Supporting Information

A Modular Strategy for Fully Conjugated Donor-Acceptor Block Copolymers

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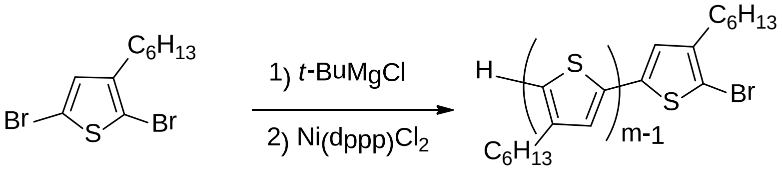
1. General methods

All reagents from commercial sources were used without further purification. Flash chromatography was performed using silica gel (particle size 40-63 μm). N,N-dimethylformamide (DMF), tetrahydrofuran (THF), and dichloromethane (DCM) were purchased from Fisher Scientific. All compounds were characterized by ^{1}H NMR (600 MHz) using Varian 600 instruments, with the solvent signal as internal reference and the spectra being acquired at room temperature. Samples were introduced using a direct insertion probe. Microwave reactions were performed using a Biotage microwave reactor. For polymer molecular weight determination, polymer samples were dissolved in chloroform at a concentration of 1 mg/mL, briefly heated, and then allowed to return to room temperature prior to filtering through a 0.45 μm filter. Gel permeation chromatography (GPC) was performed in chloroform ($CHCl_3$) on a Waters 2690 Separation Module equipped with a Waters 2414 Refractive Index Detector and a Waters 2996 Photodiode Array Detector. Molecular weights were calculated relative to linear PS standards. Differential scanning calorimetry (DSC) was performed under a nitrogen atmosphere at a heating rate of 10 °C/min. Atomic force microscopy (AFM) was conducted on an Asylum Research MFP 3D AFM, using NanoWorld Pointprobe Al-coated, non-contact mode Si cantilevers, with a resonant frequency of 190 kHz and a spring constant of 48 N/m. 2D grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements were performed at the Stanford Synchrotron Radiation Lightsource (SSRL) on Beamline 11-3, with a MAR345 image plate area detector, at 12.7 keV incident photon energy, and at incident angles of 0.10-0.12°. Thin film illumination occurred in a helium atmosphere to minimize X-ray beam damage. Specular X-ray diffraction was collected at SSRL Beamline 2-1 with an 8 keV incident photon energy.

2. Syntheses

a. Synthesis of P3HT-Br



P3HT-Br

A dried Schlenk flask equipped with a magnetic stir bar was charged with 2,5-dibromo-3-hexylthiophene (1.53 g, 4.71 mmol) in 50 mL of dry THF under argon. A solution of *t*-butylmagnesium chloride in THF (2.35 mL, 4.71 mmol, 2.00 M) was added, and the mixture was heated for 1.5 h at 40 °C. After cooling to room temperature, nickel(II)-[bis(diphenylphosphino)propane]chloride, Ni(dppp)Cl_2 (25 mg, 0.047 mmol) was quickly added. The reaction mixture was stirred for 30 min and quenched with 3 mL of hydrochloric acid (10%), and then poured into methanol. The crude product was filtered off and purified by subsequent Soxhlet extraction with methanol, hexane, and acetone to yield **P3HT-Br** polymer (270 mg, 35% yield). ^1H NMR ^1H ($CDCl_3$, 600 MHz) δ□6.96 (m, br), 2.78 (m, br), 1.68 (m, br), 1.34 (m, br), 1.32 (m, br), 1.31 (m, br), 0.89 (m, br); GPC ($CHCl_3$) M_n = 8 100 g/mol, M_w = 8 700 g/mol, PDI = 1.07.

The molecular weight of polythiophene can be calculated by analysis of the α-methyl protons of hexylthiophene from the P3HT-Br NMR spectrum. The integration of H^a/H^c is equal to 1/(m-2). The molecular weight of P3HT-Br is estimated as ~3 400 g/mol.

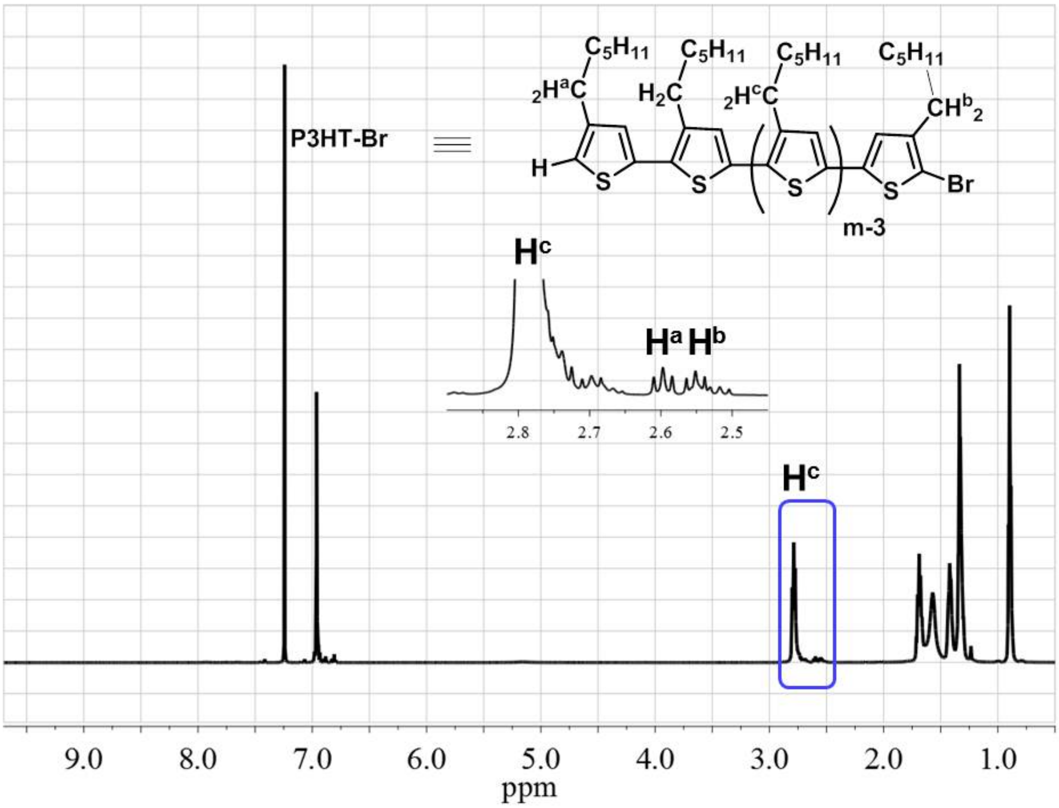
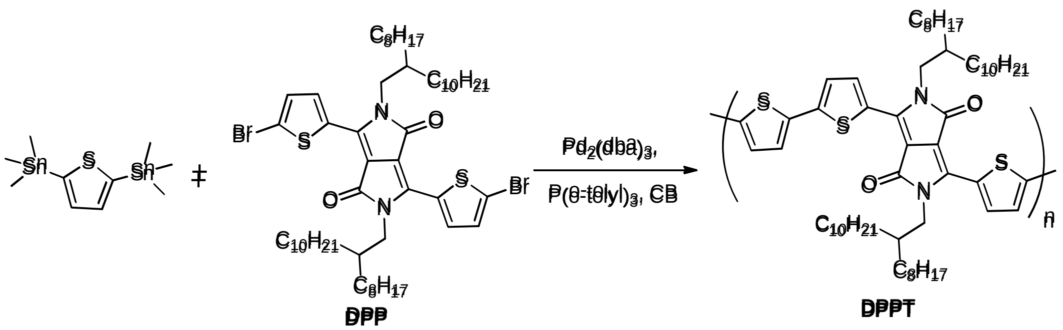


Figure S1. P3HT-Br ^1H spectrum.

b. Synthesis of DPPT homopolymer



A mixture of 2,5-bis(trimethylstannyl)thiophene (102.4 mg, 0.25 mmol), **DPP** (254.8 mg, 0.25 mmol), Pd$_2$(dba)$_3$ (4.5 mg, 0.005 mmol), and P(*o*-tolyl)$_3$ (6.1 mg, 0.02 mmol) was placed in a 10 mL microwave vial and sealed. Dry chlorobenzene (4 mL) was injected in the vial, and the mixture was sparged with argon for 20 min. The mixture was then heated at 120 °C for 3 min, 150 °C for 3 min, and finally 180 °C for 50 min under microwave irradiation. The reaction mixture was allowed to cool to 55 °C, then 30 mL of *o*-DCB was added to dissolve any precipitated polymer, and the mixture was eluted with chloroform through a silica plug. After precipitation into methanol (250 mL), the product was purified by Soxhlet extraction with methanol and acetone to yield the desired polymer, **DPPT** (230 mg, 97% yield), as a dark solid. ^{1}H NMR ^{1}H (CDCl$_3$, 600 MHz)□δ□8.92 (m, br), 7.41 (m, br), 7.06 (m, br), 4.02 (m, br), 1.93 (m, br), 1.22 (m, br), 0.86 (m, br); GPC (CHCl$_3$) M_n = 26 300 g/mol, M_w = 60 500 g/mol, PDI = 2.29.

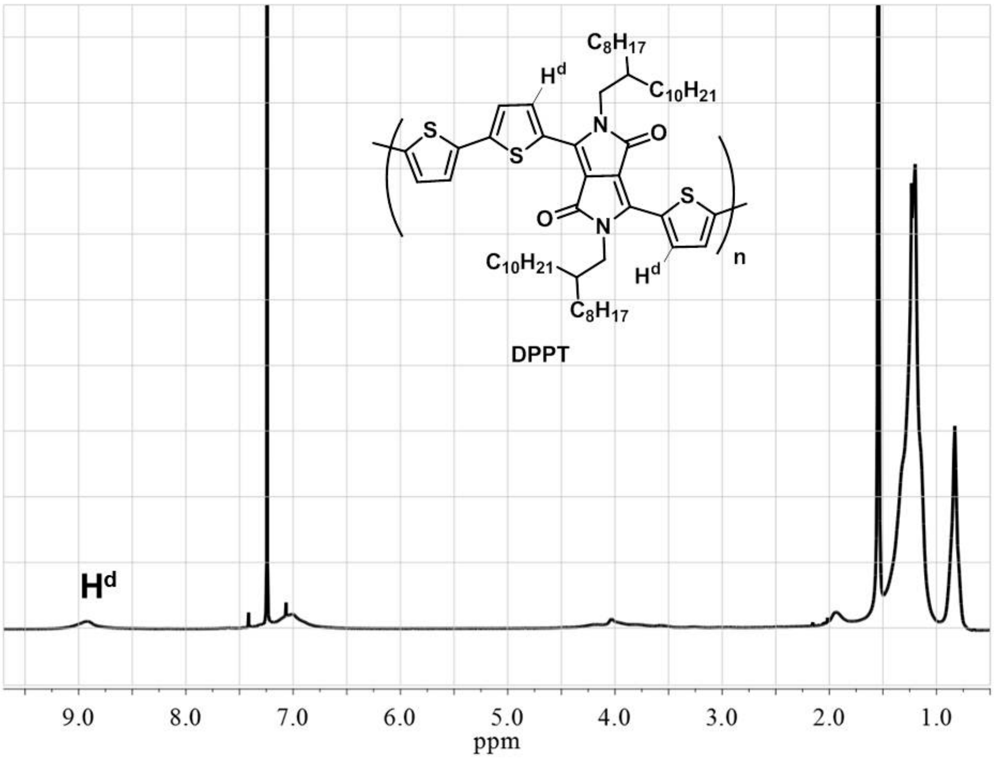
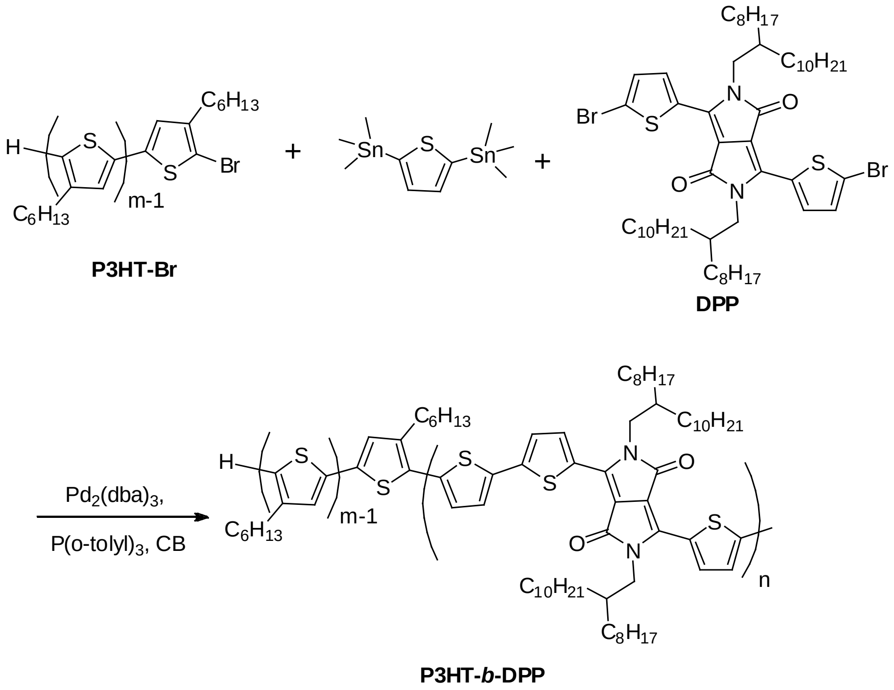


Figure S2. DPPT ^{1}H spectrum.

c. Synthesis of P3HT-*b*-DPP block copolymer



A mixture of **P3HT-Br** (8 k; GPC) (100 mg, 3 400 g/mol (NMR), 0.03 mmol), 2,5-bis(trimethylstannyl)thiophene (61.4 mg, 0.15 mmol), **DPP** (152.8 mg, 0.15 mmol), $Pd_2(dba)_3$ (2.7 mg, 0.003 mmol), and P(*o*-tolyl)$_3$ (3.7 mg, 0.012 mmol) was placed in a 10 mL microwave vial and sealed. Dry chlorobenzene (4 mL) was injected into the vial, and the mixture was sparged with argon for 20 min. The mixture was then heated at 120 °C for 3 min, 150 °C for 3 min, and finally 180 °C for 50 min under microwave irradiation. The reaction mixture was allowed to cool to 55 °C, then 30 mL of *o*-DCB was added to dissolve any precipitated polymer, and the mixture was eluted with chloroform through a silica plug. After precipitation into methanol (250 mL), the product was purified by Soxhlet extraction with methanol, hexane, and acetone to yield the desired polymer, **P3HT$_{87}$-*b*-DPP$_{13}$** (220 mg, 91% yield), as a dark solid. ^{1}H NMR ^{1}H ($CDCl_3$, 600 MHz) δ□8.92 (m, br), 6.97 (m, br), 4.02 (m, br), 2.80 (m, br), 1.95 (m, br), 1.72 (m, br), 1.51 (m, br), 1.43 (m, br), 1.35 (m, br), 0.93 (m, br), 0.85 (m, br); GPC ($CHCl_3$) M_n = 37 200 g/mol, M_w = 69 400 g/mol, PDI = 1.86.

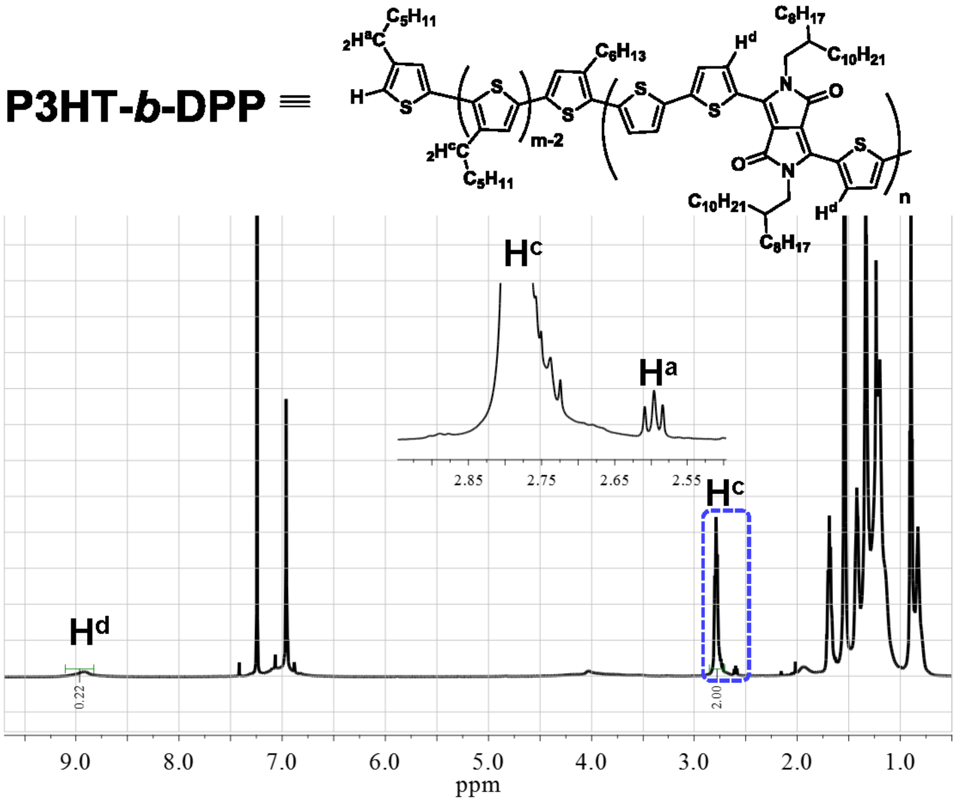
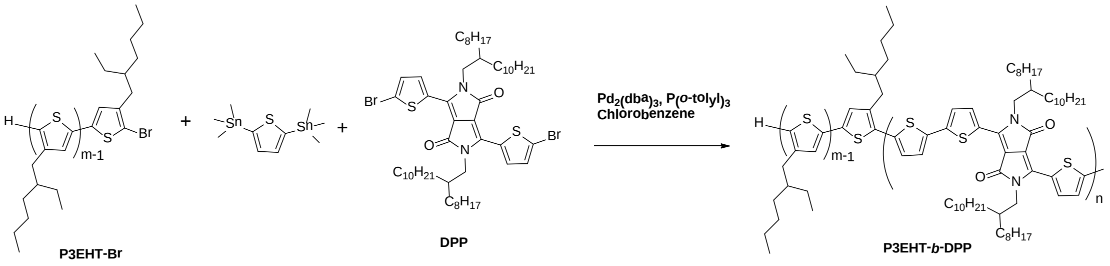


Figure S3. P3HT$_{87}$-*b*-DPP$_{13}$ ^{1}H spectrum.

d. Synthesis of P3EHT-*b*-DPP block copolymer



A mixture of **P3EHT-Br** (8 k; GPC) (60 mg, 5 000 g/mol (NMR), 0.012 mmol), 2,5-bis(trimethylstannyl)thiophene (61.4 mg, 0.15 mmol), **DPP** (152.8 mg, 0.15 mmol), Pd$_2$(dba)$_3$ (2.7 mg, 0.003 mmol), and P(*o*-tolyl)$_3$ (3.7 mg, 0.012 mmol) was placed in a 10 mL microwave vial and sealed. Dry chlorobenzene (4 mL) was injected into the vial, and the mixture was sparged with argon for 20 min. The mixture was then heated at 120 °C for 3 min, 150 °C for 3 min, and finally 180 °C for 50 min under microwave irradiation. The reaction mixture was allowed to cool to 55 °C, then 30 mL of *o*-DCB was added to dissolve any precipitated polymer, and the mixture was eluted with chloroform through a silica plug. After precipitation into methanol (250 mL), the product was dried to yield the desired polymer, **P3EHT$_{58}$-*b*-DPP$_{42}$** (200 mg, 95% yield), as a dark solid. ^{1}H NMR ^{1}H (CDCl$_3$, 600 MHz)□δ□ 8.89 (m, br), 6.91

(m, br), 4.03 (m, br), 2.75 (m, br), 1.94 (m, br), 1.70 (m, br), 1.51 (m, br), 1.43 (m, br), 1.35 (m, br), 0.93 (m, br), 0.88 (m, br); GPC ($CHCl_3$) M_n = 25 400 g/mol, M_w = 53 600 g/mol, PDI = 2.10.

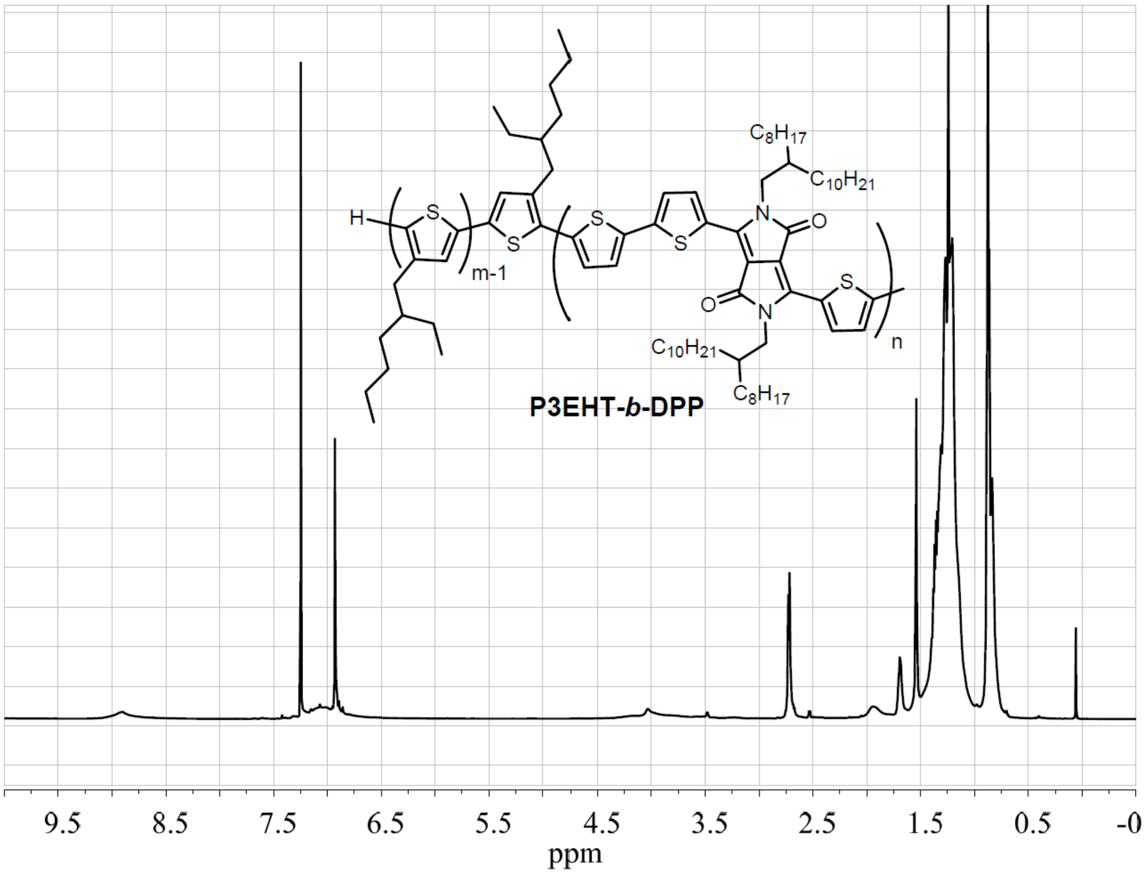
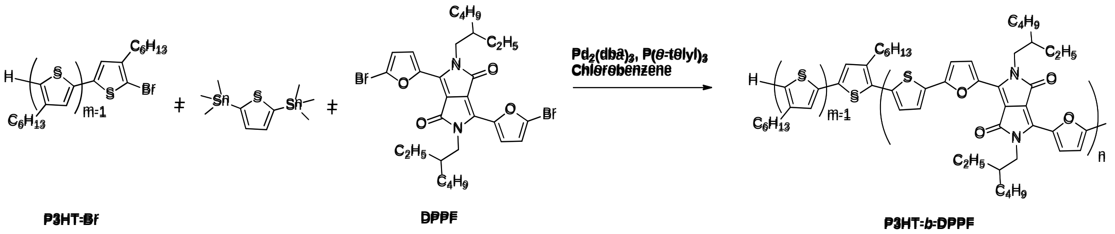


Figure S4. $P3EHT_{58}$-*b*-DPP_{42} ^1H spectrum.

e. Synthesis of P3HT-*b*-DPPF block copolymer



A mixture of **P3HT-Br** (21 k; GPC) (80 mg, 5 000 g/mol (NMR), 0.016 mmol), 2,5-bis(trimethylstannyl)thiophene (81.9 mg, 0.20 mmol), **DPPF** (130.0 mg, 0.20 mmol), $Pd_2(dba)_3$ (3.7 mg, 0.004 mmol), and P(*o*-tolyl)$_3$ (4.9 mg, 0.016 mmol) was placed in a 10 mL microwave vial and sealed. Dry chlorobenzene (4 mL) was injected into the vial, and the mixture was sparged with argon for 20 min. The mixture was then heated at 120 °C for 3 min, 150 °C for 3 min, and finally 180 °C for 50 min under microwave irradiation. The reaction mixture was allowed to cool to 55 °C, then 30 mL of *o*-DCB was added to dissolve any precipitated polymer, and the mixture was eluted with chloroform through a silica plug. After precipitation into methanol (250 mL), the product was purified by Soxhlet extraction with methanol, hexane, and acetone to yield the desired polymer, **P3HT$_{62}$-*b*-DPPF$_{38}$** (165 mg, 85% yield), as a dark solid. ^{1}H NMR ^{1}H (CDCl$_3$, 600 MHz) δ□8.81 (m, br), 6.90 (m, br), 4.83 (m, br), 2.73 (m, br), 2.05 (m, br), 1.72 (m, br), 1.51 (m, br), 1.43 (m, br), 1.35 (m, br), 0.95 (m, br), 0.86 (m, br); GPC (CHCl$_3$) M_n = 109 000 g/mol, M_w = 162 000 g/mol, PDI = 1.48.

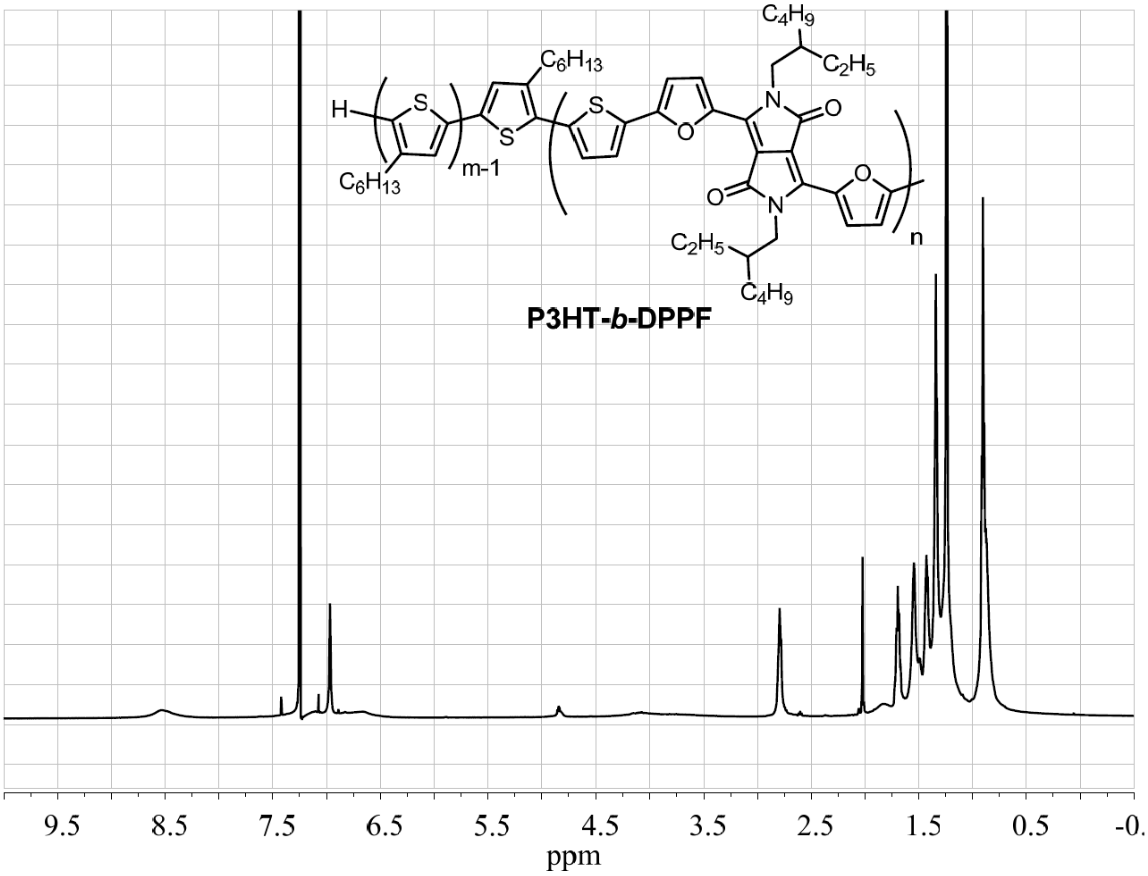


Figure S5. P3HT$_{62}$-*b*-DPPF$_{38}$ ^{1}H spectrum.

3. GPC contours based on UV detection

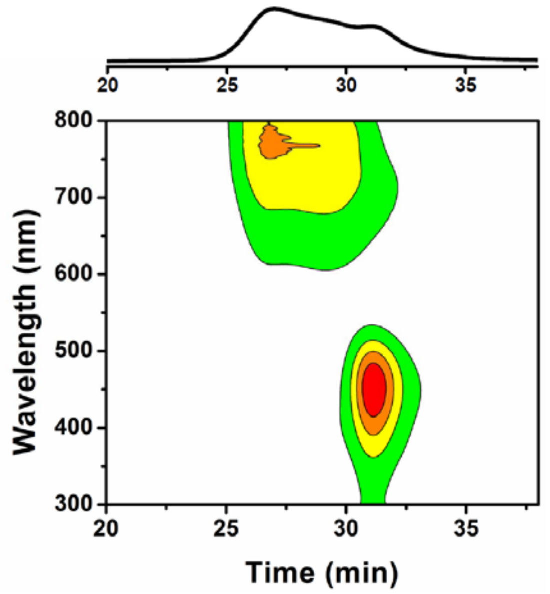


Figure S6. The GPC contour of blended P3HT and DPP homopolymers based on a UV detector.

4. Thermal transitions detected with DSC

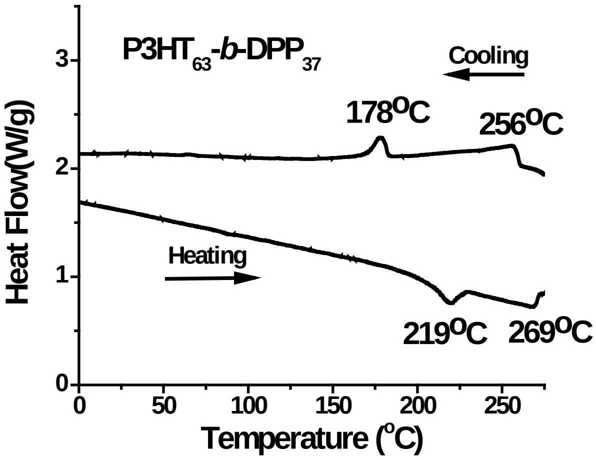


Figure S7. DSC results for P3HT$_{63}$-*b*-DPP$_{37}$.

Table S1. Enumerated DSC results for P3HT and DPPT homopolymers, as well as for two block copolymer architectures that were synthesized.

Polymer	T_m (°C)	T_m (°C)	T_c (°C)	T_c (°C)
P3HT	220			198
DPPT		252	248	
$P3HT_{87}$-*b*-DPP_{13}	218	256	245	181
$P3HT_{63}$-*b*-DPP_{37}	219	269	256	178

5. Film preparation

Thin film samples were prepared for surface morphology and bulk film microstructure studies, using AFM and GIWAXS, respectively. Substrates were cleaned by sonicating cleaved Si wafer pieces for 10 min each in acetone, *2*-propanol, and deionized water, followed by a ~3 min UV-ozone exposure. To mimic solar cell device fabrication, poly(ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (Clevios P HC V4) was spun-cast on the clean Si substrate at 4000 rpm for 55 s, and the supported film was heated at 140 °C for ~20 min.

For AFM studies, block copolymer thin films were deposited on PEDOT:PSS/Si by spin-casting the 8 mg mL^{-1} solution, in dichlorobenzene, at 800 rpm for 55 s, followed by 1500 rpm for 4 s. For GIWAXS studies, P3HT and DPP homopolymer thin films were prepared on PEDOT:PSS/Si by spin-casting the 10 mg mL^{-1} solution, in dichlorobenzene, at 1000 rpm for 60 s, followed by 2000 rpm for 20 s. Block copolymer thin films were prepared following the same procedure, except with a solution concentration in dichlorobenzene of 8 mg mL^{-1}. Films of a 1.2:1 P3HT:DPP blend were prepared on PEDOT:PSS/Si by spin-casting the 10 mg mL^{-1} solution, in dichlorobenzene, at 1000 rpm for 60 s, followed by 2000 rpm for 20 s. For these morphology experiments, annealing treatments of the supported thin films were performed at various temperatures, both below and above each melting transition, on a hot plate in an inert N_2 atmosphere.

6. P3HT:DPP blend morphology characterized with AFM

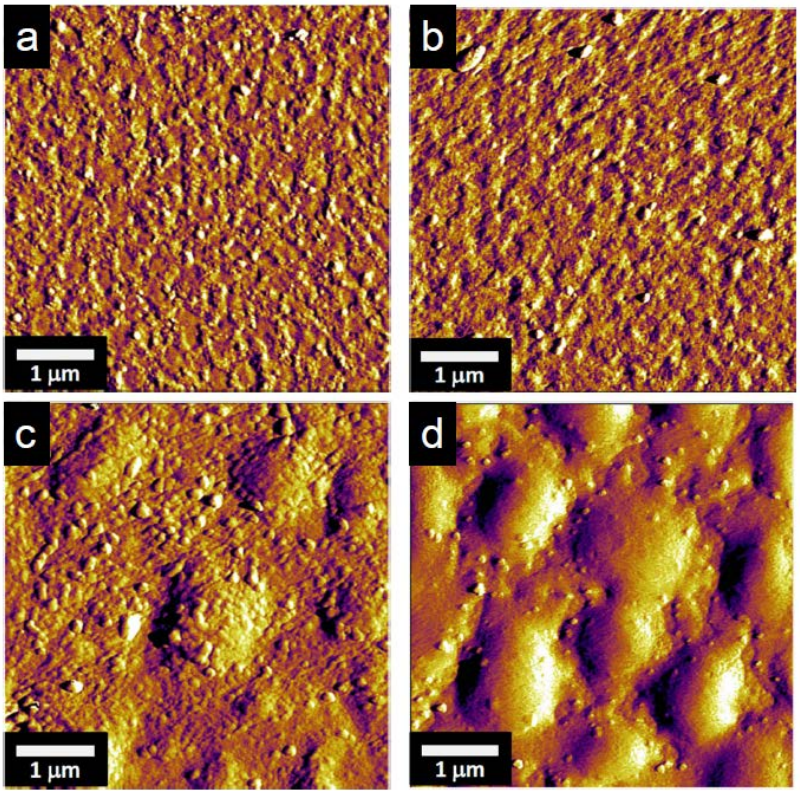


Figure S7. AFM phase images of P3HT:DPP blend thin films: (a) as-cast and (b-d) annealed at (b) 200 °C, (c) 225 °C, and (d) 265 °C.

7. P3HT:DPP blend structural characterization with GIWAXS

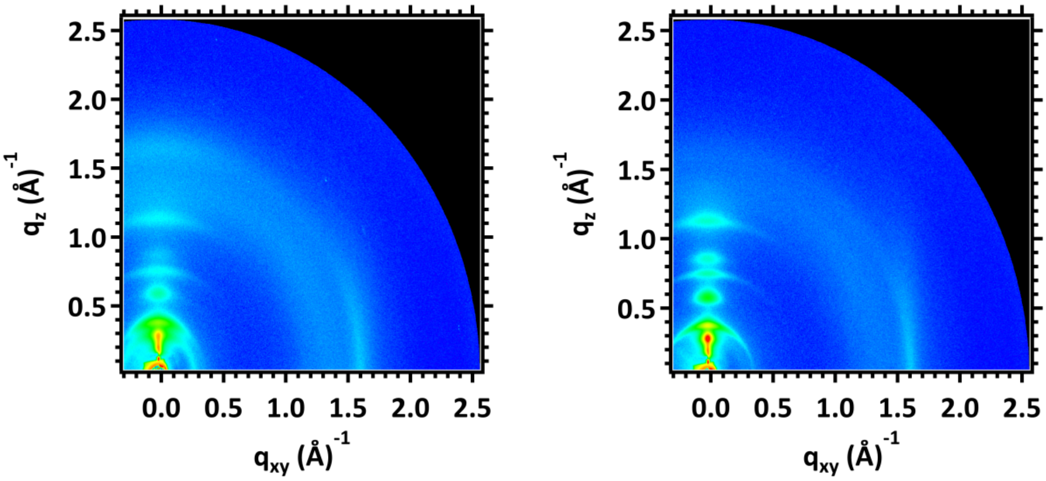


Figure S8. GIWAXS patterns of P3HT:DPP blend thin films: (left) as-cast and (right) annealed at 260 °C.