Supporting Information

Morphology Control of Solution Processable Small Molecule Bulk Heterojunction Solar Cells via Solvent Additives

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1. Experimental methods

Synthesis:

3-(5-Bromo-thiophene-2-yl)-6-(thiophene-2-yl)-2,5-bis(2-ethylhexyl)-pyrrolo[3,4-c] pyrrole-1,4-dione, 4. To a solution of 3,6-di(thiophene-2yl)-2,5-bis(2-ethylhexyl)-pyrrolo[3,4-c]pyrrole-1,4-dione (2.3 g, 7.8 mmol) in 55 mL of chloroform, N-bromosuccinimide (0.92 g, 5.2 mmol) was added. The reaction solution was stirred for 5 hrs at room temperature in the dark. After adding more chloroform, solution was washed with water and dried over magnesium sulfate. After solvent was removed under reduced pressure, the crude product was purified by column chromatography on a silica gel with chloroform/hexane from 1/1 to 2/1 (v/v) to afford **4** (1.5 g, 50 %). ^{1}H NMR (400 MHz, $CDCl_3$): 8.89 (d, 1H, J = 2.8 Hz), 8.62 (d, 1H, J = 3.6 Hz), 7.63 (d, 1H, J = 4.8 Hz), 7.26 (d, 1H, J = 4.0 Hz), 7.21 (d, 1H, J = 3.6 Hz), 3.88 – 4.05 (m, 4H), 1.84 (bs, 2H), 1.20 – 1.36 (m, 16H), 0.82 – 0.89 (m, 12H).

Compound 5. To microwave tube containing 500 mg (0.83 mmol) of compound **4**, 217 mg (0.42 mmol) of 2,6-Bis(trimethylstannyl)dithieno[3,2-b:2',3'-d]thiophene (**3**) and 25 mg (0.02 mmol) of $Pd(PPh_3)_4$ werereplaced with 15 ml of xylene. After sealed with a cap inside of glovebox, the tube was subjected to the following reaction conditions in a microwave reactor; 120 ^oC for 1 minute, 140 ^oC for 1 minute, 160 ^oC for 1 minute and 175 ^oC for 60 minutes. Upon cooling, the resulting product was precipitated in methanol (MeOH) and filtered. The residual solid was purified by column chromatography on a silica gel with chloroform/hexane gradient adding 1 % (v/v) triethylamine. After solvent removed, the purple solid was precipitated with MeOH and filtered to afford 362 mg of **5**(Yield = 70 %) ^{1}H NMR (400 MHz, C_6D_6):9.53 (d, 2H,*J* = 3.6 Hz), 9.47 (d,2H, *J* = 4.0 Hz), 7.40 (s, 2H), 7.01 (d, 2H, *J* = 3.6 Hz), 6.90 (d, 2H, *J* = 4.0 Hz), 6.81 (t, 2H, *J* = 4.4 Hz), 4.10–4.22 (m, 8H), 2.01-2.16 (bs, 4H), 1.21-1.55 (m, 32H), 0.89-1.05 (m, 24H).

Compound 6. To a solution of **5** (362 mg, 0.291 mmol) in 100 mL of chloroform, N-bromosuccinimide (109 mg, 0.61 mmol) was added. The reaction solution was stirred for 5 hrs at room temperature in the dark. After diluted with chloroform, solution was washed with water and dried over magnesium sulfate and solvent was removed under reduced pressure. The crude product was purified by column chromatography on a silica gel with chloroform with 1 % triethylamineand after removing solvent, the resulting products were precipitated with methanol to afford **6** (120mg, 30 %).^{1}H NMR (400 MHz, C_6D_6) 9.48 (d, 2H, *J* = 4.0 Hz), 9.17 (d, 2H, *J* = 4.4 Hz), 7.41 (s, 2H), 6.98 (d, 2H, *J* = 4.8 Hz), 6.74 (d, 2H, *J* = 4.0 Hz), 3.90-4.20 (m, 8H), 1.90-2.20 (m, 4H), 1.10-1.60 (m, 32H), 0.70-1.10 (m, 24H).

DTTDPP. To microwave tube containing 120 mg (0.086 mmol) of compound **6**, 71 mg (0.21mmol) of 2-trimethylstannyl-5-hexylthiphene and 25 mg (0.02 mmol) of $Pd(PPh_3)_4$ were replaced with 15 ml of xylene. After sealed with a cap inside of glovebox, the tube was subjected to the same reaction conditions in a microwave reactor as described for compound **5**. The residual solid was purified by column chromatography on a silica gel eluenting with chloroform adding 1 % (v/v) triethylamine. After solvent removed, the purple solid was precipitated with MeOH and filtered to afford 100 mg of **DTTDPP** (Yield = 74 %) ^{1}H NMR (400 MHz, $CDCl_3$) 8.90-9.04 (m, 4H), 7.39 (s, 2H), 7.17 (d, 2H, J = 4.0 Hz), 7.13 (d, 2H, J = 3.6 Hz), 7.09 (d, 2H, J = 3.2 Hz), 6.73 (d, 2H, J = 3.6 Hz), 6.69 (d, 2H, J = 3.6 Hz), 3.98-4.2 (m, 8H), 2.75-2.80 (m, 4H), 1.91-1.99 (bs, 4H), 1.65-1.68 (m, 4H), 1.20-1.50 (m, 32H), 0.85-0.99 (m, 30H).

UV-Vis absorption measurement: A thin film was prepared by spin-casting from a 0.5 wt% chloroform solution onto a glass substrate, resulting in a film thickness of ~ 60 nm. The absorption spectra were measured with a Beckman Coulter DU 800 series UV-visible spectrophotometer at room temperature.

UPS measurement: A **DTTDPP** solution was prepared in chloroform with 3 mg/mL.75 nm thick gold filmwas deposited on a pre-cleaned Si substrate with a thin native oxide. The **DTTDPP** solution was spin-cast at 2000 rpm for 40 sec on a gold film. Film fabrication was done in a N_2-atmosphere glovebox. To minimize possible influence by exposure to air, the film was then transferred from the N_2-atmosphere dry box to the analysis chamber inside an air-free holder. Subsequently, the sample was kept inside a high-vacuum chamber overnight. The UPS analysis chamber was equipped with a hemispherical electron-energy analyzer (KratosUltra Spectrometer) and was maintained at 1.0×10^{-9}Torr. The UPS measurements were carried out using the He I (hv = 21.2 eV) source. During UPS measurements, a sample bias of - 9 V was used in order to separate the sample and the secondary edge for the analyzer

Solar cell fabrication and characterization: BHJ solar cells were fabricated using **DTTDPP** as a donor and $PC_{71}BM$ as an acceptor. The ITO-coated glass substrates were cleaned with detergent, distilled water, acetone, and isopropyl alcohol in an ultrasonic bath and the dried overnight in an oven at >100°C. After UV ozone treatment of the ITO substrates for 20 min, 40 nm thick PEDOT:PSS layer was spin-cast from aqueous solution (5000 rpm for 40 sec). The substrates were dried at 140°C for 10 min in air and transferred to a N_2-glovebox for spin-casting the blend layers. The blend solutions of **DTTDPP** and $PC_{71}BM$ (1:1 w/v) in chloroform (concentration of 7 mg/ml) were prepared without or with 1% (v/v) DIO and CN. The thickness of blend layers was average 90 nm (from 2000 rpm for 40 sec) measured by profilometer. The final step in device construction involves thermal evaporation of 100 nm thick Al electrodes. The device area was 9.84 mm^2 with using an aperture. All data were obtained under AM 1.5G illumination from a calibrated solar simulator with irradiation intensity of 100 mW cm^{-2}*under ambient atmosphere*. IPCE spectra were measured using a solar cell spectral response/QE/IPCE measurement system (PV Measurements Inc.).

Atomic force microscope measurement: Tapping mode AFM images were collected under N_2-atmosphere using the Nanoscope III controller (Veeco). Silicon probes with spring constants of 5N/m and resonant frequencies of 75 KHz were used.

2. External quantum efficiency (EQE) profiles

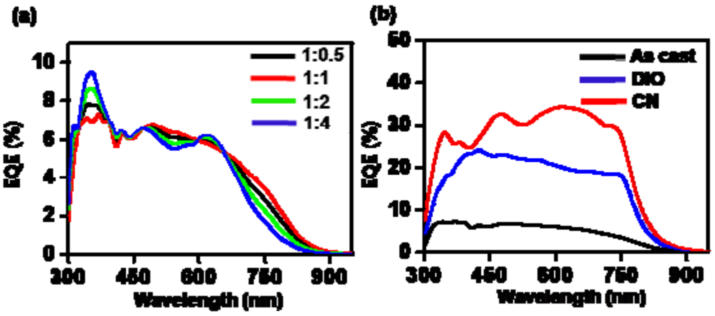

Figure S1. (a) The EQE spectra of the devices as a function of blend ratio. (b) The EQE spectra of the devices without and with 1% additives.

3. UPS spectrum of DTTDPP

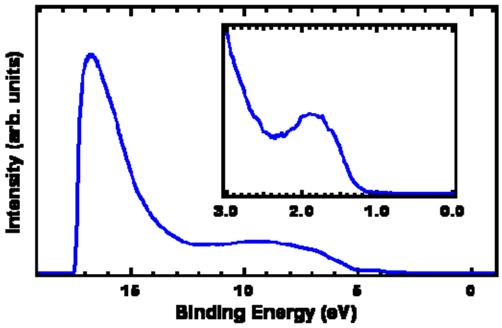

Figure S2. UPS spectrum of a **DTTDPP** film. The HOMO energy of **DTTDPP** is 5.0 eV. According to the optical gap of 1.5 eV, the LUMO energy can be estimated 3.5 eV.

4. DFT calculation

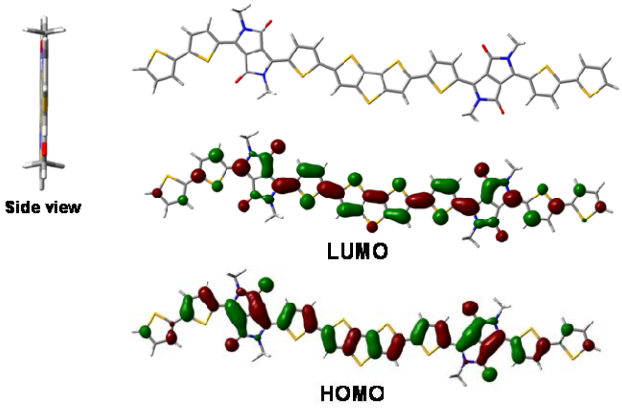

Figure S3. The optimized structure of **DTTDPP**. The DFT result shows a planar structure of **DTTDPP**.

5. XPS Spectra of DTTDPP:PC$_{71}$BM films

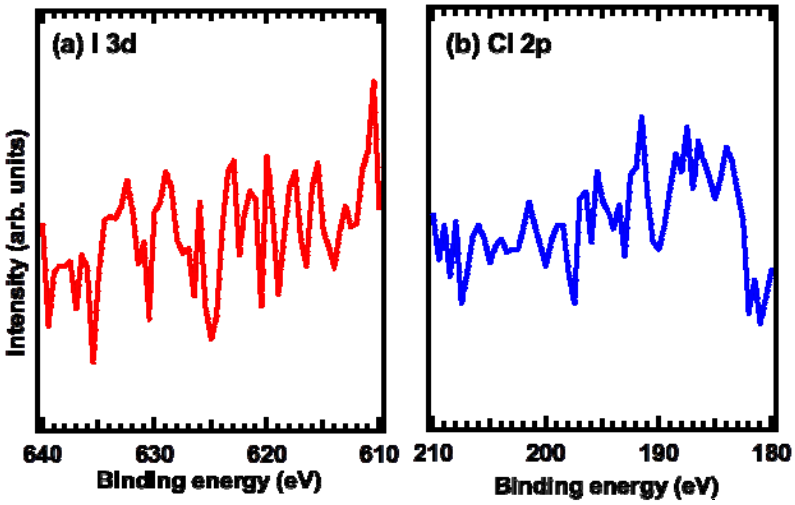

Figure S4. (a) I 3d and (b) Cl 2p XPS spectra of the **DTTDPP**:PC$_{71}$BM films with 1% DIO and 1% CN, respectively.