

Supporting Information

Surface Energy Modification of Semi-Random P3HTT-DPP

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Materials and Methods: All reagents from commercial sources were used without further purification, unless otherwise noted. All reactions were performed under dry N₂, unless otherwise noted. All dry reactions were performed with glassware that was flamed under high vacuum and backfilled with N₂. Flash chromatography was performed using a Teledyne CombiFlash R_f instrument in combination with RediSep R_f normal phase disposable columns. Solvents were purchased from VWR and used without further purification except for THF, which was dried over sodium/benzophenone before being distilled.

All compounds were characterized by ¹H NMR (500 MHz) and ¹³C NMR (500 MHz) on a Varian 500. Polymer ¹H NMRs (600 MHz) were obtained on a Varian VNMRS-600. For polymer molecular weight determination, polymer samples were dissolved in HPLC grade *o*-dichlorobenzene at a concentration of 0.5 mg/ml, briefly heated and then allowed to turn to room temperature prior to filtering through a 0.2 μm PTFE filter. SEC was performed using HPLC grade *o*-dichlorobenzene at a flow rate of 1 ml/min on one 300 x 7.8 mm TSK-Gel GMH_H R-H column (Tosoh Corporation) at 70 °C using a Viscotek GPC Max VE 2001 separation module and a Viscotek TDA 305 RI detector. The instrument was calibrated vs. polystyrene standards (1,050 – 3,800 000 g/mol) and data was analyzed using OmniSec 4.6.0 software.

Cyclic voltammetry was collected using an EG&G instruments Model 263A potentiostat under the control of PowerSuite 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) and a Pt wire counter electrode was purged with nitrogen and maintained under nitrogen atmosphere during all measurements. Acetonitrile and chloroform were distilled over

CaH₂ prior to use. Tetrabutyl ammonium hexafluorophosphate (0.1 M) was used as the supporting electrolyte for polymer films. Polymer films were made by repeatedly dipping the Pt wire in a 1% (w/w) polymer solution in chloroform or *o*-dichlorobenzene and dried under nitrogen prior to measurement.

For thin film measurements polymers were spin coated onto pre-cleaned glass slides from *o*-dichlorobenzene solutions (10 mg/mL). UV-vis absorption spectra were obtained on a Perkin-Elmer Lambda 950 spectrophotometer. The thickness and crystallinity of the thin films and GIXRD measurements were obtained using Rigaku Diffractometer Ultima IV using Cu K α radiation source (λ = 1.54 Å) in the reflectivity and grazing incidence X-Ray diffraction mode, respectively.

Surface energy studies of the neat polymers film, using the static sessile drop method, were performed on Ramé-Hart Instrument Co. contact angle goniometer model 290-F1 and analyzed using Surface Energy (one liquid) tool implemented in DROPimage 2.4.05 software. Polymer films were prepared from 10 mg/ml *o*-dichlorobenzene solutions (10 mg/mL), spin-coated on the pre-cleaned glass slides. Water and glycerol were used as two solvents in the two-liquid model to measure the static contact angle and harmonic mean Wu model was used to calculate the average surface energy values for each film according to following set of equations:

$$\gamma_w \cdot (1 + \cos(Z^w)) = \frac{4\gamma_w^d \cdot \gamma^d}{\gamma_w^d + \gamma^d} + \frac{4\gamma_w^p \cdot \gamma^p}{\gamma_w^p + \gamma^p} \quad (1)$$

$$\gamma_g \cdot (1 + \cos(Z^g)) = \frac{4\gamma_g^d \cdot \gamma^d}{\gamma_g^d + \gamma^d} + \frac{4\gamma_g^p \cdot \gamma^p}{\gamma_g^p + \gamma^p} \quad (2)$$

$$\gamma^{tot} = \gamma^d + \gamma^p \quad (3)$$

$$\gamma_w = 72.8 \frac{mJ}{m^2}; \gamma_w^d = 21.8 \frac{mJ}{m^2}; \gamma_w^p = 51.0 \frac{mJ}{m^2}$$

$$\gamma_g = 64.0 \frac{mJ}{m^2}; \gamma_g^d = 34.0 \frac{mJ}{m^2}; \gamma_g^p = 30.0 \frac{mJ}{m^2}$$

where Z^w and Z^g are the contacts angles with water and glycerol, respectively; γ^{tot} is the total surface energy, γ^p and γ^d are the polar and dispersive surface energy components.

All steps of device fabrication and testing were performed in air. ITO-coated glass substrates (10 Ω/\square , Thin Film Devices Inc.) were sequentially cleaned by sonication in detergent, de-ionised water, tetrachloroethylene, acetone, and isopropyl alcohol, and dried in a nitrogen stream. A thin layer of PEDOT:PSS (Baytron® P VP AI 4083, filtered with a 0.45 μm PVDF syringe filter – Pall Life Sciences) was first spin-coated on the pre-cleaned ITO-coated glass substrate and annealed at 130 °C for 60 minutes under vacuum. Polymer:fullerene solutions were prepared in *o*-dichlorobenzene or chloroform and stirred for 24 hours at 60 °C and 40 °C, respectively. The polymer:PC₆₁BM active layer was spin-coated (with a 0.45 μm PTFE syringe filter – Whatman) on top of the PEDOT:PSS layer. The P3HTT-DPP: PC₆₁BM film was spin-coated from *o*-dichlorobenzene solution (10 mg/mL in P3HTT-DPP, 1:1.3 w/w polymer:PC₆₁BM ratio). The P3HTMETT-DPP: PC₆₁BM film was spin-coated from *o*-dichlorobenzene solution (11 mg/mL in P3HTMETT-DPP, 1:1.3 w/w polymer:PC₆₁BM ratio). The P3HTFHTT-DPP: PC₆₁BM film was

spin-coated from chloroform solution (4 mg/mL in P3HTFHTT-DPP, 1:2 w/w polymer:PC₆₁BM ratio). Films were placed in a nitrogen cabinet for 20 minutes before being transferred to a vacuum chamber. The substrates were pumped down to a high vacuum and aluminum (100 nm) was thermally evaporated at 3 – 4 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 are 5.2 mm² P3HTT-DPP and P3HTMETT-DPP devices and 4.7 mm² for P3HTFHTT-DPP devices.

The current-voltage (I-V) characteristics of the photovoltaic devices were measured under ambient conditions using a Keithley 2400 source-measurement unit. An Oriel® Sol3A class AAA solar simulator with xenon lamp (450 Watt) and an AM 1.5G filter was used as the solar simulator. An Oriel PV reference cell system 91150V was used as the reference cell. To calibrate the light intensity of the solar simulator (to 100 mW/cm²), the power of the xenon lamp was adjusted to make the short-circuit current (J_{sc}) of the reference cell under simulated sun light as high as it was under the calibration condition. Spectral mismatch corrections were performed for each device according to previously described conditions.¹

Mobility was measured using a hole-only device configuration of both neat and blend polymer films (ITO/PEDOT:PSS/Polymer/Al, ITO/PEDOT:PSS/Polymer:PC₆₁BM/Al, respectively) or electron-only device configuration of Al/Polymer:PC₆₁BM/Al in the space charge limited current regime. The devices preparations for a hole-only device were the same as described below for solar cells. In case of electron-only device, Al was deposited on the pre-cleaned glass followed with the same steps as in case of a hole-only device. 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 4:

$$J_{SCLC} = \frac{9}{8} \epsilon_R \epsilon_0 \mu \frac{V^2}{L^3} \quad (4),$$

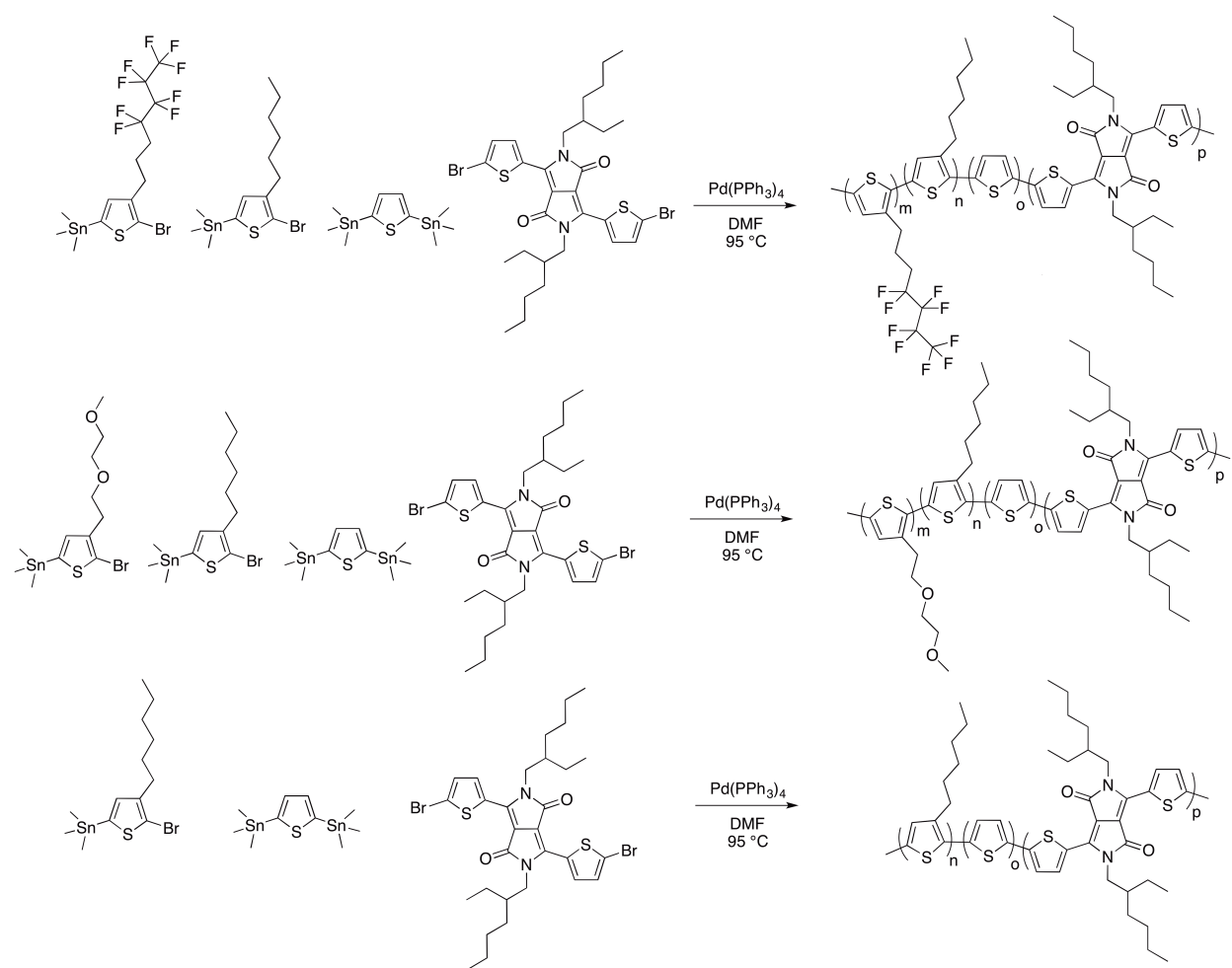
where J_{SCLC} is the current density, ϵ_0 is the permittivity of space, ϵ_R is the dielectric constant of the polymer (assumed to be 3), μ is the zero-field mobility of the majority charge carriers, V is the effective voltage across the device ($V = V_{applied} - V_{bi} - V_r$), and L is the polymer layer thickness. The series and contact resistance of the hole-only device (40-45 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 0.6 V. The series and contact resistance of the electron-only device (1.5-2 Ω) was measured using a blank (Al/Al) configuration. The built-in voltage (V_{bi}) determined from the transition between the ohmic region and the SCL region and is found to be about 2.3 V. Polymer film thicknesses were measured using GIXRD in the reflectivity mode.

Transmission electron microscopy (TEM) was performed on the JEOL JEM-2100 microscope equipped with the Gatan Orius CCD camera. The accelerating voltage was 200 kV. Films for the TEM measurements were prepared from the *o*-dichlorobenzene solutions of Polymer:PC₆₁BM blends at the optimized processing conditions indicated for BHJ devices listed above. Films for TEM were prepared by first spin-casting on PEDOT:PSS coated glass, which were then placed in de-ionized water and upon PEDOT:PSS dissolution the floated films were picked up with the 400 hex mesh copper grid (Electron Microscopy Sciences).

Photoluminescence (PL) measurements were performed on a Horiba Jobin Yvon NanoLog Spectrofluorometer System Model FL-1039/40 with a 450 W Xe Lamp. Neat and blend films were prepared using the same polymer concentration and fullerene ratios as those used in devices: P3HTT-DPP (10 mg/mL, *o*-DCB), P3HTT-DPP:PC₆₁BM (1:1.3, 10 mg/mL, *o*-DCB), P3HTMETT-DPP (11 mg/mL, *o*-DCB), P3HTMETT-DPP:PC₆₁BM (1:1.3, 11 mg/mL, *o*-DCB), P3HTFHTT-DPP (4 mg/mL, chloroform), P3HTFHTT-DPP:PC₆₁BM (1:2, 4 mg/mL, chloroform).

Synthetic Procedures:

Synthetic procedures for the synthesis of 2-bromo-5-trimethyltin-3-hexylthiophene, 2,5-bis(trimethyltin)thiophene, (5-bromo-4-(4,4,5,5,6,6,7,7,7-nonafluoroheptyl)thiophen-2-yl)trimethylstannane, (5-bromo-4-(2-(2-methoxyethoxy)ethyl)thiophen-2-yl)trimethylstannane (7), 2,5-Diethylhexyl-3,6-bis(5-bromothiophene-2-yl)pyrrolo[3,4-*c*]-pyrrole-1,4-dione, were used without modifications as reported in the literature.^{1,2}



Scheme S1. Copolymerizations of P3HTFHTT-DPP, P3HTMETT-DPP, and P3HTT-DPP polymers.

Stille Copolymerizations for P3HTT-DPP Polymers. Monomers 2-bromo-5-trimethyltin-3-hexylthiophene (*n*), 2,5-bis(trimethyltin)thiophene (*o*), and 2,5-Diethylhexyl-3,6-bis(5-bromothiophene-2-yl)pyrrolo[3,4-*c*]-pyrrole-1,4-dione (*p*) were added to 3-necked RBFs at varied molar ratios (*n* = 0.8 for P3HTT-DPP, or *n* = 0.4 eq for P3HTFHT-DPP and P3HTMETT-DPP, *o* = 0.1 eq, *p* = 0.1 eq.) Comonomer (5-bromo-4-(4,4,5,5,6,6,7,7,7-nonafluoroheptyl)thiophen-2-yl)trimethylstannane or (5-bromo-4-(2-(2-methoxyethoxy)ethyl)thiophen-2-yl)trimethylstannane was added at a molar ratio of 0.4 eq for semi-fluoro alkyl and oligoether co-polymers,

respectively. Dry DMF (0.04 M) was added via syringe followed by quickly adding palladium tetrakis(triphenylphosphine) (0.04 eq) in one portion. The solution was degassed with N₂ for 20 m, then heated to 95 °C for 48 h. Reaction mixtures were cooled to room temperature and precipitated into stirring methanol, followed by addition of ammonium hydroxide. Polymers were decanted into a thimble and purified via Soxhlet extraction with methanol, hexanes, dichloromethane and then collected in chloroform. Polymer chloroform solutions were concentrated *in vacuo* and precipitated in cold MeOH and collected via filtration.

P3HTFHTT-DPP: $m = 0.4, n = 0.4, o = 0.1, p = 0.1$. Yield 64% (171 mg). $M_n = 10.9$ kDa, $\bar{D} = 3.06$. ¹H NMR (600 MHz, CDCl₃) δ 8.91 (s, 0.10H), 7.32 (s, 0.13H), 7.17 – 7.14 (m, 0.20H), 7.00 (s, 0.30H), 4.10 – 4.04 (m, 0.20H), 2.95 (m, 0.34H), 2.82 (m, 0.40H), 2.72 (m, 0.08H), 2.60 (m, 0.03H), 2.20 (m, 0.37H), 2.05 – 1.96 (m, 0.51H), 1.74 – 1.72 (m, 0.47H), 1.48 – 1.28 (m, 2.76H), 0.96 – 0.89 (m, 1.40H).

P3HTMETT-DPP: $m = 0.4, n = 0.4, o = 0.1, p = 0.1$. Yield 79% (240 mg). $M_n = 16.2$ kDa, $\bar{D} = 3.13$. ¹H NMR (600 MHz, CDCl₃) δ 8.91 (s, 0.10H), 7.34 (s, 0.72H), 7.17 – 6.93 (m, 0.43H), 4.08 (m, 0.23H), 3.81 (m, 0.37H), 3.67 (m, 0.38H), 3.58 (m, 0.37H), 3.41 (s, 0.54H), 3.12 (m, 0.33H), 2.94 (m, 0.04H), 2.83 (m, 0.34H), 2.60 (m, 0.04H), 1.97 (m, 0.12H), 1.74 (m, 0.36H), 1.50 – 1.28 (m, 2.41H), 0.97 – 0.90 (m, 1.35H).

P3HTT-DPP: $n = 0.8, o = 0.1, p = 0.1$. Yield 64% (118 mg). $M_n = 13.5$ kDa, $\bar{D} = 5.20$. ¹H NMR (600 MHz, CDCl₃) δ 8.91 (s, 0.10H), 7.32 (s, 0.08H), 7.17 (d, 0.20H), 7.00 (s, 0.34H), 4.10 – 4.04 (m, 0.19H), 2.82 (m, 0.78H), 2.60 (m, 0.05H), 1.96 (m, 0.10H), 1.72 (m, 0.93H), 1.48 – 1.28 (m, 3.93H), 0.89 (m, 2.13H).

¹H NMR of Polymers:

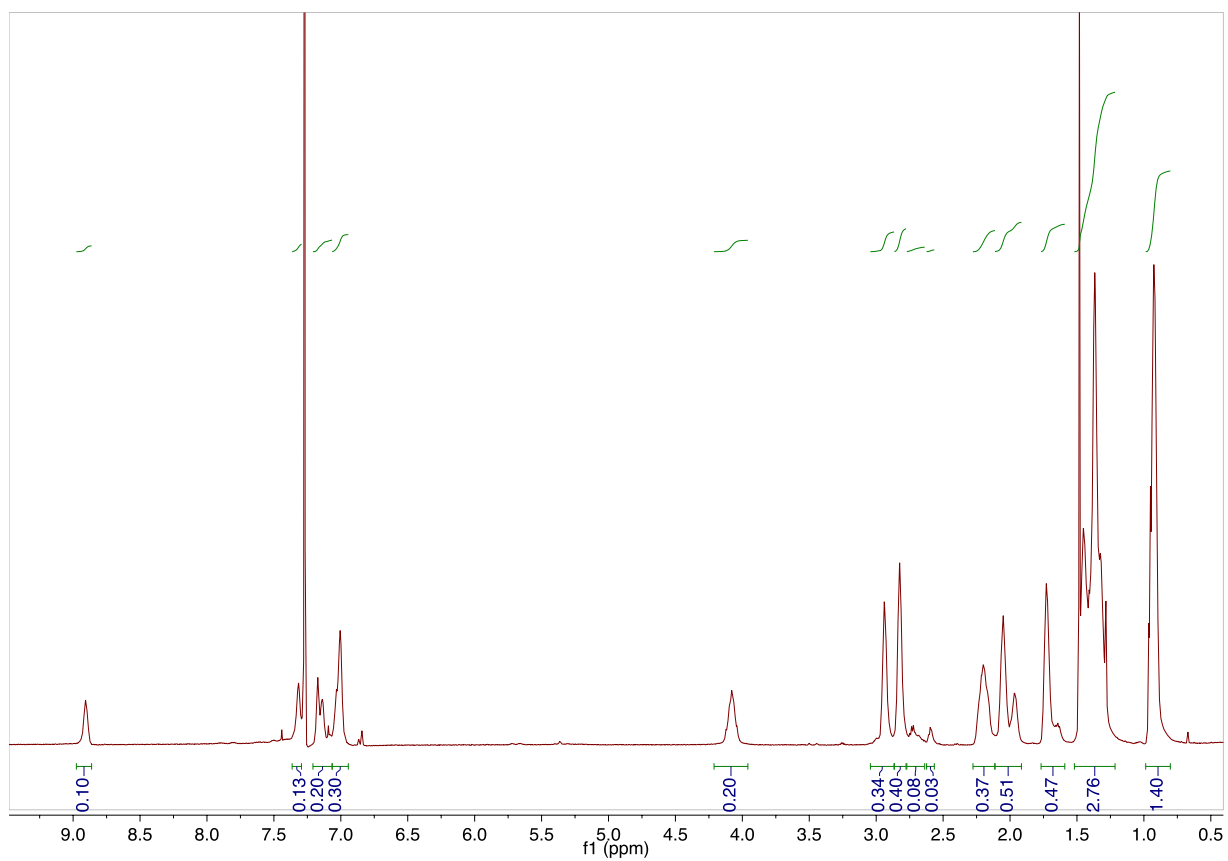


Figure S1. ¹H NMR of P3HTFHT-DPP in CDCl₃.

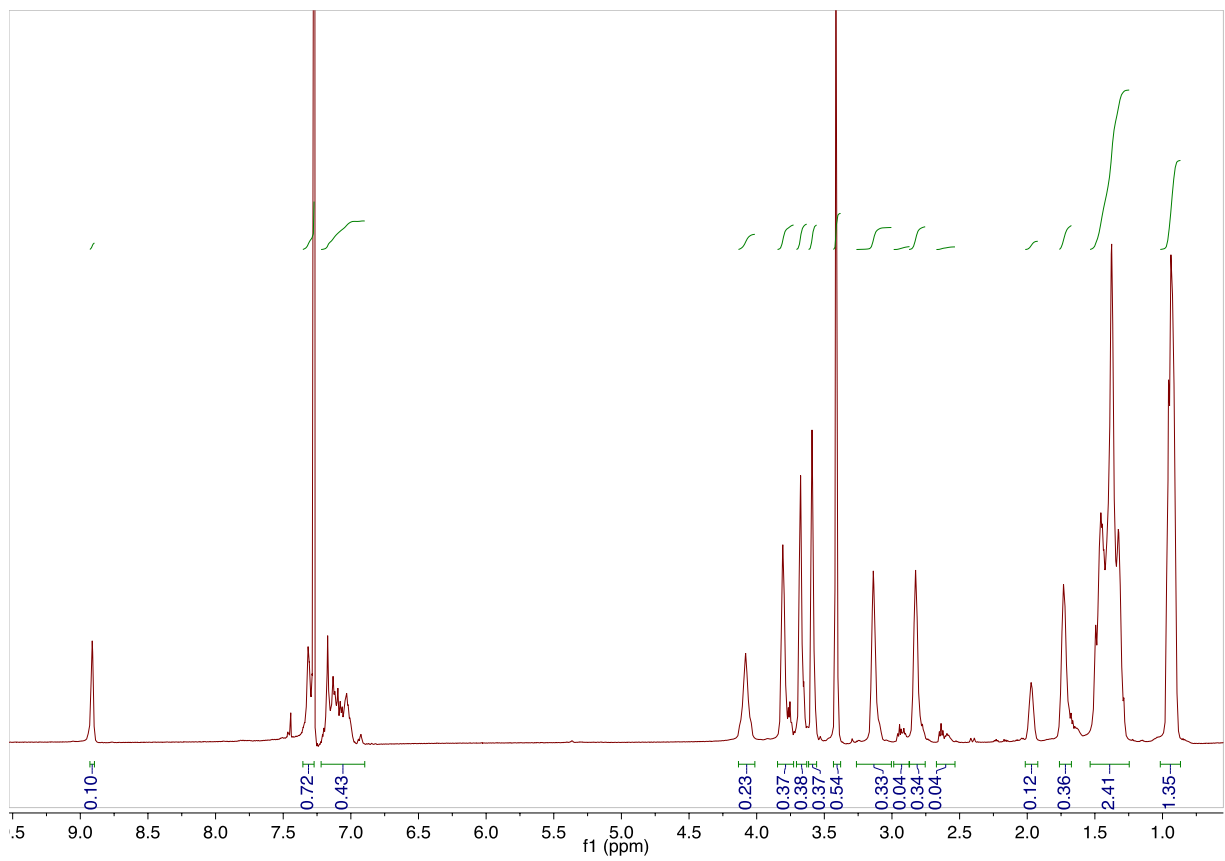


Figure S2. ^1H NMR of P3HTMETT-DPP in CDCl_3 .

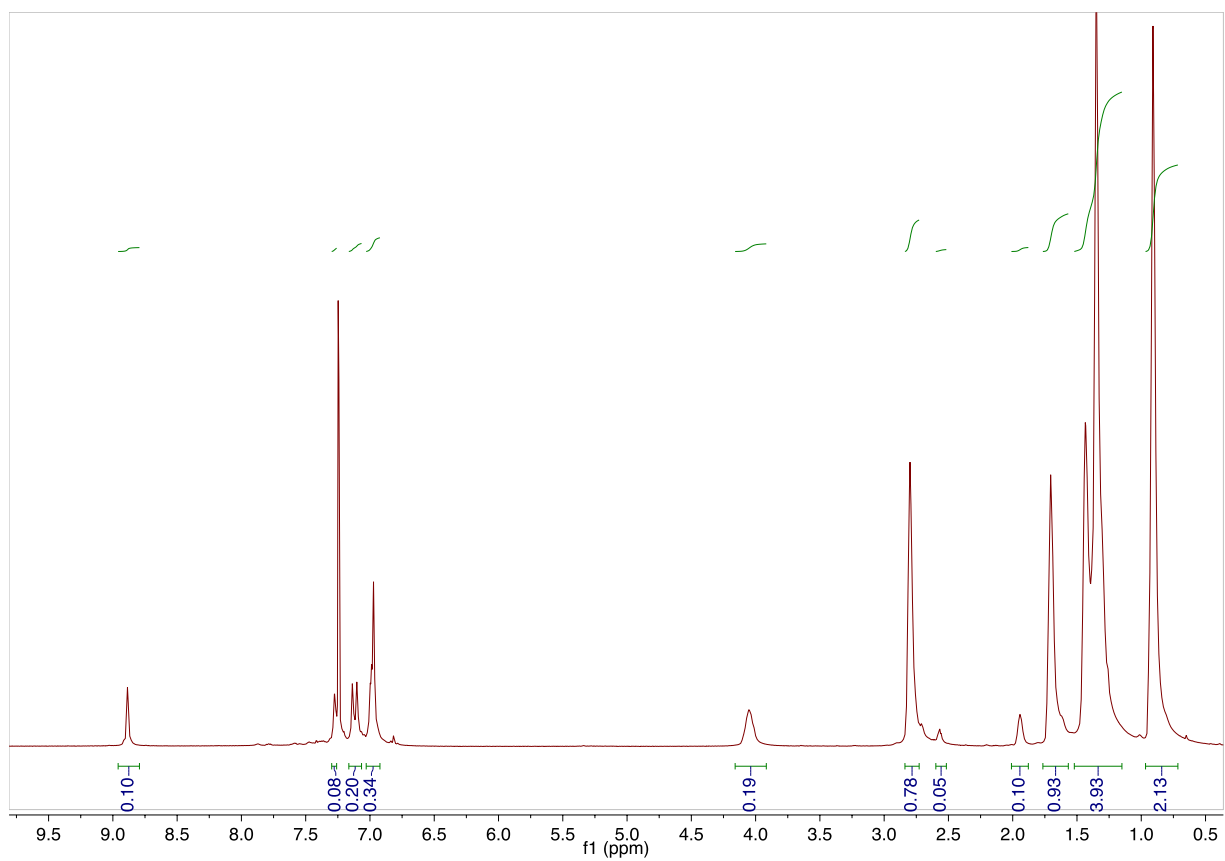


Figure S3. ^1H NMR of P3HTT-DPP in CDCl_3 .

Cyclic Voltammetry:

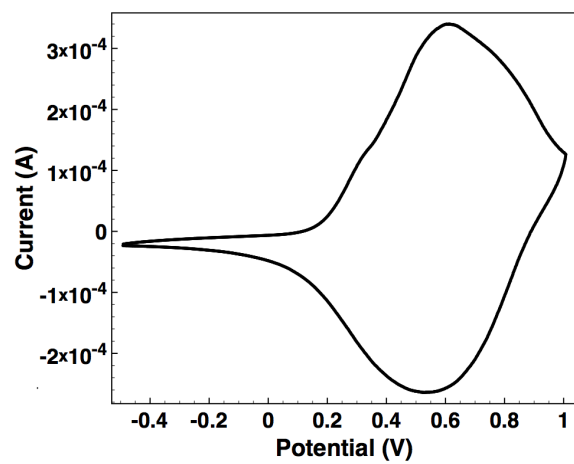


Figure S4. P3HTFHTT-DPP

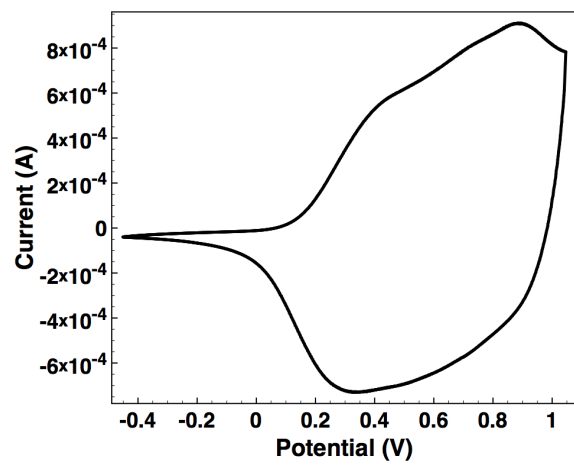


Figure S5. P3HTMETT-DPP

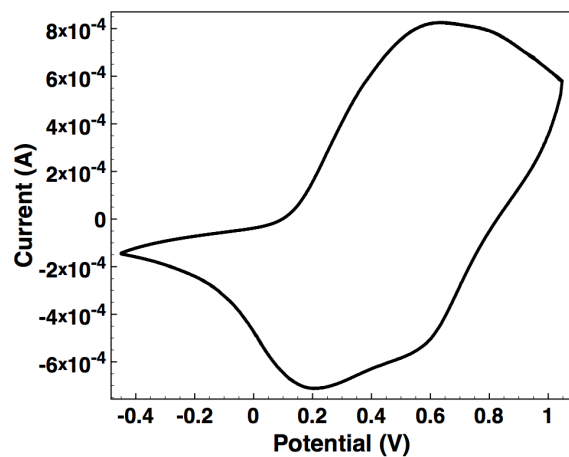


Figure S6. P3HTT-DPP

Differential Scanning Calorimetry:

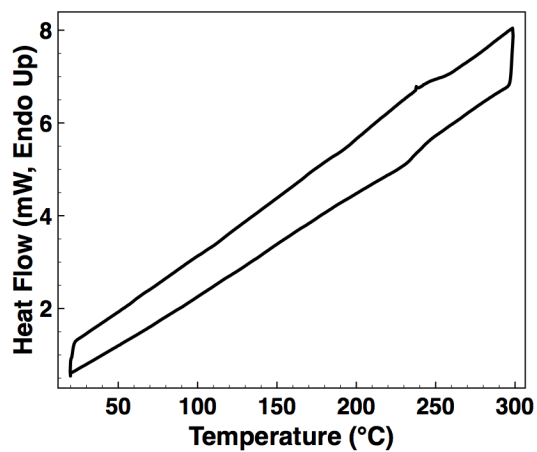


Figure S7. DSC trace of P3HTFHTT-DPP

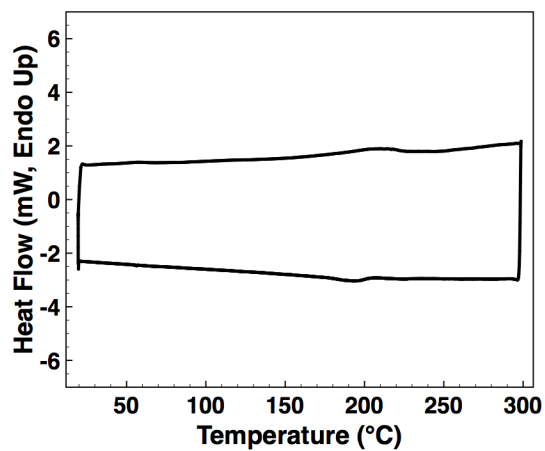


Figure S8. DSC trace of P3HTMETT-DPP.

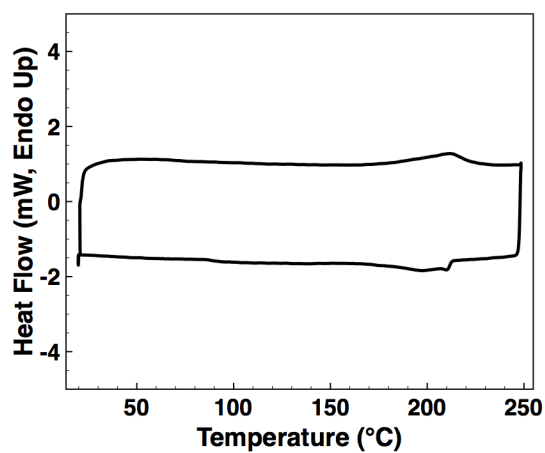


Figure S9. DSC trace of P3HTT-DPP.

Surface Energy Data

Table S1. Surface energies of neat polymer films calculated from one and two-liquid models based on the static sessile drop method.

Polymer	One-Liquid Surface Energy	Wu Model Surface Energy
	As Cast	As Cast
P3HTT-DPP	18.7 ± 0.32	20.6 ± 0.70
P3HTMETT-DPP	29.1 ± 0.39	25.7 ± 0.25
P3HTFHDT-DPP	15.9 ± 0.09	15.0 ± 1.16

Mobility Data

Table S2. Hole, electron mobilities, and hole/electron mobility ratios of polymer:PC₆₁BM blends in thin films spin-coated from *o*-DCB.

Polymer:PC ₆₁ BM (Ratio)	Hole Mobility (μ_h) (cm ² V ⁻¹ s ⁻¹)	Electron Mobility (μ_e) (cm ² V ⁻¹ s ⁻¹)	μ_h/μ_e	Thickness (nm)
P3HTT-DPP (1:1.3)	4.50x10 ⁻³	1.57x10 ⁻⁴	28.66	77
P3HTMETT-DPP (1:1.3)	6.27x10 ⁻³	2.08x10 ⁻⁴	30.14	98.6
P3HTFHTT-DPP (1:2)	9.29x10 ⁻⁴	1.77x10 ⁻⁴	5.25	115

TEM

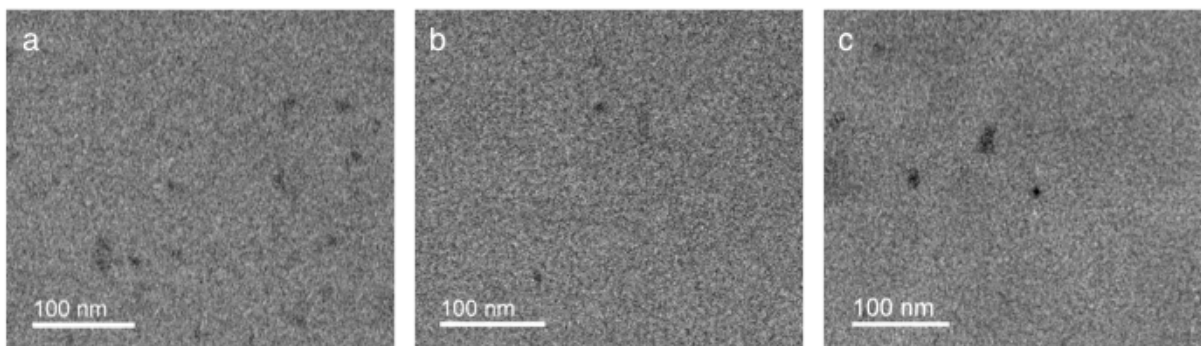


Figure S10. TEM images of a) P3HTT-DPP:PC₆₁BM (1:1.3), b) P3HTMETT-DPP:PC₆₁BM (1:1.3) and c) P3HTFHTT-DPP:PC₆₁BM (1:2) blends.

References:

- (1) Khlyabich, P. P.; Ng, C. F.; Thompson, B. C. *Macromolecules* **2011**, *44* (13), 5079–5084.
- (2) Howard, J. B.; Noh, S.; Beier, A. E.; Thompson, B. C. *ACS Macro Lett.* **2015**, 725–730.