF) syringe filter—Pall Life Sciences) was spin-coated on the freshly cleaned ITO-coated glass substrates and then annealed at 120 °C for 50 min under high vacuum to generate a 40 nm thick film. Separate solutions of the polymers and $PC_{61}BM$ were prepared in *o*-DCB. The solutions were stirred for 8 h before they were mixed at the desired ratios and stirred for 24 h to form a homogeneous solution prior to spin-coating.

The polymer:$PC_{61}BM$ active layer was filtered (with a 0.45 µm polytetrafluoroethylene (PTFE) syringe filter—Pall Life Sciences) and spin-coated on top of the PEDOT:PSS layer. Concentrations of the blends were 11 mg/mL respective to the total polymer weight. For consistency across all polymers, every device was kept in a nitrogen box for 30 min after spin-coating and then placed in the vacuum chamber for aluminium deposition. The substrates were pumped down to high vacuum ($<9.0\times10^{-7}$ torr) and aluminium (100 nm) was thermally evaporated at 3–6 Å/s using a

Denton Benchtop Turbo IV Coating System onto the active layer through shadow masks to define the active area of the devices as 5.18 mm^2.

The current density–voltage (J–V) characteristics of the photovoltaic devices were measured under ambient conditions using a Keithley 2400 source-measurement unit. An Oriel® Sol3A class AAA S11 solar simulator with a Xenon lamp (450 W) and an AM 1.5G filter was used as the solar simulator. An Oriel PV reference cell system 91150 V was used as the reference cell to calibrate the light intensity of the solar simulator (to 100 mW/cm^2), achieved by making the J_{sc} of the reference cell under simulated sunlight as high as it was under the calibration condition.

External quantum efficiency (EQE) measurements were performed using a 300 W Xenon arc lamp (Newport Oriel), chopped and filtered monochromatic light (250 Hz, 10 nm FWHM) from a Cornerstone 260 1/4 M double grating monochromator (Newport 74125) together with a light bias lock-in amplifier. A silicon photodiode calibrated at Newport was utilized as the reference cell.

Mobility was measured using a hole-only device configuration of ITO/PEDOT:PSS/Polymer/Al in the space charge limited current regime as described in literature.[11] The device preparation for a hole-only device was the same as that described above for solar cells and thicknesses were determined by GIXRD in the reflectivity mode. The dark current was measured under ambient conditions and humidity.

2. Small Molecule NMR Spectra

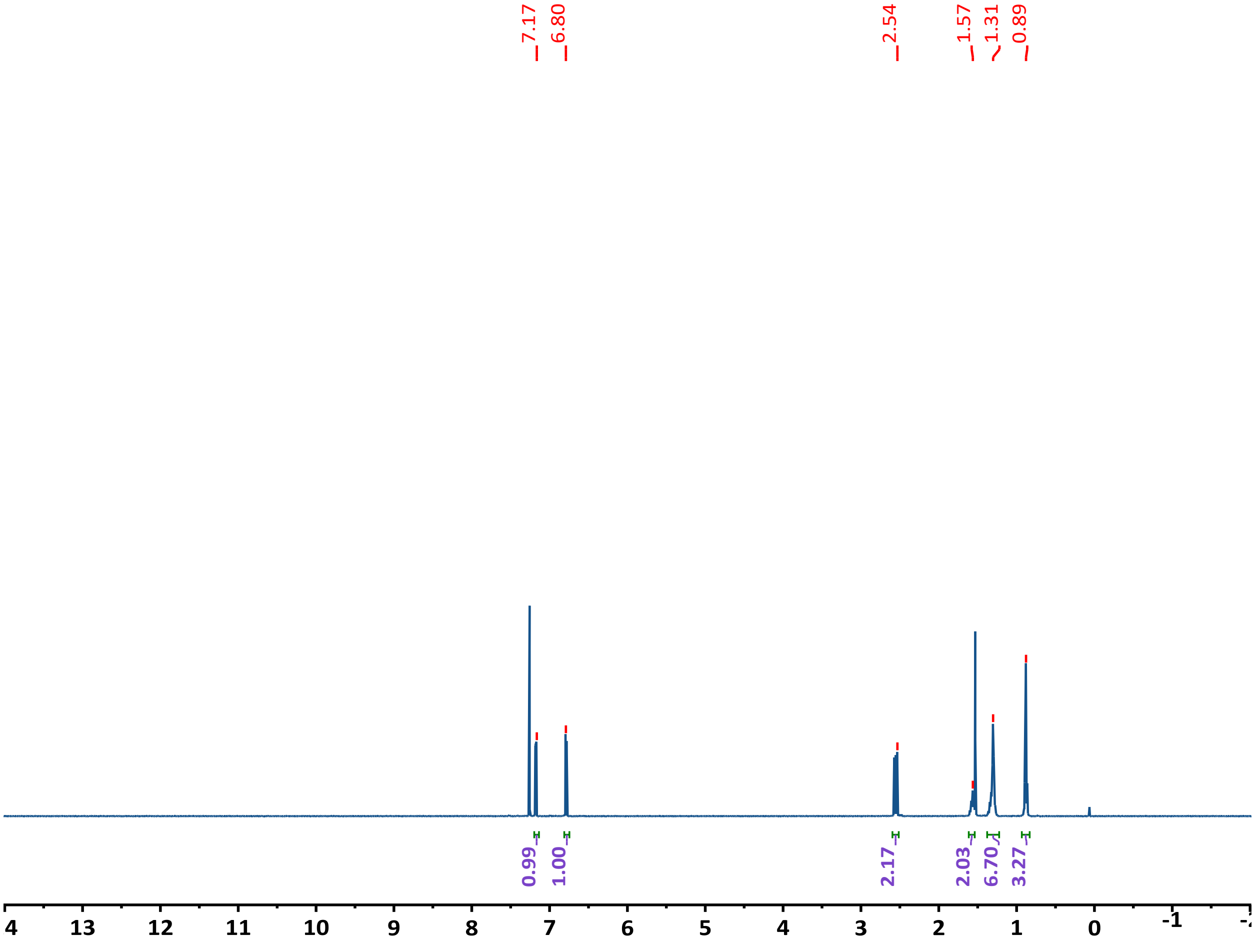

Figure S1. ^{1}H NMR for monomer, **2-bromo-3-hexylthiophene (2Br-3HT)**, in $CDCl_3$.

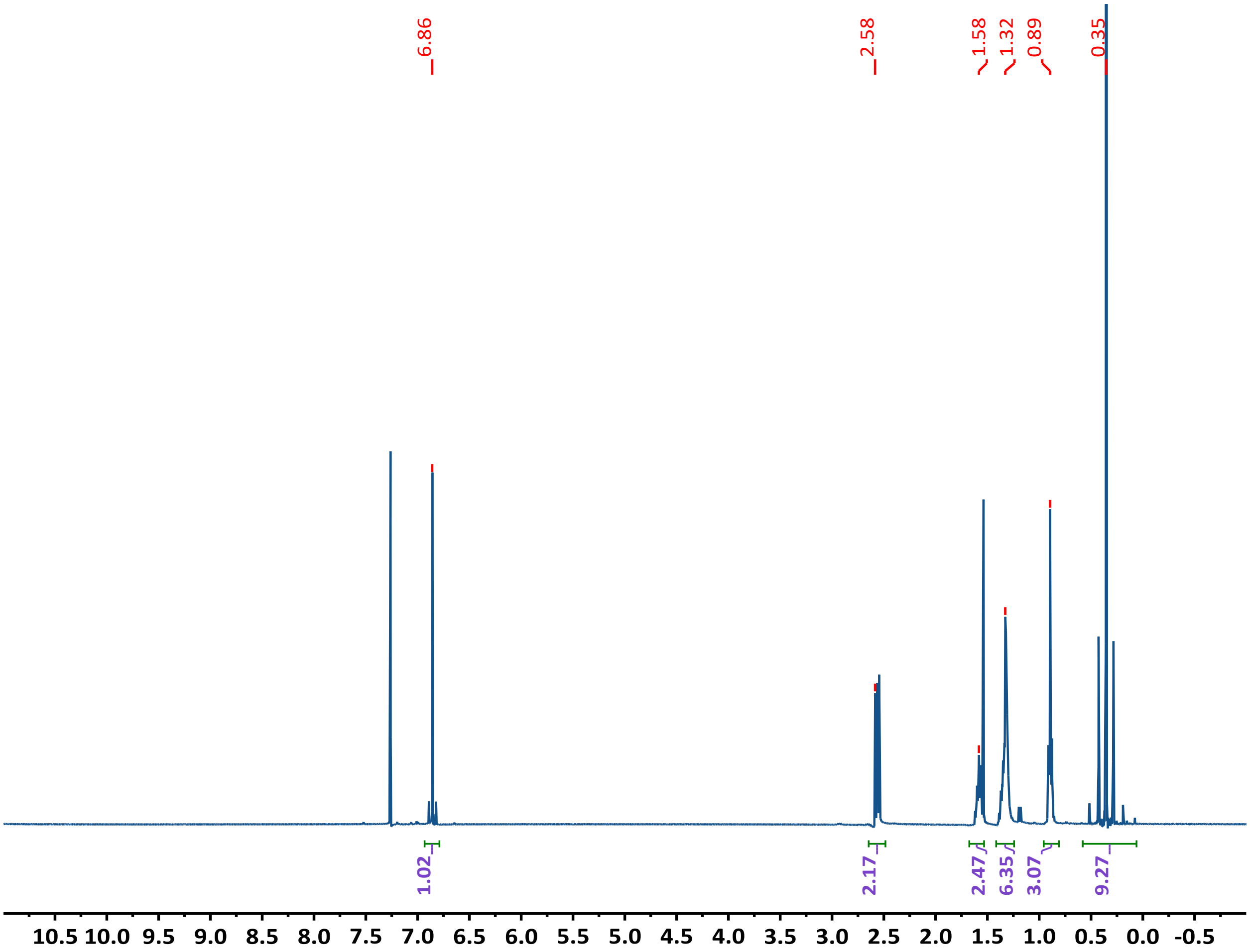

Figure S2. ^{1}H NMR for monomer, **2-bromo-5-trimethyltin-3-hexylthiophene**, in $CDCl_3$.

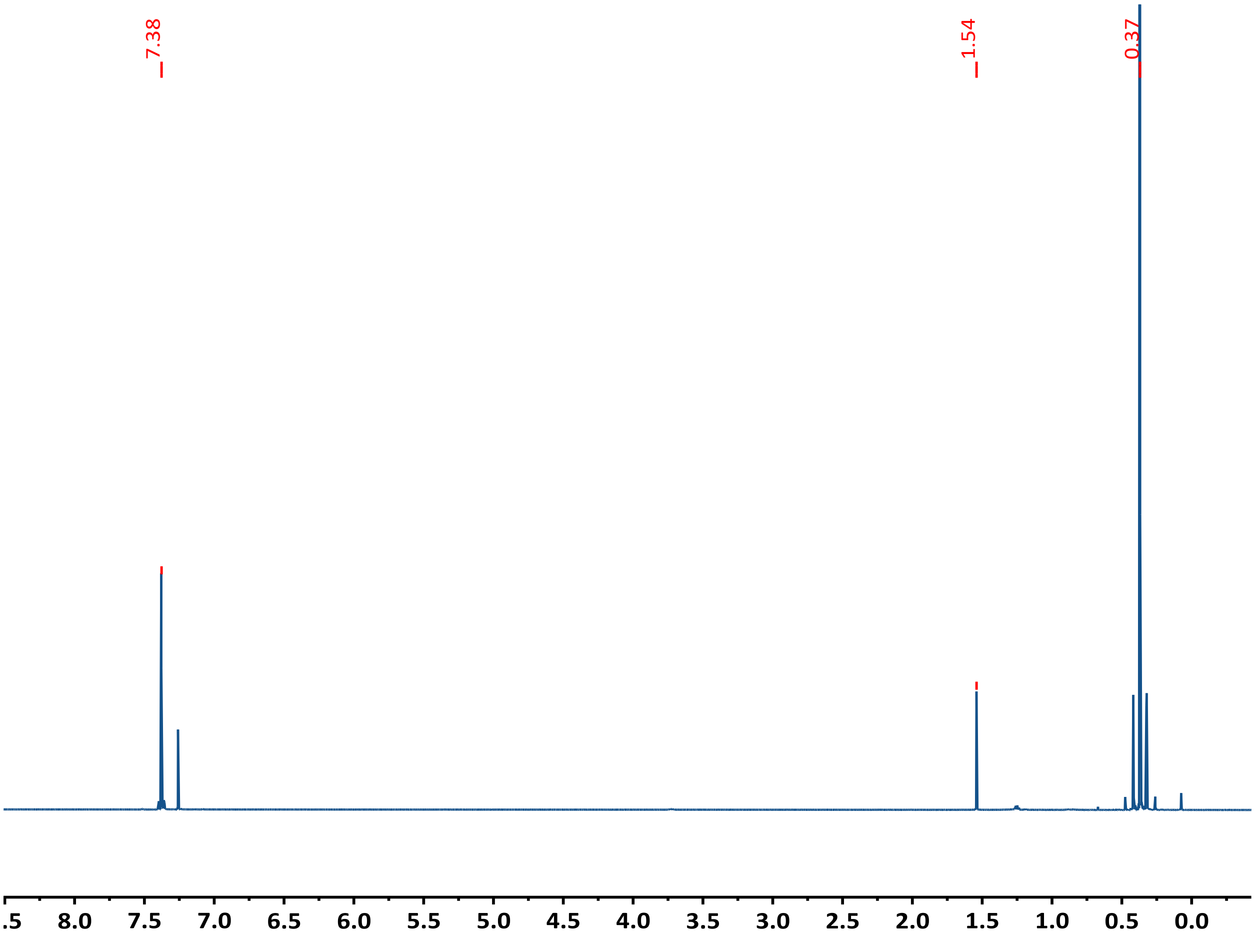

Figure S3. ^{1}H NMR for monomer, **2,5-bis(trimethyltin)thiophene**, in $CDCl_3$.

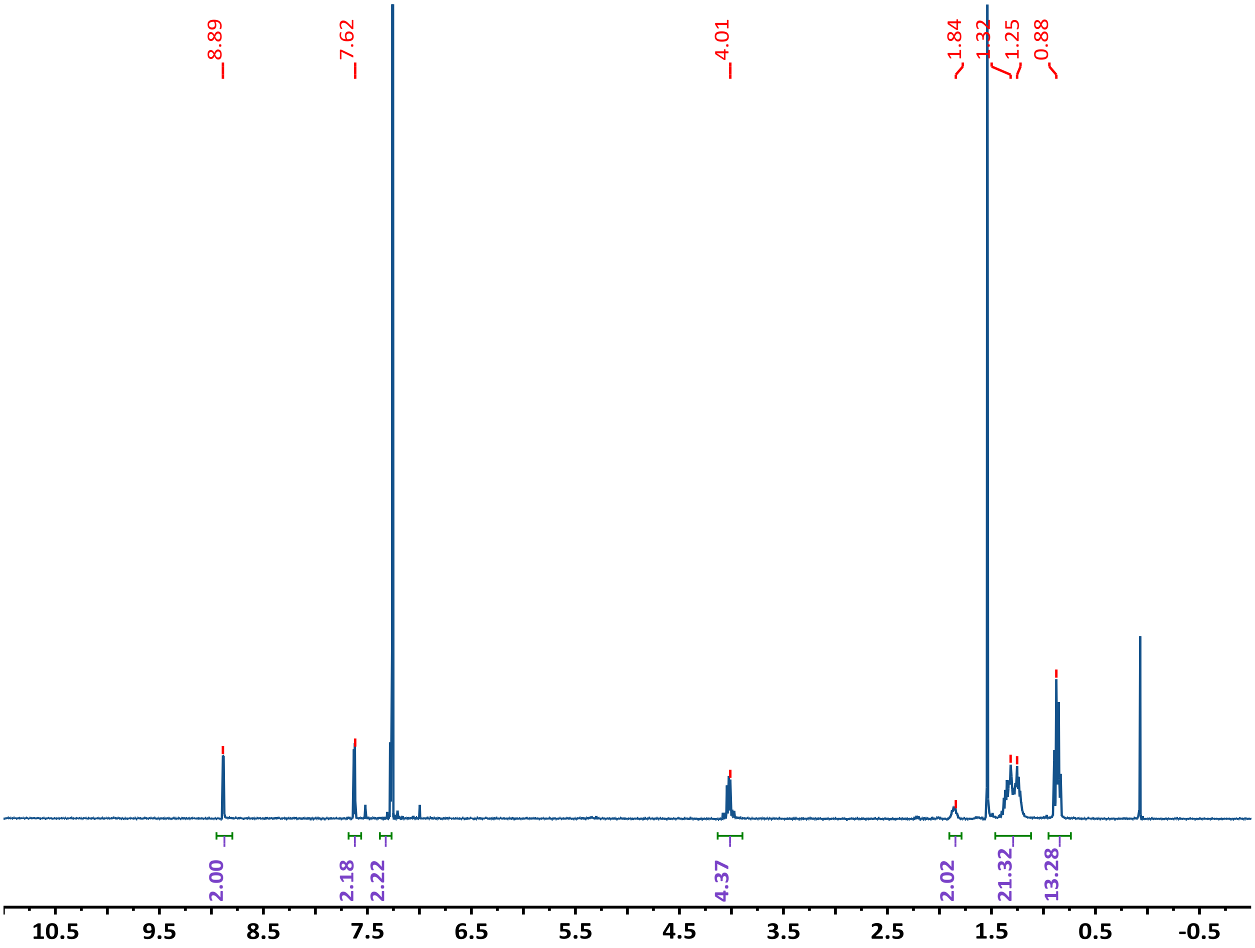

Figure S4. ^{1}H NMR for monomer, **2,5-diethylhexyl-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (EH-DPP)**, in $CDCl_3$.

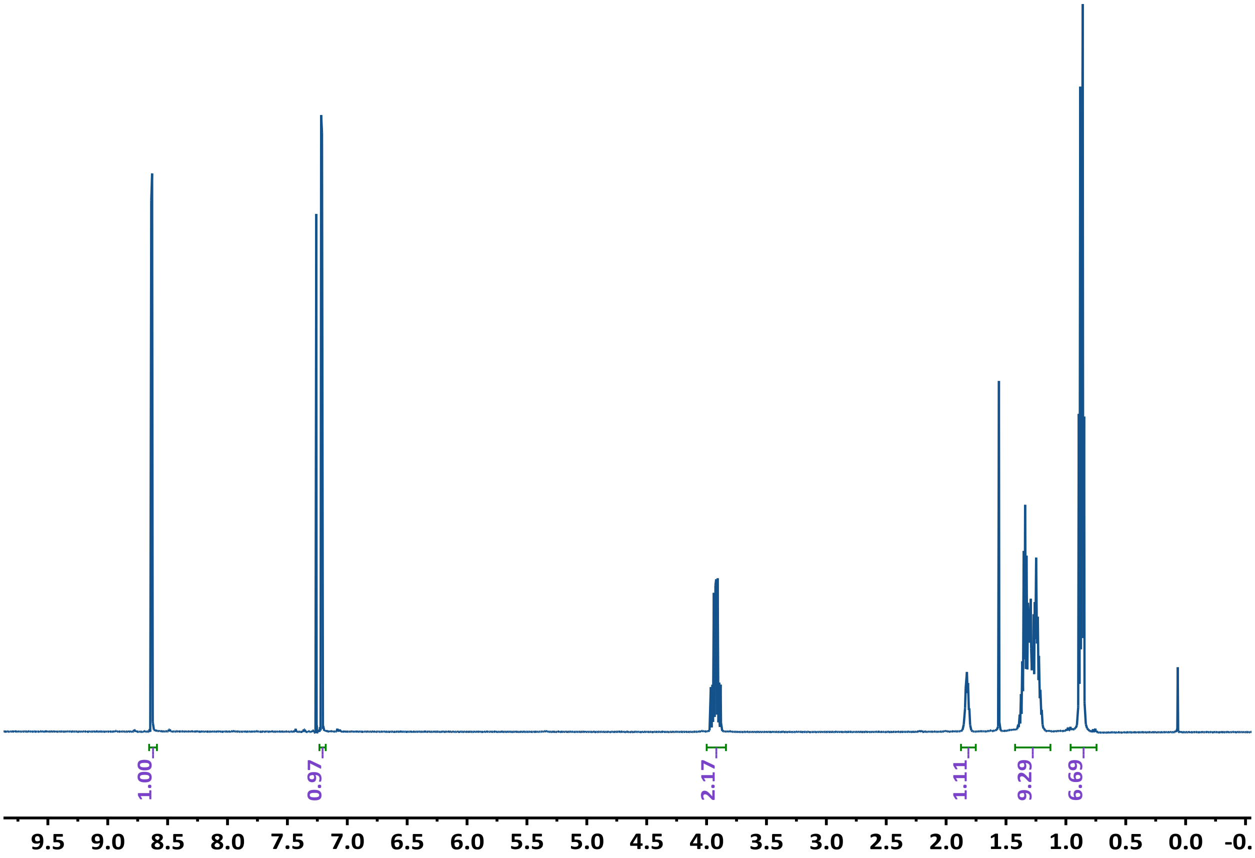

Figure S5. ^{1}H NMR for monomer, **2,5-diethylhexyl-3,6-bis(5-bromothiophene-2-yl)pyrrolo[3,4-c]-pyrrole-1,4-dione (Br-DPP)**, in $CDCl_3$.

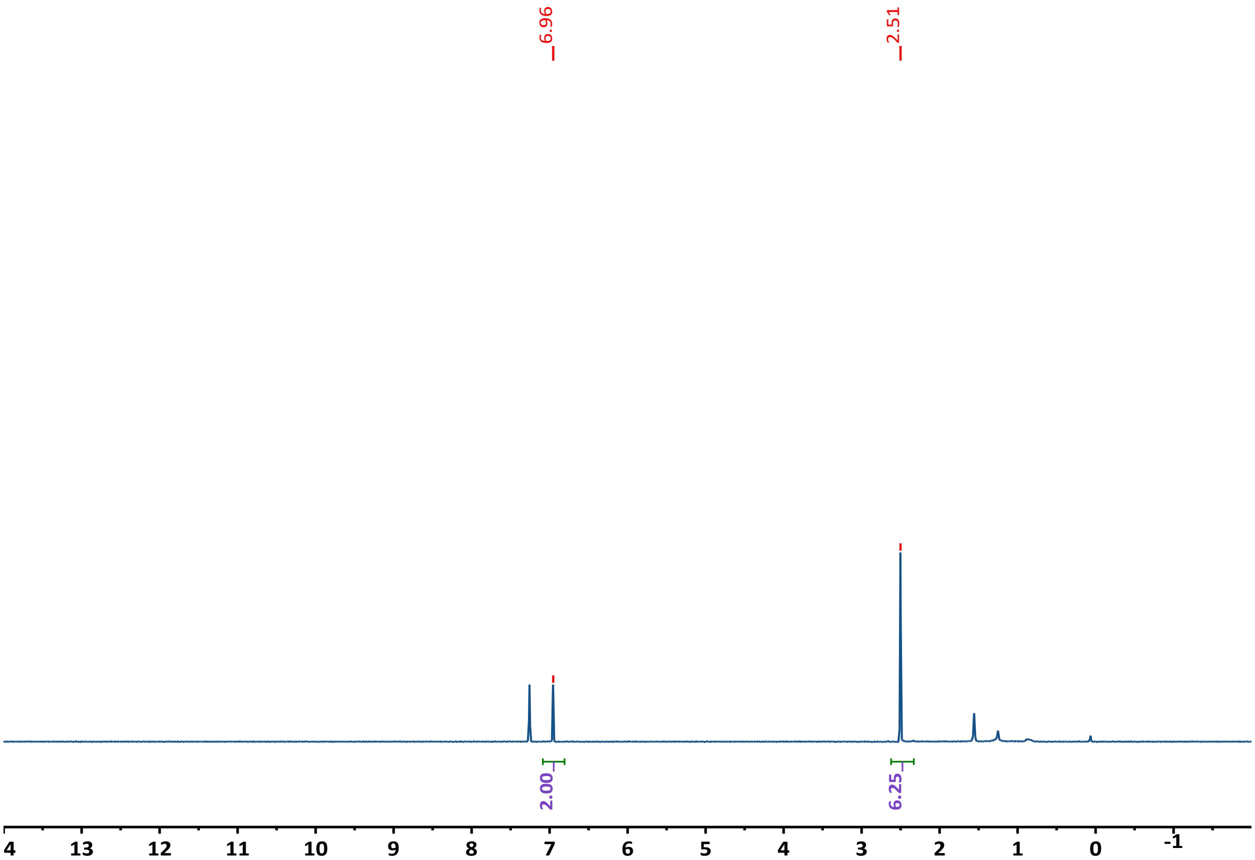

Figure S6. ^{1}H NMR for monomer, **4,4'-dimethyl-2,2'-bithiazole (BTz)**, in CDCl$_3$.

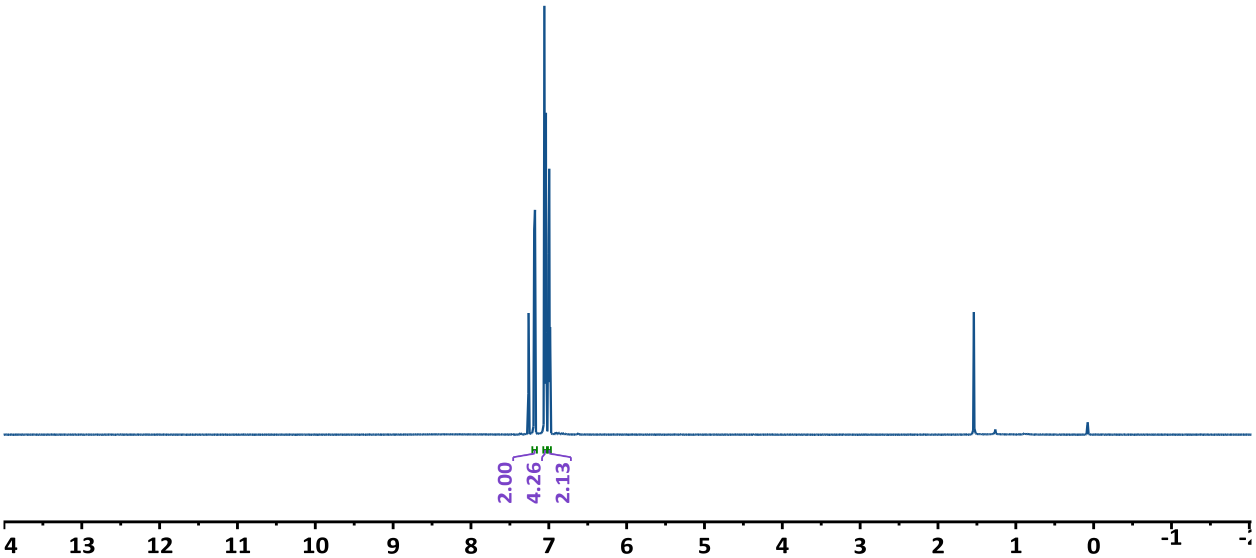

Figure S7. ^{1}H NMR for monomer, **(E)-2-(2-(thiophen-2-yl)vinyl)thiophene (TvT)**, in $CDCl_3$.

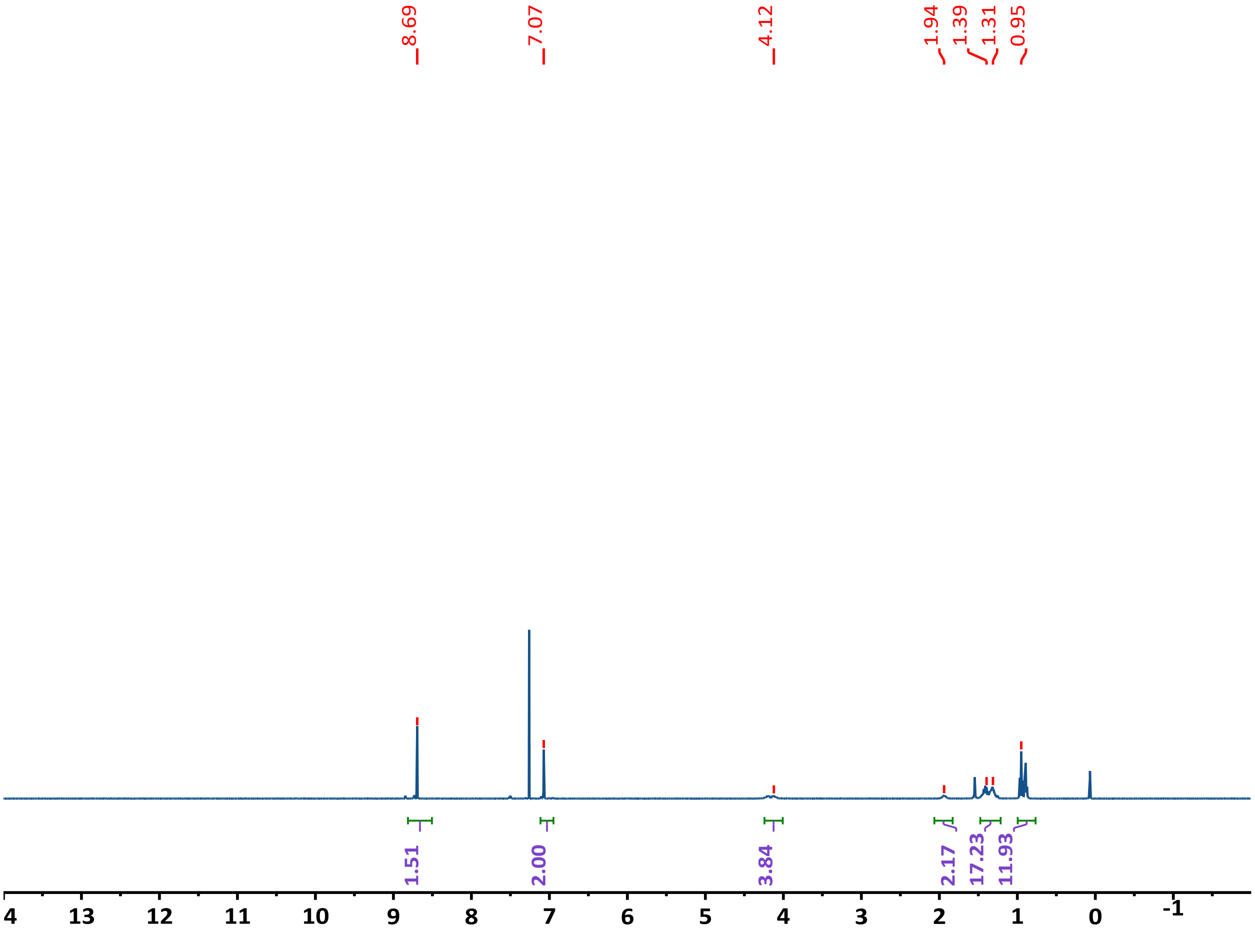

Figure S8. ^{1}H NMR for monomer, **2,8-dibromo-4,10-bis(2-ethylhexyl)thieno[2',3':5,6]pyrido[3,4-g]thieno[3,2-c]isoquinoline-5,11(4H,10H)-dione (Br-TPTI)**, in $CDCl_3$.

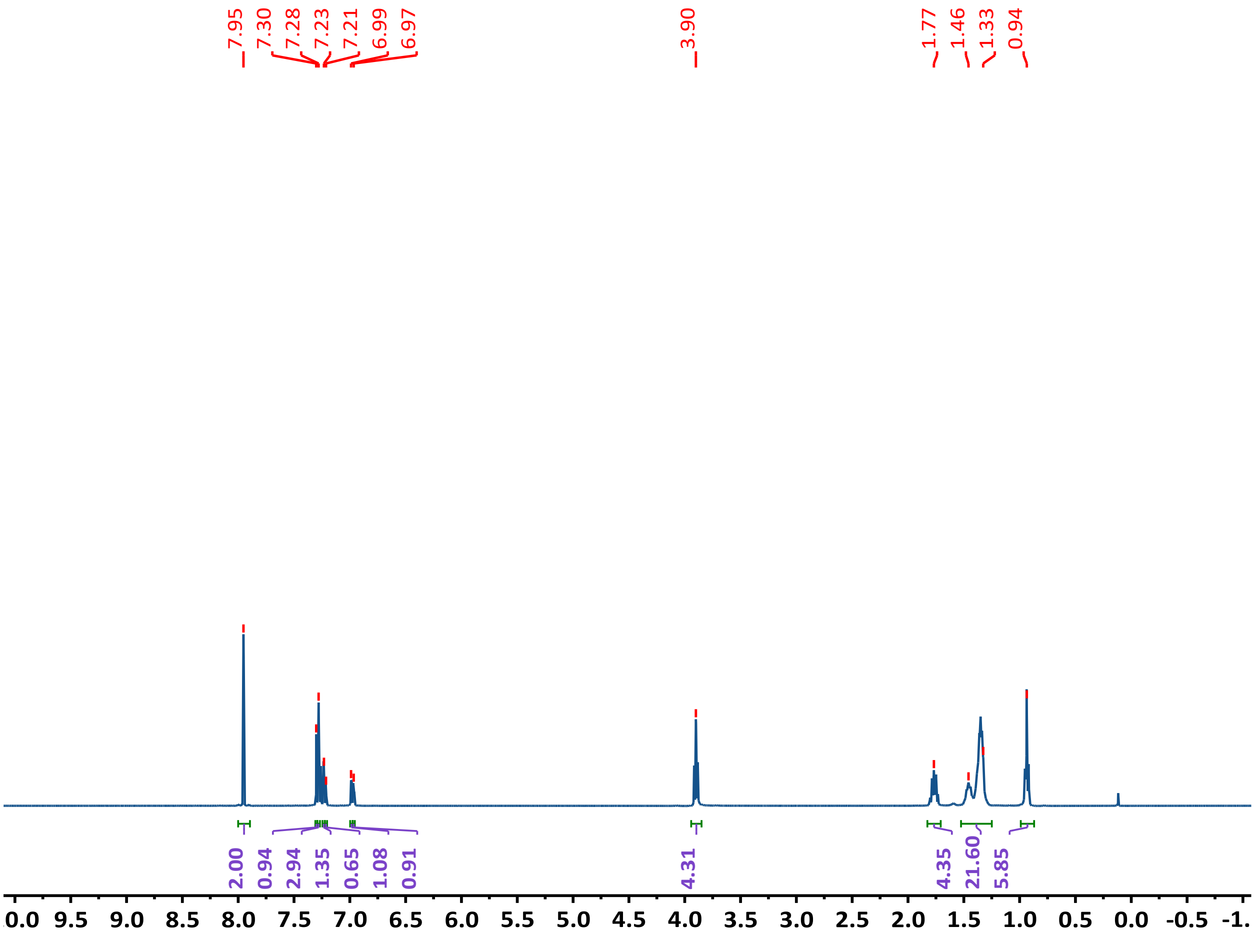

Figure S9. ^{1}H NMR for monomer, **5,8-dibromo-2,3-bis(3-(octyloxy)phenyl)quinoxaline (Br-QX)**, in $CDCl_3$.

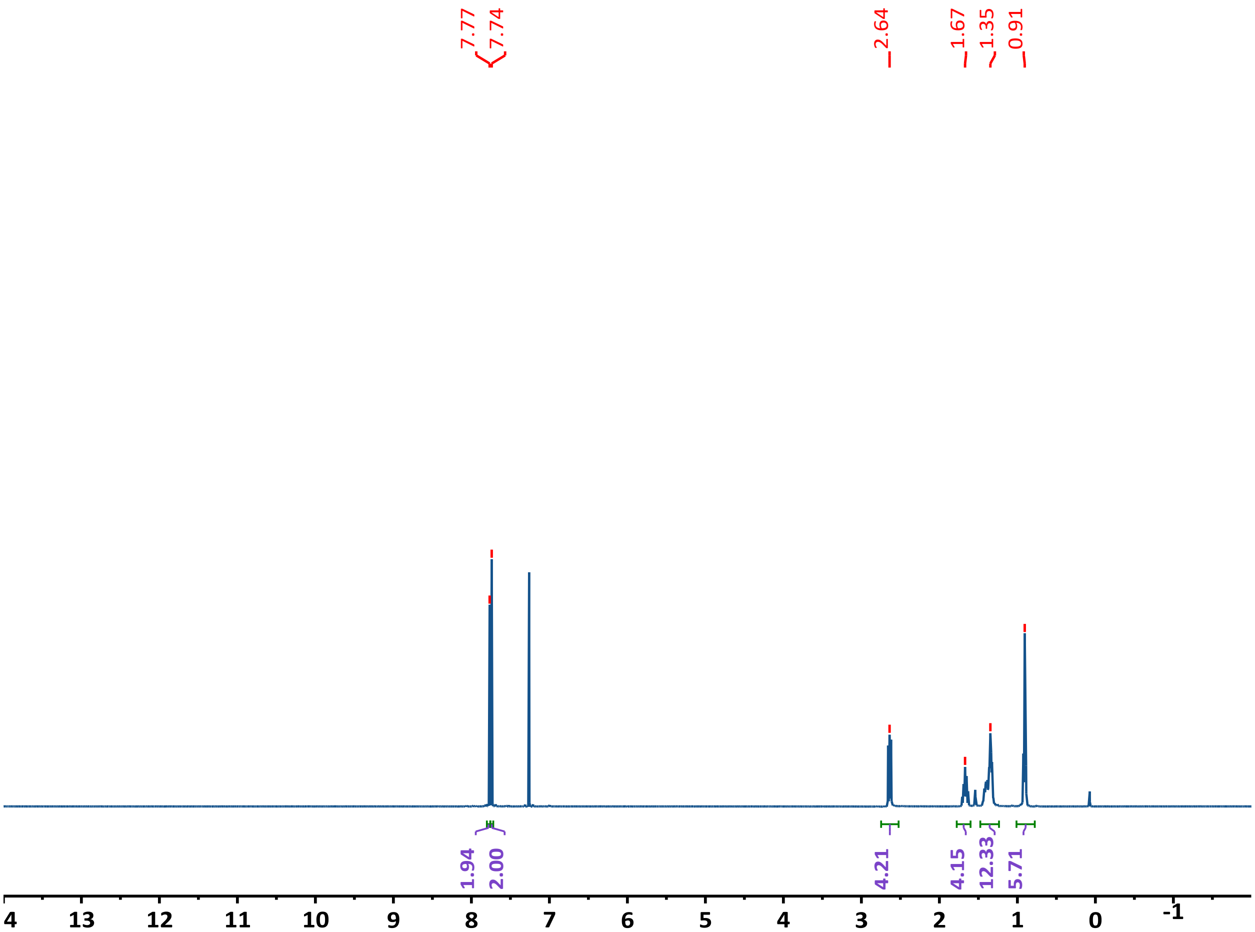

Figure S10. ^{1}H NMR for monomer, **4,7-bis(5-bromo-4-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (Br-BTD)**, in $CDCl_3$.

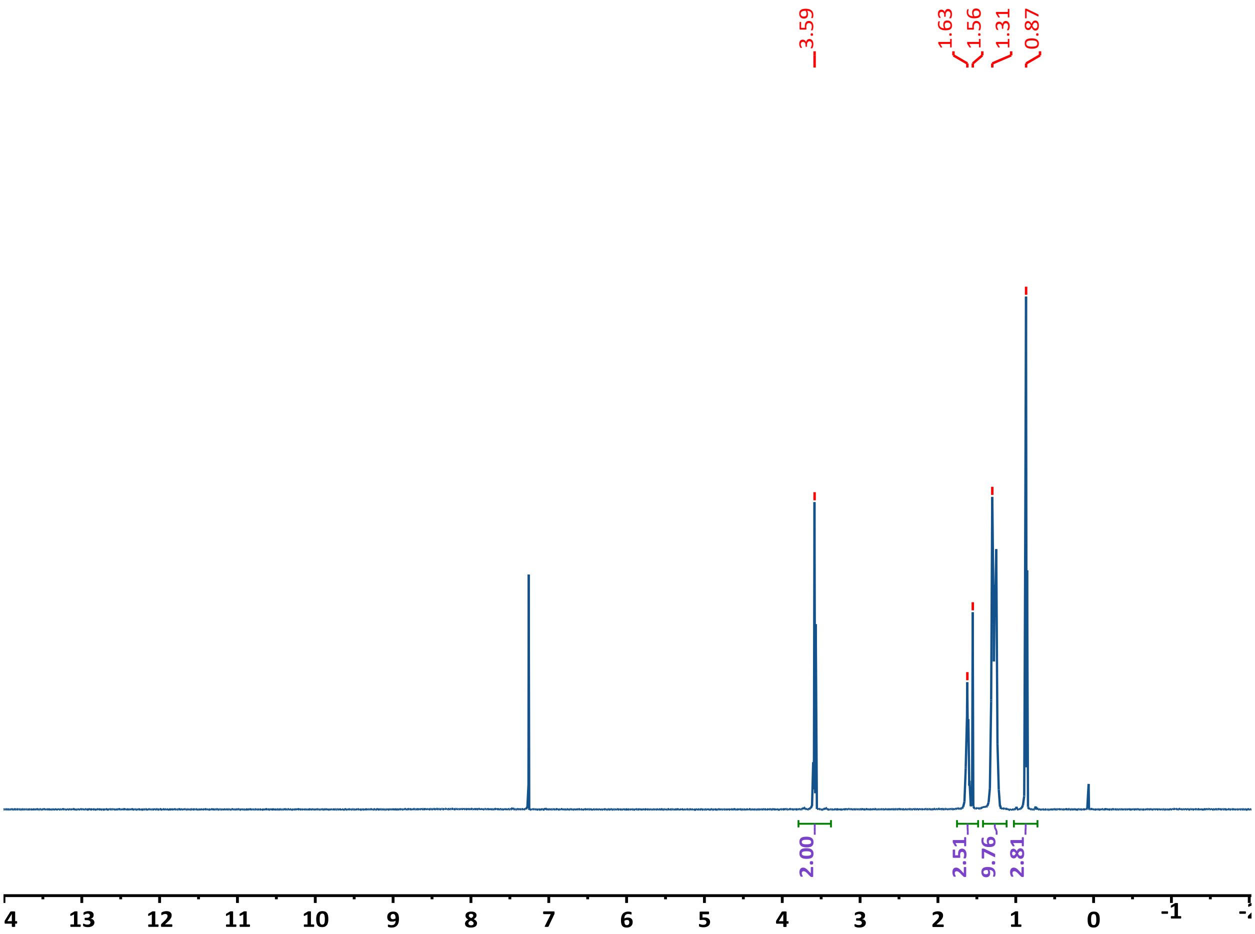

Figure S11. ^{1}H NMR for monomer, **1,3-dibromo-5-octayl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (Br-TPD)**, in $CDCl_3$.

3. Polymer NMR Spectra

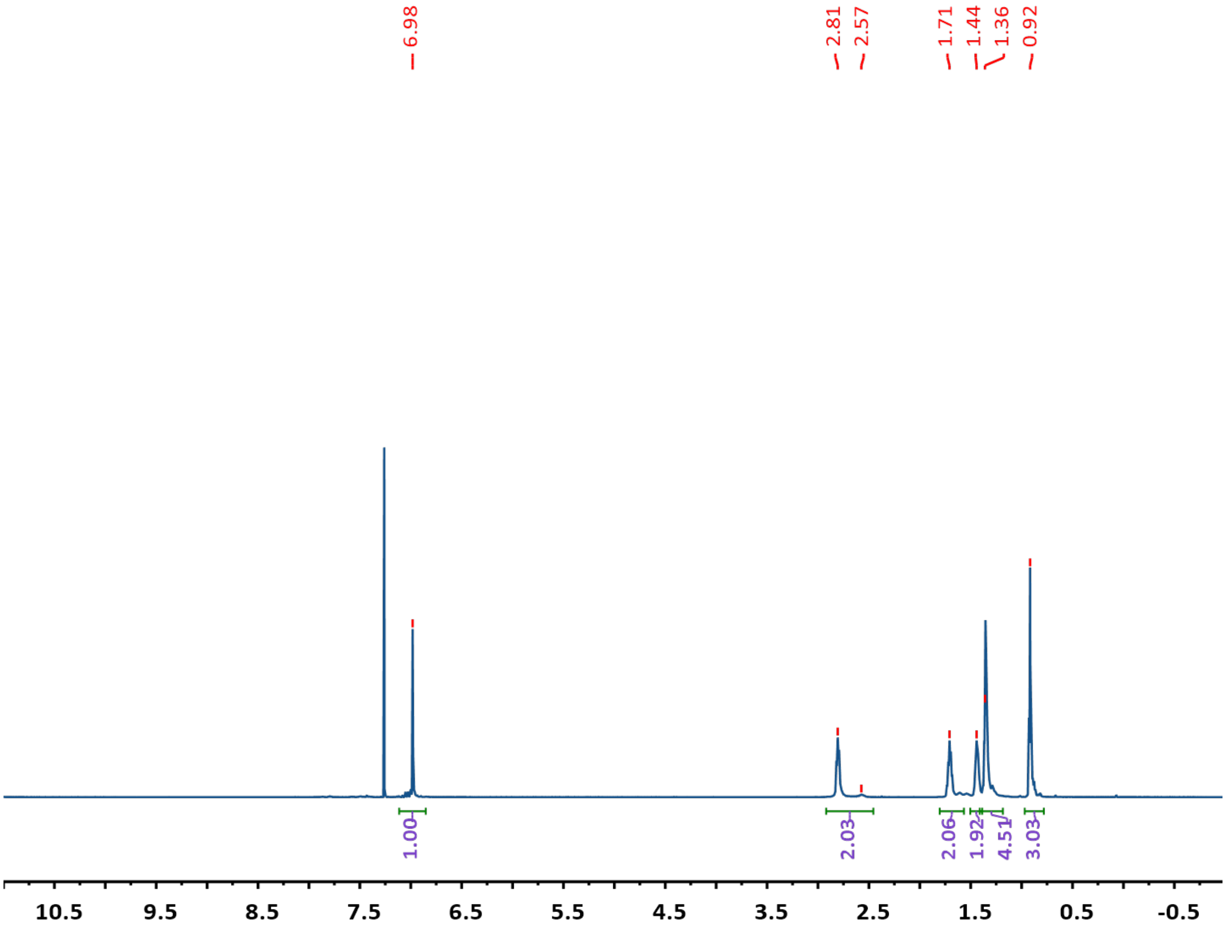

Figure S12. ^{1}H NMR Spectra of **Stille P3HT (A1).**

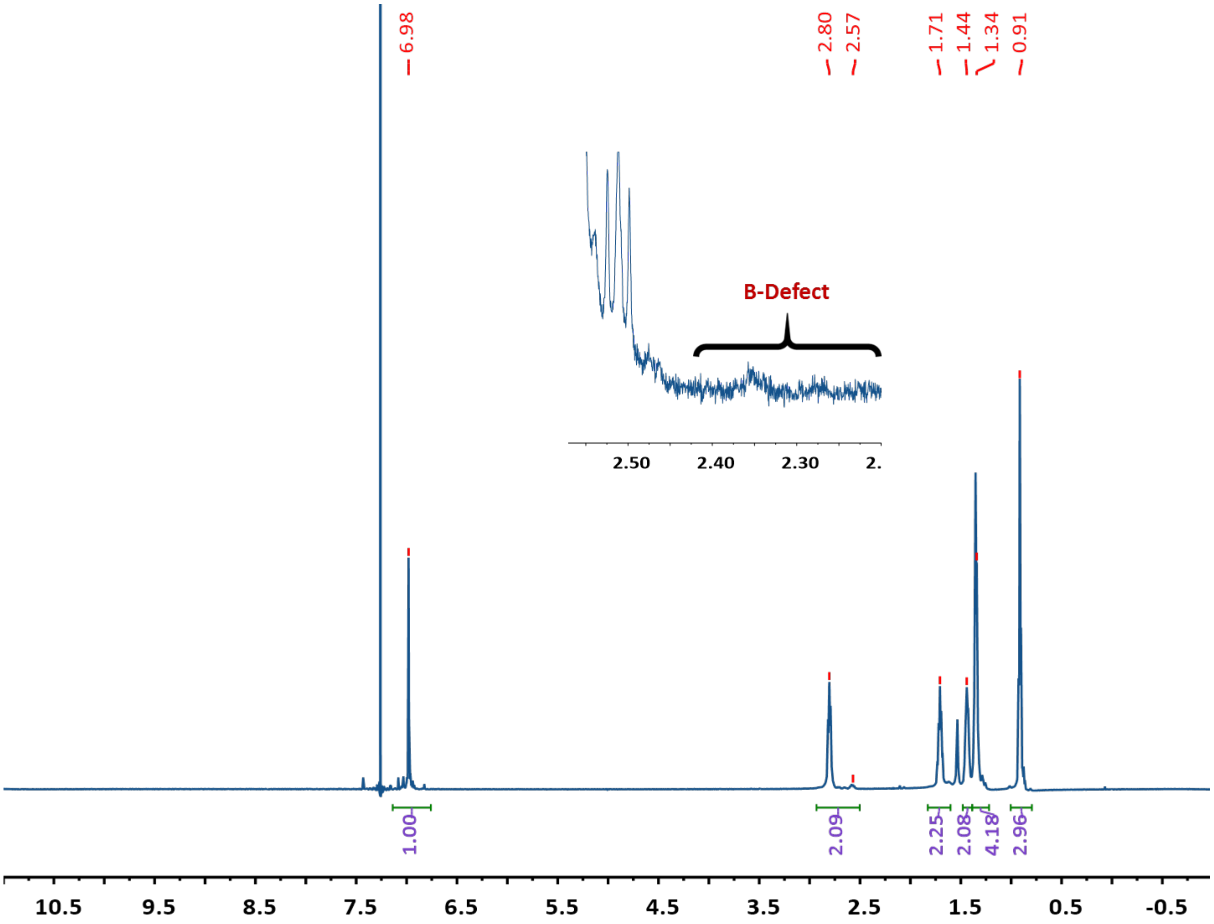

Figure S13. ^{1}H NMR Spectra of **DArP P3HT (A2).**

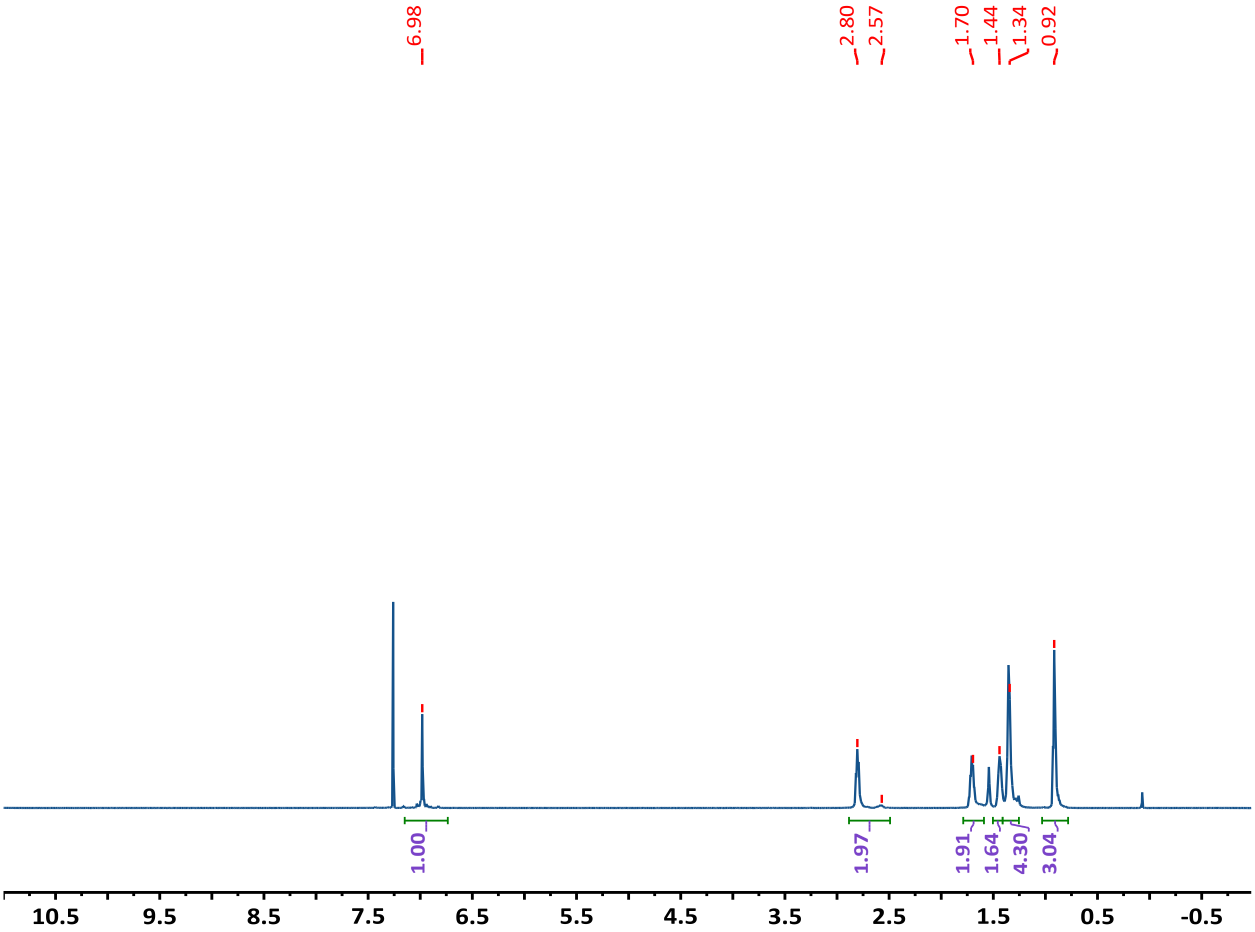

Figure S14. ^{1}H NMR Spectra of **DArP P3HT (A3).**

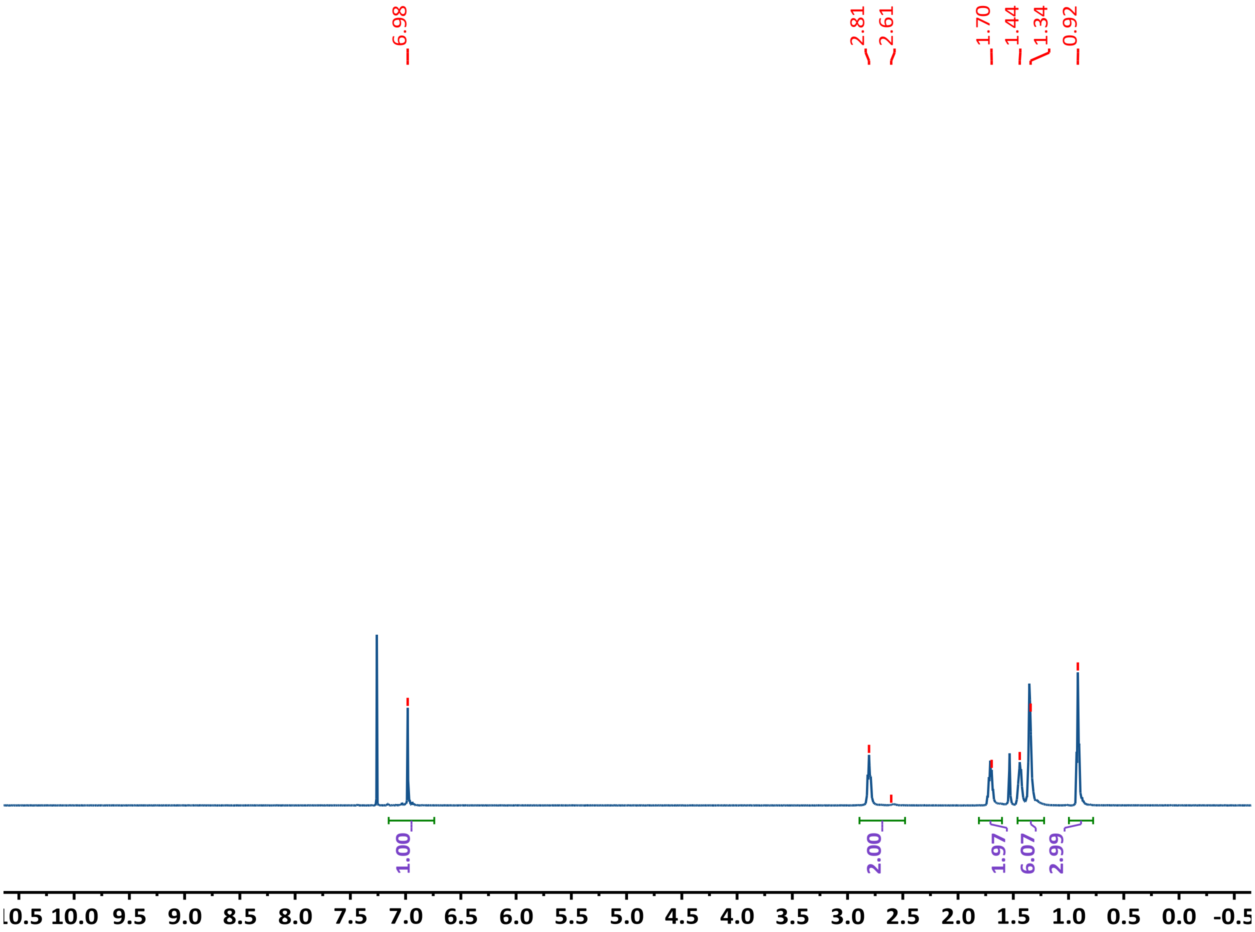

Figure S15. ^{1}H NMR Spectra of **DArP P3HT (A4).**

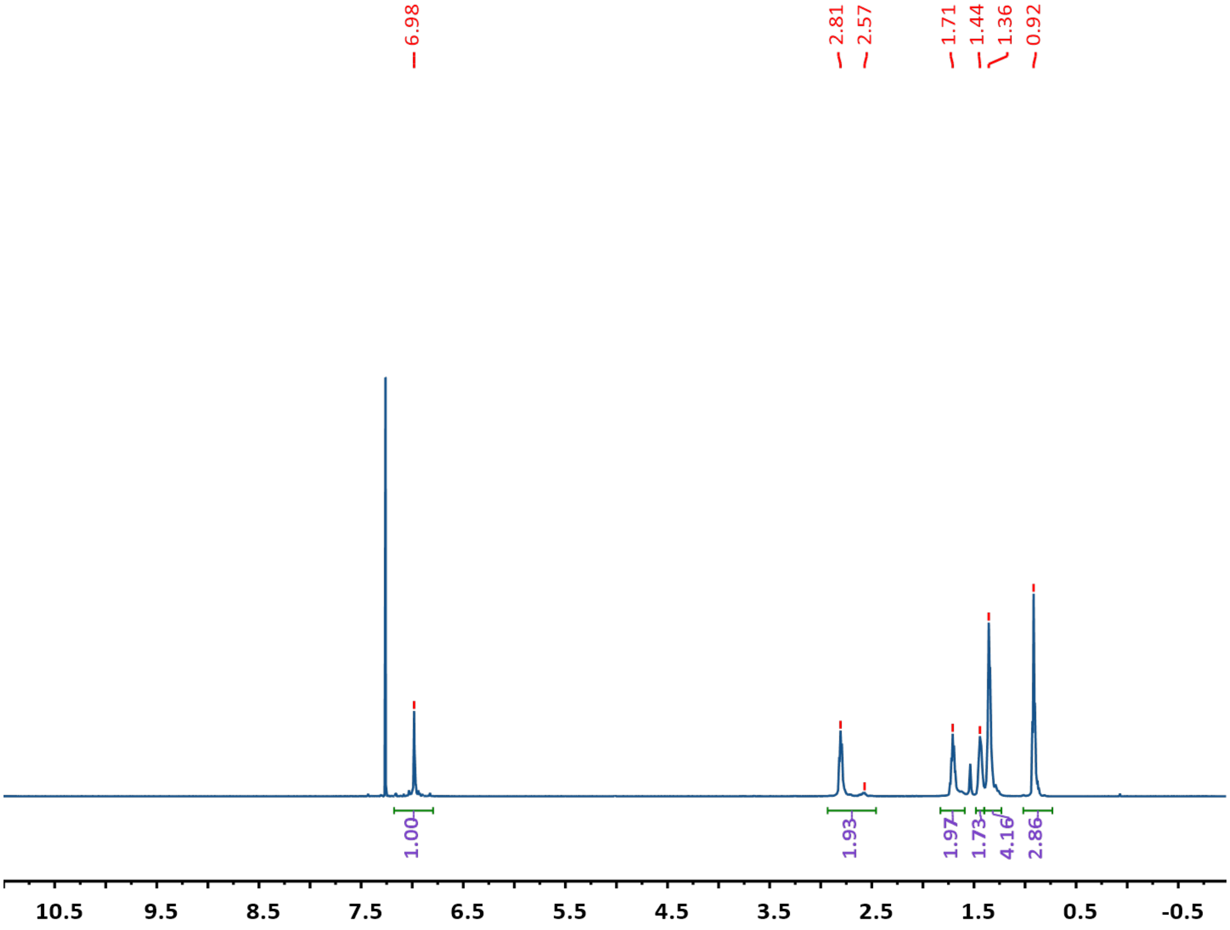

Figure S16. ^{1}H NMR Spectra of **DArP P3HT (A5).**

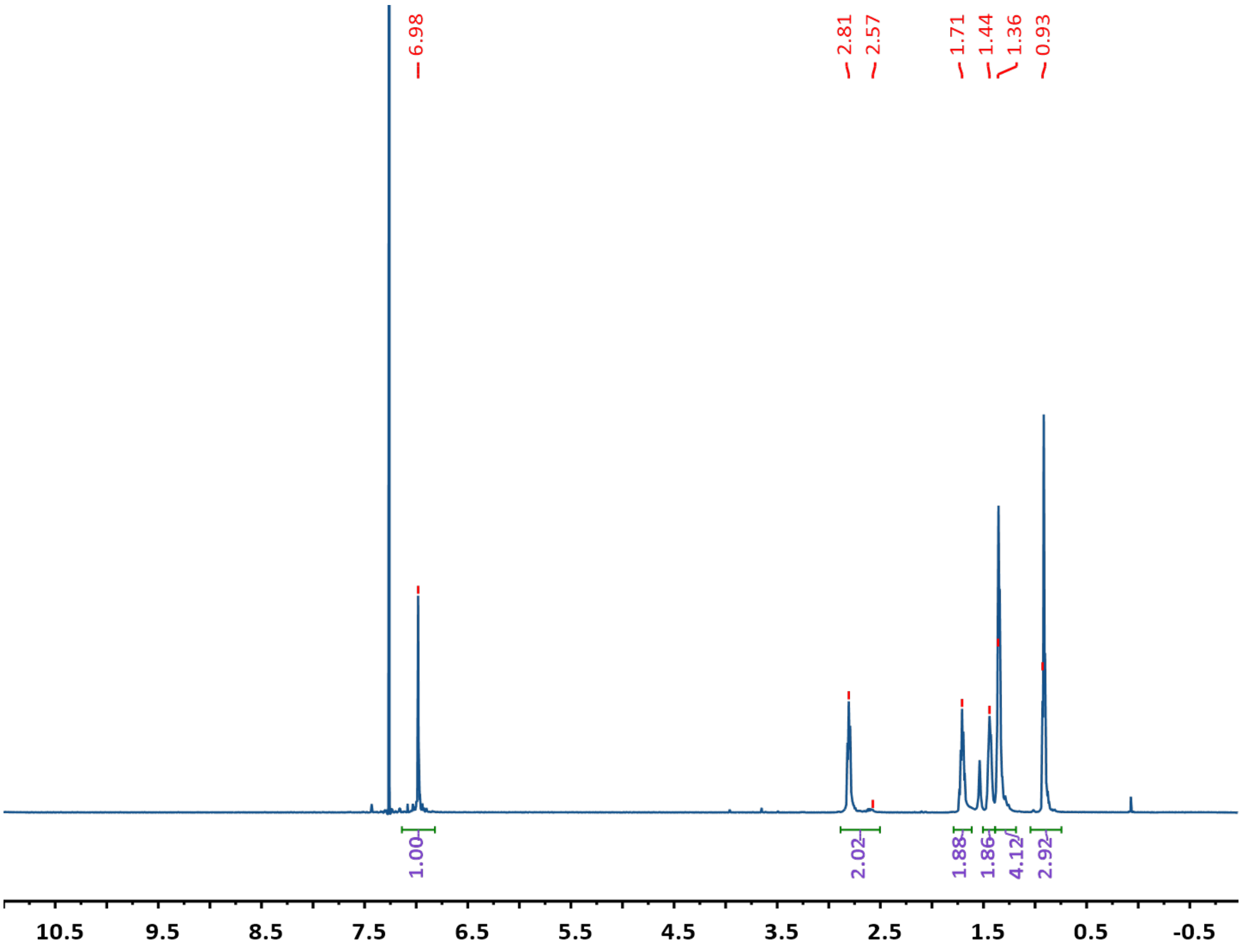

Figure S17. ^{1}H NMR Spectra of **DArP P3HT (A6).**

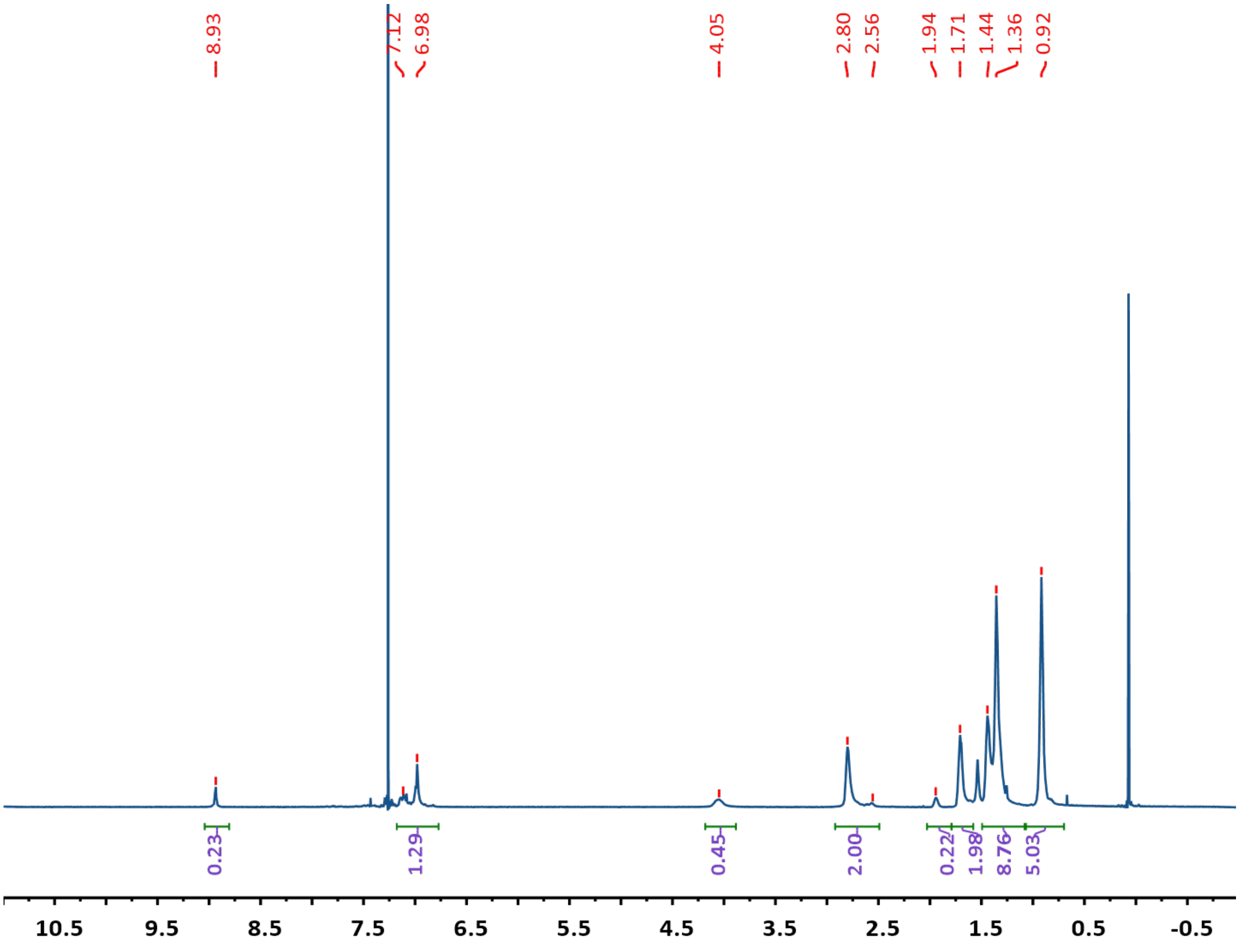

Figure S18. ^{1}H NMR Spectra of **Stille P3HTT-DPP (B1).**

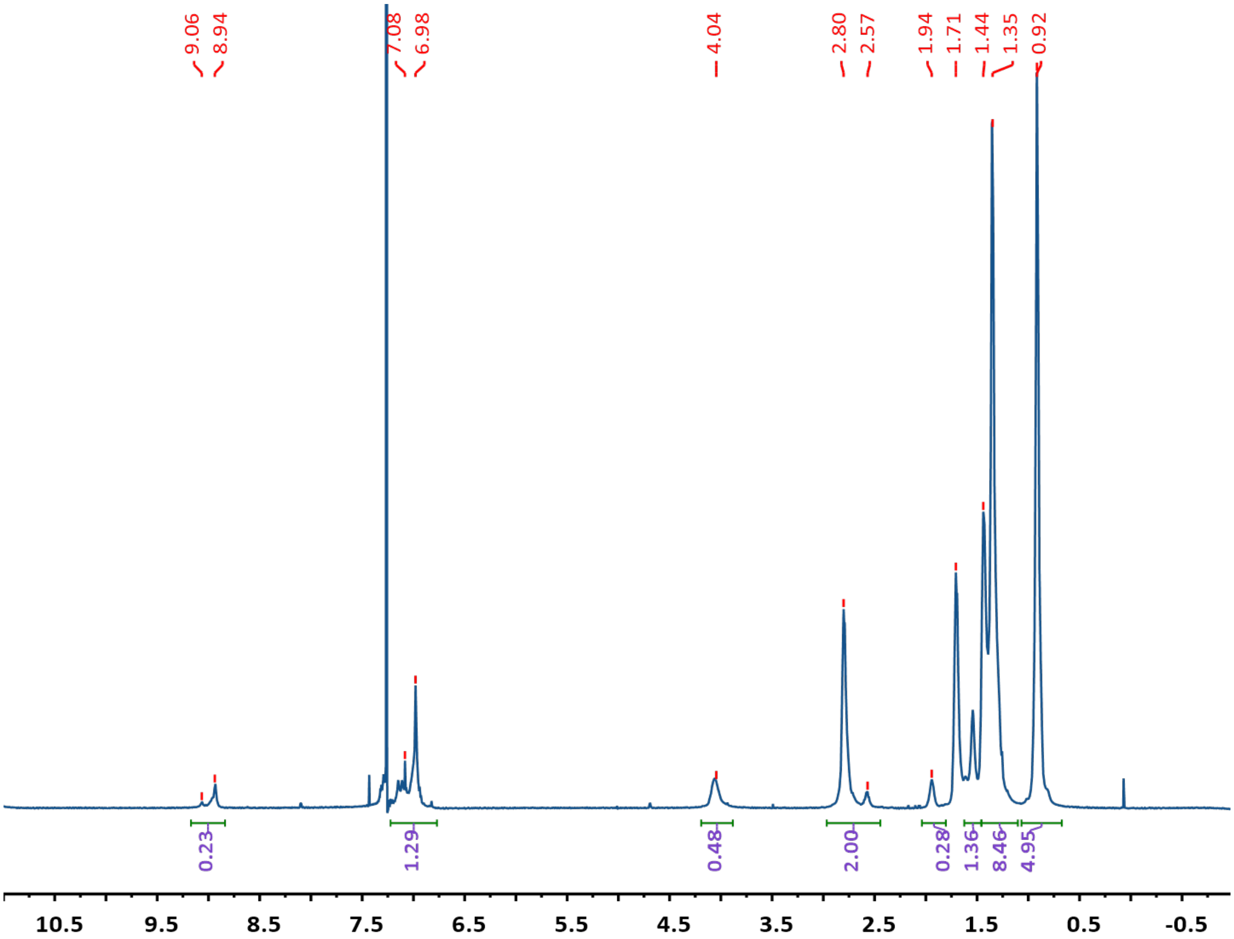

Figure S19. ^{1}H NMR Spectra **of DArP P3HTT-DPP (B2).**

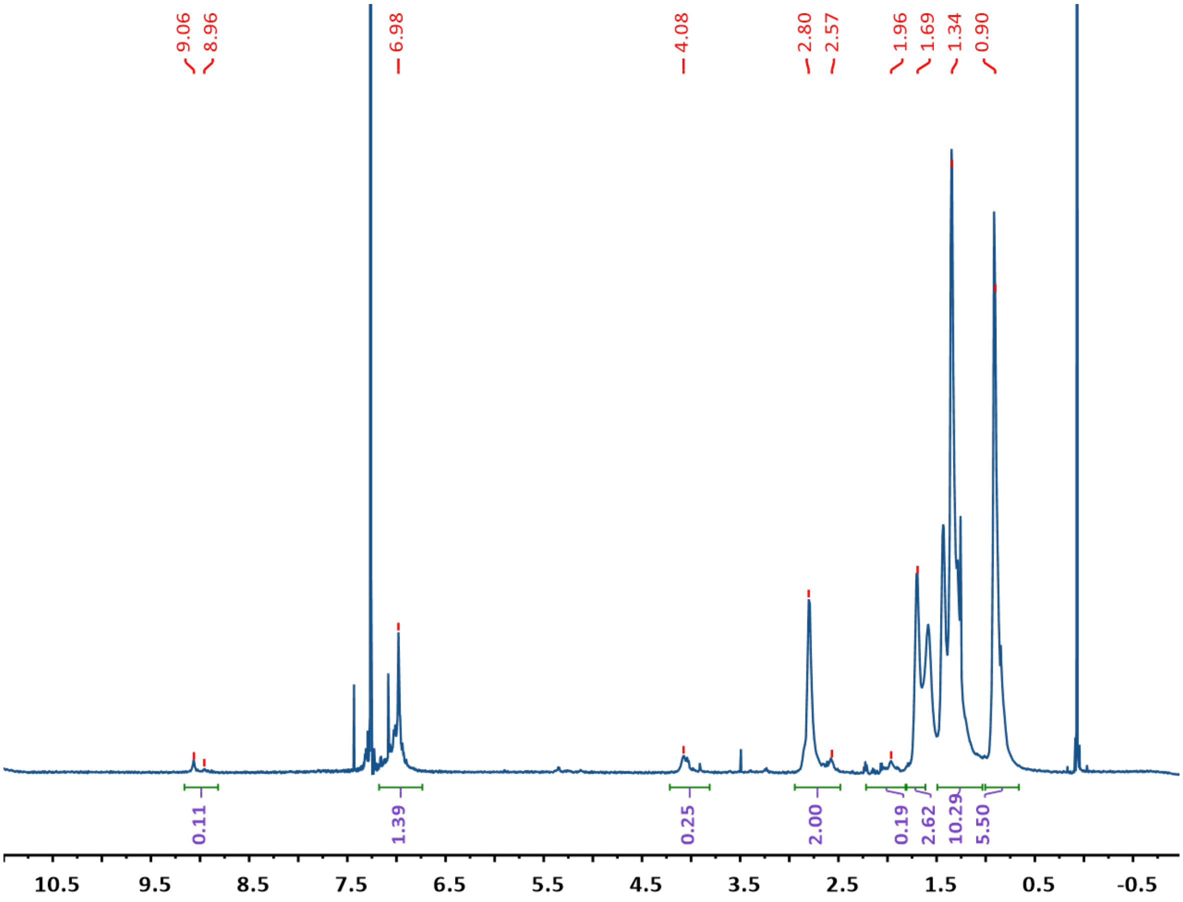

Figure S20. ^{1}H NMR Spectra of **DArP P3HTT-DPP (B3).**

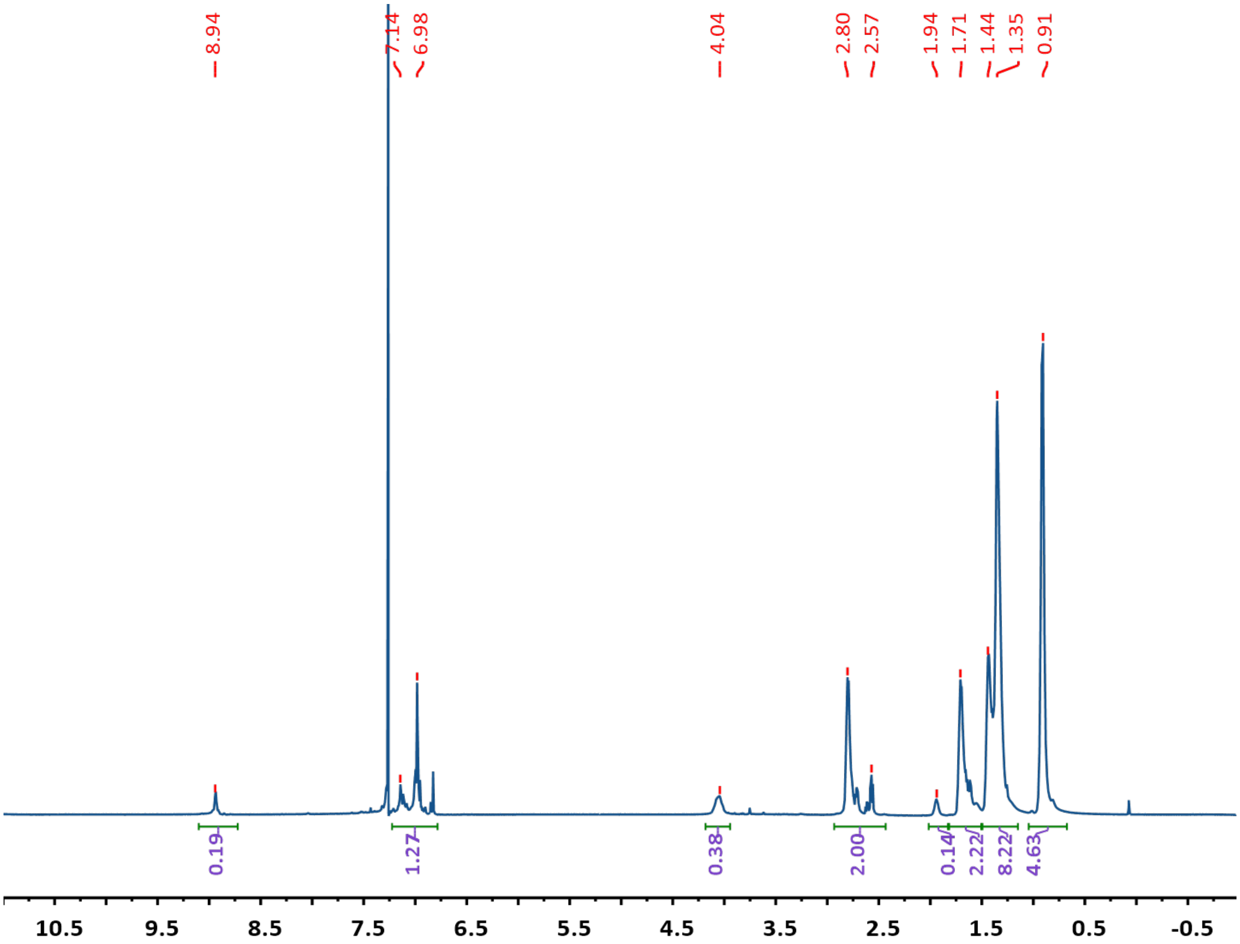

Figure S21. ^{1}H NMR Spectra of **DArP P3HTT-DPP (B4).**

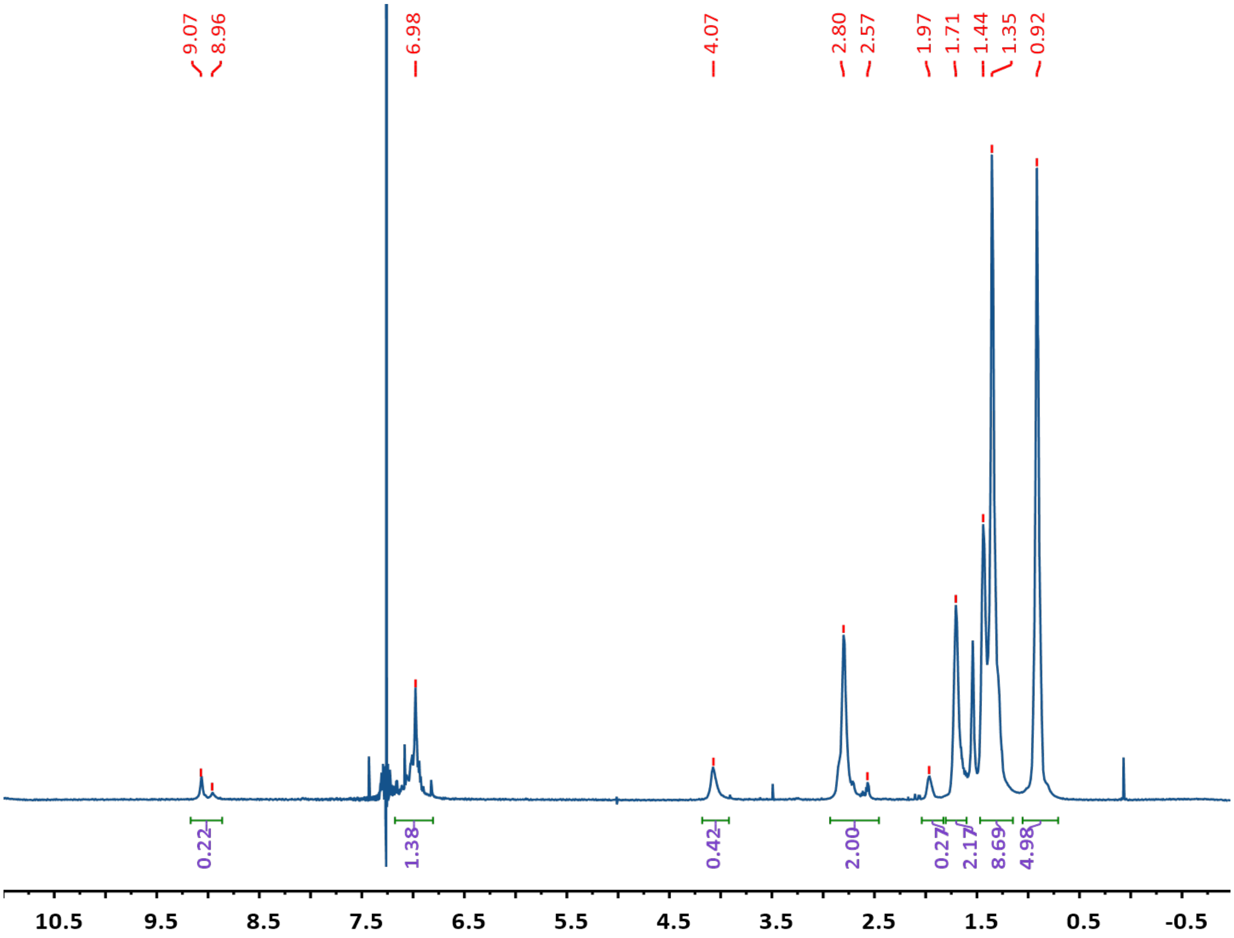

Figure S22. ^{1}H NMR Spectra of **DArP P3HTT-DPP (B5).**

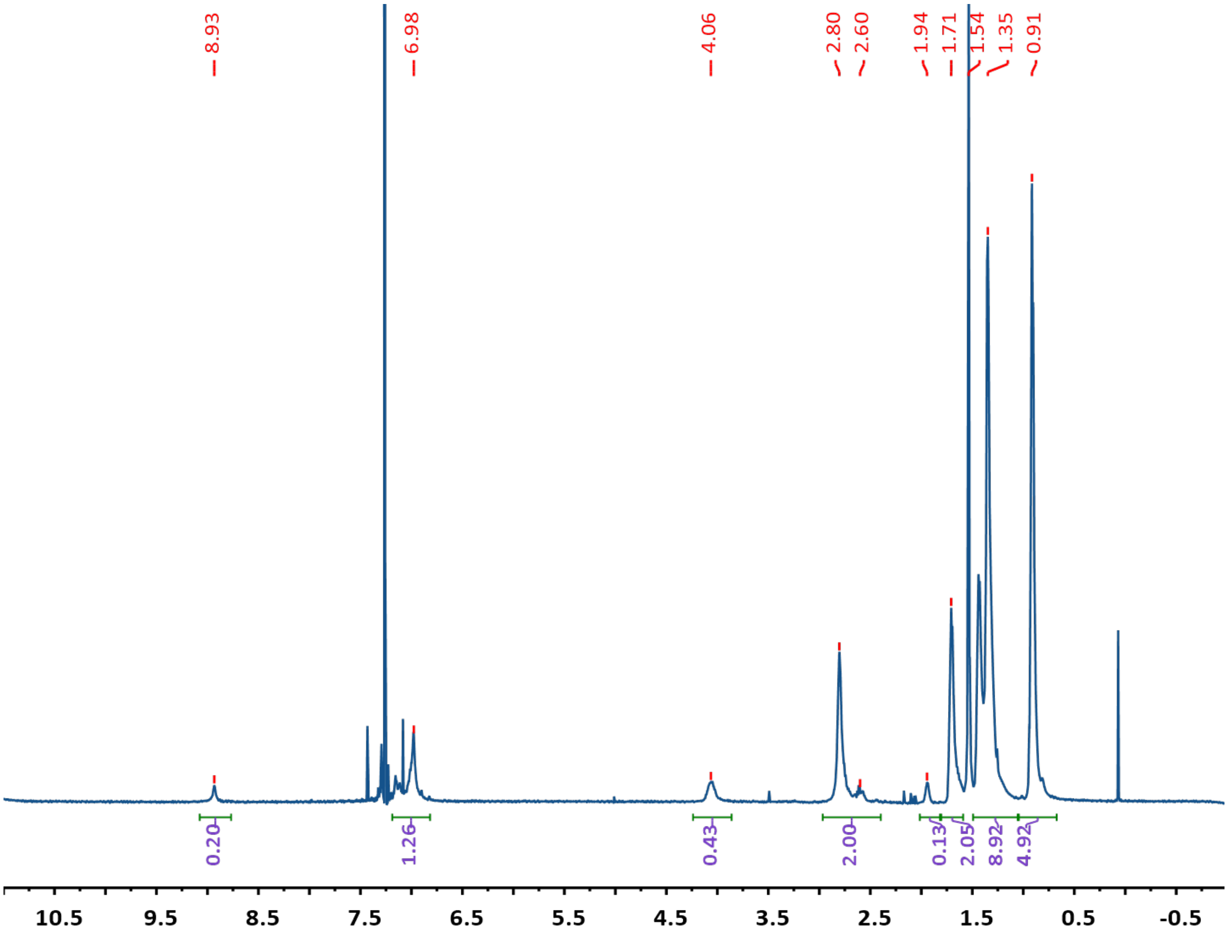

Figure S23. ^{1}H NMR Spectra of **DArP P3HTT-DPP (B6).**

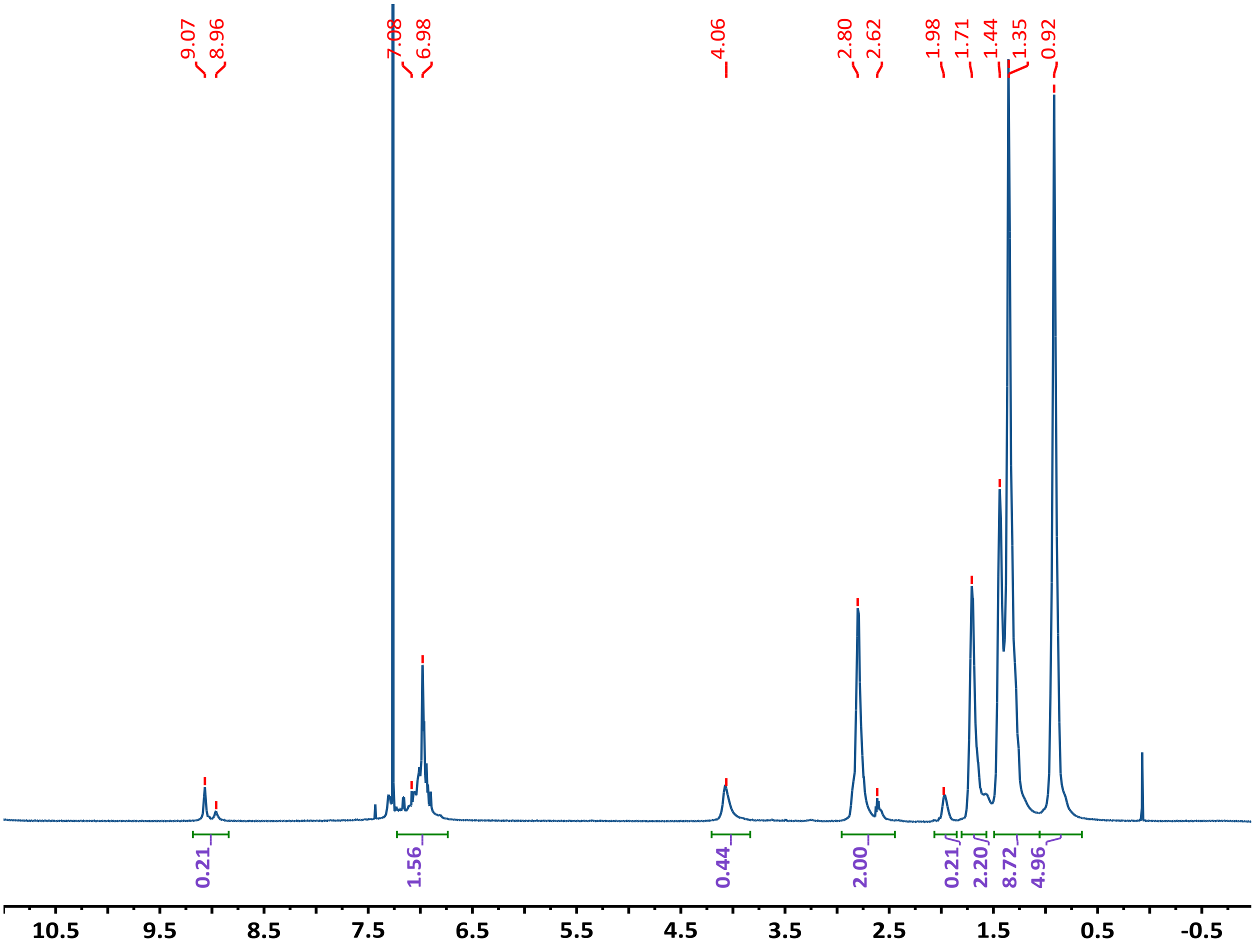

Figure S24. ^{1}H NMR Spectra of **DArP P3HTT-DPP (B7).**

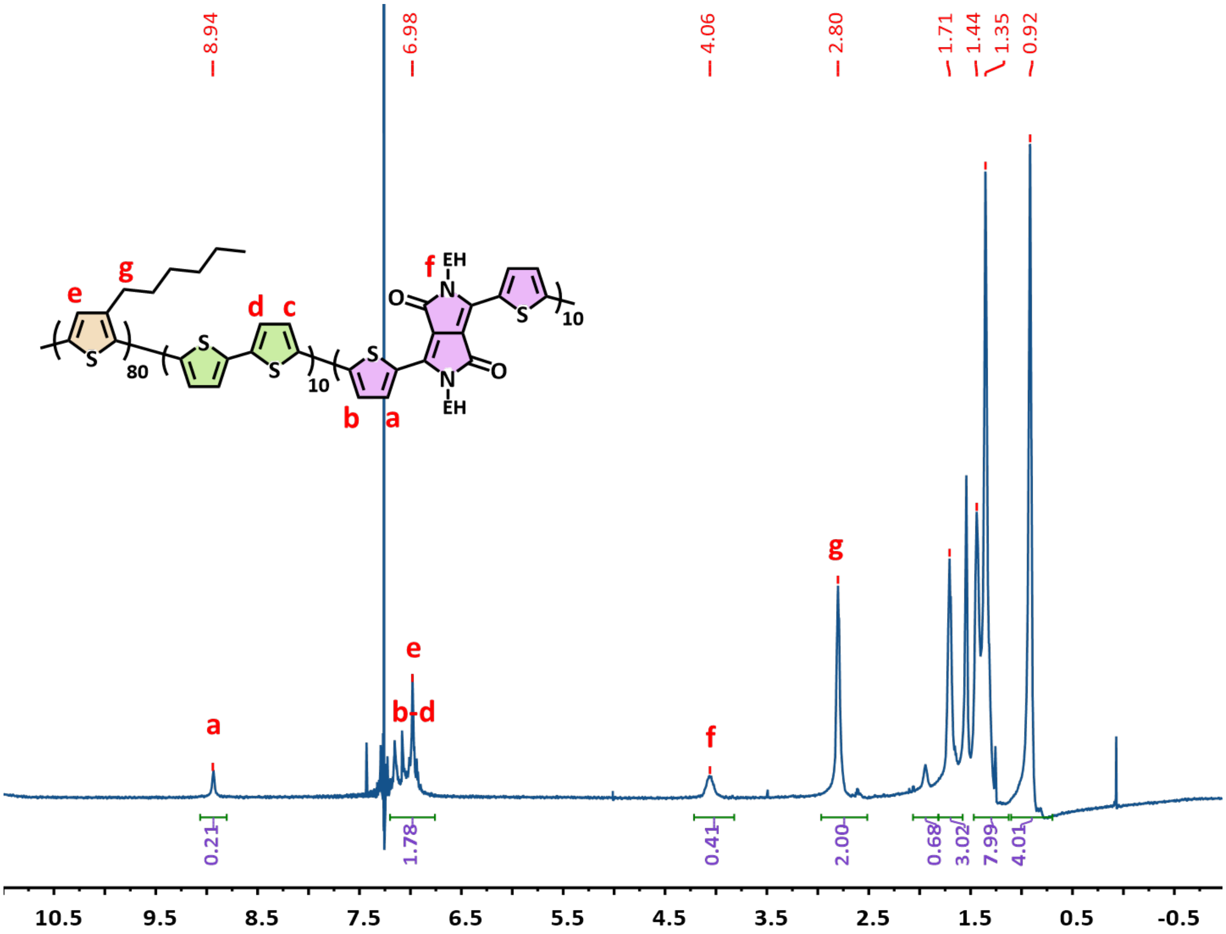

Figure S25. ^{1}H NMR Spectra of **DArP P3HT-BT-DPP (P1).** Peaks for b-d overlap with the 3HT couplings (around 6.98 ppm).

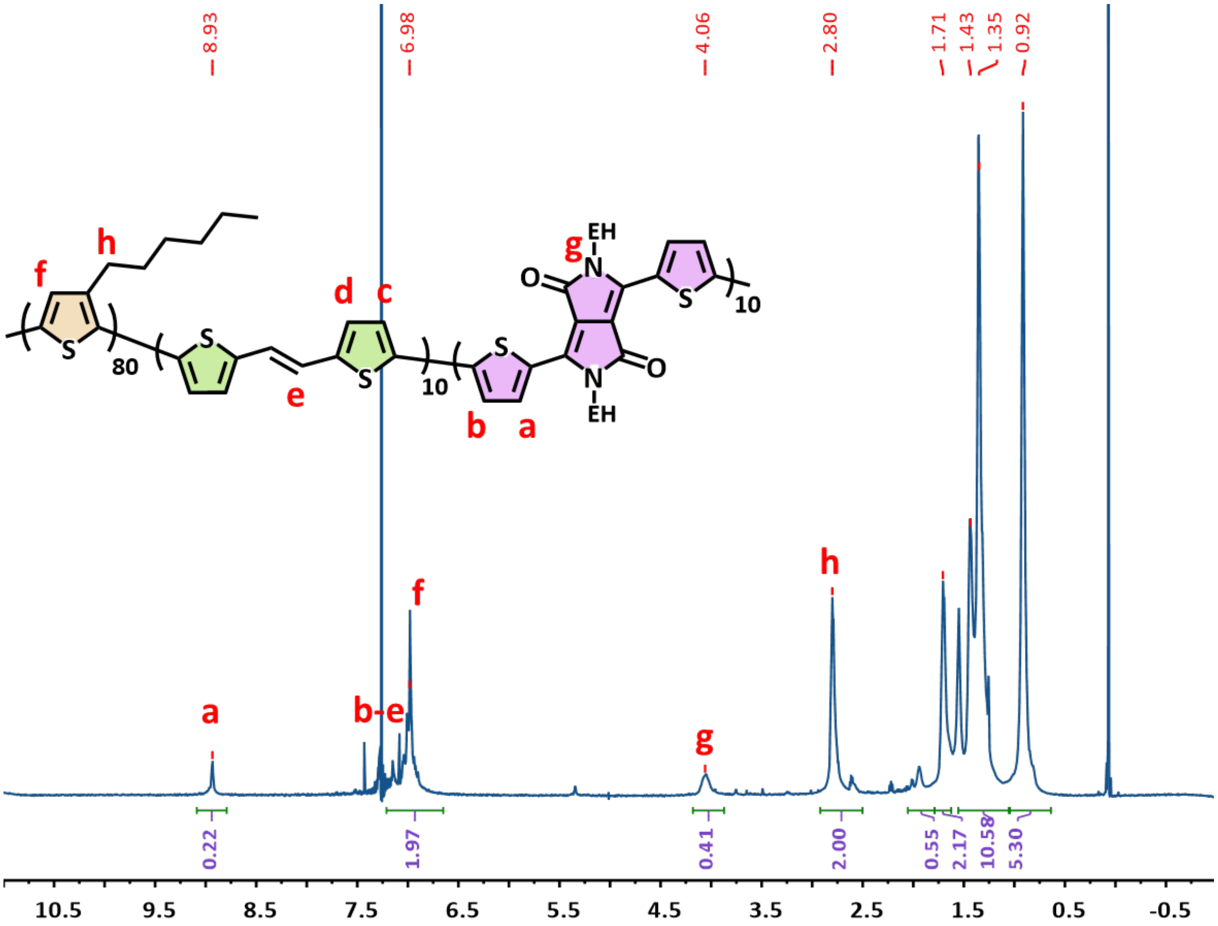

Figure S26. ^{1}H NMR Spectra of **DArP P3HT-TvT-DPP (P2).** Peaks for b-e overlap with the 3HT couplings (around 6.98 ppm).

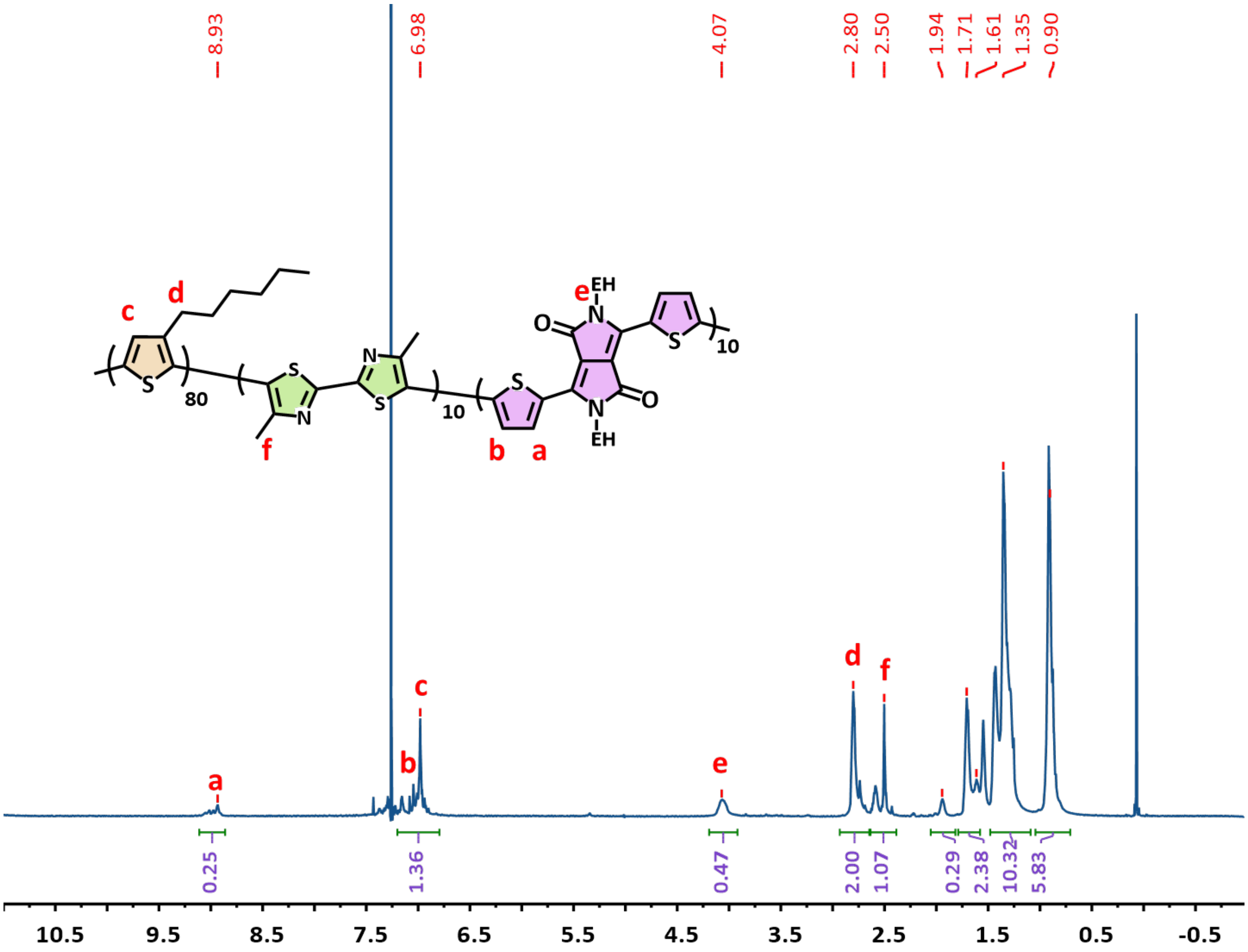

Figure S27. ^{1}H NMR Spectra of **DArP P3HT-BTz-DPP (P3).**

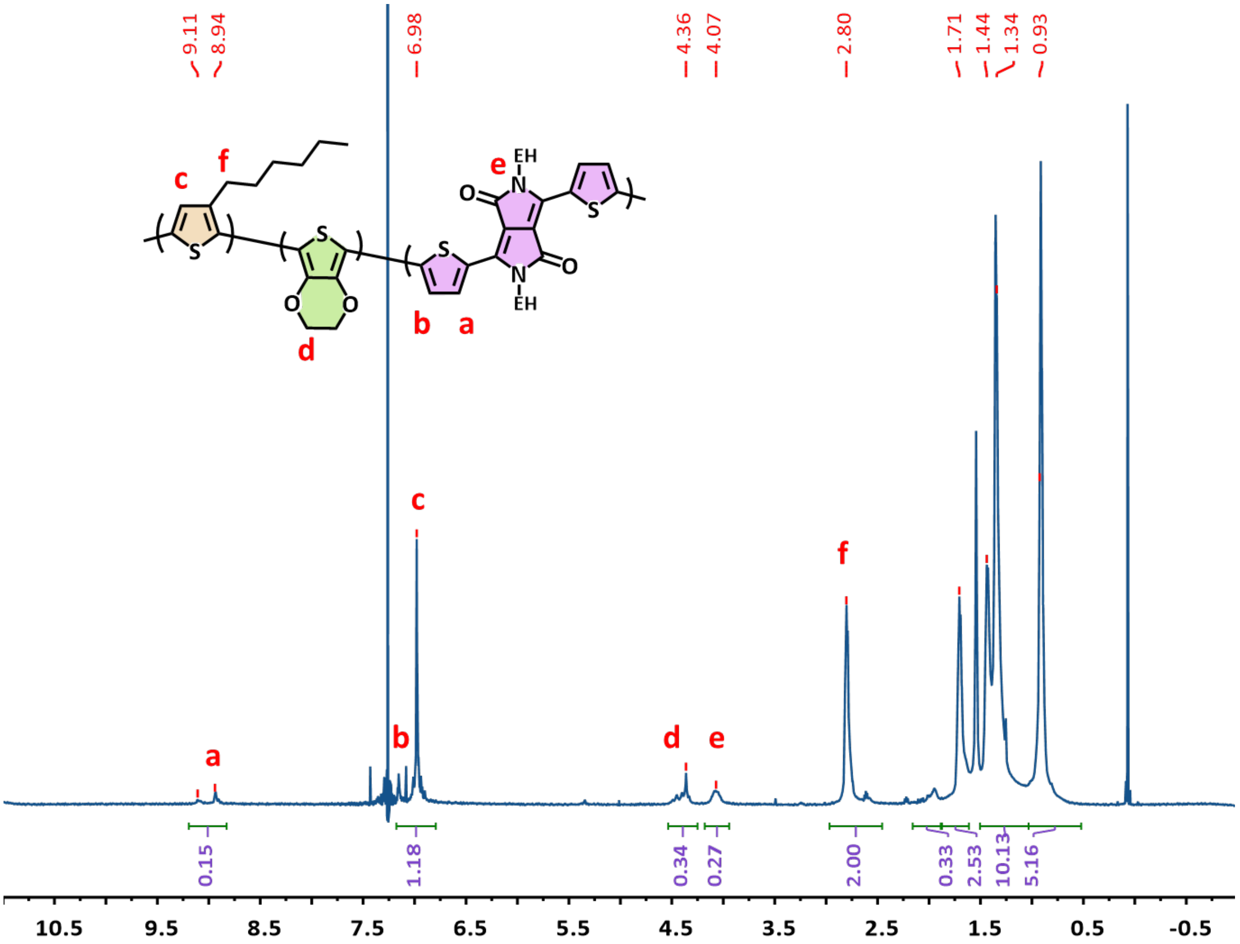

Figure S28. ^{1}H NMR Spectra of **DArP P3HT-EDOT-DPP (P4).**

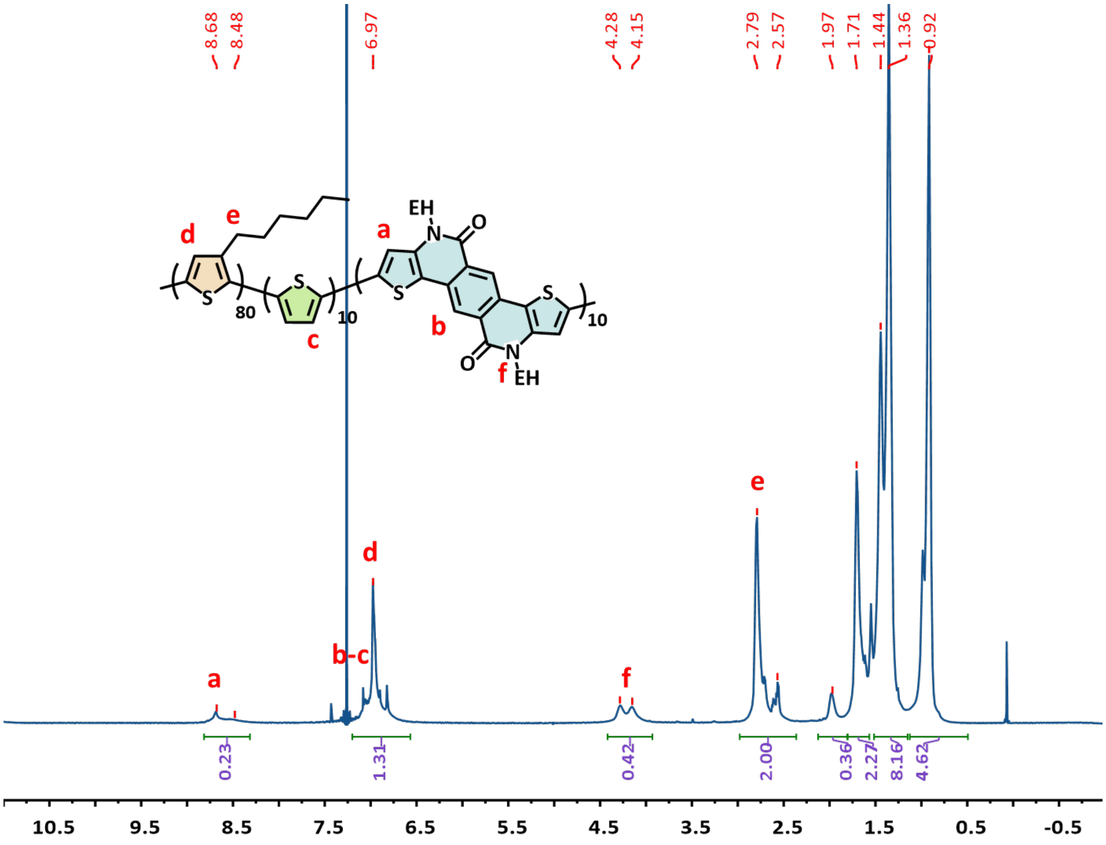

Figure S29. ^{1}H NMR Spectra of **DArP P3HTT-TPTI (P5).** Peaks for b-c overlap with the 3HT couplings (around 6.98 ppm).

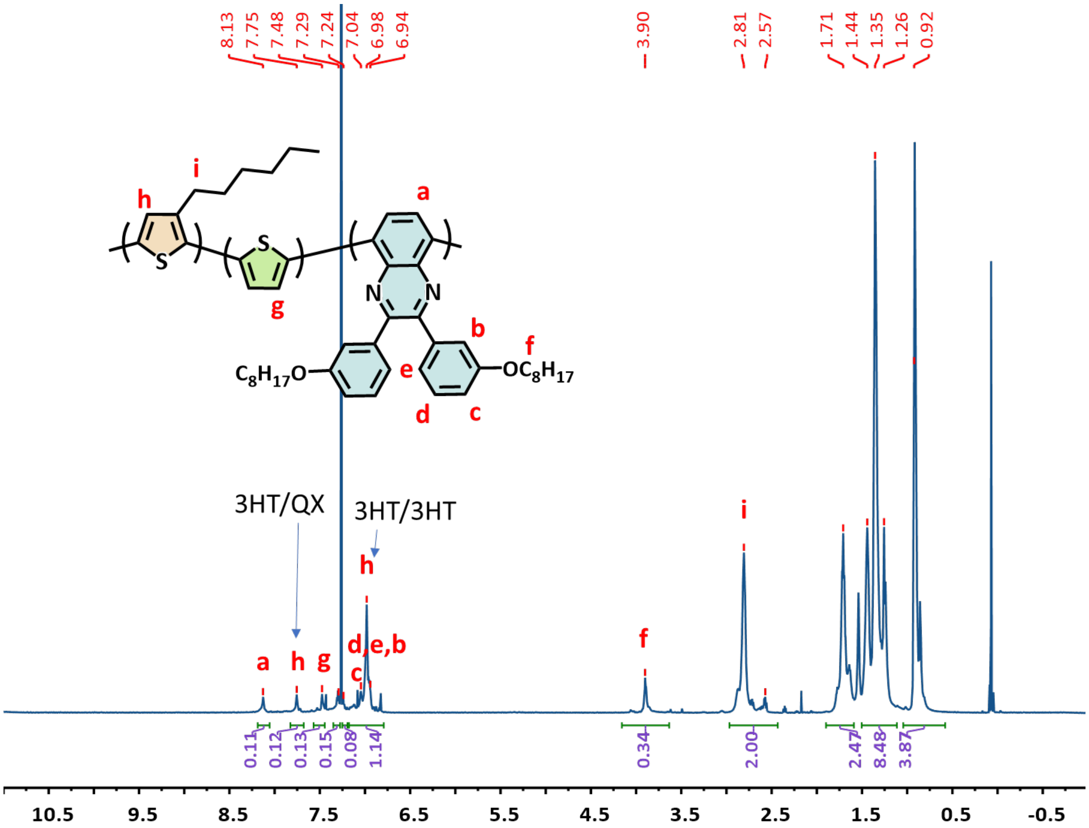

Figure S30. ^{1}H NMR Spectra of **DArP P3HTT-QX (P6).** Peaks for b-e overlap with majority 3HT couplings (around 6.98 ppm).

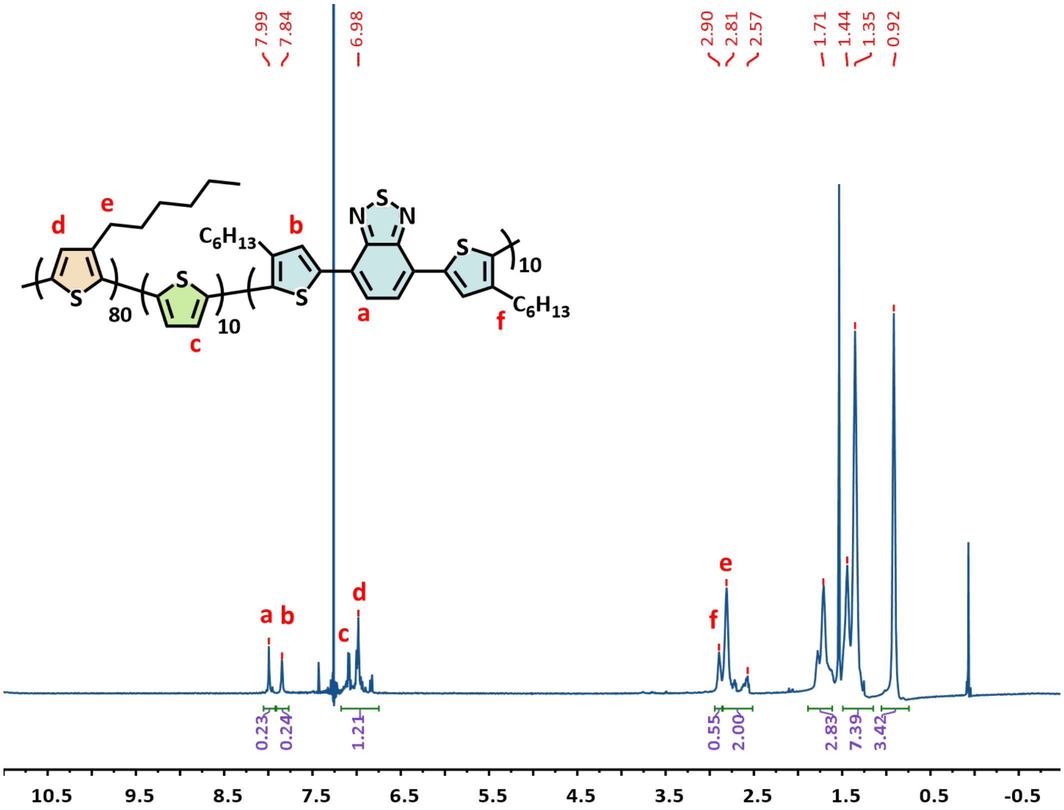

Figure S31. ^{1}H NMR Spectra of **DArP P3HTT-BTD (P7).**

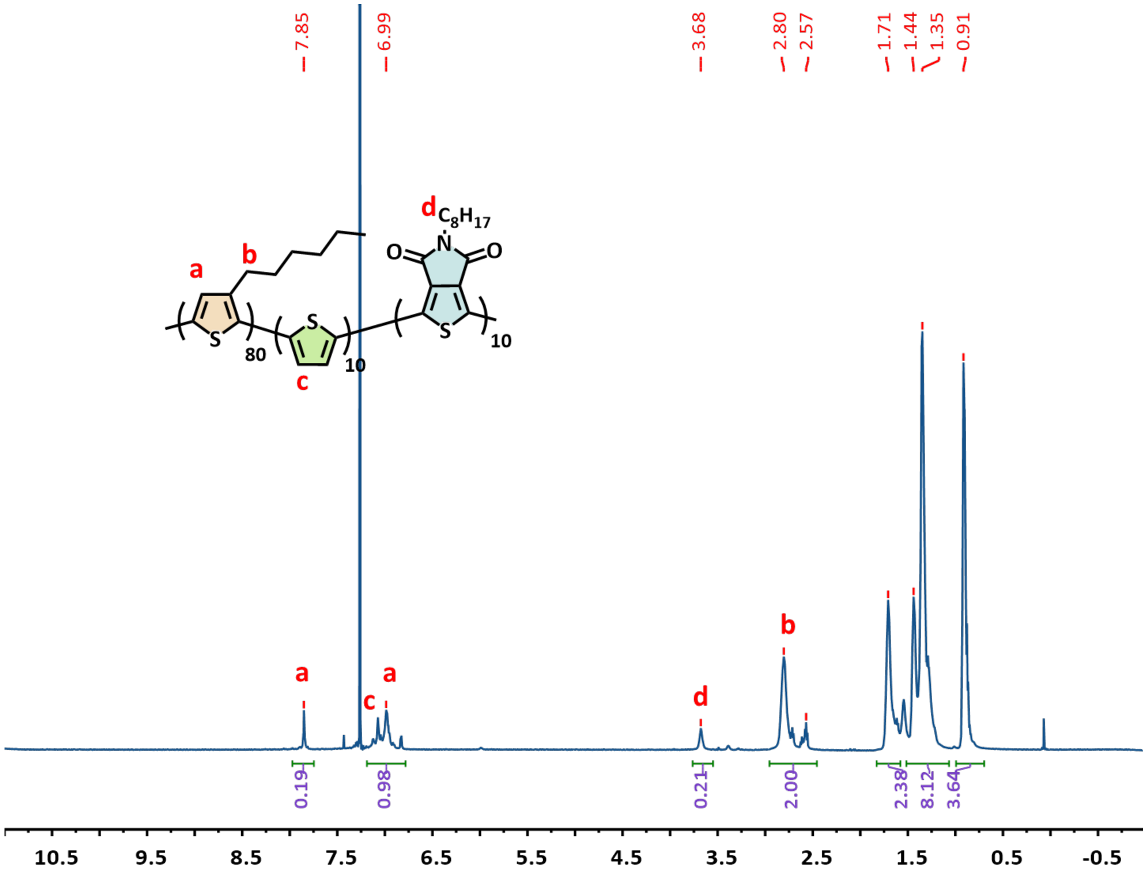

Figure S32. ^{1}H NMR Spectra of **DArP P3HTT-TPD (P8).**

4. CV Traces

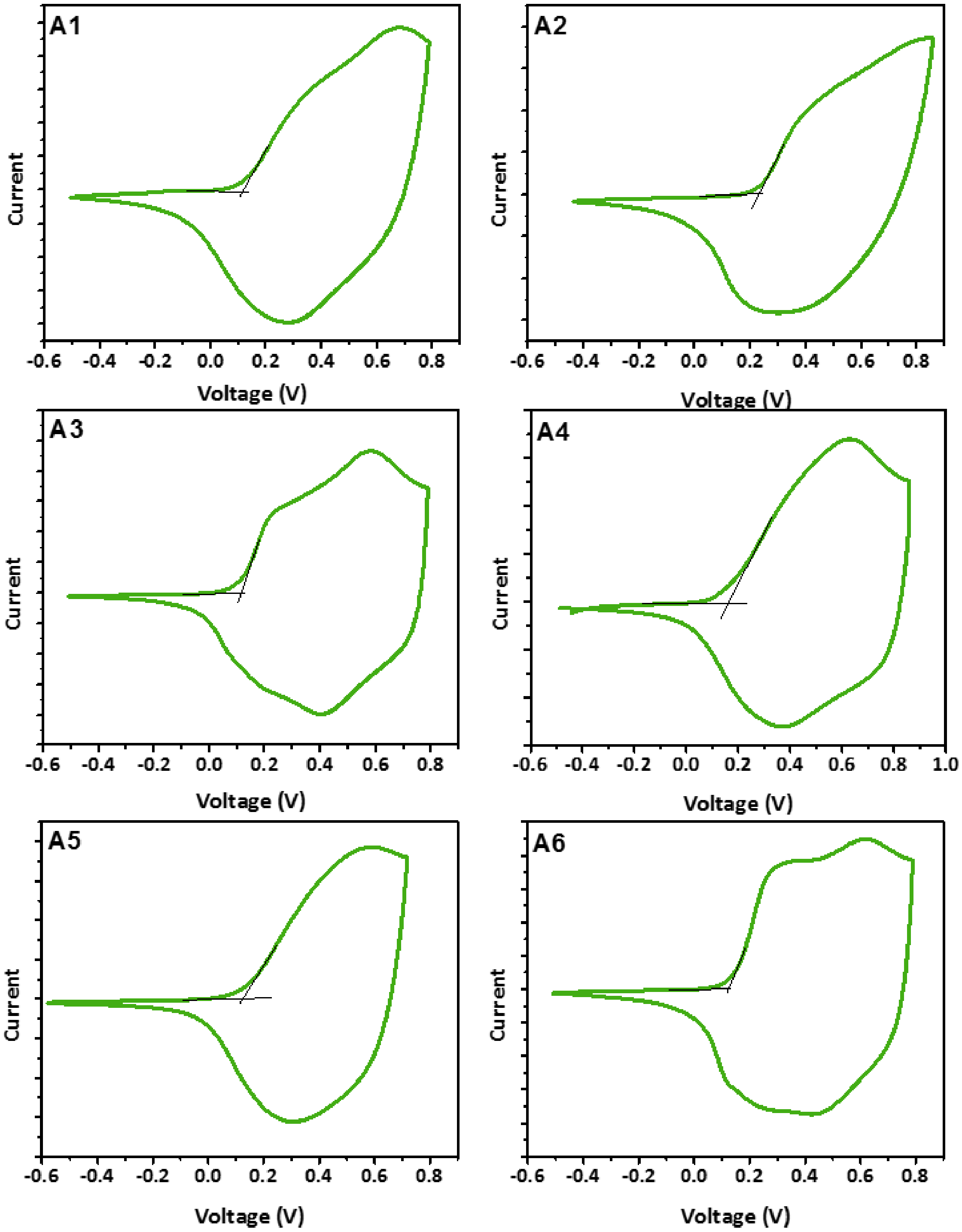

Figure S33. Cyclic voltammetry traces of P3HT Series.

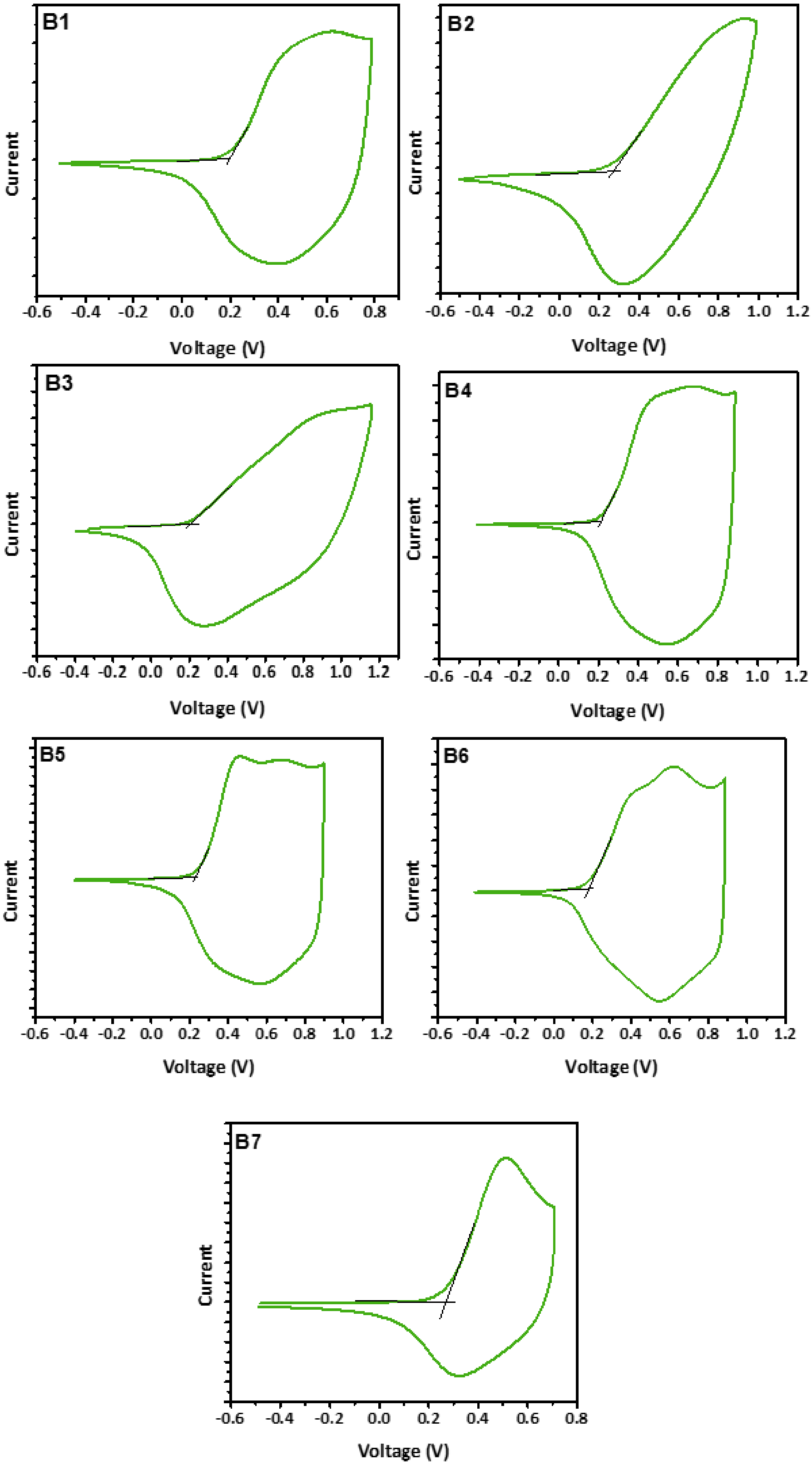

Figure S34. Cyclic voltammetry traces of P3HTT-DPP Series.

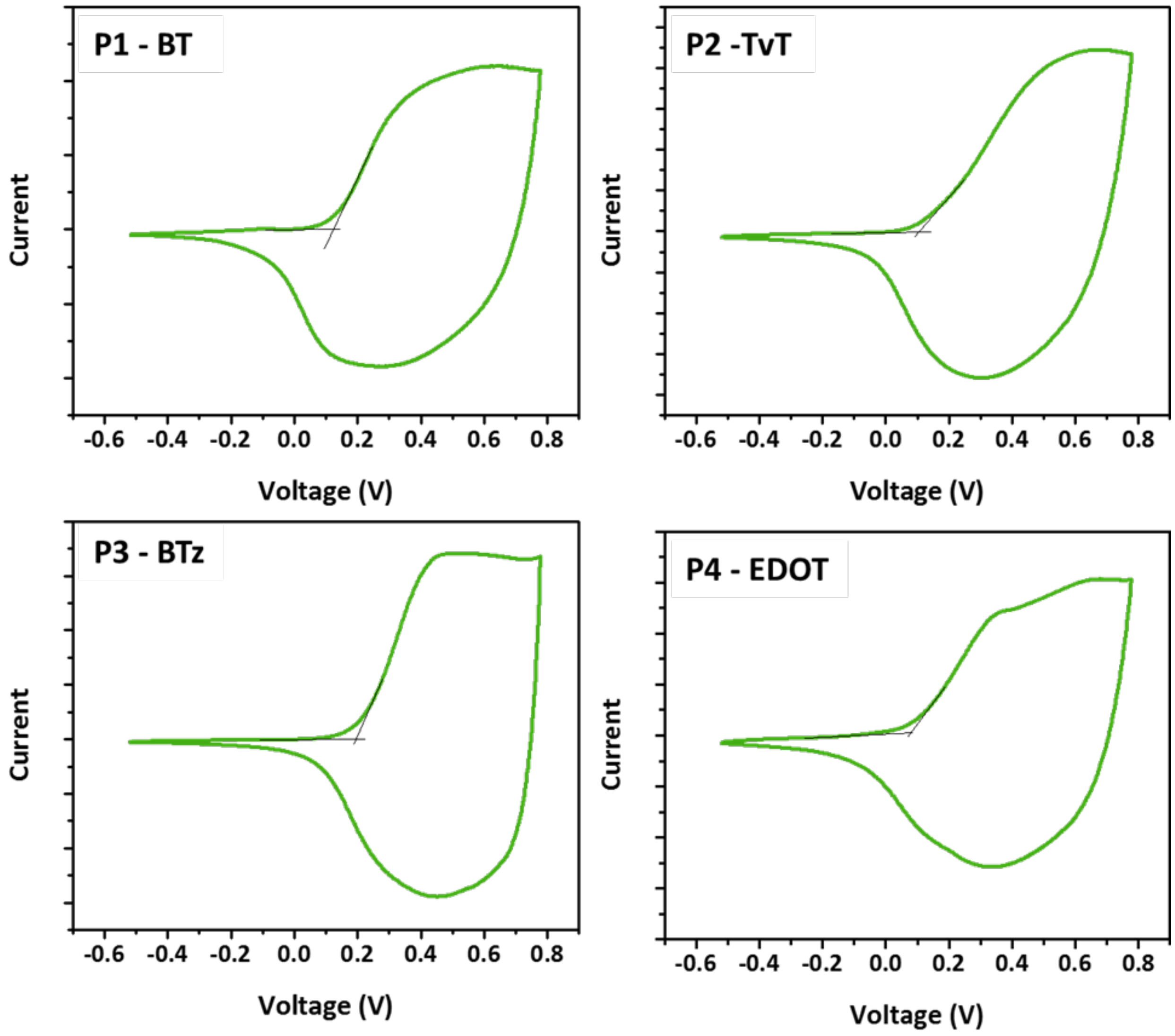

Figure S35. Cyclic Voltametry of the P3HT-X-DPP Series.

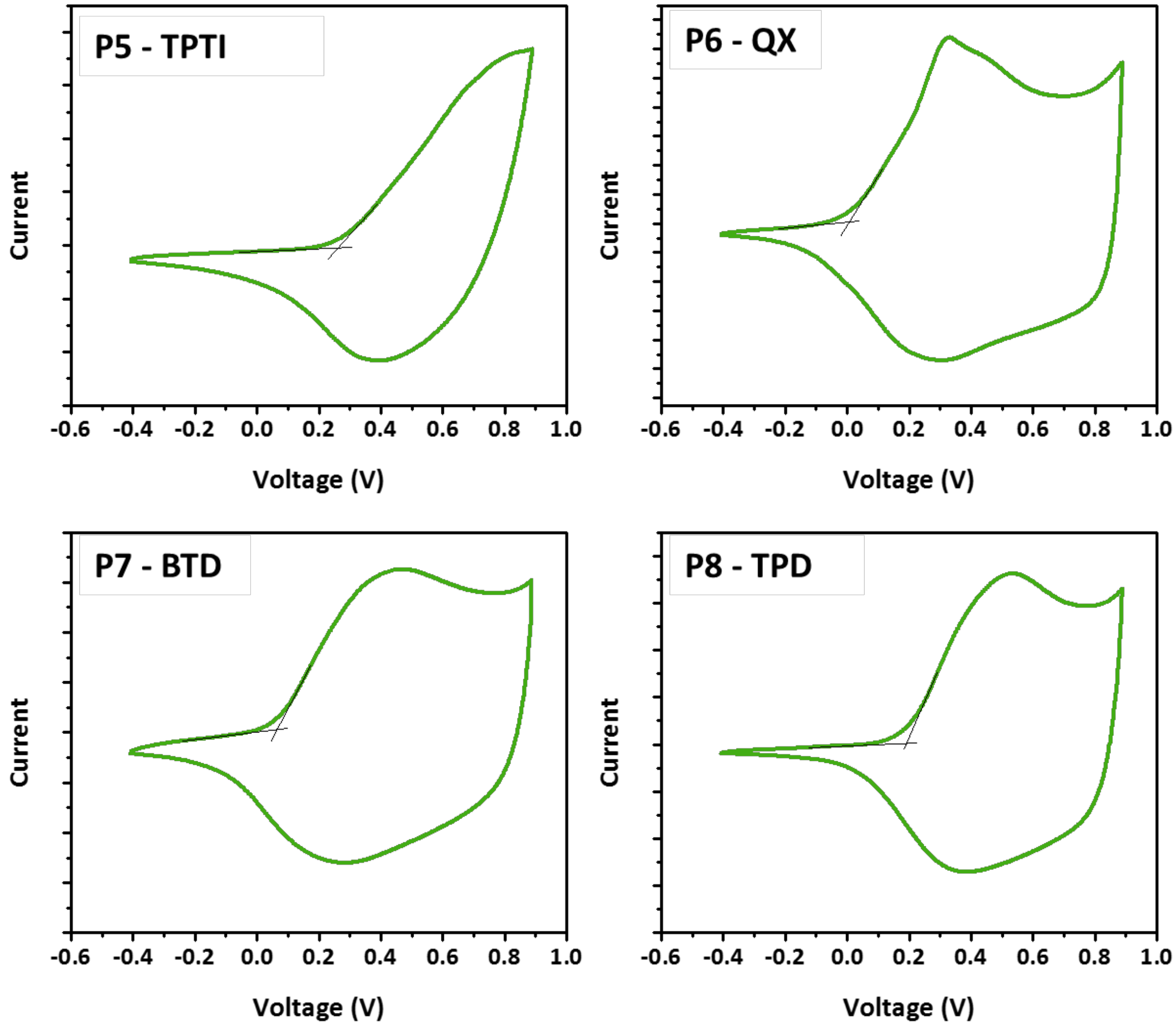

Figure S36. Cyclic Voltametry of the P3HTT-Y Series.

5. DSC Traces

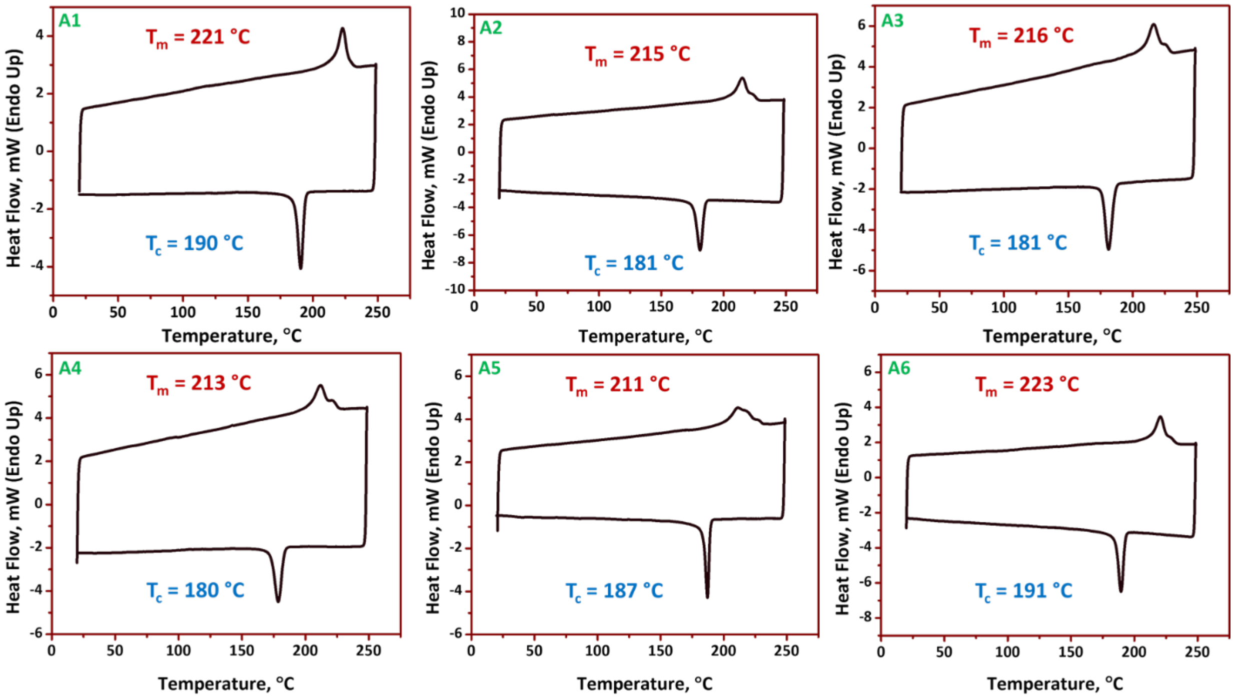

Figure S37. DSC Traces of the P3HT Series

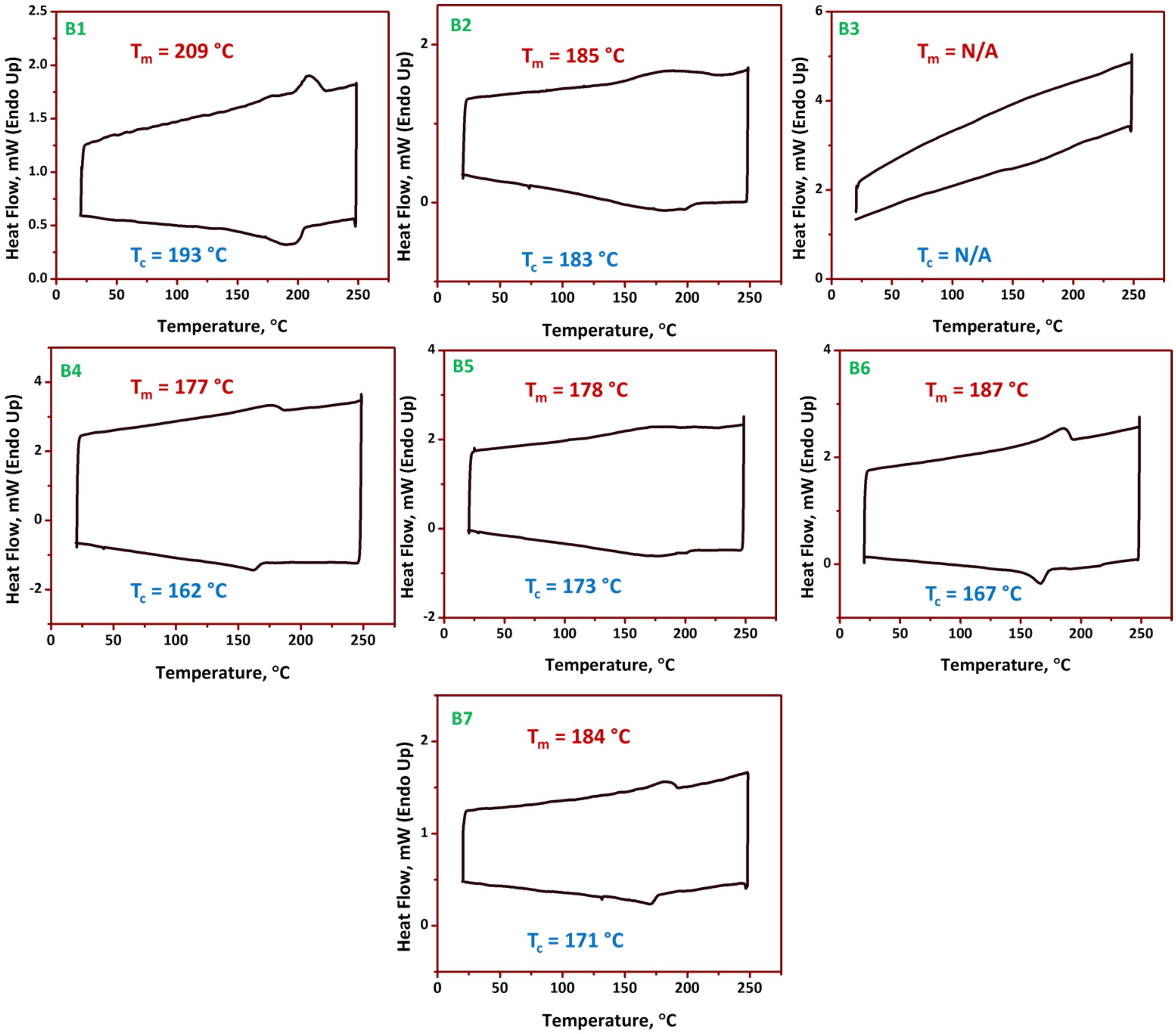

Figure S38. DSC Traces of P3HTT-DPP Series

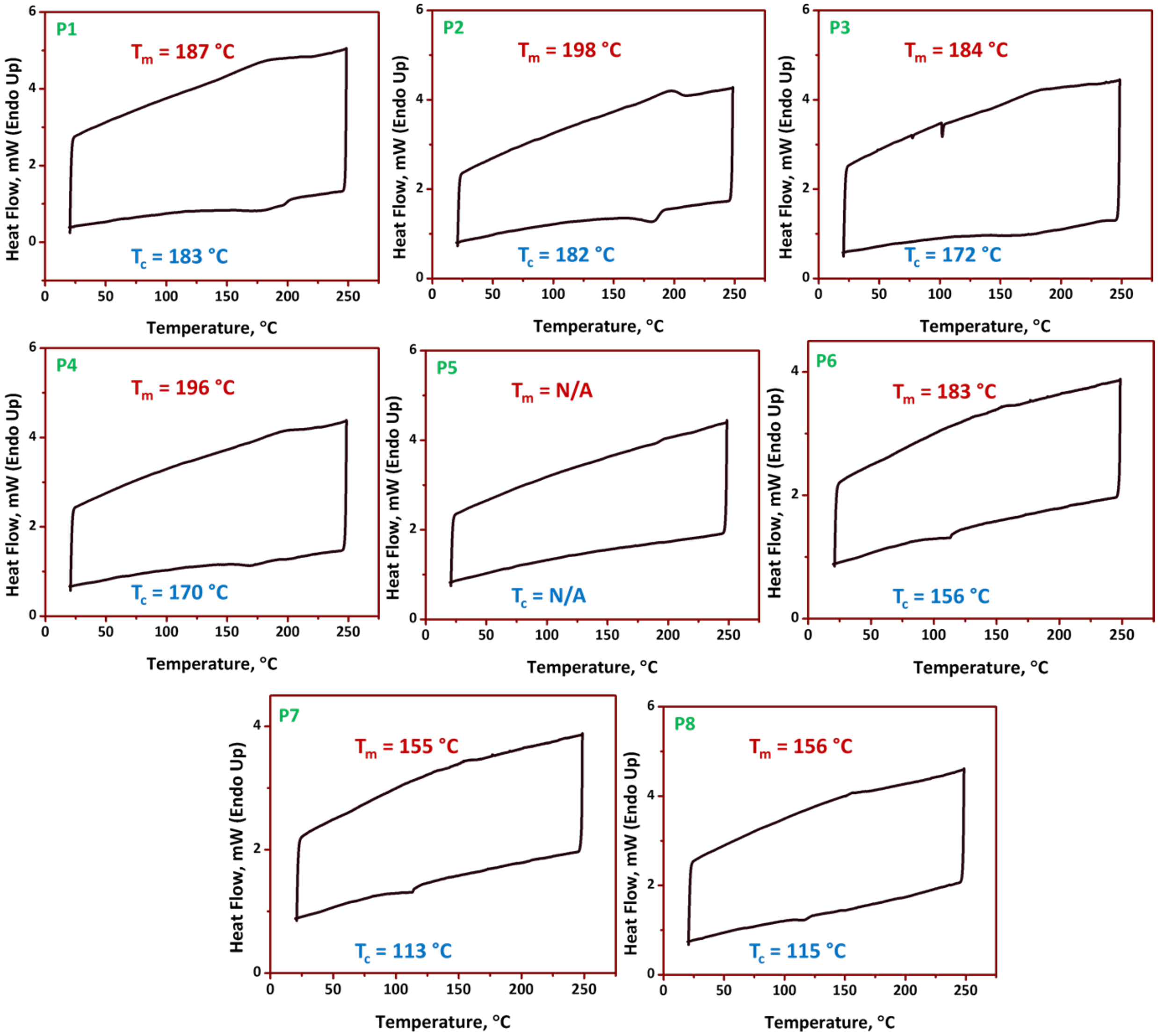

Figure S39. DSC Traces of DArP Semi-Random P3HT Analogs

6. Thin Film Measurements

For thin film measurements, solutions were spin-coated onto pre-cleaned 2.5 cm^2 glass slides (sonicated for 10 minutes in water, acetone, and isopropyl alcohol then dried under high N_2 flow) from o-dichlorobenzene solutions. The thickness of films and GIXRD measurements were obtained using Rigaku Diffractometer Ultima IV using Cu Kα radiation source ($\lambda = 1.54$ Å) in the reflectivity and grazing-incidence X-ray diffraction mode, respectively.

Crystallite size was estimated using Scherrer's equation[12,13]:

$$\tau = K\lambda/(\beta \cos\theta) \quad (1)$$

where τ is the mean size of the ordered domains, K is the dimensionless shape factor (K = 0.9), λ is the x-ray wavelength, β is the line broadening at half the maximum intensity (FWHM) in radians, and θ is the Bragg angle.

SCLC Hole Mobility:

Mobility was measured using a hole-only device configuration of ITO/PEDOT:PSS/Polymer/Al in the space charge limited current regime (SCLC).[11] The devices preparations for a hole-only device were the same as described below for solar cells. The dark current was measured under ambient conditions. At sufficient potential the mobilities of charges in the device can be determined by fitting the dark current to the model of SCL current and described by equation 2:

$$J_{SCLC} = \frac{9}{8}\varepsilon_R \varepsilon_0 \mu \frac{V^2}{L^3} \qquad (2),$$

where J_{SCLC} is the current density, ε_0 is the permittivity of space, ε_R is the dielectric constant of the polymer (assumed to be 3), μ is the zero-field mobility of the majority charge carriers, V is the effective voltage across the device ($V = V_{applied} - V_{bi} - V_r$), and L is the polymer layer thickness. The series and contact resistance of the hole-only device (18 – 23 Ω) was measured using a blank (ITO/PEDOT/Al) configuration and the voltage drop due to this resistance (V_r) was subtracted from the applied voltage. The built-in voltage (V_{bi}), which is based on the relative work function difference of the two electrodes, was also subtracted from the applied voltage. The built-in voltage can be determined from the transition between the ohmic region and the SCL region and is found to be about 1 V. Polymer film thicknesses were measured using GIXRD in the reflectivity mode.

7. Tabulated Polymer Data from GIXRD and UV-Vis Measurements

Table S1. Data Table of electrochemical oxidative HOMO levels, peak absorption, peak absorption coefficient, optical bandgaps, 2θ, GIXRD reflection intensity, d_{100} spacing, full width at half the maximum (FWHM), and crystallite size as estimated from Scherrer's equation.

Polymer	**$\lambda_{max,abs}$ (nm)**	**Absorption Coefficient (cm^{-1})**	**GIXRD Intensity (a.u.)**	**FWHM (deg.)**	**Crystallite Size (nm)**
A1	556	104039	585	0.60	13.2
A2	520	102776	723	0.52	15.3
A3	552	110500	1014	0.53	15.0
A4	556	104206	734	0.49	16.2
A5	552	109489	895	0.50	15.9
A6	556	121110	872	0.54	14.7
Polymer	**$\lambda_{max,abs}$ (nm)**	**Absorption Coefficient (cm^{-1})**	**GIXRD Intensity (a.u.)**	**FWHM (deg.)**	**Crystallite Size (nm)**
B1	511	51598	270	0.78	10.2
	684	72252			
B2	526	50118	712	0.57	13.9
	687	61058			
B3	493	32819	--	--	--
	682	22689			
B4	522	54836	712	0.58	13.7
	682	63625			
B5	516	55114	847	0.55	14.5
	679	55253			
B6	523	55507	1374	0.50	15.9
	684	67002			
B7	506	47274	1209	0.51	15.6
	682	70772			
Polymer	**$\lambda_{max,abs}$ (nm)**	**Absorption Coefficient (cm^{-1})**	**GIXRD Intensity (a.u.)**	**FWHM (deg.)**	**Crystallite Size (nm)**
P1	525	59439	584	0.59	13.5
	686	71408			
P2	541	61289	317	0.53	15.0
	689	73432			
P3	507	47615	277	0.51	15.6
	685	67042			
P4	526	53021	334	0.53	15.0
	753	69558			
P5	548	92859	543	0.54	14.7
P6	516	77826	1752	0.41	19.4
P7	511	54871	1078	0.37	21.5
P8	541	55218	165	0.47	16.9

8. Polymer OPV Data

Spectral Mismatch Determination

As emphasized by Shrotriya et al.,[14] there can be a spectral error in the measured short-circuit current due to differences in the spectra irradiance of the light source and the reference spectrum or differences in the spectral responses of the reference detector and test cell. This error can be conveyed by a spectra mismatch correction factor (*M*)[15] which is defined as:

$$M = \frac{\int_{\lambda_1}^{\lambda_2} E_{Ref}(\lambda) S_R(\lambda) d\lambda}{\int_{\lambda_1}^{\lambda_2} E_{Ref}(\lambda) S_T(\lambda) d\lambda} \frac{\int_{\lambda_1}^{\lambda_2} E_S(\lambda) S_T(\lambda) d\lambda}{\int_{\lambda_1}^{\lambda_2} E_S(\lambda) S_R(\lambda) d\lambda} \quad (2),$$

where $E_{Ref}(\lambda)$ is the reference spectral irradiance; $E_S(\lambda)$ is the source spectral irradiance; $S_R(\lambda)$ is the spectral responsivity; and $S_T(\lambda)$ is the spectral responsivity of the test cell, each as a function of wavelength (λ). Spectral responsivities $S(\lambda)$ for the tested devices were calculated based on the external quantum efficiency (EQE) values, according to equation 3:

$$S(\lambda) = \frac{q\lambda}{hc} EQE(\lambda) \quad (3),$$

where the constant term q/hc equals 8.0655 x 10^5 for wavelength in units of meters and $S(\lambda)$ in units of AW^{-1}. Based on the spectral responsivities $S(\lambda)$ obtained using equation 3, integrated short-circuit current densities ($J_{sc,EQE}$) can be obtained:

$$J_{sc,EQE} = \int_{\lambda_1}^{\lambda_2} E_{Ref}(\lambda) S_T(\lambda) d\lambda \quad (4).$$

In order to mismatch-correct the efficiencies of the BHJ solar cells, short-circuit current densities (J_{sc}) were divided by the M, as defined in equation 5. The raw data (J_{sc}), spectral-mismatch factor (M) and the spectral mismatch-corrected short-circuit current densities ($J_{sc,corr}$) are summarized in **Table S2**.

$$J_{sc,corr} = \frac{J_{sc}}{M} \quad (5).$$

Table S2. Summary of raw short-circuit current densities ($J_{sc,raw}$), spectral-mismatch factor (M), spectral mismatch-corrected short-circuit current densities ($J_{sc,corr}$) and integrated shortcircuit current densities ($J_{sc,EQE}$) for BHJ solar cells based on semi-random copolymers

P3HT:PC$_{61}$BM	**$J_{sc,raw}$ (mA/cm^2)**	**M**	**$J_{sc,corr}$ (mA/cm^2)**	**$J_{sc,EQE}$ (mA/cm^2)**	**J_{sc} error (%)**
A1	8.04	0.96	8.34	8.44	1.20
A2	5.74	0.98	5.85	6.11	4.44
A3	8.38	1.02	8.22	8.31	1.09
A4	8.70	1.01	8.61	8.70	1.05
A5	8.59	1.01	8.5	8.63	1.53
A6	9.87	1.05	9.4	9.66	2.77
P3HTT-DPP:PC$_{61}$BM	**$J_{sc,raw}$ (mA/cm^2)**	**M**	**$J_{sc,corr}$ (mA/cm^2)**	**$J_{sc,EQE}$ (mA/cm^2)**	**J_{sc} error (%)**
B1	10.60	0.812	13.06	13.20	1.07
B2	4.27	0.819	5.21	5.11	1.92
B3	3.59	0.814	4.41	4.30	2.49
B4	8.25	0.811	10.17	10.06	1.08
B5	7.42	0.817	9.08	9.44	3.96
B6	10.78	0.814	13.24	13.30	0.45
B7	9.99	0.817	12.23	12.16	0.57
Polymer:PC$_{61}$BM	**$J_{sc,raw}$ (mA/cm^2)**	**M**	**$J_{sc,corr}$ (mA/cm^2)**	**$J_{sc,EQE}$ (mA/cm^2)**	**J_{sc} error (%)**
P1	8.53	0.828	10.3	9.82	4.66
P2	9.07	0.810	11.2	10.77	3.84
P3	5.98	0.808	7.4	7.31	1.22
P4	3.71	0.728	5.1	5.12	0.39
P5	9.48	0.987	9.6	10.21	6.35
P6	4.51	0.960	4.7	4.89	4.04
P7	2.70	0.872	3.1	3.22	3.87
P8	5.07	0.874	5.8	6.00	3.45

J-V Curves

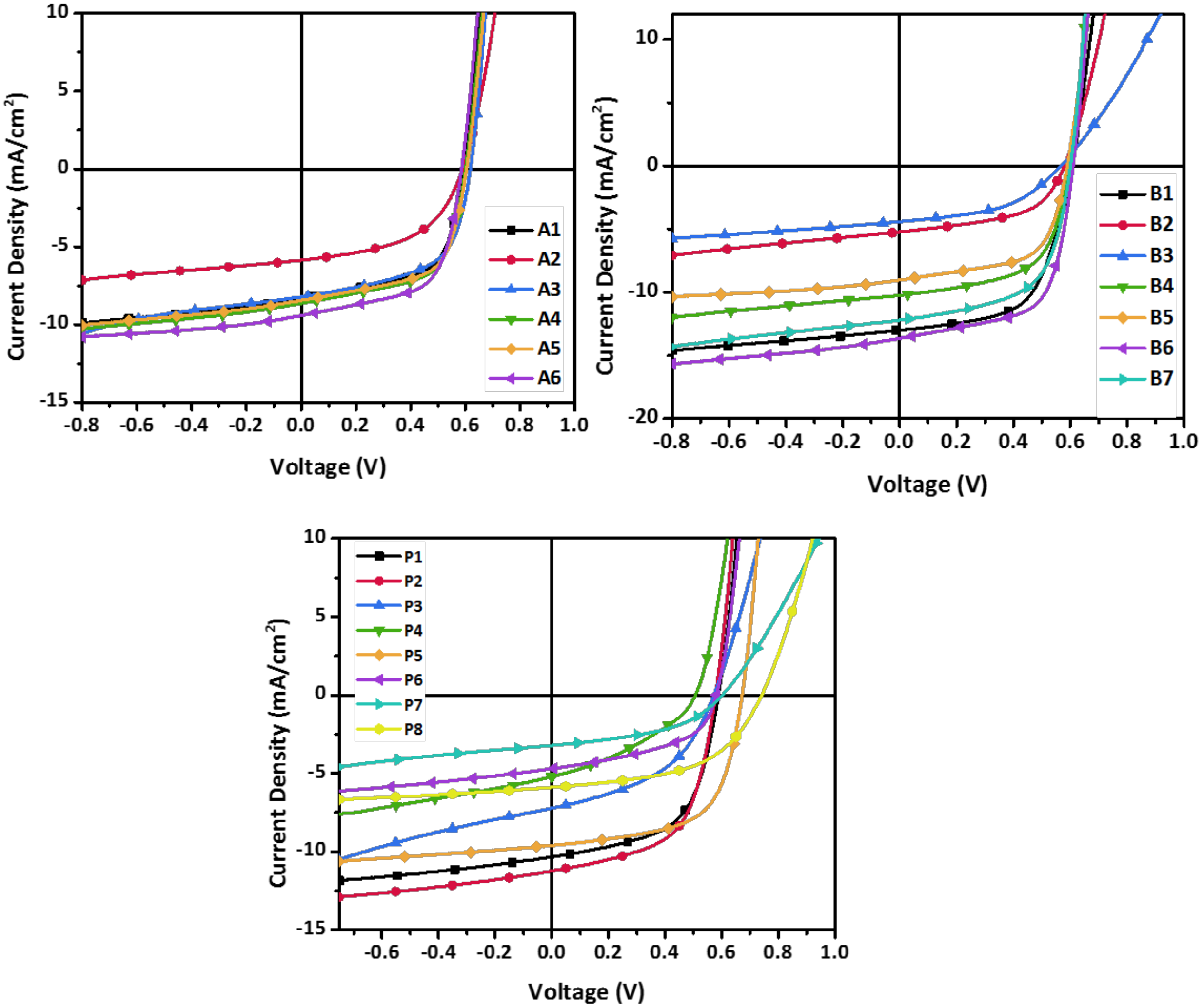

Figure S40. J-V Curves for P3HT (A1-A6), P3HTT-DPP (B1-B7), and Semi-Random P3HT Analogs (P1-P8).

Table S3. Averages and Standard Deviations for Polymer Solar Cell Data

Polymer: PC$_{61}$BM	**J$_{sc}$ [a] (mA/cm^2)**	**(±)**	*σ*	**V$_{oc}$ (V)**	**(±)**	*σ*	**FF**	**(±)**	*σ*	**PCE [a] (%)**	**(±)**	*σ*
A1	8.34	±	0.09	0.59	±	0.002	0.581	±	0.01	2.86	±	0.2
A2	5.85	±	0.22	0.59	±	0.002	0.464	±	0.02	1.60	±	0.2
A3	8.22	±	0.11	0.61	±	0.003	0.556	±	0.01	2.79	±	0.2
A4	8.61	±	0.04	0.60	±	0.003	0.578	±	0.01	2.99	±	0.1
A5	8.5	±	0.15	0.60	±	0.002	0.573	±	0.01	2.92	±	0.1
A6	9.4	±	0.07	0.59	±	0.001	0.591	±	0.01	3.28	±	0.1
Polymer: PC$_{61}$BM	**J$_{sc}$ [a] (mA/cm^2)**	**(±)**		**V$_{oc}$ (V)**	(±)		**FF**	(±)		**PCE [a] (%)**	(±)	*σ*
B1	13.06	±	0.17	0.60	±	0.001	0.590	±	0.01	4.62	±	0.2
B2	5.21	±	0.24	0.58	±	0.001	0.520	±	0.02	1.57	±	0.3
B3	4.41	±	0.14	0.57	±	0.002	0.449	±	0.01	1.13	±	0.3
B4	10.17	±	0.09	0.60	±	0.003	0.585	±	0.01	3.57	±	0.1
B5	9.08	±	0.11	0.59	±	0.001	0.580	±	0.02	3.11	±	0.1
B6	13.24	±	0.13	0.61	±	0.007	0.597	±	0.02	4.82	±	0.2
B7	12.23	±	0.16	0.60	±	0.005	0.567	±	0.02	4.16	±	0.2
Polymer: PC$_{61}$BM	**J$_{sc}$ [a] (mA/cm^2)**	**(±)**		**V$_{oc}$ (V)**	(±)		**FF**	(±)		**PCE [a] (%)**	(±)	*σ*
P1	10.3	±	0.08	0.59	±	0.001	0.549	±	0.01	3.34	±	0.1
P2	11.2	±	0.06	0.58	±	0.001	0.563	±	0.01	3.64	±	0.1
P3	7.4	±	0.09	0.57	±	0.002	0.440	±	0.02	1.86	±	0.1
P4	5.1	±	0.12	0.49	±	0.008	0.318	±	0.05	0.80	±	0.3
P5	9.6	±	0.19	0.67	±	0.001	0.590	±	0.02	3.79	±	0.2
P6	4.7	±	0.23	0.58	±	0.004	0.490	±	0.02	1.34	±	0.2
P7	3.1	±	0.29	0.60	±	0.001	0.439	±	0.01	0.82	±	0.1
P8	5.8	±	0.16	0.73	±	0.009	0.512	±	0.01	2.16	±	0.1

[a] Mismatch corrected.

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