# **Supplementary Information**

# A non-fullerene electron acceptor based on fluorene and diketopyrrolopyrrole building blocks for solution-processable organic solar cells with an impressive open-circuit voltage

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### Section 1: Synthetic Details

DPP1 was synthesized as per the reaction scheme 1 depicted in the main text.

# 1.1 6,6'-((9,9-dioctyl-9H-fluorene-2,7-diyl)bis(thiophene-5,2-diyl))bis(2,5-bis(2-ethylhexyl) - 3-(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione) (**DPP1**)

2,2'-(9,9-dioctyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-Compounds dioxaborolane (1) (150 mg, 0.23 mmol) and 3-(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (2) (308 mg, 0.51 mmol) were mixed in 15.0 mL of dioxane in a 50.0 mL round bottom flask at room temperature. The reaction mixture was stirred for 15 minutes followed by the addition of aqueous 2 M K<sub>2</sub>CO<sub>3</sub> (5.00 mL). The resulting suspension was degassed for 10 minutes by purging argon, and tetrakis(triphenylphosphine)palladium(0) [Pd(PPh<sub>3</sub>)<sub>4</sub>] catalyst (115 mg, 0.10 mmol) was added to the reaction mixture. The reaction mixture was heated at 90 °C in an oil bath for 24 hrs in the absence of light and the reaction progress was followed by thin-layer chromatography (TLC), which indicated the consumption of starting 1. The reaction mixture was cooled to room temperature, extracted with chloroform (25 mL) and the organic layer was separated. The organic layer was washed with water  $(2 \times 100 \text{ mL})$  followed by brine (50 mL), dried over anhydrous MgSO<sub>4</sub> and recovered to get a crude solid which was purified through column chromatography on silica gel (chloroform/hexane = 1 : 1 as eluent) to afford DPP1 (250 mg) as a black powder. Yield: 74%. M.p.: 130-132 °C. FT-IR (thin solid film, cm<sup>-1</sup>): 3080, 2955, 2925, 2855, 1661, 1555, 1443, 1419, 1401, 1316, 1231, 1100, 857, 812, 735. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, δ/ppm): 9.07–9.06 (m, 2H), 8.91–8.90 (m, 2H), 7.85–7.83 (m, 2H), 7.79–7.77 (m, 2H), 7.74–7.71 (m, 4H), 7.65–7.64 (m, 2H), 7.36–7.32 (m, 2H), 4.19– 4.03 (m, 8H), 2.16–2.12 (m, 4H), 2.07–1.96 (m, 2H), 1.95–1.83 (m, 2H), 1.51–1.28 (m, 32H), 1.22–1.04 (m, 24H), 1.00–0.89 (m, 24H), 0.83–0.80 (m, 6H). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, δ/ppm): 161.83, 161.64, 152.39, 150.47, 141.46, 140.22, 139.78, 136.97, 134.93, 132.57, 130.63, 130.22, 128.84, 128.37, 125.47, 124.45, 120.78, 120.47, 108.33, 108.16, 77.68, 45.85, 39.50, 39.29, 31.89, 30.51, 30.32, 30.05, 29.32, 28.72, 28.52, 23.99, 23.80, 23.66, 23.21, 22.72, 14.03, 13.94, 10.50, 10.39; HRMS (APCI): [M]<sup>+</sup>, found 1434.8021.  $C_{89}H_{118}N_4O_4^{32}S_4$  requires 1434.8030.

# Spectra of DPP1

## IR Spectrum



<sup>1</sup>H NMR Spectrum



# <sup>13</sup>C NMR Spectrum



## **HRMS Spectrum**



## $[\mathbf{M}]^+$

m/z	Theo. Mass	Delta (ppm)	Composition
1434.8021	1434.8022	-0.04	C88 H114 O9 N4 S2
	1434.8024	-0.16	C95 H112 O N5 S3
	1434.8019	0.17	C95 H120 N S5
	1434.8024	-0.19	C81 H122 O6 N6 S5
	1434.8017	0.27	C73 H126 O8 N8 S6
	1434.8017	0.29	C88 H122 O8 S4
	1434.8017	0.29	C87 H116 O3 N7 S4
	1434.8026	-0.32	C89 H126 O3 S6
	1434.8029	-0.52	C81 H114 O7 N10 S3
	1434.8012	0.62	C87 H124 O2 N3 S6
	1434.8030	-0.64	C89 H118 O4 N4 S4
	1434.8031	-0.67	C75 H128 O9 N5 S6

1434.8011	0.74	C80 H126 O10 N2 S5
1434.8010	0.75	C79 H120 O5 N9 S5
1434.8010	0.77	C94 H116 O5 N S3
1434.8010	0.77	C93 H110 N8 S3
1434.8008	0.90	C86 H112 O8 N7 S2
1434.8035	-0.97	C89 H110 O5 N8 S2
1434.8035	-0.97	C90 H116 O10 N S2
1434.8036	-1.00	C75 H120 O10 N9 S4

## Section 2: Experimental

#### 2.1. Materials

All the reagents and chemicals used, unless otherwise specified, were purchased from Sigma-Aldrich Co. The solvents used for reactions were obtained from Merck Speciality Chemicals (Sydney, Australia) and were used as such. 3-(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione was purchased from Luminescence Technology Corporation, Taiwan and was used as such.

#### 2.2. Instruments and characterization

Unless otherwise specified, all <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded using a Bruker AV400 spectrometer at 400 MHz and 100.6 MHz, respectively, or a Bruker AV200 spectrometer at 200 MHz and 50 MHz, respectively. Chemical shifts ( $\delta$ ) are measured in parts per million. Thin Layer Chromatography (TLC) was performed using 0.25 mm thick plates precoated with Merck Kieselgel 60 F<sub>254</sub> silica gel, and visualised using ultraviolet (UV) light (254 nm and 365 nm). Melting points were measured using a Gallenkamp MPD350 digital melting point apparatus and are uncorrected. High resolution mass spectra (atmospheric-pressure chemical ionization (APCI)) experiments were carried out on a Thermo Scientific Q-Exactive FTMS, ionizing by APCI from an ASAP probe [S1].

All ultraviolet-visible (UV-vis) absorption spectra were recorded on a Hewlett Packard HP 8453 Diode array UV-visible spectrophotometer. Thin films were spin-coated from *o*-chlorobenzene (*o*-DCB) at a spin speed of 2000 rpm for 1 min onto cleaned glass slides. **DPP1** was spin-coated from solutions at a concentration of 30 mg/mL. P3HT: **DPP1** blend solutions were prepared in the same manner as for devices, i.e. P3HT (15 mg) and **DPP1** (15 mg) in a total volume of 1 mL. Where specified, films were annealed at 150 °C for 5 min. Fluorescence spectra were recorded using a Perkin-Elmer LS50B fluorimeter. Photoelectron Spectroscopy in Air (PESA) measurements were recorded using a Riken Keiki AC-2 PESA spectrometer with a power setting of 5 nW and a power number of 0.5. Samples for PESA

were prepared on clean glass substrates. The thermal stability of **DPP1** was investigated by thermogravimetric analysis (TGA). TGA was run at a heating rate of 10 °C/min, from room temperature to 800 °C.

#### 2.3. Device fabrication and characterization of photovoltaic devices

Indium tin oxide (ITO)-coated glass ( $10\Omega/\Box$ ) was cleaned by standing in a stirred solution of 5% (v/v) Deconex 12PA detergent at 90 °C for 20 min. The ITO-coated glass was then successively sonicated for 10 min each in distilled water, acetone, and isopropanol. The substrates were then exposed to a UV-ozone clean at room temperature for 10 min. UV/ozone cleaning of glass substrates was performed using a Novascan PDS-UVT, UV/ozone cleaner with the platform set to maximum height. The intensity of the lamp was greater than 36 mW/cm<sup>2</sup> at a distance of 10 cm. At ambient conditions, the ozone output of the UV cleaner is greater than 50 ppm. Aqueous solutions of PEDOT/PSS (HC Starck, Baytron P AI 4083) were filtered (0.45 µm PVDF filter) and deposited onto glass substrates in air by spin coating (Laurell WS-400B-6NPP lite single wafer spin processor) at 4000 rpm for 60 s to give a layer having a thickness of  $35 \pm 5$  nm. The PEDOT/PSS layer was then annealed on a hotplate in a glove box at 120 °C for 10 min. For OPV devices, the newly synthesized organic n-type material (DPP1) and P3HT (Nano-C) were separately dissolved in individual vials by magnetic stirring. Blend ratios and solution concentrations were varied to optimize device performance. The solutions were then combined, filtered (0.45 µm PTFE filter), and deposited by spin coating (SCS G3P spin coater) onto the ITO-coated glass substrates inside a glove box (with  $H_2O$  and  $O_2$  levels both <1 ppm). Film thicknesses were determined on identical samples using a Dektak 6M Profilometer. The coated substrates were then transferred (without exposure to air) to a vacuum evaporator inside an adjacent nitrogen-filled glove box. Samples were placed on a shadow mask in a tray. The area defined by the shadow mask gave device areas of exactly 0.09 cm<sup>2</sup>. Deposition rates and film thicknesses were monitored using a calibrated quartz thickness monitor inside the vacuum chamber. Layers of calcium (Ca) (Aldrich), from an open tungsten boat, and aluminum (Al) (3 pellets of 99.999%, KJ Lesker), from an alumina-coated graphite boat, having thicknesses of 20 nm and 100 nm, respectively, were evaporated onto the active layer by thermal evaporation at pressures less than  $2 \times 10^{-6}$  mbar Current density-voltage

(J–V) characteristics of OSCs were measured under AM1.5G illumination at 100 mW/cm2 (SAN-EI Electric XEC-301S solar simulator). Light intensity of the solar simulator was calibrated using a monosilicon detector (with KG-5 visible color filter) to minimize the spectral mismatch.

For incident photon conversion efficiency (IPCE) measurements, the devices were in suit tested in glove-box. IPCE data were collected using an Oriel 150W lamp coupled to a monochromator and an optical fibre. The output of the optical fibre was focused to give a beam that was contained within the area of the device. IPCE data were calibrated with a standard, unfiltered Si cell.

AFM topographic maps were performed directly on the active layer of the P3HT: **DPP1** blends using an Asylum Research MFP-3D-SA instrument. The AFM was run in intermittent contact mode (tapping mode) using MicroMasch NSC18 tips (typical resonant frequency ~100 kHz, typical probe radius ~10 nm and typical aspect ratio 3:1).

#### 2.4. Device preparation for thin film transistors

We used thin film transistor (TFT) substrates Gen. 5: "end-of-line test substrates for customized semiconductor" purchased from Fraunhofer IMPS. Gate dielectric layers were thermally oxidized 230 ±10 nm SiO<sub>2</sub>. Test chip sizes were  $15 \times 15 \text{ mm}^2$ . Via Gate contact pads were  $0.5 \times 0.5 \text{ mm}^2$  structured by lift off technique.

The SiO<sub>2</sub> layer was cleaned with acetone followed by 2-propanol, and then treated with UV ozone. Bottom contact TFTs with prepatterned source drain electrodes having a fixed channel width of 2000  $\mu$ m and varying channel lengths of 2.5, 5, 10, 20  $\mu$ m, with a total of 16 devices in one test chip were employed. Gate via, source drain contacts were 30 nm of Au with 10 nm high work function adhesion layer (ITO) (structured by lift off techniques). HMDS and OTS were applied as a passivation layer prior to the deposition of active layer. Device fabrication was completed by deposition of **DPP1 (dissolved in CHCl3)** by spin coating at 3000 rpm for 1 minute. Measurements of the transistor characteristics were done using an Agilent parameter analyser B1500A. Estimation of the carrier mobility was done using the standard transistor equation (1) in saturation mode:

$$\mu = \frac{2L}{WC_i} \left(\frac{\delta \sqrt{I_D}}{\delta V_G}\right)^2 \qquad (1)$$

where  $\mu$  is the two probe field effect mobility, L= channel length, C<sub>i</sub> is the gate insulator capacitance.

	Solvent	Surface treatment	ТА	hole		
				$\mu [cm^{2}V^{-1}s^{-1}]$	V <sub>T</sub> [V]	On/off
DPP1	CHC13	OTS	Xa	4.8×10 <sup>-4</sup>	-6	1.8×10 <sup>5</sup>
	CHC13	OTS	A80	5.2×10 <sup>-4</sup>	-10	1.3×10 <sup>4</sup>
	CHCl3	HMDS	Xa	1.2×10 <sup>-4</sup>	-19	6.7×10 <sup>3</sup>
	CHC13	HMDS	A80	1.1×10 <sup>-5</sup>	-15	1.6×10 <sup>3</sup>

TA- thermal annealing, OTS-octyl trichlorosilane, HMDS-hexamethyldisilazane, V<sub>T</sub>-threshold voltag

Section 3: Supporting Figures



**Fig. S1** Fluorescence spectra of pristine film of **DPP1** (black curve; **DPP1 P**) along with its blend with P3HT [as-cast (red curve; **DPP1 B**) and annealed blend at 150 °C for 5 min (blue curve; **DPP1 BA**)], spin-coated from *o*-dichlorobenzene ( $\lambda_{ex} = 600$  nm).



**Fig. S2** Orbital density distribution for the HOMOs and LUMOs of **DPP1**. Density functional theory calculations were performed using the Gaussian 09 suite of programs and B3LYP/6-311+G(d,p)/B3LYP/6-31G(d) level of theory.







**Fig. S3** PESA spectrum of thin film of **DPP1** from *o*-DCB. The dashed-lines show the fits to extract ionisation potential (-5.30eV) which corresponds to the HOMO energy level.



**Fig. S4** TGA trace of **DPP1** under nitrogen atmosphere. Heating rate: 10 °C/min from room temperature to 800 °C.



**Fig. S5** (a) DSC curve of DPP1. Heating rate: 20 °C/min; scan run from 50 °C to 500 °C (b) amplified DSC thermogram section between 241 °C to 270 °C



**Fig. S6** Transfer (left) and output (right) characteristics of **DPP1** OFET devices processed at room temperature. Device dimensions: channel length =  $100 \mu m$ ; channel width = 1 mm.

## References

[S1] C.N. McEwen, R.G. McKay, B.S. Larsen, Anal. Chem. 77 (2005) 7826.