Supplementary Information:

General procedure for alkylation

Starting compound 1 (0.05 mol) and K2CO3 (27.6 g, 0.2 mol) were suspended in 250 ml of dry DMF under inert atmosphere of nitrogen. The mixture was heated to 120 °C and appropriate alkylating reagent (0.2 mol) was added dropwise. The mixture was heated at 130 °C for 5 or 12 h, cooled to 25 °C and 250 ml of water was added. The suspension was filtered and the filter cake was washed with water. Pure compound was obtained through washing with methanol, filtration and drying.

General procedure for bromination

NBS (3.47 g; 19.5 mmol) was added to a alkylated DPP derivative (9.5 mmol) dissolved in 100 ml of chloroform. The mixture was stirred at 25 °C for 3 h whereupon acetone (2 ml) was added to quench the reaction. The mixture was succesively washed with water and brine. The organic solvents were removed in vacuo. Pure product was obtained through washing with methanol, filtration and drying.

General procedure for Suzuki-Miyaura cross-coupling

2-(1-Benzofuran-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaboralane (1.61 g, 6.6 mmol) and appropriate dibromo DPP derivative (3.2 or 6.4 mmol) were dissolved in the mixture of THF/H_2O (240 ml, 4:1). Argon was bubbled through the solution for 15 min whereupon [$PdCl_2(PPh_3)_2$] (90 mg, 0.04 mmol) and Na_2CO_3 (0.7 g, 6.6 mmol) were added and the reaction mixture was stirred at 65 °C for 6 h. The reaction was diluted with water (10 ml) and extracted with CH_2Cl_2 (2 × 100 ml). The combined organic extracts were dried (Na_2SO_4), the solvents were evaporated *in vacuo* and the crude product was purified by column chromatography (SiO_2; indicated solvent system).

2,5-Bis(2-ethylhexyl)-3,6-bis(thiophen-2-yl)-1*H*,2*H*,4*H*,5*H*-pyrrolo[3,4-*c*]pyrrole-1,4-dione (2A)

General procedure for the alkylation of compound 1 (15 g, 0.05 mol) and 1-bromo-2-ethylhexane (38.6 g, 0.2 mol) gave compound 2A (9.7 g, 37 %). ^{1}H NMR (400 MHz, $CDCl_3$), δ = 8.89 (dd, J = 3.88 Hz, 1.08 Hz, 2H), 7.63 (dd, J = 5 Hz, 1,04 Hz, 2H), 7.27 (dd, J = 5.12 Hz, 3.96 Hz, 2H), 4.04-4.01 (m, 4H), 1.86-1.85 (m, 2H), 1.38-1.25 (m, 16H), 1.23-0.85 (m, 12H) ppm; ^{13}C NMR (400 MHz, $CDCl_3$), δ = 161.71, 140.39, 135.25, 129.79, 128.39, 109.33, 107.87, 45.81, 39.03, 30.15, 28.31, 23.49, 23.03, 13.99, 10.44 ppm.

3,6-Bis(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-1*H*,2*H*,4*H*,5*H*-pyrrolo[3,4-*c*]pyrrole-1,4-dione (3A)

General procedure for the bromination of compound 2A (5 g, 9.5 mmol) gave 5.2 g (80 %) of compound 3A. ^{1}H NMR (400 MHz, $CDCl_3$), δ = 8.64 (d, J = 4.2 Hz, 2H), 7.22 (d, J = 4.16 Hz, 2H), 3.95-3.91 (m, 4H), 1.84 (m, 2H), 1.37-1.24 (m, 16H), 0.9 (m, 12H) ppm; ^{13}C NMR (400 MHz, $CDCl_3$), δ = 161.38, 139.38, 135.38, 131.45, 131.13, 119.01, 107.97, 45.98, 39.07, 30.14, 28.29, 23.52, 23.01, 14.00, 10.51 ppm.

3,6-Bis[5-(1-benzofuran-2-yl)thiophen-2-yl]-2,5-bis(2-ethylhexyl)-1*H*,2*H*,4*H*,5*H*-pyrrolo[3,4-*c*]pyrrole-1,4-dione (A)

General procedure for the Suzuki-Miyaura cross-couping with compound 3A (2.2 g, 3.2 mmol) afforded the crude product, which was purified by column chromatography (SiO_2; hex/$CHCl_3$ 1:2) to give A (2.03 g, 81 %). ^{1}H NMR (400 MHz, $CDCl_3$), δ = 9.00 (d, 2H. J = 4.2 Hz), 7.57-7.22 (m, 10H), 7.01 (s, 2H), 4.13-4.01 (m, 4H), 1.94-1.93 (m, 2H), 1.43-1.22 (m, 16H), 0.95-0.84 (m, 12H) ppm; ^{13}C NMR (400 MHz, $CDCl_3$), δ = 161.56, 154.95, 149.99, 139.52, 137.89, 136.55, 129.52, 128.83, 125.42, 125.32, 123.50, 121.16, 111.25, 108.69, 103.62, 46.06, 39.26, 30.33, 28.52, 23.66, 23.11, 14.09, 10.55 ppm. HR-FT-MALDI-MS (DHB) m/z: 756.3062 (M^+) requires. 756.3056. Anal. Calcd for $C_{46}H_{48}N_2O_4S_2$ (757.01): C 72.98, H 6.39, N 3.7, O 8.45, S 8.47; Found C 72.94, H 6.45, N 3.84, S 8.39.

2-Ethylhexyl2-(5-{2-[(2-ethylhexyl)oxy]-2-oxoethyl}-1,4-dioxo-3,6-bis(thiophen-2-yl)-1*H*,2*H*,4*H*,5*H*-pyrrolo[3,4-*c*]pyrrol-2-yl)acetate (2B)

General procedure for the alkylation of compound 1 (10 g, 0.033 mol) and 2-ethylhexyl-2-bromoacetate (33.2 g, 0.132 mol) afforded crude product, which was diluted with dichloromethane. The organic phase was washed several time with water and dried over Na_2SO_4. After removal of the solvent, the residue was recrystallized from methanol to give 2B (14.6 g, 68 %). ^{1}H NMR (400 MHz, $CDCl_3$), δ = 8.77 (d, J = 2.36 Hz, 2H), 7.62 (d, J = 4.2 Hz, 2H), 7.27 (m, 2H), 4.91 (m, 4H), 4.08-4.07 (m, 4H), 1.54 (m, 2H), 1.30-1.21 (m, 16H), 0.84-0.82 (m, 12H) ppm; ^{13}C NMR (400 MHz, $CDCl_3$), δ = 162.21, 160.91, 139.83, 135.13, 130.80, 129.50, 128.88, 107.56, 68.16, 43.63, 38.58, 30.22, 28.76, 23.59, 22.89, 13.98, 10.86 ppm.

2-Ethylhexyl2-[3,6-bis(5-bromothiophen-2-yl)-5-{2-[(2-ethylhexyl)oxy]-2-oxoethyl}-1,4-dioxo-1*H*,2*H*,4*H*,5*H*-pyrrolo[3,4-*c*]pyrrol-2-yl]acetate (3B)

General procedure for the bromination of compound 2B (2 g, 0.003 mol) and 0.5 ml CH_3COOH gave pure product 3B (2.15 g, 86 %). ^{1}H NMR (400 MHz, $CDCl_3$), δ = 8.48 (d, J = 4.2 Hz, 2H), 7.21 (d, J = 4.2 Hz, 2H), 4.82 (m, 4H), 4.11-4.09 (m, 4H), 1.57 (m,

4H), 1.33-1.24 (m, 16H), 0.87-0.83 (m, 12H) ppm; ^{13}C NMR (400 MHz, $CDCl_3$), δ = 167.94, 160.55, 137.73, 135.15, 131.88, 130.86, 119.45, 107.65, 68.32, 43.53, 38.62, 30.23, 28.79, 23.61, 22.90, 14.00, 10.88 ppm.

2-Ethylhexyl 2-{3,6-bis[5-(1-benzofuran-2-yl)thiophen-2-yl]-5-{2-[(2-ethylhexyl)oxy]-2-oxoethyl}-1,4-dioxo-1*H*,2*H*,4*H*,5*H*-pyrrolo[3,4-*c*]pyrrol-2-yl}acetate (B)

General procedure for the Suzuki-Miyaura cross-couping with compound 3B (1.5 g, 1.9 mmol) afforded crude product, which was purified by column chromatography (SiO_2; CH_2Cl_2) to give B (1.17 g, 71 %). ^{1}H NMR (400 MHz, $CDCl_3$), δ = 8.85 (d, 2H, *J* = 4,24 Hz), 7.53–7.45 (m, 6H), 7.33–7.20 (m, 4H), 6.97 (s, 2H), 4.97 (s, 4H), 4.13-4.11 (m, 4H), 1.6–1.57 (m, 2H), 1.35–1.19 (m, 16H), 0.86–0.79 (m, 12H) ppm, ^{13}C NMR (400 MHz, $CDCl_3$), δ = 168.17, 160.71, 154.91, 149.61, 138.84, 138.21, 136.37, 129.18, 128.70, 125.72, 125.47, 123.51, 121.21, 111.20, 103.97, 68.24, 43.71, 38.63, 30.26, 28.82, 23.65, 22.89, 13.97, 10.90 ppm. HR-FT-MALDI-MS (DHB) m/z: 872.3189 (M^+) requires. 872.3165. Anal. Calcd for $C_{50}H_{52}N_2O_8S_2$ (873.09): C 68.78, H 6.00, N 3.21, O 14,66, S 7.35; Found C 68.79, H 6.05, N 3.20, S 7.33.

2,5-Bis(2,2-diethoxyethyl)-3,6-bis(thiophen-2-yl)-1*H*,2*H*,4*H*,5*H*-pyrrolo[3,4-*c*]pyrrole-1,4-dione (2C)

General procedure for the alkylation of compound 1 (9.0 g, 0.03 mol) and 2-bromo-1,1-diethoxyethane (23.6 g, 0.12 mol) afforded crude product, which was diluted with dichlormethane. The organic phase was washed several times with water and dried over Na_2SO_4. After removal of the solvent, the residue was recrystallized from methanol to give 2C (5.3 g, 33 %). ^{1}H NMR (400 MHz, $CDCl_3$), δ = 8.66 (dd, *J* = 3.88 Hz, 1.12 Hz, 2H), 7.63 (dd, *J* = 5 Hz, 1,08 Hz, 2H), 7.23 (dd, *J* = 5 Hz, 3.92 Hz, 2H), 4.86 (t, *J* = 5.64 Hz, 2H), 4.15 (d, *J* = 5.68 Hz, 4H), 3.81-3.74 (m, 4H), 3.58-3.50 (m, 4H), 1.17-1.13 (m, 12H) ppm; ^{13}C NMR (400 MHz, $CDCl_3$), δ = 161.83, 140.82, 134.45, 131.03, 129.70, 128.11, 107.72, 100.78, 64.03, 45.41, 15.28 ppm.

3,6-Bis(5-bromothiophen-2-yl)-2,5-bis(2,2-diethoxyethyl)-1*H*,2*H*,4*H*,5*H*-pyrrolo[3,4-*c*]pyrrole-1,4-dione (3C)

General procedure for the bromination of compound 2C (1.0 g, 1.9 mmol) gave product 3C (1.26 g, 96 %). ^{1}H NMR (400 MHz, $CDCl_3$), δ = 8.40 (d, *J* = 4.16 Hz, 2H), 7.18 (d, *J* = 4.16 Hz, 2H), 4.82 (m, 2H), 4.05 (d, *J* = 5.64 Hz, 2H), 3.81-3.77 (m, 4H), 3.56-3.52 (m, 4H), 1.18-1.14 (m, 12H) ppm; ^{13}C NMR (400 MHz, $CDCl_3$), δ = 161-57. 139.81, 134.63, 131.13, 131.11, 119.72, 107.75, 100.80, 64.36, 45.72, 15.30 ppm.

3,6-Bis[5-(1-benzofuran-2-yl)thiophen-2-yl]-2,5-bis(2,2-diethoxyethyl)-1*H*,2*H*,4*H*,5*H*-pyrrolo[3,4-*c*]pyrrole-1,4-dione (C)

General procedure for the Suzuki-Miyaura cross-couping with compound 3C (1.5 g, 3.2 mmol) gave the crude product, which was filtered and washed with water and acetone to give pure product C (1.69 g, 76 %). ^{1}H NMR (400 MHz, $CDCl_3$), δ = 8.78 (d, 2H, *J* = 4.16 Hz), 7.60-7.52 (m, 6H), 7.33-7.26 (m, 4H), 7.08 (s, 2H), 4.90 (t, 2H, *J* = 5.56 Hz), 4.23 (d, 4H, *J* = 5.56 Hz), 3.84-3.80 (m, 4H), 3.60-3.56 (m, 4H), 1.20-1.17 (m, 12H) ppm; ^{13}C NMR (400 MHz, $CDCl_3$), δ = 161.78, 154.96, 150.06, 140.00, 138.40, 135.70, 129.65, 128.85, 125.24, 123.45, 121.18, 111.29, 108.41, 103.76, 101.00, 64.24, 63.34, 45.74, 15.35 ppm. HR-FT-MALDI-MS (DHB) m/z: 764.2245 (M^+) requires. 764.2226. Anal. Calcd for $C_{42}H_{40}N_2O_8S_2$ (764.91): C 65.95, H 5.27, N 3.66, O 16,73, S 8.38; Found C 65.69, H 5.15, N 3.65, S 8.28.

Pd(0) precatalysts was purchased from Precmet.

Solvents were obtained from Penta, Lach-ner or Sigma Aldrich.

Thin-layer chromatography (TLC) was conducted on aluminum sheets coated with silica gel 60 F254 with visualization by a UV lamp (254 or 360 nm).

Absorption spectra of in DCM solutions were recorded with a Unicam Helios Beta spectrophotometer.

Electrochemical measurements were carried out in *N*,*N*-dimethylformamide (DMF) containing 0.1 M Bu_4NPF_6 in a three electrode cell by cyclic voltammetry (CV) and rotating disk voltammetry (RDV). The working electrode was platinum disc (2mm in diameter) for CV and RDV experiments. As the reference and auxiliary electrodes were used saturated calomel electrode (SCE) separated by a bridge filled with supporting electrolyte and Pt wire, respectively. All potentials are given *vs.* SCE. Voltammetric measurements were performed using a potentiostat PGSTAT 128N (AUTOLAB, Metrohm Autolab B.V., Utrecht, The Netherlands) operated via NOVA 1.10 software.

^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz at 25°C with a Bruker AVANCE III 400 instruments equipped with BBO/Prodigy cryoprobe. Chemical shifts are reported in ppm relative to the signal of TMS. The residual solvent signal in the ^{1}H and ^{13}C NMR spectra was used as an internal reference ($CDCl_3$ 7.25 and 77.23 ppm). Apparent resonance multiplicities are described as s (singlet), d (doublet), and m (multiplet).

High resolution MALDI MS spectra were measured on a MALDI mass spectrometer LTQ Orbitrap XL (Thermo Fisher Scientific, Bremen, Germany) equipped with nitrogen UV laser (337 nm, 60 Hz). The LTQ Orbitrap instrument was operated in positive-ion mode over a normal mass range (m/z 50 - 1500) with the following setting of tuning parameters: resolution 100,000 at m/z = 400, laser energy 17 mJ, number of laser shots 5, respectively. The survey crystal positioning system (survey CPS) was set for the random choice of shot position by automatic crystal recognition. The isolation width Δm/z 4, normalised collision energy 25 %, activation Q value 0.250, activation time 30 ms and helium as the collision gas were used for CID experiments in LTQ linear ion trap. The used matrix was 2,5-dihydroxybenzoic acid (DHB). Mass spectra were averaged over the whole MS record (30 s) for all measured samples.

Elemental analyses were performed on an EA 1108 Fisons instrument.

S2. Absorption spectra in DCM.

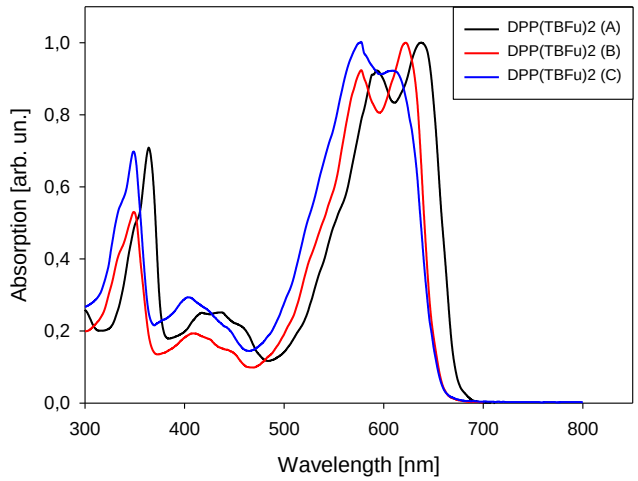

Figure S1: Normalized absorption of the compounds under study in DCM.

S3. Further characterization of photovoltaic devices.

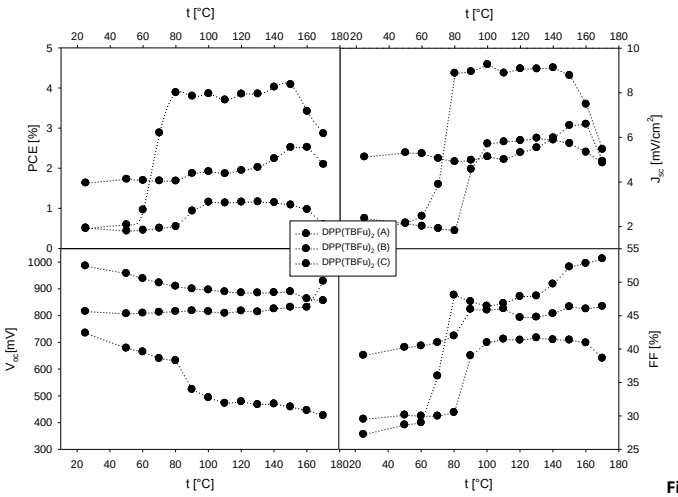

Figure S2: Main photovoltaic parameters of the gradually annealing of the devices with PEDOT:PSS anode material.

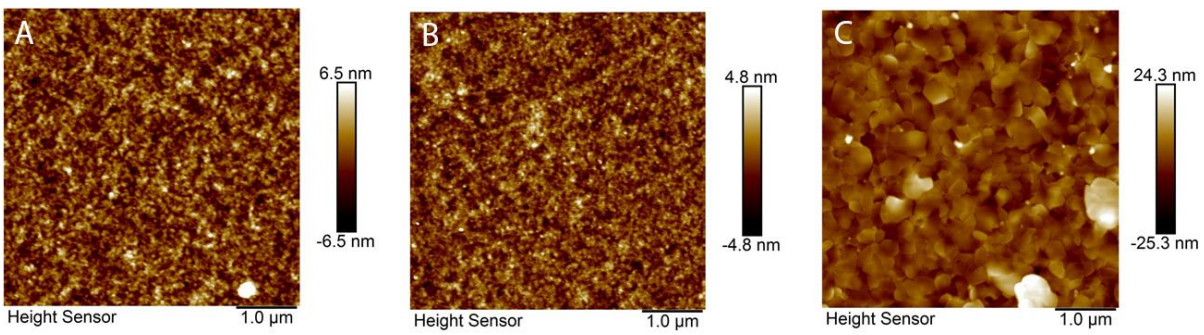

Figure S3: AFM images of the ethyl-hexyl acetatylated (compound (B)) DPP(TBFu)$_2$:PC$_{60}$BM blend: as-cast (A) and annealed at 140°C (B), and 170°C (C).