Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.
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Diketopyrrolopyrrole (DPP) Functionalized Tetrathienothiophene (TTA) Small Molecules for Organic Thin Film Transistors and Organic Photovoltaic Cells

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1. Materials and Methods:

All chemicals and solvents (from Aldrich, Arco, or TCI Chemical Co.) were of reagent grade. Reaction solvents (toluene, ether, and THF) were distilled under nitrogen from sodium/benzophenone ketyl, and halogenated solvents were distilled from CaH_2. ^1H and ^{13}C NMR spectra were recorded using a Bruker 500 or a 300 instrument, with reference to solvent signals. Differential scanning calorimetry (DSC) was carried out on a Mettler DSC 822 instrument at a scan rate of 10 K/min. Thermo gravimetric analysis (TGA) was performed on a Perkin Elmer TGA-7 thermal analysis system using dry nitrogen as a carrier gas at a flow rate of 40 mL/min. UV–Vis absorption and fluorescence spectra were obtained in the indicated solvents at room temperature using JASCO V-530 and Hitachi F-4500 spectrometers, respectively. Differential pulse voltammetry experiments were performed with a conventional three-electrode configuration (a platinum disk working electrode, an auxiliary platinum wire electrode, and a non-aqueous Ag reference electrode, with a supporting electrolyte of 0.1 M tetrabutylammonium hexafluorophosphate (dry $TBAPF_6$) in the specified dry solvent, using a CHI621C Electrochemical Analyzer (CH Instruments). Under N_2, the anhydrous OSC material was dissolved in above 0.1 M *o*-$C_6H_4Cl_2$ solution to prepare a 10^{-3} M test solution. In each DPV experiment, 5 mL of the test solution is scanned together with Fc^+/Fc (also 10^{-3} M; as internal standard) under N_2. All electrochemical potentials were referenced to an Fc^+/Fc internal standard (at +0.6 V). Mass spectrometric data were obtained with a JMS-700 HRMS instrument. 3-(2-thienyl)-6-(5-bromo-2-thienyl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4-dione(**5**),[1] and 3-(5-bromothiophen-2-yl)-2-(2-ethylhexyl)-4-(2-ethylhexyloxy)-6-(thiophen-2-yl)pyrrolo[3,4-c]pyrrol-1(2H)-one(**5'**) were prepared according to the literature procedures.[2]

*Synthesis of 2,6-di(trimethylstannyl)-3,7-dipentadecylthieno[3,2-b]thieno[2',3':4,5]thieno[2,3-d]thiophene (**2**):* Under nitrogen and anhydrous condition at 0 °C, 2.5 M *n*-BuLi (1.3 mL in hexanes, 3.26 mmol) was slowly added to a 30 mL THF solution of compound **1** (1.0 g, 1.48 mmol), and the mixture was stirred for 40 min. Next, trimethyltin chloride (0.65 g, 3.26 mmol) in THF (10 mL) was added slowly through syringe to the reaction mixture and the mixture was stirred at 0 °C for 30 min, then warmed to room temperature and stirred for overnight. Workup was performed by addition of water followed by extraction with ether. The combined organic phases were washed with water and then brine before drying over Na_2SO_4 and evaporation of the solvent. The crude product was purified by recrystallization from ether yielding the pure product as white solid (1.0 g, 67%). ^1H NMR ($CDCl_3$**;** 300 MHz): δ 2.72 (t, J=7.5 Hz, 4H), 1.79 – 1.68 (m, 4H), 1.34 ─ 1.25 (m, 48H), 0.88 (t, J=6.6 Hz, 6H), 0.43 (s, 18H). ^{13}C NMR (75MHz; $CDCl_3$): 142.71, 142.55, 136.70, 133.84, 132.29, 32.06, 31.92, 30.06, 29.68, 29.53, 29.48, 29.36, 22.69, 14.12.

*Synthesis of (DDPP-TTAR; **1**):* In a two-necked, 100 mL round-bottom flask was charged with compound **2** (0.20 g, 0.20 mmol), compound **5** (0.26 g, 0.44 mmol) and $Pd(PPh_3)_4$ (0.01 g, 0.01 mmol). The glassware was purged with nitrogen before adding degassed, anhydrous toluene the reaction mixture was then heated at 110 °C and stirred for overnight. After cooling back to room temperature, the mixture was filtered through a celite column. Toluene was used to extract the product from the celite pad. The toluene solutions were combined and evaporated, the desired product was recrystallized from CH_2Cl_2, giving 225 mg of blue solid in a yield of 65%. Mp: 225 °C. ^1H NMR ($CDCl_3$**;** 300 MHz): δ 9.06 (d, J=4.2 Hz, 2H), 8.91 (dd, J=3.9, 1.1 Hz, 2H), 7.61 (dd, J=5.0, 1.1 Hz, 2H), 7.32 (d, J=4.2 Hz, 2H), 7.27 ─ 7.24 (m, 2H), 4.11 – 3.97 (m, 8H), 3.01 (t, J=7.6 Hz, 4H), 1.96 – 1.77 (m, 8H), 1.47 – 1.25 (m, 80H), 0.95 – 0.84 (m, 30H). ^{13}C NMR (125MHz; $CDCl_3$): 161.65, 161.52, 143.72, 141.77, 139.82, 139.74, 136.59, 135.24, 134.06, 132.68, 130.83, 130.38, 129.95, 129.91, 129.09, 128.40, 126.54 108.11, 46.12, 45.94, 39.36, 39.13, 31.92, 30.25, 29.92, 29.67, 29.63, 29.54, 29.40, 29.36, 29.07, 28.44, 28.38, 23.61, 23.55, 23.18, 23.08, 22.68, 14.09, 14.03, 10.54, 10.49. HRMS (EI, m/z) calcd.: 1716.8640 (M^+). Found: 1716.8646.

Synthesis of (DDPP'-TTAR; ***2****). Following similar synthetic procedure of DDPP-TTAR (****1****)*: compound **6** (0.26 g, 0.44 mmol) was used instead of compound **5**. After similar work up steps to those employed for the synthesis of **DDPP-TTAR** (**1**), the desired product was purified by column chromatography (CH_2Cl_2), giving 230 mg of blue solid in a yield of 62%. Mp: 130 °C. ^1H NMR ($CDCl_3$**;** 300 MHz): δ 8.46 (d, J=4.1 Hz, 2H), 8.20 (dd, J=4.1, 1.1 Hz, 2H), 7.66 (dd, J=5.0, 1.0 Hz, 2H), 7.28 (d, J=1.4 Hz, 2H), 7.23 ─ 7.20 (m, 2H), 4.55 – 4.52 (m, 4H), 4.01 – 3.87 (m, 4H), 3.01 (t, J=6.6 Hz, 4H), 1.82 – 1.80 (m, 8H), 1.48 – 1.24 (m, 80H), 1.02 – 0.84 (m, 30H). ^{13}C NMR (125MHz; $CDCl_3$): 166.17, 161.47, 148.64, 143.53, 141.75, 141.11, 138.40, 134.77, 133.48, 132.44, 132.37, 132.12, 131.38, 130.11, 129.60, 127.92, 127.58, 114.33, 111.51, 72.42, 45.52, 39.12, 31.92, 30.78, 30.26, 29.77, 29.67, 29.63, 29.43, 29.36, 29.24, 29.10, 28.92, 28.37, 24.11, 23.57, 23.04, 22.68, 14.10, 14.09, 11.31, 10.49. HRMS (EI, m/z) calcd.: 1716.8640 (M^+). Found: 1716.8629.

Solar Cell Fabrication and Characterization: Pre-patterned ITO-coated glass (Thin Film Devices, Inc.) with a series resistance of ∼10Ω/□ was used as the substrate. It was cleaned by sequential sonication in hexane, DI water, methanol, isopropanol, and acetone, and finally UV/ozone treated (Jelight Co.) for 30 min. For the fabrication of inverted solar cells, ZnO electron transport/hole blocking layer was prepared by spin-coating at 5000 rpm from a ZnO precursor solution prepared from 0.5 M zinc acetate dehydrate in 0.5 M monoethanolamine and 2-methoxyethanol under N_2. After cleaning the electrical contacts, substrates were immediately baked in air 150 °C for 5 min. The films were then rinsed with DI water, isopropanol, and acetone, and then dried in a glovebox. Active layer solutions were prepared in CF or CF/DIO with varying vol% of DIO. For optimum performance **1** and **2** devices, active layers were spin-coated at 3000 rpm and 3500 rpm to obtain thicknesses of 80 nm and 85 nm, respectively. Thin layers of 5 nm MoO_x and 100 nm of Ag were then thermally evaporated through a shadow mask at $\sim 10^{-6}$ Torr. Device I-V characteristics measured under AM1.5G light (100 mW/cm^2) using the Xe arc lamp of a Spectra-Nova Class A solar simulator. The light intensity was calibrated using an NREL-certified monocrystalline Si diode coupled to a KG3 filter to bring spectral mismatch to unity. Four-point contact measurements were performed and electrical characterizations were measured with a Keithley 2400 unit. The area of all devices was 6 mm^2, and an aperture with size of 6 mm^2 was used on top of cells during measurements. EQEs were characterized using an Oriel model QE-PV-SI instrument equipped with an NIST-certified Si diode. Monochromatic light was generated from an Oriel 300W lamp source.

2. Atomic Force Microscope (AFM), Transmission Electron Microscope (TEM), and Grazing Incidence Wide-Angle X-ray Scattering (GIWAXS)

AFM measurements were performed using a Dimension Icon Scanning Probe Microscope (Veeco) in tapping mode, and GIXRD measurements on an 18 kW Rigaku ATXG diffractometer using a multilayer parabolic mirror, a NaI scintillation detector, and X-rays of wavelength $\lambda = 1.541$ Å. TEM measurements were performed using a JEOL JEM-2100F instrument, with samples prepared directly from films prepared under identical conditions as actual devices. GIWAXS measurement was performed at Beamline 8ID-E of the Advanced Photon Source at Argonne National Laboratory. The experimental setup was described by Jiang et al.[3] The sample was irradiated with 7.35 keV x-rays in air at an incidence angle of 0.20° for up to 30s using attenuations between 0 and 2 and the scattering was recorded on a Pilatus 1M detector located 204 mm from the sample.

3. Differential pulse voltammograms (DPV)

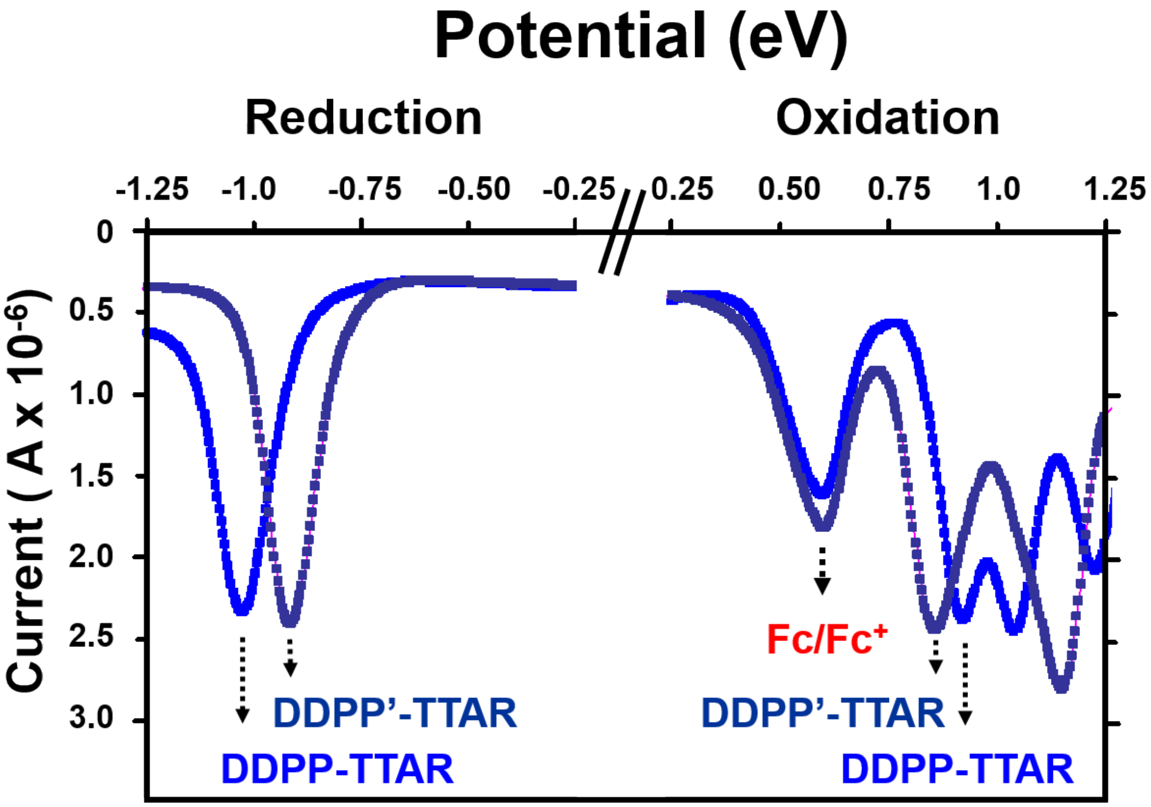

Figure S1. DPV redox spectra of **DDPP-TTAR** and **DDPP'-TTAR** with Fc/Fc$^+$ as the internal standard.

4. Photovoltaic (PV) performance of 2:PC$_{71}$BM

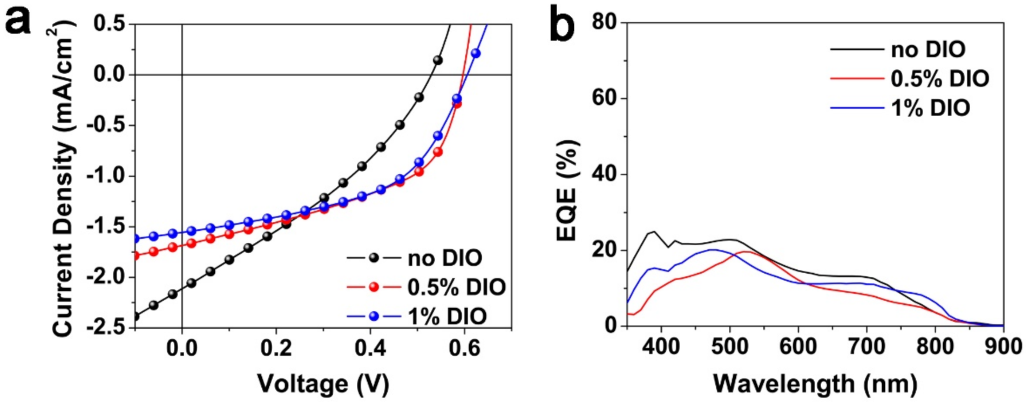

Figure S2. Inverted OSC performance: (a) illuminated *J-V* characteristics of **2**:PC$_{71}$BM (1:1) with varying DIO vol%. (b) External quantum efficiency (EQE) spectra of best performing OSCs.

5. Summary of PV parameters based on other conditions

Table S1. Summary of PV metrics based on other solvent combinations and D:A ratios.

Compound	Solvent	D:A, w/w	V_{oc} (V)	J_{sc} (mA/cm^2)	*FF* (%)	PCE (%) (average PCE)*
1	CF:DIO=98% /2%, v/v	1:1	0.715	9.11	54.1	3.52 (3.48)
1	CF:DIO = 97%/3%, v/v	1:1	0.712	8.28	54.0	3.18 (3.09)
1	CF:DIO=99% /1%, v/v	1:1.5	0.727	9.07	53.8	3.55 (3.50)
1	CF:DIO=99% /1%, v/v	1:2	0.724	8.56	54.0	3.35 (3.31)
1	CF:DIO=99% /1%, v/v	2:1	0.730	6.96	44.7	2.27 (2.21)
1	CB:DIO=99% /1%, v/v	1:1	0.723	9.41	50.8	3.45 (3.39)
2	CF:DIO=98% /2%, v/v	1:1	0.598	1.51	52.0	0.47 (0.42)
2	CF:DIO = 97%/3%, v/v	1:1	0.597	1.43	52.2	0.45 (0.42)

*Average PCE is obtained from at least 8 devices.

6. Photoluminescence (PL)

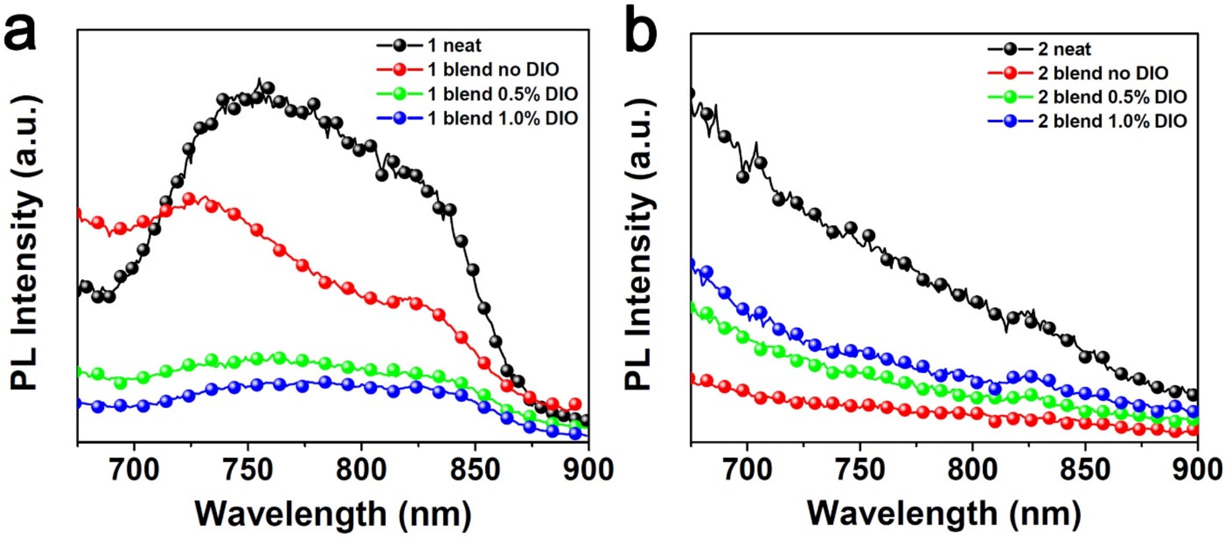

Figure S3. PL spectra of **1** and **2** neat films and blend films based on **1**:$PC_{71}BM$ and **2**:$PC_{71}BM$ with varying DIO vol%.

7. SCLC mobilities.

Table S2. Summary of SCLC mobilities based on hole-only devices.

Donor	*Acceptor*	*DIO*	μ_h *(cm²V⁻¹s⁻¹)*
1	NA	0%	$(2.5 \pm 0.1) \times 10^{-2}$
1	$PC_{71}BM$	0%	$(1.6 \pm 0.1) \times 10^{-4}$
1	$PC_{71}BM$	0.5%	$(6.2 \pm 0.1) \times 10^{-3}$
1	$PC_{71}BM$	1%	$(1.1 \pm 0.1) \times 10^{-2}$
1	$PC_{71}BM$	2%	$(3.2 \pm 0.1) \times 10^{-3}$
2	NA	0%	$(4.9 \pm 0.1) \times 10^{-3}$
2	$PC_{71}BM$	0%	$(2.3 \pm 0.1) \times 10^{-3}$
2	$PC_{71}BM$	0.5%	$(4.6 \pm 0.1) \times 10^{-4}$
2	$PC_{71}BM$	1%	$(5.0 \pm 0.1) \times 10^{-5}$
2	$PC_{71}BM$	2%	$(5.5 \pm 0.1) \times 10^{-5}$

Reference:

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