Supporting Information

A Naphthodithiophene-Diketopyrrolopyrrole Donor Molecule for Efficient Solution-Processed Solar Cells

Stephen Loser, Carson J. Bruns, Hiroyuki Miyauchi, Rocío Ponce Ortiz, Antonio Facchetti, Samuel I. Stupp*, and Tobin J. Marks**

Materials and Methods

TDPP[1] and compound **1**[2] were prepared according to published literature procedures. *N*-Bromosuccinimide (NBS), *n*-butyllithium (2.5 M in hexanes), $BF_3 \cdot OEt_2$, Me_3SnCl and $Pd(PPh_3)_4$ were purchased from Aldrich. Bis(2,2-diethoxyethyl) disulfide was purchased from TCI America. NBS was recrystallized from H_2O and all other reagents were used as received without further purification. THF was distilled from Na/benzophenone. All reactions were carried out under an inert atmosphere of N_2. Analytical thin-layer chromatography (TLC) was performed on aluminum sheets, precoated with silica gel 60-

F_{254} (Merck 5554). Flash column chromatography was carried out using silica gel 60 (Silicycle) as the stationary phase. NMR spectra were recorded on either a Bruker Avance III 500 spectrometer or a Varian Unity Plus 500 spectrometer, with working frequencies of 499.4 MHz for ^{1}H and 125.6 MHz for ^{13}C. Chemical shifts are reported in ppm and referenced to the residual non-deuterated solvent frequencies ($CDCl_3$: δ 7.27 ppm for ^{1}H, δ 77.0 ppm for ^{13}C). High resolution mass spectra were recorded on an Agilent 6210 LC-TOF multimode ionization (MMI) mass spectrometer. Electrospray mass spectrometry was performed with a Thermo Finnegan model LCQ Advantage mass spectrometer. UV-Visible spectroscopy was performed on a Varian Cary 5000 UV-Vis-NIR spectrophotometer. Electrochemistry was performed on a C3 Cell Stand electrochemical station equipped with BAS Epsilon software (Bioanalytical Systems, Inc., Lafayette, IN). Thin films were analyzed using wide-angle X-ray diffractometry (WAXRD) on a Rigaku ATX-G using standard θ-2θ techniques, with monochromatic CuKα radiation. OFET device measurements were carried out at room temperature in a customized probe station in air. Coaxial and/or triaxial shielding was incorporated into Signatone probes to minimize noise levels. Organic field effect transistor (OFET) characterizations were performed with a Keithley 6430 subfemto ammeter (drain) and a Keithley 2400 (gate) source meter, operated by a locally written Labview program. OPV characterization was performed on a Spectra-Nova Class A Solar Simulator with AM1.5G light (100 mW/cm^2) from a Xe arc lamp. The light source was calibrated with a NREL-certified Si diode equipped with a KG3 filter to bring spectral mismatch to unity. Current vs potential (J-V) measurements were recorded with a Keithly 2400 digital source meter. External quantum efficiency (EQE) was performed using an Oriel Model

QE-PV-SI (Newport Instruments) equipped with a NIST-certified Si-diode and a Merlin lock-in amplifier and optical chopper. Monochromatic light was generated from a 300 W Xe arc lamp.

Synthesis and Characterization

TDPP-Br. Protected from light, NBS (522 mg, 2.93 mmol) in $CHCl_3$ (50 mL) was added to a solution of **TDPP** (1.54 g, 2.93 mmol) in $CHCl_3$ (100 mL) at 0 °C over 6 h. The reaction was stirred at ambient temperature overnight and the solvent was removed under reduced pressure. The residue was chromatographed on SiO_2 (hexanes–$CHCl_3$, gradient from 9:1 to 3:2) to afford the title compound as a purple solid (934 mg, 53%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): ∂ = 8.92 (d, *J* = 3.5 Hz, 1H), 8.65 (d, *J* = 4.0 Hz, 1H), 7.65 (d, *J* = 5.0 Hz, 1H), 7.28 (dd, *J* = 5.0 Hz, 4.0 Hz, 1H), 7.23 (d, *J* = 4.0 Hz, 1H), 4.07–3.90 (m, 4H), 1.90–1.82 (m, 2H), 1.38–1.22 (m, 16H), 0.91–0.82 (m, 12H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): ∂ = 161.6, 161.5, 140.9, 138.9, 135.6, 135.1, 131.4, 131.2, 130.9, 129.7, 128.5, 118.6, 108.1, 107.7, 45.9, 45.9, 39.1, 39.0, 30.1, 30.1, 28.3, 23.5, 23.5, 23.0, 23.0, 14.0, 10.4 ppm. HRMS (ESI-TOF-MS): *m/z* calcd for $C_{30}H_{40}BrN_2O_2S_2$ $[M+H]^+$ 603.1714, found 603.1715. Anal. Calcd for $C_{30}H_{39}BrN_2O_2S_2$: C, 59.69; H, 6.51. Found: C, 59.72; H, 6.45.

Compound 2. *n*-Butyllithium (2.5 M solution in hexane, 13.0 mL, 32.5 mmol) was added dropwise to a solution of **1** (7.04 g, 13.0 mmol) in dry THF (240 ml) at -78 °C. The mixture was stirred at this temperature for 2 h and then bis(2,2-diethoxyethyl) disulfide (10.5 g, 35.2 mmol) was added. After stirring for 30 min, the reaction was allowed to warm up to room temperature and stirred overnight. The reaction was quenched with water and extracted with ether (3 × 100 mL), then dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Volatile impurities were further removed *in vacuo* at 150 °C. The residue was chromatographed on SiO_2 (hexanes-EtOAc, gradient from 99:1 to 97:3) to afford the title compound as a yellow oil (6.36 g, 72%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): ∂ = 7.77 (d, J = 9.0 Hz, 2H), 7.49 (d, J = 9.0 Hz, 2H), 4.65 (t, J = 5.5 Hz, 2H), 3.96 (d, J = 6.0 Hz, 4H), 3.97–3.51 (m, 8H), 3.21 (d, J = 5.5 Hz, 4H), 1.94–1.86 (m, 2H), 1.76–1.35 (m, 16H), 1.18 (t, J = 7.0 Hz, 12H) , 1.03 (t, J = 7.0 Hz, 6H) , 0.95 (t, J = 7.0 Hz, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): ∂ = 153.8, 128.7, 128.1, 125.1, 118.0, 102.0, 76.4, 62.1, 40.7, 36.4, 30.3, 29.2, 23.7, 23.1, 15.2, 14.2, 11.3 ppm. Anal. Calcd for $C_{38}H_{64}O_6S_2$: C, 67.02; H, 9.47. Found: C, 67.71; H, 9.39.

NDT. A Pomeranz-Fritsch type cyclization reaction was utilized to afford the named compound using a modified literature procedure.[3] A solution of **2** (4.89g, 7.18 mmol) in dry CH_2Cl_2 (800 mL) was added dropwise over 4.5 h to a refluxing solution of $BF_3{\cdot}OEt_2$ (2.0 mL, 16 mmol) in dry CH_2Cl_2 (2000 mL). The mixture was refluxed overnight and poured into sat. $NaHCO_3$ (aq) (1000 mL) and cooled to ambient temperature. The organic layer was separated and combined with CH_2Cl_2 extracts (2 × 100 mL), dried over $MgSO_4$, filtered, and concentrated. The residue was chromatographed on SiO_2 (hexanes–EtOAc, gradient from 100:0 to 99.3:0.7) to afford the title compound as a yellow powder (495 mg, 14%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): ∂ = 8.47 (s, 2H), 7.46 (m, 4H), 4.28 (d, J = 5.5 Hz, 4H), 2.00–1.93 (m, 2H), 1.84–1.40 (m, 16H), 1.08 (t, J = 7.5 Hz, 6H), 0.95 (t, J = 7.5 Hz, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): ∂ = 149.8, 139.7, 128.0, 127.1, 124.8, 124.6, 110.8, 75.5, 40.8, 30.5, 29.2, 23.9, 23.2, 14.2, 11.4 ppm. Anal. Calcd for $C_{30}H_{40}O_2S_2$: C, 72.53; H, 8.12. Found: C, 72.68; H, 8.16.

NDT(SnMe$_3$)$_2$. *n*-Butyllithium (2.5 M solution in hexane, 0.6 mL, 1.5 mmol) was added dropwise to a solution of **NDT** (295.3 mg, 0.595 mmol) in dry THF (50 mL) at -78 °C. The mixture was stirred at this temperature for 30 min and then at room temperature for 30 min. After cooling down to -78 °C, Me_3SnCl (1 M solution in hexane, 1.5 mL, 1.5 mmol) was added dropwise. After stirring for 30 min at this temperature, the reaction was returned to room temperature and stirred overnight. The reaction was quenched with $NaHCO_3$ (aq) and solvent was removed *in vacuo*. The residue was dissolved in hexane and washed with $NaHCO_3$ aq (1 × 25 mL) and with water (2 × 25 mL), then dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Recrystallization in *i*PrOH yielded the target compound as a yellow powder (411.2 mg, 84%). ^1H NMR (500 MHz, $CDCl_3$, 298 K): ∂ = 8.44 (s, 2H), 7.52 (s, 2H), 4.30 (d, *J* = 5.5 Hz, 4H), 2.00–1.92 (m, 2H), 1.84–1.40 (m, 16H), 1.08 (t, *J* = 7.5 Hz, 6H), 0.98 (t, *J* = 7.0 Hz, 6H), 0.48 (s, 18H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): ∂ = 149.2, 142.7, 141.2, 132.6, 130.1, 124.5, 109.6, 75.2, 40.8, 30.5, 29.2, 23.9, 23.2, 14.2, 11.4, -8.4 ppm. Anal. Calcd for $C_{36}H_{56}O_2S_2Sn_2$: C, 52.58; H, 6.86. Found: C, 53.03; H, 6.86.

NDT(TDPP)$_2$: Dry toluene (10 mL) and dry DMF (2 mL) were added to **NDT(SnMe$_3$)$_2$** (80.4 mg, 0.0978 mmol), **TDPP-Br** (147 mg, 0.243 mmol) and $Pd(PPh_3)_4$ (11.5 mg, 0.00996 mmol). The reaction was heated to 120 °C and stirred for 24 h, then poured into MeOH (150 mL) and stirred for 20 min. The resulting precipitate was collected by vacuum filtration and chromatographed on SiO_2 (hexanes–$CHCl_3$, gradient from 30:70 to 0:100) to afford the title compound as a shiny, bronze-colored solid (120 mg, 80%). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): ∂ = 8.97 (d, J = 4.5 Hz, 2H), 8.95 (d, J = 4.0 Hz, 2H), 8.35 (s, 2H), 7.65–7.64 (m, 4H), 7.50 (d, J = 4.0 Hz, 2H), 7.29 (d, J = 4.5 Hz, 2H), 4.30 (d, J = 5.5 Hz, 4H), 4.14–4.02 (m, 8H), 2.02–1.20 (m, 54H), 1.12 (t, J = 7.5 Hz, 6H), 1.01 (t, J = 7.0 Hz, 6H), 0.97–0.86 (m, 24H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): ∂ = 161.6, 161.5, 149.2, 142.1, 140.3, 140.2, 139.3, 136.9, 136.5, 135.5, 130.7, 129.8, 129.6, 128.5, 126.5, 126.4, 125.7, 121.7, 111.3, 108.5, 108.1, 75.6, 45.91, 40.8, 39.3, 39.1, 30.4, 30.4, 30.2, 29.7, 29.2, 28.6, 28.3, 23.9, 23.7, 23.5, 23.2, 23.2, 23.1, 14.3, 14.2, 14.1, 11.4, 10.6, 10.5 ppm. MS (ESI): m/z calcd for $C_{90}H_{117}N_4O_6S_6$ $[M+H]^+$ 1541.7, found 1541.5. Anal. Calcd for $C_{90}H_{116}N_4O_6S_6$: C, 70.09; H, 7.58; N 3.63. Found: C, 70.19; H, 7.55; N, 3.54.

Cyclic Voltammetry (CV)

NDT(TDPP)$_2$ was drop cast from a 0.2% (w/w) chloroform solution onto the working electrode. The thin film was immersed into anhydrous acetonitrile under N_2 and scanned at a rate of 100 mV/s using tetrabutylammonium hexafluorophosphate (NBu_4PF_6) as the electrolyte. A platinum working and counter electrode and a silver wire pseudoreference electrode were used. A ferrocene/ferrocenium (Fc/Fc$^+$) redox couple was used as the internal standard and was assigned an absolute energy level of -4.8 eV vs vacuum.[4] Electrochemical potential is reported vs SCE, which has an energy of -4.44 eV vs vacuum.[5] The HOMO level of **NDT(TDPP)$_2$** was determined by eq 1 (E_{ox}^{onset} =onset oxidation potential vs Fc/Fc$^+$). The LUMO level of **NDT(TDPP)$_2$** was determined by eq 2 (E_g^{opt} = optical band gap).

$$E_{\mathrm{HOMO}} = -\,(E_{ox}^{\mathrm{onset}} + 4.80)\ (\mathrm{eV}) \qquad (1)$$

$$E_{\mathrm{LUMO}} = E_g^{\mathrm{opt}} + E_{\mathrm{HOMO}}\ (\mathrm{eV}) \qquad (2)$$

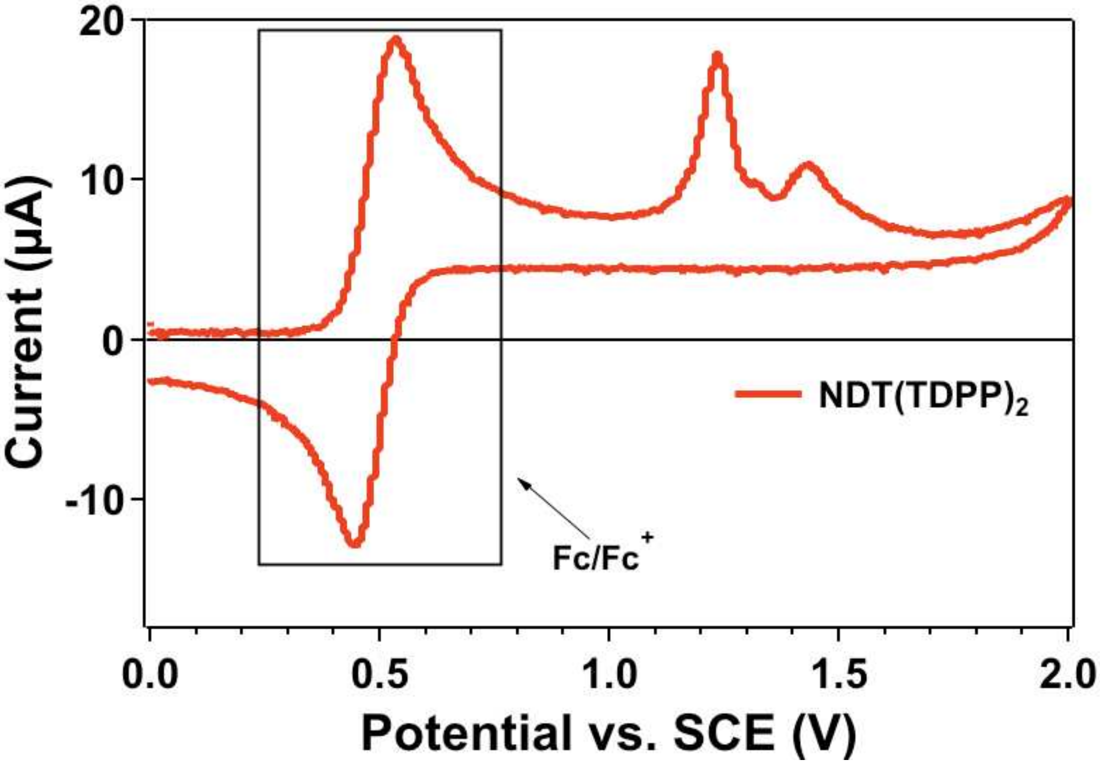

Figure S1. Cyclic voltammogram of a **NDT(TDPP)$_2$** thin film. Note: Fc/Fc$^+$ redox couple was used as internal standard.

OFET Device Fabrication

Bottom-gate/top-contact OFETs were fabricated on hexamethyldisilazane (HMDS)-treated, *p*-doped Si (001) wafers with 300 nm of thermally grown SiO_2 as dielectric layer. The capacitance of the 300 nm SiO_2 gate insulator is ~12 nF·cm^{-2}. Si wafers were cleaned by sonication in ethanol followed by 5 minutes of O_2 plasma. Trimethylsilation of the Si/SiO_2 surface was completed by exposure of the Si wafer to HMDS vapor in an air-free reaction vessel under N_2 at room temperature. The semiconductor layer was deposited by placing 5 drops of **NDT(TDPP)$_2$** or **NDT(TDPP)$_2$**:PC$_{61}$BM (w:w) at 10 mg·mL^{-1} and 20 mg·mL^{-1} , repectively, from anhydrous chloroform on an HMDS-treated wafer. After 30 seconds, the remaining solution not dried was flung off by hand. This drop casting technique was used because spin coating did not yeild consistent films due to hydrobic HMDS layer. After the semiconductor was deposited, the device was annealed at 110 °C. To complete the device fabrication, 50 nm of Au was thermally evaporated through a shadow mask at ~1 × 10^{-6} Torr to yield the source and drain electrodes with a channel length and width of 100 and 5000 μm, respectively. Device characterization was carried out in air.

OPV Device Fabrication and Characterization

Patterned ITO-coated glass (Thin Film Device, Inc.), with a resistivity of <10Ω/□ and thickness of 280 nm was cleaned in sequential sonications at 50 °C in soap/DI water, DI water, methanol, isopropanol, and acetone for 30 min. After the final sonication step, substrates were blown dry with a stream of N_2 gas. ITO substrates were then treated for 30 minutes in a UV/O_3 oven (Jelight Co.). PEDOT:PSS (Clevios P VP Al 4083) was then spun-cast at 5000 rpm for 30 sec and subsequently annealed at 150 °C for 15 min. Immediately following PEDOT:PSS annealing, samples were blown with a stream of N_2 gas to drive off moisture. Samples were then transferred to a N_2-filled glove box for active layer and top contact deposition. Active layers containing donor **NDT(TDPP)$_2$** and acceptor PC$_{61}$BM (>99.5% pure, American Dye Source) were formulated inside the glove box in various ratios (w:w) at a total concentration of 20 mg mL^{-1} in distilled chloroform. Active layer solutions were then allowed to stir at 600 – 800 rpm for 1.5 h at 40 °C. The active layer solutions were spun-cast at 4000 rpm for 15 sec to afford an active layer thickness of ~75 nm (by AFM). Samples were then either thermally annealed at various temperatures (60 – 150 °C) for 10 min on a temperature-controlled hot plate or left as cast. To finish device fabrication, LiF(1.0 nm)/Al(100 nm) were thermal evaporated, sequentially, at a base pressure of ~4.0×10^{-6} torr. The top Al electrodes were then encapsulated with epoxy and a glass slide before testing. *J-V* characteristics were measured using the methods stated previously. Each pixel of the device was carefully masked with black rubber to prevent parasitic charge leakage and inaccurate electrode overlap. Each substrate had 4 pixels with a defined area of 0.06 cm^2.

OFET and WAXRD Data

Table S1. Summary of top-contact OFET performance of drop cast **NDT(TDPP)$_2$** and various blend ratios between **NDT(TDPP)$_2$** and PC$_{61}$BM on HMDS-treated Si/SiO$_2$ wafer annealed at 110 °C, measured in air.

Blend Ratio [D:A]	**μ_h [cm^2 V s^{-1}]^a**	**V_t [V]**	**I_{on}/I_{off}**
2.3:1	2.57×10^{-3} ($\pm 2.90 \times 10^{-4}$)	-19.4	8.00×10^{2}
1.5:1	3.28×10^{-3} ($\pm 3.87 \times 10^{-5}$)	-19.5	4.80×10^{2}
1:1	3.54×10^{-3} ($\pm 5.67 \times 10^{-4}$)	-17.5	4.58×10^{2}
NDT(TDPP)$_2$	7.18×10^{-3} ($\pm 2.20 \times 10^{-4}$)	-14.9	3.83×10^{3}

[a] Average response with standard deviation in parenthesis

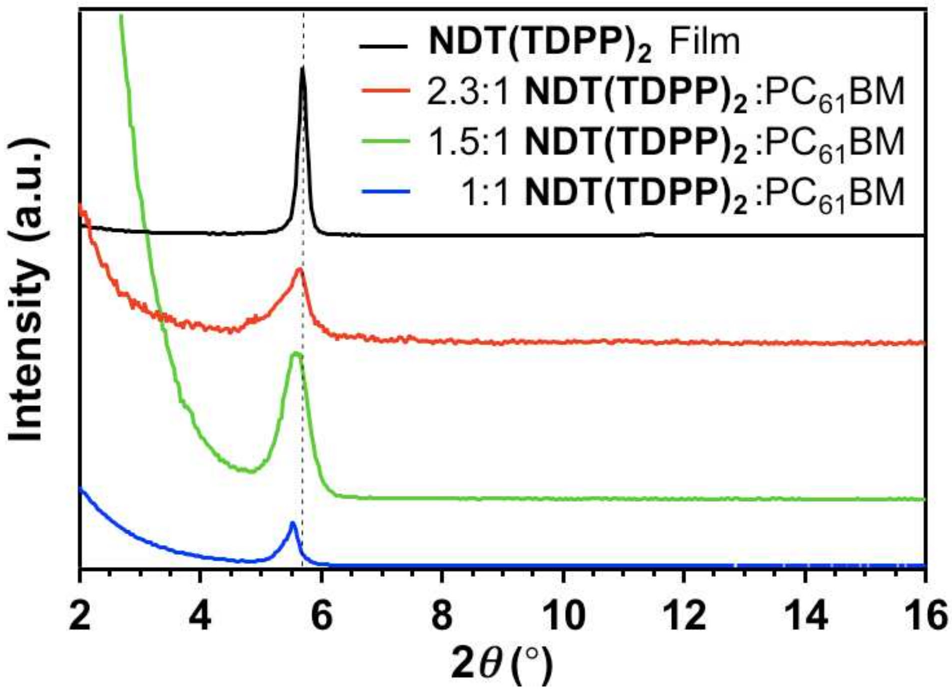

Figure S2. WAXRD of various **NDT(TDPP)$_2$**:PC$_{61}$BM blend films and neat **NDT(TDPP)$_2$** on HMDS-treated Si/SiO$_2$ wafer annealed at 110 ºC.

OPV Device Optimization Screening

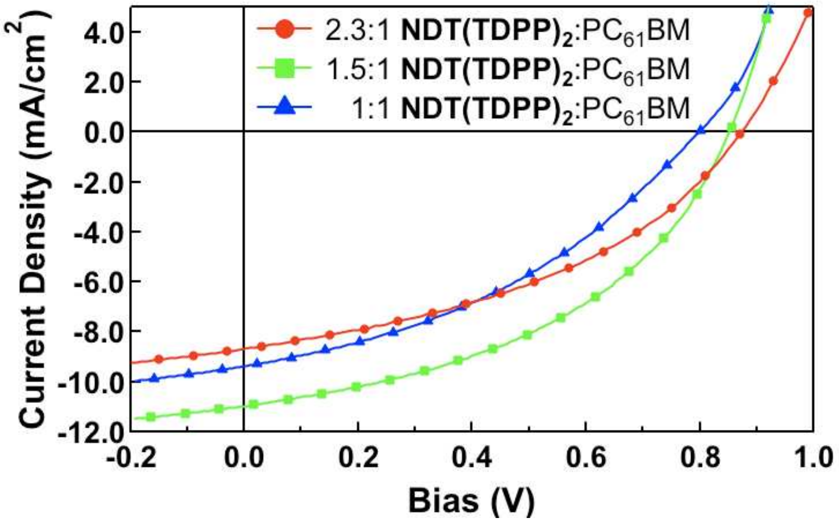

Figure S3. Typical *J-V* response of OPV devices based on various blend ratios between **NDT(TDPP)$_2$** and PC$_{61}$BM annealed at 110 °C for 10 min.

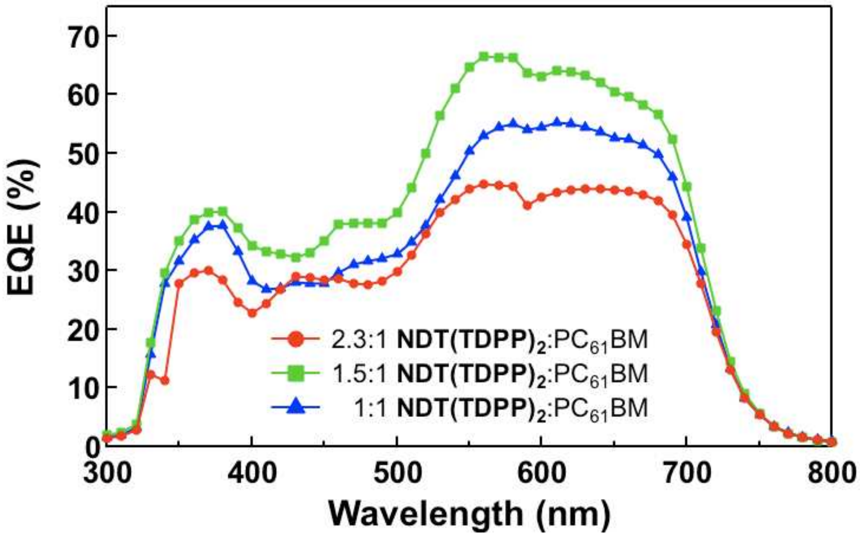

Figure S4. Typical EQE response of OPV devices based on various blend ratios between **NDT(TDPP)$_2$** and PC$_{61}$BM annealed at 110 °C for 10 min.

Table S2. Summary of *J*-*V* and EQE response of various of OPV devices based on blend ratios between **NDT(TDPP)$_2$** and PC$_{61}$BM annealed at 110 °C for 10 min.

Blend Ratio [D:A]	**V_{OC} [mV]**[a]	**J_{SC} [mA/cm^2]**[a]**, measured**	***FF* (%)**[a]	***PCE* (%)**[a]	**EQE$_{\lambda=570}$ (%)**	**J_{SC} [mA/cm^2], calculated**[b]
2.3:1	873(±3)	8.38(±0.20)	39.8(±0.9)	2.91(±0.14)	44.6	8.36
1.5:1	844(±6)	11.27(±0.21)	42.7(±1.5)	4.06(±0.06)	66.4	11.11
1:1	797(±2)	9.45(±0.06)	38.1(±1.0)	2.87(±0.02)	54.4	9.40

[a] Device metrics with average response and standard deviation in parenthesis

[b] Calculated J_{SC} from integrating entire EQE spectrum

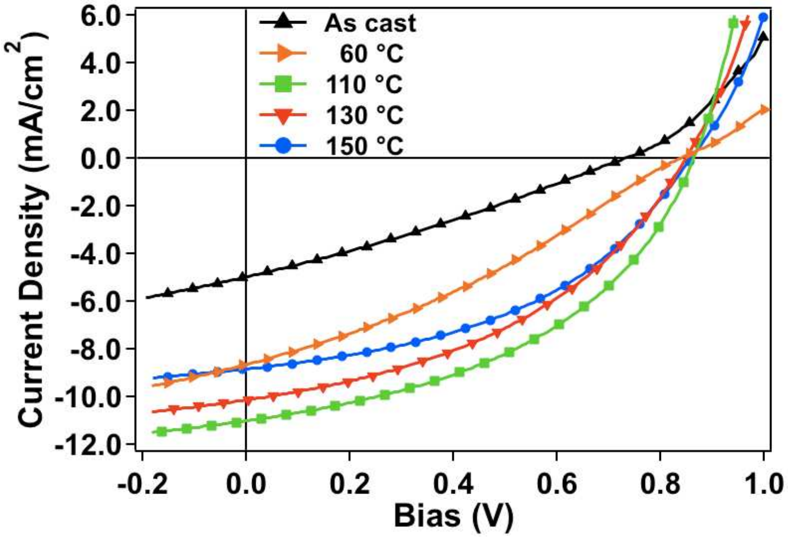

Figure S5. Typical *J*-*V* response of an OPV device based on a 1.5:1 **NDT(TDPP)$_2$**:PC$_{61}$BM blend. Active layer films were either evaluated with no additional processing or thermally annealed between 60 – 150 °C for 10 min.

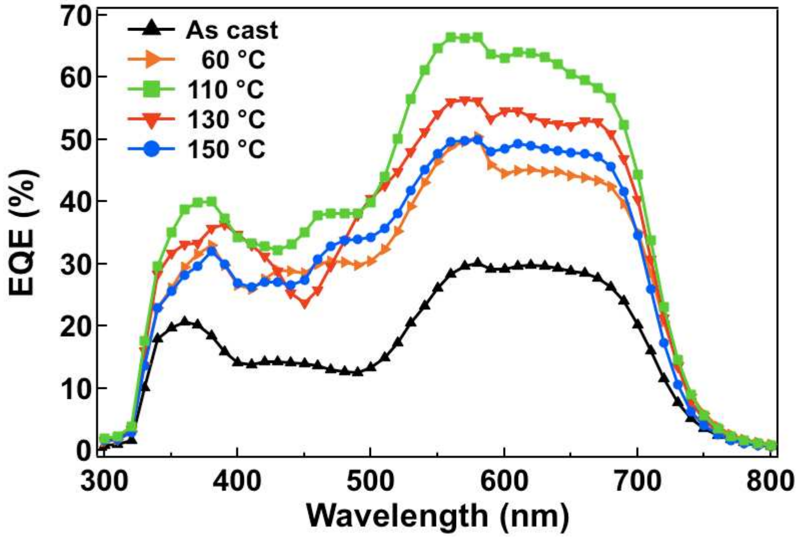

Figure S6. Typical EQE response of an OPV device based on a 1.5:1 **NDT(TDPP)$_2$**:PC$_{61}$BM blend. Active layer films were either evaluated with no additional processing or thermally annealed between 60 – 150 °C for 10 min.

Table S3. Summary of *J-V* and EQE response of OPV devices based on a 1.5:1 **NDT(TDPP)$_2$**:PC$_{61}$BM blend with no treatment and thermal annealing between 60 – 150 °C for 10 minutes.

Annealing Temperature (°C)	V_{OC} **[mV]**[a]	J_{SC} **[mA/cm^2]**[a], **measured**	***FF* (%)**[a]	***PCE* (%)**[a]	**EQE$_{\lambda=570}$ (%)**	J_{SC} **[mA/cm^2], calculated**[b]
As Cast	691(±43)	4.99(±0.06)	28.8(±0.3)	0.99(±0.05)	29.6	4.96
60	802(±32)	8.40(±0.28)	31.7(±0.42)	2.10(±0.14)	49.7	8.59
110	844(±6)	11.27(±0.21)	42.7(±1.5)	4.06(±0.06)	66.4	11.11
130	838((±2)	10.07(±0.07)	41.2(±0.44)	3.47(±0.04)	56.4	9.90
150	843(±3)	8.83(±0.13)	45.4(±1.3)	3.32(±0.02)	49.7	8.87

[a] Device metrics with average response and standard deviation in parenthesis

[b] Calculated J_{SC} is from integrating entire EQE spectrum

Atomic Force Microscopy (AFM)

Figure S7 displays AFM tapping mode height images of as-cast and annealed **NTD(TDPP)$_2$**:PC$_{61}$BM blend ratios on ITO/PEDOT:PSS substrates. As the concentration of PC$_{61}$BM increases, more discrete donor and acceptor domains are formed. In addition, annealing at 110 ºC for 10 minutes reduces the roughness of the films and appears to increase the size of the donor and acceptor domains. It is difficult to discern which morphology is ideal, but according to the device *J-V* metrics a ratio of 1.5:1 **NTD(TDPP)$_2$**:PC$_{61}$BM annealed at 110 ºC gives the best performance and hence the best morphology.

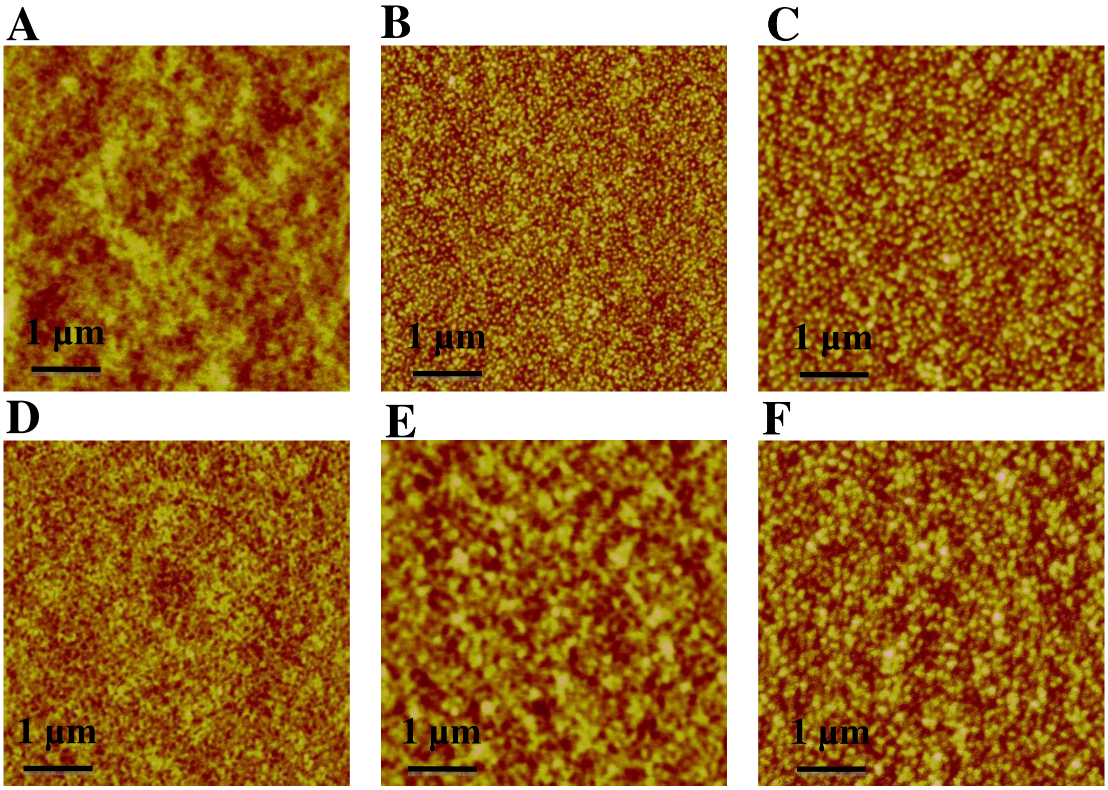

Figure S7. 5×5 µm tapping mode AFM height images of **NDT(TDPP)$_2$**:PC$_{61}$BM active layers on ITO/PEDOT:PSS. (**A**) 2.3:1, (**B**) 1.5:1, and (**C**) 1:1 active layer blend ratios as-cast, and (**D**) 2.3:1, (**E**) 1.5:1, and (**F**) 1:1 blend ratios annealed at 110 °C for 10 min. Note: RMS roughness = 0.45 (**A**), 1.1 (**B**), 3.09 (**C**), 0.45 (**D**), 0.47 (**E**), and 2.55 nm (**F**).

Complete Ref. 13a

Bronstein, H.; Chen, Z.; Ashraf, R. S.; Zhang, W.; Du, J.; Durrant, J. R.; Shakya Tuladhar, P.; Song, K.; Watkins, S. E.; Geerts, Y.; Wienk, M. M.; Janssen, R. A. J.; Anthopoulos, T.; Sirringhaus, H.; Heeney, M.; McCulloch, I., *J. Am. Chem. Soc.* **2011,** *133*, 3272–3275.

References

[1] Tamayo, A. B.; Tantiwiwat, M.; Walker, B.; Nguyen, T.-Q. *J. Phys. Chem. C* **2008**, *112*, 15543–15552.

[2] Mori, T.; Kijima, M. *Opt. Mater.* **2007**, *30*, 545–552.

[3] Bevis, M. J.; Forbes, E. J.; Naik, N. N.; Uff, B. C., *Tetrahedron* **1971**, *27*, 1253-1259.

[4] Pommerehne, J.; Vestweber, H.; Guss, W.; Mahrt, R. F.; Bassler, H.; Porsch, M.; Daub, J. *Adv. Mater.* **1995**, *7*, 551–554.

[5] Meerholz, K.; Heinze, J. *Electrochim. Acta* **1996**, *41*, 1839–1854.