# **Supporting Information**

# Use of Side-Chain in Rational Design of N-Type Diketopyrrolopyrrole-based Conjugated Polymers: What did we find out?

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### **Experimental Section**

All the monomers were synthesised by previously reported literature procedures.<sup>1,2</sup> Thiophene 2- carbonitrile, *n*-butyllithium (1.6 M solution in hexane), potassium tertiary butoxide,  $(Pd_2(dba)_3)$ ,  $(o-tol)_3P$  and tetrabutylammoniumhexafluorophosphate ((TBA)PF<sub>6</sub>) were obtained from Aldrich. Organic solvents (THF, CHCl<sub>3</sub>, NMP and diisopropylamine)

were dried by Na/Benzophenone,  $P_2O_5$ , calcium hydride, KOH respectively. The other materials were used as received. 2,5-Bis(2-octyldodecyl)-3,6-bis[5-(4,4,5,5-tetramethyl-1,3,2-dioxo borolan-2-yl)thiophene-2-yl]-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dionewas synthesized by freshly prepared LDA and 2-isopropoxy- 4,4,5,5-tetramethyl-1,3,2-dioxoborolane.<sup>1</sup> All the copolymers have been synthesized by Suzuki coupling reaction under inert atmosphere.

<sup>1</sup>**H NMR** spectra were recorded on a Bruker 400 MHz (<sup>13</sup>C on a 100 MHz) NMR spectrometer in CDCl<sub>3</sub> using TMS as an internal standard. Chemical shifts are reported in parts per million.

**Thermogravimetric analysis** (TGA) measurements were conducted on a Mettler Toledo TGA SDTA 851 apparatus at a heating rate of 10 °C/min under a nitrogen atmosphere.

**UV-Visible** spectra were recorded on Perkin-Elmer (Lambda 35) UV–Vis Spectrometer. The spectra in solution were recorded in CHCl<sub>3</sub> and solid state spectra were recorded from thin films of polymers spin coated on quartz substrates.

Average molecular weights ( $M_w$ ,  $M_n$ ) were determined by Gel permeation chromatography (GPC) against polystyrene standards. THF and 1, 3, 5 trichloro benzene were used as eluents with a flow rate of 1ml/min.

**Atomic force microscopy** (AFM) was carried out in close-contact mode using an Agilent Technologies 5500 AFM. Films were prepared by drop casting from 2 mg/mL solutions of the polymers in *o*-dichlorobenzene or in chloroform at room temperature.

**Grazing incidence X-ray Scattering** (GIXS) measurements were performed at beam line 11-3 at the Stanford Synchrotron Radiation Light source (SSRL, Stanford, CA, USA) with a sample-to-detector distance of 401.51 mm. The diffraction patterns were calibrated using Lanthanum Hexaborade (LaB6). An incident X-ray beam of 12.735 keV is used at SSRL and the critical incidence angle was evaluated to be about 0.12 ° for good scattering of the thin films. A MAR345 Imaging Plate was used to record the scattering patterns and the exposure time was set to 30 seconds.

#### **Organic Field effect transistor fabrication**

The OFET devices were fabricated using (1) bottom-gate bottom-contact (**BG-BC**) and (2) top-gate bottom-contact (**TG-BC**) transistor configurations. Devices were made from Si/SiO<sub>2</sub>

substrates with pre-patterned Au source/drain electrodes. The surface of SiO<sub>2</sub> was treated with hexamethyldisilazane (**HMDS**) in order to passivate its surface and prevent formation of charge trapping states. Copolymers were dissolved in anhydrous chlorobenzene (CB) under inert conditions. Prior to spin-casting, the solutions were filtered through a 0.22  $\mu$ m PTFE filter to ensure no traces of un-dissolved impurities remained. The polymer semiconductor layer was spun on top of the substrates at 1500 rpm to complete the transistor fabrication followed by thermal annealing at 140 °C in nitrogen. **TG-BC** transistors were fabricated onto glass substrates containing pre-patterned Al source/drain electrodes.<sup>3</sup> The semiconducting polymer solution was then spun-cast onto the substrates at room temperature in nitrogen atmosphere. Following, the insulating fluoropolymer **CYTOP** (Ashai Glass) was sequentially spin cast directly onto the semiconducting polymer at room temperature followed by annealing at 100 °C for 5 minutes. Device fabrication was completed with the evaporation of the Al gate electrodes by thermal evaporation under high vacuum (10<sup>-6</sup> mbar). Typical S-D channel length and width for FETs ranged from 10-30 µm and 7.5 mm-20 mm, respectively.

#### **Synthesis of Monomers**

#### General procedure for N-alkylation (1a-d)

3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(*2H*,5*H*)-dione (TDPP) (0.5 g, 1.66 mmol), potassium carbonate (0.81 g, 5.83 mmol) were taken in freshly distilled dimethylformamide (10 mL) stirred at 120 °C for 1 h. Corresponding alkyl halide (4.32 mmol) was added slowly drop wise over 30 minutes. After the complete drop wise addition the reaction was stirred at 130 °C for 20 h. The progress of the reaction was monitored by thin layer chromatography (TLC). On completion, DMF was removed under vacuum distillation. To the concentrated solution distilled water was added (200 mL). The organic phases was extracted with  $CH_2Cl_2$  (3 x 50 mL), washed with brine and dried over anhydrous MgSO<sub>4</sub>. Crude mixture obtained was purified with silica gel chromatography eluting with hexane: ethyl acetate (9:1 to 7:3) solvent mixture.

#### 2,5-dihexyl-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (1b)

#### **Yield:** 75 %

<sup>1</sup>**H NMR:** (400 MHz, CDCl<sub>3</sub>): δ (ppm) 8.93 (d, *J* = 3.9 Hz, 2H), 7.64 (d, *J* = 5.1 Hz, 2H), 7.29 (d, *J* = 4.9, 4.0 Hz, 2H), 4.12–4.01 (m, 4H), 1.80–1.69 (m, 4H), 1.48–1.37 (m, 4H), 1.36–1.26 (m, 8H), 0.88 (t, *J* = 7.0 Hz, 6H)

<sup>13</sup>C NMR: (100 MHz, CDCl<sub>3</sub>): δ (ppm) 161.38, 140.03, 135.22, 130.63, 129.80, 128.59, 107.73, 42.22, 31.40, 29.91, 26.53, 22.53, 13.98

**MS (ESI-TOF)** Calculated for  $C_{26}H_{32}N_2O_2S_2$ : m/z: 468.19; Found: 491.18 (M + Na)<sup>+</sup>

Melting Point: 174 °C

## 2,5-bis(2-ethylhexyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (1c) Yield: 65 %

<sup>1</sup>**H NMR:** (400 MHz, CDCl<sub>3</sub>): δ (ppm) 8.89 (d, *J* = 3.7 Hz, 2H), 7.63 (d, *J* = 5.0 Hz, 2H), 7.28 (d, *J* = 4.3 Hz, 2H), 4.12 – 3.91 (m, 4H), 1.86 (d, *J* = 6.0 Hz, 2H), 1.49 – 1.08 (m, 16H), 0.87 (dd, *J* = 16.6, 7.3 Hz, 12H)

<sup>13</sup>C NMR: (100 MHz, CDCl<sub>3</sub>): δ (ppm) 161.70, 140.37, 135.21, 130.46, 129.77, 128.36, 107.86, 45.79, 39.01, 30.13, 28.29, 23.47, 22.99, 13.96, 10.41

**MS (ESI-TOF):** Calculated for  $C_{30}H_{40}N_2O_2S_2$ : m/z: 524.24; Found: 547.24 (M + Na)<sup>+</sup>

Melting Point: 127 °C

2,5-bis(2-octyldodecyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (1d) Yield: 72 %

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>): δ (ppm) 8.87 (d, *J* = 3.8 Hz, 2H), 7.62 (d, *J* = 5.0 Hz, 2H), 7.27 (d, *J* = 5.1 Hz, 2H), 4.02 (d, *J* = 7.6 Hz, 4H), 1.90 (s, 2H), 1.58 (s, 4H), 1.38–1.20 (m, 60H), 0.86 (q, *J* = 6.1 Hz, 12H)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 162.16, 140.37, 135.15, 130.39, 129.78, 128.32, 107.88, 46.15, 37.67, 31.85, 31.81, 31.11, 29.94, 29.58, 29.49, 29.43, 29.29, 29.23, 26.14, 22.62, 22.60, 14.06

**MS (ESI-TOF)** Calculated for  $C_{54}H_{88}N_2O_2S_2$ : m/z: 860.62; Found 883.61 (M + Na)<sup>+</sup>

Melting Point: 77 °C

# Synthesis of 2,5-Bis(2-octyldodecyl)-3,6-bis[5-(4,4,5,5-tetramethyl-1,3,2-dioxo borolan-2-yl)thiophene-2-yl]-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (M1)

Diisopropylamine (700 mg, 0.98 mL, 6.94 mmol) was taken in a 100 mL round bottom flask with 15 mL of dry THF and *n*-Butyllithium in *n*-hexane (2.55 mL, 6.38 mmol) was added slowly to this at 0 °C under argon atmosphere. The freshly prepared LDA solution was added slowly at -25 °C to a 15 mL THF solution of 2,5-bis(2-octyldodecyl)-3,6-dithiophene-2-yl-2,5-dihydropyrrolo[3,4-c]pyrrole- 1,4-dione (1d) (2.0 g, 1 mmol) and 2-isopropoxy- 4,4,5,5-tetramethyl-1,3,2-dioxoborolane (1.64 g, 1.80 mL, 8.79 mmol). This reaction mixture was stirred at 0 °C for 2 h and quenched with 10 mL of 1 M HCl solution. After extraction with chloroform (3 X 20 mL) the combined organic fractions were dried over magnesium sulfate and the solvent was removed under reduced pressure. The residue was dissolved in 2 mL of dichloromethane, and the solution was precipitated into 200 mL of cold acetone under

vigorous stirring. The precipitate was filtered off and washed with cold acetone to afford 1.74 g (2.25 mmol, 78%) of M1 as a pink solid. Yield: 78 %

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ (ppm) 8.91 (d, *J* = 3.7 Hz, 2H), 7.71 (d, *J* = 3.8 Hz, 2H), 4.05 (d, *J* = 7.6 Hz, 4H), 1.89 (s, 2H), 1.37 (s, 24H), 1.31 – 1.16 (m, 64H), 0.86 (m, 12H)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,): δ (ppm) 162.17, 140.94, 138.08, 136.58, 136.08, 109.14, 85.01, 46.67, 38.19, 32.35, 32.31, 31.68, 30.45, 30.06, 30.02, 29.95, 29.79, 29.72, 26.75, 25.20, 23.12, 23.09, 14.56

**Elemental analysis:** Anal. Calcd for C<sub>66</sub>H<sub>110</sub>B<sub>2</sub>N<sub>2</sub>O<sub>6</sub>S<sub>2</sub> C, 71.20; H, 9.96; B, 1.94; N, 2.52; O, 8.62; S, 5.76 Found: C, 71.50; H, 9.19; N, 3.21; S, 6.71

Melting point: 90 °C

Synthesis of 3,6-bis-(5-bromo-thiophen-2-yl)-N,N'-bis(2-(2-(2-methoxy ethoxy) ethoxy)ethyl)-1,4-dioxo-pyrrolo [3,4- c]pyrrole (M2):

2,5-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4 (2H,5H)-dione(1a) (1 mmol) was taken in freshly distilled dry CHCl<sub>3</sub> (20 mL). Nbromosuccinimide (2.01 mmol) was added slowly portion wise for over 10 minutes to the reaction mixture at 0 °C. The reaction mixture was stirred at the same temperature for 1 h and kept at room temperature for 48 h. Completion of the reaction was confirmed by TLC. Water was added to the crude mixture and extracted with  $CH_2Cl_2$  (3 x 50 mL), washed with water and brine. The combined organic layers were collected and dried over anhydrous MgSO<sub>4</sub>. The crude solid obtained was precipitated in methanol to give a pure product as purple solid. **Yield:** 85 %

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.79 (d, J = 5.1 Hz, 2H), 7.27 (d, J = 5.1 Hz, 2H), 4.29 (t, J = 6.3 Hz, 4H), 3.80 (t, J = 6 Hz, 4H), 3.65–3.47 (m, 16H), 3.34 (s, 6H) ppm.

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 161.72, 139.94, 135.31, 131.83, 131.54, 119.78, 108.40, 72.34, 71.20, 71.00, 70.97, 69.37, 59.46, 42.68

**Elemental analysis:** Anal. Calcd for C<sub>28</sub>H<sub>34</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>8</sub>S<sub>2</sub>: C, 44.81; H, 4.57; Br, 21.29; N, 3.73; O, 17.05; S, 8.54 Found: C, 45.71; H, 5.07; N, 4.40; S, 7.79

Melting point: 98 °C

#### General procedure for the synthesis of M3-M5

2,5-bis(2-alkyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(*2H*,5*H*)-dione(alkylated TDPP) (1mmol) was taken in freshly distilled dry CHCl<sub>3</sub> (20 mL). Bromine (2.01 mmol) was

diluted with CHCl<sub>3</sub> (5 mL) and added slowly drop wise for over 30 minutes to the reaction mixture at 0 °C. Reaction mixture was stirred at the same temperature for 1 h and kept at room temperature for 8 h. Completion of the reaction was confirmed by TLC and the excess bromine was quenched with sodium bisulfite. The reaction mixture was washed with water and extracted with  $CH_2Cl_2$  (3 x 50 mL), washed with brine and dried over anhydrous MgSO<sub>4</sub>. Crude mixture obtained was precipitated in methanol to give a pure product as purple solid.

3,6-Di(2-bromothien-5-yl)-2,5-di(2-hexyl)- pyrrolo[3,4-c]pyrrole-1,4-dione (M3)

**Yield:** 75 %

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.68 (d, J = 4.2 Hz, 2H), 7.24 (d, J = 4.2 Hz, 2H), 4.03 – 3.94 (m, 4H), 1.70 (dd, J = 15.3, 8.3 Hz, 2H), 1.47 – 1.24 (m, 12H), 1.00 (s, 2H), 0.90 (d, J = 6.5 Hz, 6H)

<sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>) δ (ppm) 165.72, 142.24, 139.31, 131.83, 128.54, 118.78, 113.40, 45.20, 31.1, 31.97, 26.37, 22.46, 14.68

**Elemental analysis:** Anal. Calcd for C<sub>26</sub>H<sub>30</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: C, 49.85; H, 4.83; Br, 25.51; N, 4.49; O, 5.11; S, 10.24. Found: C, 49.42; H, 4.74; N, 4.87; S, 10.23

Melting point: 130 °C

3,6-Di(2-bromothien-5-yl)-2,5-di(2-ethylhexyl)-pyrrolo[3,4-c]pyrrole-1,4-dione (M4) Yield: 65 %

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.66 (d, *J* = 4.2 Hz, 2H), 7.23 (d, *J* = 4.2 Hz, 2H), 4.04 – 3.85 (m, 4H), 1.84 (s, 2H), 1.41 – 1.19 (m, 16H), 0.88 (m, *J* = 7.4 Hz, 12H).

<sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>) δ (ppm) 165.12, 142.64, 139.21, 131.4, 128.64, 118.98, 113.60, 49.20, 37.9, 32.17, 29.12, 26.37, 23.46, 11.23, 14.68

**Elemental analysis:** Anal. Calcd for C<sub>30</sub>H<sub>38</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: C, 52.79; H, 5.61; Br, 23.41; N, 4.10; O, 4.69; S, 9.40. Found: C, 53.19; H, 5.21; N, 3.90; S, 9.22

Melting point: 120 °C

# 3,6-Di(2-bromothien-5-yl)-2,5-di(2-octyldodecyl)- pyrrolo[3,4-c]pyrrole-1,4-dione (M5) Yield: 72 %

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ (ppm) 8.87 (d, J = 3.8 Hz, 2H), 7.27 (d, J = 5.1 Hz, 2H), 4.02 (d, J = 7.6 Hz, 4H), 1.90 (s, 2H), 1.58 (s, 4H), 1.38 – 1.20 (m, 60H), 0.86 (q, J = 6.1 Hz, 12H) <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>) δ (ppm) 165.12, 142.66, 139.11, 131.4, 128.74, 118.80, 113.60, 49.20, 37.9, 32.17, 31.25, 29.92, 29.46, 29.36, 27.1, 22.23, 14.68

Melting point: 95 °C

#### General synthetic procedure of DPP-DPP copolymers (2DPP-OD-HE)

3,6-Di(2-bromothien-5-yl)-2,5-di(2-hexyl)- pyrrolo[3,4-c]pyrrole-1,4-dione (M3) (1 mmol) and M1 (1 mmol) were taken in degassed dry Toluene (40 mL) and two drops aliquat 336 was added. The reaction container was loaded with the ligand  $P(o-tol)_3$  (20 mg) and catalyst precursor  $Pd_2(dba)_3$  (10 mg) and purged with N<sub>2</sub> for 10 min to remove O<sub>2</sub>. Degassed aqueous solution of K<sub>3</sub>PO<sub>4</sub> (1 mL) was added through syringe and this mixture was purged with N<sub>2</sub> for 10 min and refluxed at 90 °C for 48 h. Reaction mixture was cooled to room temperature, washed with water and extracted with CHCl<sub>3</sub>. Solvent was evaporated and the concentrated polymer solution in CHCl<sub>3</sub>was precipitated by slowly adding into vigorously stirred methanol solution. The precipitates were collected by filtration and then washed with methanol, hexane and acetone. The polymer was dried under vacuum for overnight.

**Yield:** 170 mg (66 %).

<sup>1</sup>**H NMR** (CDCl<sub>3</sub>, 400 MHz): δ (ppm) 9.2-8.7 (br, 4H), 7.3- 6.70 (br, 4H), 4.5 (br, 8H), 2.03 (br, 2H), 1.5-0.8 (m, 98H)

**Elemental analysis:** Anal. Calcd for C<sub>80</sub>H<sub>118</sub>N<sub>4</sub>O<sub>4</sub>S<sub>4</sub>: C, 72.35; H, 8.96; N, 4.22; S, 9.66. Found: C, 72.35; H, 8.44; N, 4.15; S, 9.53

**Molecular Weight Data:** $M_n = 13.2 \text{ kg/mol}; M_w = 93.2 \text{ kg/mol}; PDI = 7.07$ Synthesis of 2DPP-OD-EH:

A procedure similar to the synthesis of **2DPP**-OD-HE was followed for the synthesis of **2DPP**-OD-EH. 3,6-Di(2-bromothien-5-yl)-2,5-di(2-ethylhexyl)- pyrrolo[3,4-c]pyrrole-1,4-dione (M4) (1 mmol) and M1 (1 mmol) monomers were used up for the polymerisation. **Yield:** 190 mg (75 %).

<sup>1</sup>**H NMR** (CDCl<sub>3</sub>, 400 MHz): δ (ppm) 9.1-8.7(br, 4H), 7.4-6.8 (m, 4H), 4.5-3.7 (br, 4H), 2.10-2.01 (m, 4H), 1.5-0.6 (m, 104H)

**Elemental analysis:** Anal. Calcd for C<sub>84</sub>H<sub>126</sub>N<sub>4</sub>O<sub>4</sub>S<sub>4</sub>: C, 72.89; H, 9.18; N, 4.05; S, 9.27. Found: C, 71.85; H, 8.63; N, 4.01; S, 9.33

**Molecular Weight Data:** M<sub>n</sub>=13.3 kg/mol; M<sub>w</sub> = 100 kg/mol PDI = 7.53

#### Synthesis of 2DPP-OD-OD:

A procedure similar to the synthesis of **2DPP**-OD-EHwas followed for the synthesis of **2DPP**-OD-ODusing 3,6-Di(2-bromothien-5-yl)-2,5-di(2-octyldodecyl)- pyrrolo[3,4-c]pyrrole-1,4-dione (M5) (1 mmol) and M1 (1 mmol) monomers were used up for the polymerisation.

**Yield:** 190 mg (75 %)

<sup>1</sup>**H NMR** (CDCl<sub>3</sub>, 400 MHz): δ (ppm) 9.4-8.7 (br, 2H), 7.5- 7.0 (m, 2H), 4.4-3.7 (br, 4H), 2.15 (br, 2H), 1.5-0.8 (m, 76H)

**Elemental Analysis:** Anal. Calcd for C<sub>54</sub>H<sub>88</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: C, 75.29; H, 10.30; N, 3.25; S, 7.44. Found: C, 75.09; H, 9.92; N, 3.42; S, 7.74

**Molecular Weight Data:**  $M_n = 20.8 \text{ kg/mol}; M_w = 27.5 \text{ kg/mol}; PDI = 1.32$ 



Figure SI 1: TGA of DPP-DPP Copolymers.



Figure SI 2: Cyclic voltammogram of DPP-DPP copolymers in dry acetonitrile with a scan rate of 100 mV/s



Figure SI 3: Multiple reduction cycles of 2DPP-OD-TEG in dry acetonitrile

Polymer	Oxidation	Reduction	
	E <sub>onset</sub> <sup>ox</sup> (V) / HOMO (eV)	E <sub>onset</sub> <sup>red</sup> (V) / LUMO (eV)	E <sub>g</sub> <sup>elc</sup> (eV)
2DPPOD-HE	0.89 / - 5.35	-0.82 /-3.64	1.71
2DPPOD-EH	0.89 / -5.35	-0.86 / -3.6	1.75
2DPPOD-OD	0.94 / -5.4	-0.94 /-3.52	1.88
2DPPOD-TEG	0.79 / -5.25	-0.80 /-3.66	1.59

Table SI 1: Electrochemical properties of the polymers.



Figure SI 4: Optimized electron delocalization MO diagram of the model dimer

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