Supporting Information

Linear Side-Chains in Benzo[1,2-*b*:4,5-*b'*]dithiophene–Thieno[3,4-*c*]pyrrole-4,6-dione Polymers Direct Self-Assembly & Solar Cell Performance

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Synthetic Details

Methods and Materials: All reagents from commercial sources were used without further purification. Reactions were carried out under nitrogen atmosphere. Solvents were dried and purified using standard techniques. Flash chromatography was performed with analytical-grade solvents using Silicycle SiliaFlash P60 (particle size 40-63 μm, 60 Å, 230 – 400 mesh) silica gel. Flexible plates PE SilG/UV 250 μm from Whatman® were used for TLC. Compounds were detected by UV irradiation or staining with I_2, unless otherwise stated. All compounds were characterized by ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) on a Bruker Avance III Ultrashielded 400 Plus instrument and acquired at room temperature. High-resolution mass spectrometry (HRMS) data were recorded using a Thermo Scientific - LTQ Velos Orbitrap MS in positive electro spray ionization (+ESI) or positive atmospheric pressure photoionization (+APPI) mode. Elemental analyses were carried out on a Flash 2000 - Thermo Scientific CHNO Analyzer. Size exclusion chromatography (SEC) was performed with HPLC-grade chloroform at an elution rate of at 1.0 mL/min through three PLgel Mixed-C columns (5 μm), at room temperature. The SEC system consisted of a Waters 2695 Separation Module and a Waters 486 Tunable Absorption Detector. The apparent molecular weights

and polydispersities (M_w/M_n) were determined with a calibration based on linear polystyrene standards using Millennium software from Waters.

Synthetic Procedures:
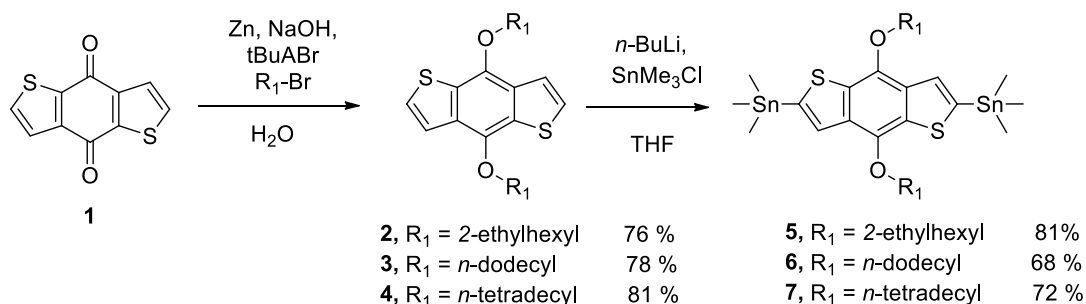
Benzo[1,2-b:4,5-b']dithiophene-4,8-dione (**1**) was synthesized according to previously reported methods.[1] The syntheses of derivatives **2**, **3**, and **4** were adapted from those described in earlier work.[1,2]

General procedure for the alkylation of Benzo[1,2-b:4,5-b']dithiophene-4,8-dione (1): Compound **1** (2.2 g, 10 mmol) was suspended in 30 mL of water into a 100 mL flask equipped with a condenser. Zinc powder (1.43 g, 22 mmol) was added under vigorous stirring, followed by 6 g of NaOH. As the temperature was raised from room temperature to reflux, the color of the mixture changed from yellow, to dark red, and then to orange. After 1 h, the alkyl bromide (30 mmol) and a catalytic amount of tetrabutylammonium bromide were added to the reaction mixture (Note: an excess amount of zinc powder (0.65 g, 10 mmol) can be added if the color doesn't turn to yellow within two hours). After an additional 4 h, the reaction mixture was poured into iced water, and extracted with diethyl ether (x4). The organic layers were combined, washed with brine, dried over anhydrous MgSO$_4$, and concentrated under *vacuum*. The crude product was finally purified by column chromatography (hexane, then hexane/chloroform: 9/1) to afford the desired compound.

4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene (2): (3.4 g, 76%). ^{1}H NMR (CDCl$_3$, 400 MHz): δ (ppm) = 7.49 (d, *J* = 5.54 Hz, 2H), 7.37 (d, *J* = 5.54 Hz, 2H), 4.19 (d, *J* = 5.50 Hz, 4H), 1.86-1.34 (m, 18H), 1.02 (t, *J* = 7.42 Hz, 6H), 0.94 (t, *J* = 7.20 Hz, 6H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ (ppm) = 144.9, 131.8, 130.2, 126.2, 120.5, 76.3, 40.9, 30.7, 29.5, 24.2, 23.4, 14.5, 11.6. HRMS (+APPI, *m/z*): calcd. for C$_{26}$H$_{38}$O$_2$S$_2$ [M]$^{+·}$: 446.2313; found, 446.2305.

4,8-bis(dodecyloxy)benzo[1,2-b:4,5-b']dithiophene (3): (4.3 g, 78%). ^{1}H NMR (CDCl$_3$, 400 MHz): δ (ppm) = 7.48 (d, *J* = 5.53 Hz, 2H), 7.37 (d, *J* = 5.53 Hz, 2H), 4.27 (t, *J* = 6.57 Hz, 4H), 1.87 (m, 4H), 1.55 (m, 4H), 1.27 (m, 32H), 0.88 (t, *J* = 6.52 Hz, 6H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ (ppm) = 144.7, 131.8, 130.3, 126.1, 120.5, 74.1, 32.1, 30.7, 29.9, 29.8, 29.7, 29.6, 29.5, 26.2, 22.8, 14.3. HRMS (+APPI, *m/z*): calcd. for C$_{34}$H$_{54}$O$_2$S$_2$ [M]$^{+·}$: 558.3565; found, 558.3544.

4,8-bis(tetradecyloxy)benzo[1,2-b:4,5-b']dithiophene (**4**): (4.9 g, 81%).^{1}H NMR (CDCl₃, 400 MHz): δ (ppm) = 7.48 (d, J = 5.53 Hz, 2H), 7.37 (d, J = 5.53 Hz, 2H), 4.27 (t, J = 6.55 Hz, 4H), 1.87 (m, 4H), 1.56 (m, 4H), 1.30 (m, 40H), 0.88 (t, J = 6.53 Hz, 6H).^{13}C NMR (CDCl₃, 100 MHz): δ (ppm) = 144.5, 131.6, 130.1, 125.9, 120.3, 73.9, 31.9, 30.5, 29.7, 29.6, 29.5, 29.4, 26.1, 22.7, 14.1. HRMS (+APPI, m/z): calcd. for $C_{38}H_{62}O_2S_2$ [M]⁺: 614.4191; found, 614.4163.

The syntheses of derivatives **5**, **6**, and **7** were adapted from those described in earlier work.[1,3]
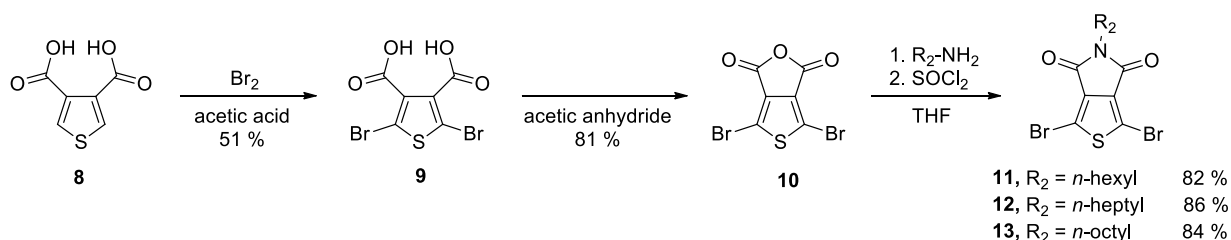
General procedure for the stanyllation of 4,8-bis(alkyloxy)benzo[1,2-b:4,5-b']dithiophene (BDT): Compound **2**, **3** or **4** (4 mmol) were solubilized in 75 mL of dry THF under inert atmosphere. The mixture was cooled down to -78°C using a dry ice-acetone bath, and 4.55 mL of n-butyllithium (8.8 mmol, 2.5 M in n-hexane) was added dropwise. After being stirred at -78°C for 1 h, the solution was slowly warmed up to room temperature and stirred for 30 min. The cloudy mixture was cooled in the dry ice-acetone bath, and trimethyltin chloride (1.99 g, 10 mmol) was added in one portion (the mixture turned clear). The reaction mixture was stirred overnight at room temperature, was then poured into 200 mL of cool water, and was extracted with diethyl ether (x4). The organic layers were combined, washed with brine (x1), dried over anhydrous MgSO₄ and concentrated under *vacuum*. The residue was recrystallized twice from ethanol to yield the desired compounds as colorless needles.

(4-((2-ethylhexyl)oxy)-8-((3-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene-2,6 diyl)bis(trimethylstannane) (5): (2.5 g, 81%). ^{1}H NMR (CDCl₃, 400 MHz): δ (ppm) = 7.51 (s, 2H), 4.19 (d, J = 5.41 Hz, 4H), 1.81 (m, 2H), 1.73-1.31 (m, 16H), 1.02 (t, J = 7.44 Hz, 6H), 0.94 (t, J = 6.77 Hz, 6H), 0.44 (s, 18H). ^{13}C NMR (CDCl₃, 100 MHz): δ (ppm) = 142.9, 140.0, 133.5, 132.5, 127.6, 75.3, 40.3, 30.2, 28.9, 23.6, 22.8, 13.9, 11.0, 8.7. HRMS (+APPI, m/z): calcd. for $C_{32}H_{54}O_2S_2Sn_2$ [M]⁺: 774.1609; found, 774.1595.

(4,8-bis(dodecyloxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (6): (2.4 g, 68%). ^{1}H NMR (CDCl₃, 400 MHz): δ (ppm) = 7.51 (s, 2H), 4.29 (t, J = 5.58 Hz, 4H), 1.88 (quintuplet, J = 7.05 Hz, 4H), 1.58 (m, 4H), 1.27 (m, 32H), 0.88 (m, 6H), 0.44 (s, 18H).^{13}C NMR (CDCl₃, 100 MHz): δ (ppm) =143.1, 140.4, 134.0, 132.0, 128.0, 73.6, 31.9, 30.5, 29.7, 29.6, 29.5, 29.4, 26.12, 22.7, 14.12, 8.3. HRMS (+APPI, m/z): calcd. for $C_{40}H_{70}O_2S_2Sn_2$ [M]⁺: 886.2861; found, 886.2864.

(4,8-bis(tetradecyloxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (7): (2.7 g, 72%). ^{1}H NMR (CDCl$_3$, 400 MHz): δ (ppm) = 7.51 (s, 2H), 4.29 (t, J = 6.56 Hz, 4H), 1.88 (quintuplet, J = 7.15 Hz, 4H), 1.55 (m, 4H), 1.36 (m, 40H), 0.87 (t, J = 6.53 Hz, 6H), 0.44 (s, 18H).^{13}C NMR (CDCl$_3$, 100 MHz): δ (ppm) = 143.1, 140.5, 134.0, 132.9, 128.0, 73.6, 31.9, 30.5, 29.7, 29.6, 29.5, 29.4, 26.1, 22.7, 14.1, 8.3. HRMS (+APPI, m/z): calcd. for C$_{44}$H$_{78}$O$_2$S$_2$Sn$_2$ [M]$^+$: 942.3487; found, 942.3482.

2,5-Dibromothiophene-3,4-dicarboxylic acid (9)[4] and **4,6-Dibromothieno[3,4-c]furan-1,3-dione (10)** [5] were synthesized according to previously reported methods.
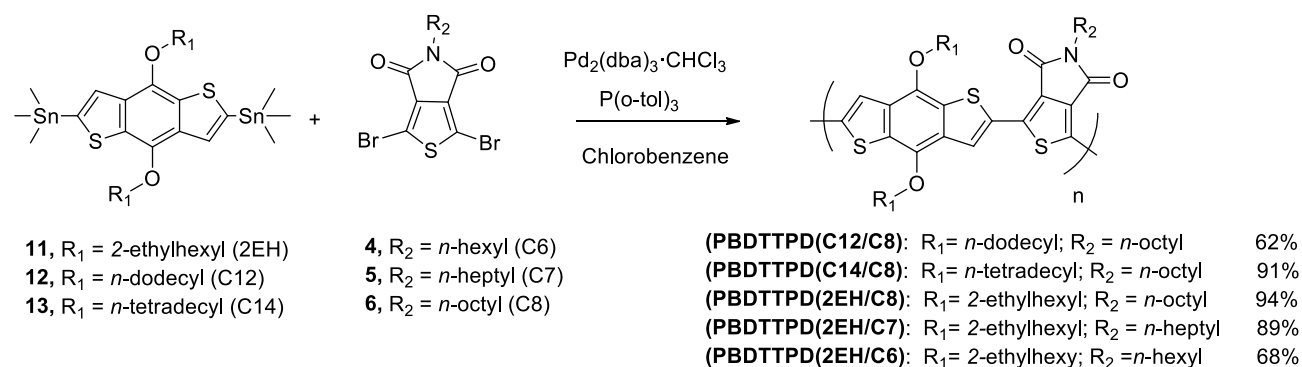
General procedure for the preparation of 1,3-Dibromo-5-(n-alkyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (TPD). Compound **10** (1.46 g, 4.68 mmol) was combined with 12 mL of dry THF in a 50 mL flask, and n-alkylamine (4.90 mmol) was added. The reaction mixture was stirred at 50°C for 3 h. The volatiles were removed in vacuo, thionyl chloride (5 mL) was added to the residue, and the reaction mixture was stirred at 55°C for 4 h. The reaction contents were added dropwise to a mixture of water (100 mL) and methanol (50 mL). The precipitate was filtered, dried and purified by column chromatography using CHCl$_3$ as the eluent. The CHCl$_3$ solution was concentrated by evaporation, and the solid was finally recrystallized from ethanol to yield the corresponding TPD monomer as white flakes (**11-13**).

1,3-Dibromo-5-(n-hexyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (11): (1.51 g, 82%). ^{1}H NMR (CDCl$_3$, 400 MHz): δ (ppm)= 3.58 (t, J = 7.30 Hz, 2H), 1.62 (m, 2H), 1.29 (m, 6H), 0.82 (t, J = 6.60Hz, 3H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ (ppm) =159.7, 134.2, 112.3, 38.2, 30.7, 27.6, 25.8, 21.8, 13.4. HRMS (+ESI, m/z): calcd. for C$_{12}$H$_{14}$Br$_2$NO$_2$S [M+H]$^+$: 393.9112; found, 393.9108. Anal. calcd. for C$_{12}$H$_{13}$Br$_2$NO$_2$S: C, 36.48; H, 3.32; N, 3.55; S, 8.12; found: C, 36.88; H, 3.33; N, 3.57; S, 8.27.

1,3-Dibromo-5-(n-heptyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (12): (1.64 g, 86%). ^{1}H NMR (CDCl$_3$, 400 MHz): δ (ppm) = 3.58 (t, J = 7.28 Hz, 2H), 1.64 (m, 2H), 1.30 (m, 8H), 0.87 (t, J = 6.65 Hz, 3H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ (ppm) = 160.2, 134.6, 112.7, 38.6, 31.4, 28.6, 28.1, 26.6, 22.4, 13.9. HRMS (+ESI, m/z): calcd. for C$_{13}$H$_{16}$Br$_2$NO$_2$S [M+H]$^+$: 422.9268; found, 407.9263.

Anal. calcd. for $C_{13}H_{15}Br_2NO_2S$: C, 38.16; H, 3.10; N, 3.42; S: 7.84; found: C, 38.33; H, 3.66; N, 3.46; S: 7.87.

1,3-Dibromo-5-(n-octyl)-4H-thieno[3,4-*c*]pyrrole-4,6(5H)-dione (13): (1.66 g, 84%). ^{1}H NMR (CDCl$_3$, 400 MHz): δ (ppm) = 3.58 (t, J = 7.28 Hz, 2H), 1.60 (m, 2H), 1.29 (m, 10H), 0.86 (t, J = 6.49 Hz, 3H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ (ppm) = 160.0, 134.5, 112.6, 38.5, 31.4, 28.7, 27.9, 26.4, 22.3, 13.7. HRMS (+ESI, *m/z*): calcd. for $C_{14}H_{18}Br_2NO_2S$ $[M+H]^+$: 421.9425; found, 421.9408. Anal. calcd. for $C_{14}H_{17}Br_2NO_2S$: C, 39.74; H, 4.05; N, 3.31; S: 7.58; found: C, 39.90; H, 4.03; N, 3.38; S: 7.56.

11, R$_1$ = 2-ethylhexyl (2EH)
12, R$_1$ = *n*-dodecyl (C12)
13, R$_1$ = *n*-tetradecyl (C14)

4, R$_2$ = *n*-hexyl (C6)
5, R$_2$ = *n*-heptyl (C7)
6, R$_2$ = *n*-octyl (C8)

(PBDTTPD(C12/C8): R$_1$= *n*-dodecyl; R$_2$ = *n*-octyl   62%
(PBDTTPD(C14/C8): R$_1$= *n*-tetradecyl; R$_2$ = *n*-octyl   91%
(PBDTTPD(2EH/C8): R$_1$= 2-ethylhexyl; R$_2$ = *n*-octyl   94%
(PBDTTPD(2EH/C7): R$_1$= 2-ethylhexyl; R$_2$ = *n*-heptyl   89%
(PBDTTPD(2EH/C6): R$_1$= 2-ethylhexy; R$_2$ =*n*-hexyl   68%

General procedure for the polymerization: 1,3-Dibromo-5-(n-alkyl)-4H-thieno[3,4-*c*]pyrrole-4,6(5H)-dione (516 µmol), (4,8-bis(alkyloxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (500 µmol), tris(dibenzylideneacetone)dipalladium (14.2 mg, 15.5 µmol) and tri-o-tolylphosphine (18.9 mg, 62.1 µmol) were combined in a 50 mL Schlenk flask. Then, 9.1 mL of chlorobenzene freshly degassed *via* F.P.T cycles were added to the flask and the reaction mixture was stirred for 36 h at 110°C. Next, the polymerization mixture was cooled down to 55°C, and the strong complexing ligand N,N-diethyl-2-phenyldiazenecarbothioamide (34 mg, 155 µmol) was added with CHCl$_3$ (20 mL). After stirring for 3 h under inert atmosphere, the mixture was slowly precipitated into methanol (200 mL). The precipitate was filtered through a Soxhlet thimble and purified via Soxhlet extraction for 2 h with methanol, 20 h with dichloromethane **(PBDTTPD(2EH/C8)**, **(PBDTTPD(2EH/C7)** and **(PBDTTPD(2EH/C6))** or hexane **((PBDTTPD(C12/C8)** and **(PBDTTPD(C14/C8))**, the polymer was finally collected from chlorobenzene. The chlorobenzene solution was then concentrated by evaporation, precipitated into methanol (400 mL) and filtered to yield the desired polymers. The polymerization yields and SEC results are shown in Table S1.

Table S1. SEC analyses of the **PBDTTPD** derivatives ([*]: poor solubility)

Polymers	Yield	M_n (kDa)	M_w (kDa)	PDI
(PBDTTPD(2EH/C8)	333 mg, 94 %	36	70	2.0
(PBDTTPD(C14/C8)	399 mg, 91 %	38	71	1.9
(PBDTTPD(C12/C8)	254 mg, 62 %	n/a*	n/a	n/a
(PBDTTPD(2EH/C7)	309 mg, 89 %	32	63	2.0
(PBDTTPD(2EH/C6)	231 mg, 68 %	24	51	2.2

References

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Device Fabrication

The solar cells were prepared on glass substrates with tin-doped indium oxide (ITO, 15 Ω sq^{-1}) patterned on the surface. Substrates were first scrubbed with dilute Extran 300 detergent solution to remove organic residues before immersing in an ultrasonic bath of dilute Extran 300 for 15 min. Samples were rinsed in flowing deionized water for 5 min before being sonicated for 15 min each in successive baths of acetone and isopropanol. After a final 5 min rinse in flowing deionized water, samples were dried with pressurized nitrogen before being exposed to a UV−ozone plasma for 15 min. An aqueous solution of PEDOT:PSS (Clevios P VP AI 4083) was spin-cast at 4,000 rpm onto the substrates and baked at 140°C for 15 min. All steps above were performed in a laminar flow hood to prevent adsorption of dust particles on the substrates. Immediately after baking the substrates, the samples were then transferred into a dry nitrogen glovebox (<3 ppm O2) for active layer deposition.

All solutions were prepared in the glovebox using the polymers synthesized as previously described (*vide supra*) and PC$_{71}$BM purchased from SOLENNE. The polymers and PC$_{71}$BM were dissolved in chlorobenzene containing 5% (by volume) of 1-chloronaphthalene (CN) additive, and the solutions were stirred overnight at 115°C. Optimized devices were prepared using a polymer:PC$_{71}$BM ratio of 1:1.5 (by weight), with a concentration of 20 mg mL^{-1}. The effects of various solvents, solution concentrations, additive concentrations, and blend ratios on device performance were also examined.

The active layers were spin-cast from the solutions at 115°C at an optimized speed for 45 s, using a programmable spin coater from Laurell Technologies (WS-650-NPPLITE), resulting in a film of 100 to 120 nm in thickness. The samples were then dried at room temperature for 1 hour. Next, the samples were placed in a thermal evaporator for evaporation of 7 nm thickness calcium evaporated at 1 Å s^{-1} and 150 nm of aluminum electrodes evaporated at 5 Å s^{-1}, at a pressure less than 1x10^{-6} Torr. Following electrode deposition, samples underwent J−V testing.

J-V measurements of solar cells were performed in the glovebox with a Keithley 2400 source meter and a Spectra-Physics 91160-1000 solar simulator calibrated to 1 sun, AM1.5 G, with a NREL certified KG-5 filtered silicon photodiode.
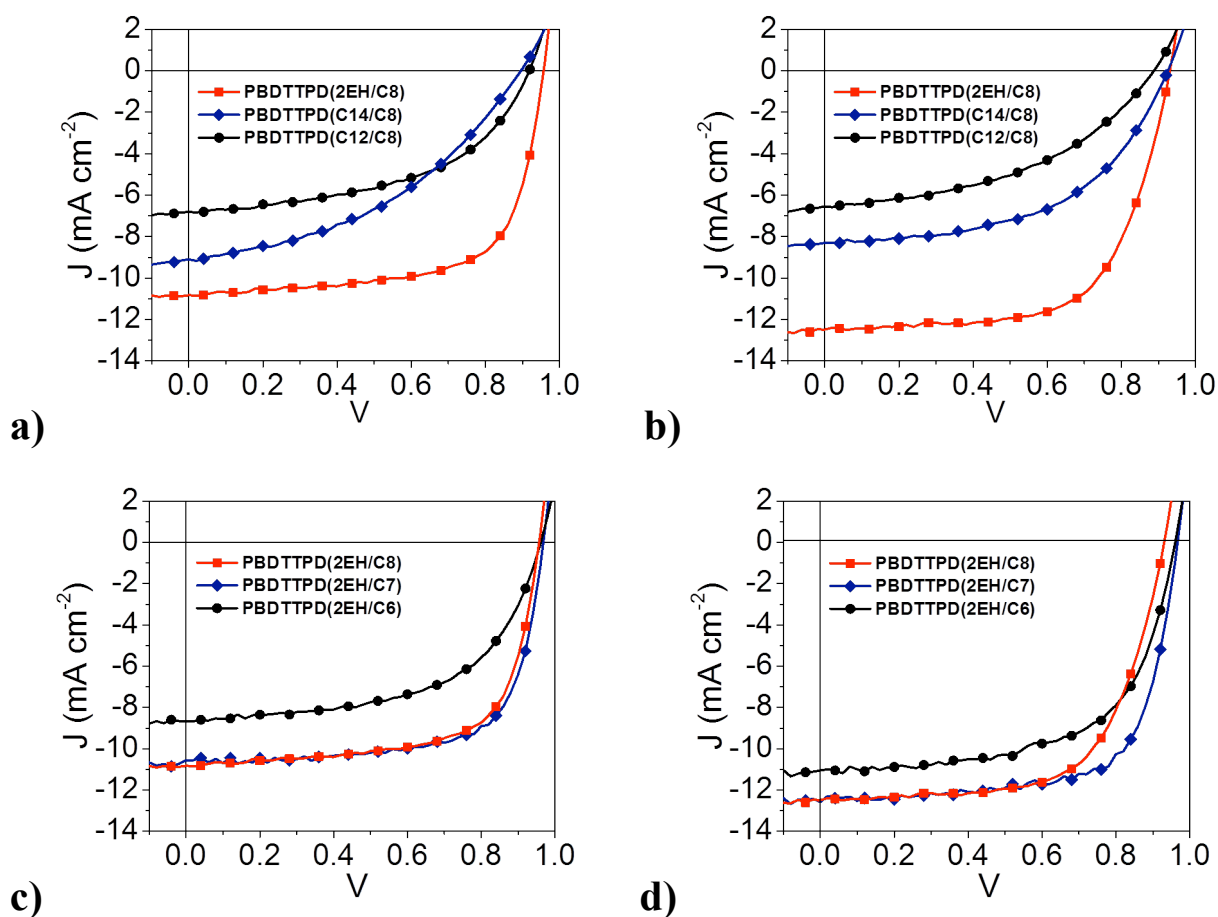
PV Performance – No Additive *vs.* 5%CN

a) **b)** **c)** **d)**

Figure S1. (a) Characteristic *J-V* curves of BHJ solar cells fabricated from PBDTTPD(2EH/C8), PBDTTPD(C14/C8), and PBDTTPD(C12/C8), with PC$_{71}$BM (under AM1.5G illumination, 100 mW.cm^{-2}); all films were prepared from CB solutions with no additive. (b) BHJ devices prepared from blends containing 5% CN (v/v). (c) BHJ devices fabricated from PBDTTPD(2EH/C8), PBDTTPD(2EH/C7), and PBDTTPD(2EH/C6), with PC$_{71}$BM; all films were prepared from CB solutions with no additive. (d) BHJ devices prepared from blends containing 5% CN (v/v).

Grazing Incidence X-ray Scattering (GIXS)

Silicon substrates were cleaned using the ITO cleaning procedure outlined in the Device Fabrication section, except the substrates were not scrubbed with or sonicated in dilute Extran 300 detergent solution. The substrates were then coated with PEDOT:PSS using the procedure outlined in the Device Fabrication section and the PBDTTPD thin films were spin-cast using the same procedures as those used for solar cell fabrication.

GIXS experiments were performed at the Stanford Synchrotron Radiation Lightsource beamline 11-3 using a photon energy of 12.7 keV, a MAR345 image plate area detector, and an incident X-ray beam angle of ~0.12°. During measurement, samples were kept in a helium-filled chamber to prevent beam damage and to minimize X-ray scattering due to air.

All X-ray diffraction data analysis was performed with the WxDiff software package developed by Dr. Stefan Mannsfeld. Cake segments from 70 to 110° were used to determine the π-π stacking peak location and d-spacing. Peak locations were obtained using multiple peak fitting (using pseudo-Voigt peaks) and background subtraction. For all samples, cake segments were fit with flat and power law backgrounds and the appropriate number of diffraction peaks to obtain a proper fit.
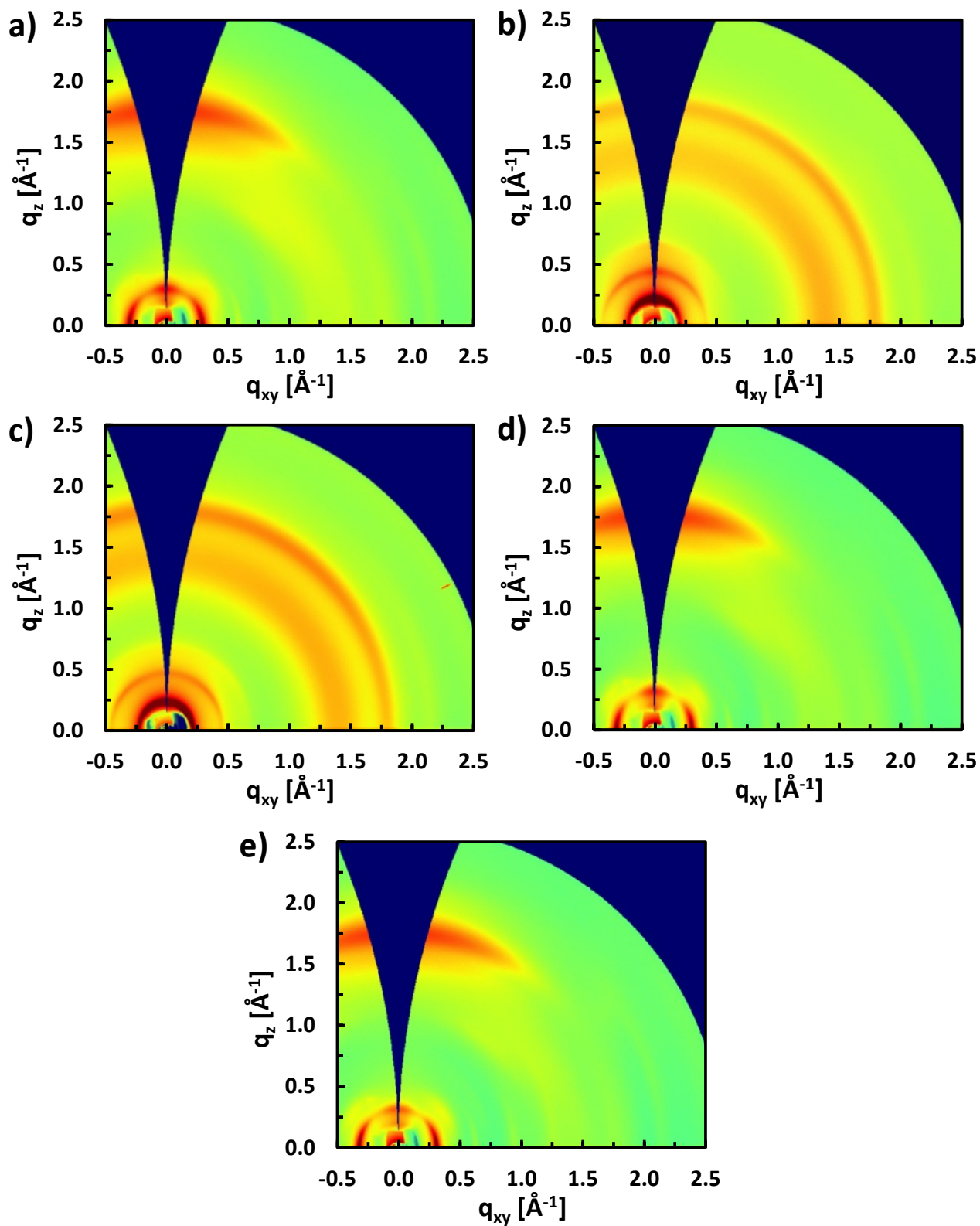
Figure S2. GIXS patterns of neat polymer films of (a) PBDTTPD(2EH,C8), (b) PBDTTPD(C14,C8), (c) PBDTTPD(C12,C8), (d) PBDTTPD(2EH,C7), (e) PBDTTPD(2EH,C6); all films were prepared from CB solutions containing 5% CN (v/v)
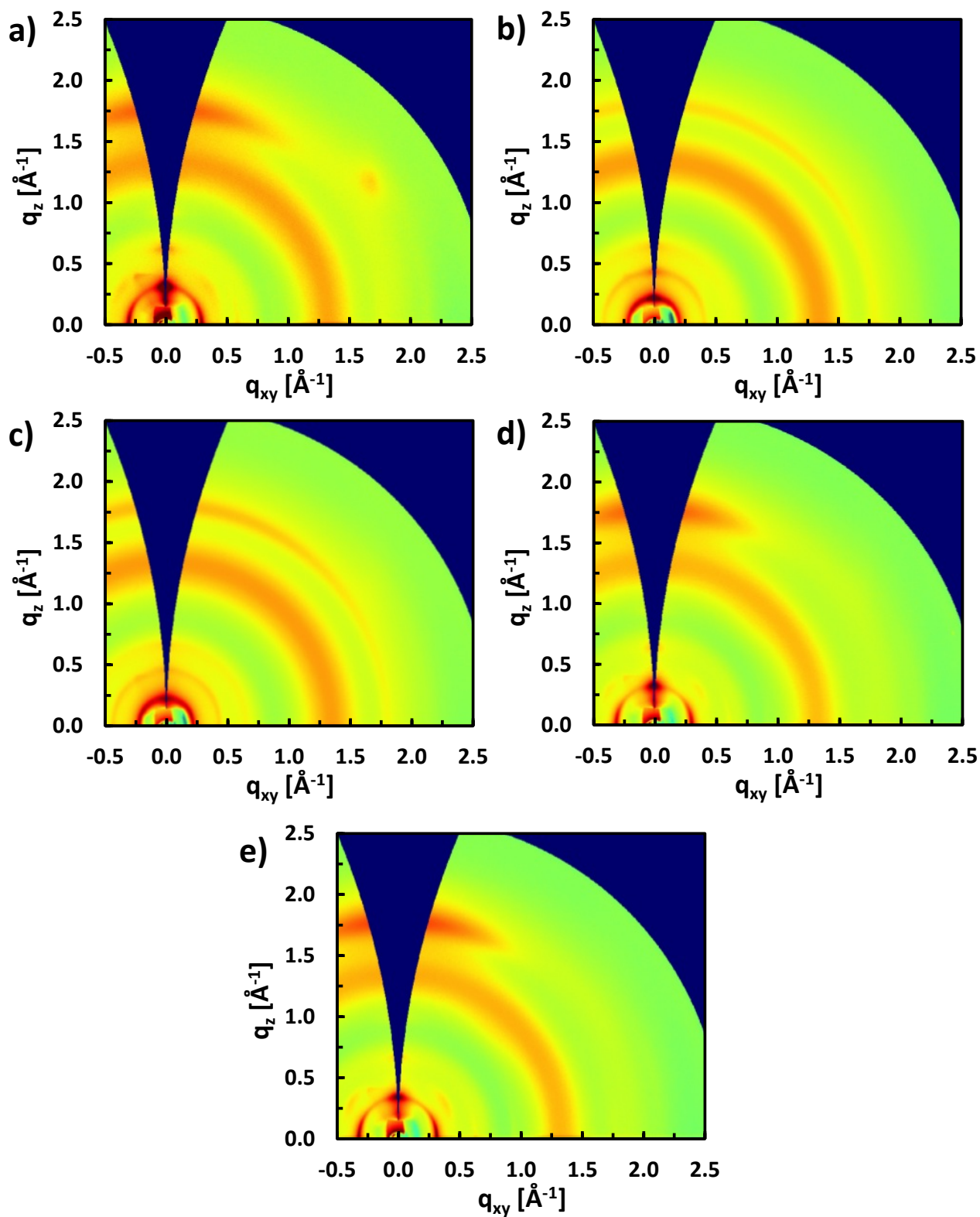
Figure S3. GIXS patterns of (a) PBDTTPD(2EH,C8), (b) PBDTTPD(C14,C8), (c) PBDTTPD(C12,C8), (d) PBDTTPD(2EH,C7), (e) PBDTTPD(2EH,C6) in BHJs with PC$_{71}$BM; all films were prepared from CB solutions containing 5% CN (v/v)