Thieno[3,2-*b*]thiophene-Diketopyrrolopyrrole containing polymers for high performance OFETs and OPV devices

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S1 Synthetic Procedures

9-(Bromomethyl)nonadecane was prepared according to literature procedure.¹ Thieno[3,2-b]thiophene-2-carbonitrile was purchased from Butt Park LTD. UK. All other chemicals were purchased from Aldrich or Fisher and used as received. All reactions were carried out in under Argon using solvents and reagents as commercially supplied, unless otherwise stated. ¹H and ¹³C NMR spectra were recorded on a Bruker AV-400 (400 MHz), using the residual solvent resonance of CDCl₃ or TMS as an internal reference and are given in ppm. Melting points were determined with electrothermal Mel-Temp apparatus and are uncorrected. Number-average (Mn) and weight average (Mw) were determined by Agilent Technologies 1200 series GPC running in chlorobenzene at 80 °C, using two PL mixed B columns in series, and calibrated against narrow polydispersity polystyrene standards. Electrospray mass spectrometer, UV-vis spectra were recorded on a UV-1601 Shimadzu

Uv-vis spectrometer. Flash chromatography (FC) was performed on silica gel (Merck Kieselgel 60 F254 230-400 mesh) unless otherwise indicated. Thin Layer Chromatography (TLC) was performed on Merck aluminium-backed plates precoated with silica (0.2 mm, 60 F254). Microwave experiments were performed in a Biotage initiator V 2.3. Photo Electron Spectroscopy in Air (PESA) measurements were recorded with a Riken Keiki AC-2 PESA spectrometer with a power setting of 5nW and a power number of 0.5. Samples for PESA were prepared by spin-coating a solution of the sample on glass substrates from chlorobenzene at a concentration of 5 mg/mL.

S2 Monomer Synthesis



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

Sodium (0.26 g, 11.3 mmol) and iron(III) chloride (~10 mg) was added to 6 mL of 2methyl-2-butanol and the mixture was heated to reflux until full consumption of the sodium was observed (~3 hrs). The solution was cooled to 85 °C and thieno[3,2b]thiophene-2-carbonitrile **1** (1.24 g, 7.5 mmol) was added, followed by diisopropyl succinate (0.60 g, 3.0 mmol). After stirring for 2hr, the reaction was cooled to 50 °C, and methanol (10 mL) was added. The reaction was quenched by addition of glacial acetic acid (3 mL) and refluxed for 15 min. The reaction mixture was filtered and washed with water (2 x 50 mL), hot methanol (2 x 50 mL), acetone (2 x 25 mL) and hexane (25 mL) to afford the product as a dark blue solid (1.1 g, 73 %), which was used without further purification.

2,5-Bis(2-octyldodecyl)-3,6-di(thieno[3,2-*b*]thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione 3

To a mixture of 3,6-di(thieno[3,2-*b*]thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)dione **2** (1.00 g, 2.43 mmol), potassium carbonate (1.12 g, 8.11 mmol) and 18-crown-6 (12 mg) in DMF (40 mL) was added 9-(bromomethyl)nonadecane (3.00 g, 8.11 mmol). The reaction mixture was stirred at 120 °C for 18 hr and then cooled to room temperature. Chloroform (100 mL) and water were added (200 mL) and the layers separated. The organic layer was washed with sat. brine (3 x 200 mL) and concentrated *in vacuo*. Hexane (25 mL) was added and the mixture was sonicated briefly (5 mins) and then filtered to afford a dark solid which was washed with methanol (2 x 20 mL) to afford the pure product (0.8 g, 34%).

¹H NMR (400 MHz, CDCl₃) δ : 9.29 (s, 2H, Ar*H*), 7.60 (d, *J* = 5.3, 2H, Ar*H*), 7.31 (d, *J* = 5.2, 2H, Ar*H*), 4.07 (d, *J* = 7.7 Hz, 4H, NC*H*₂), 2.14 – 1.86 (m, 2H, NCH2C*H*(CH₂R)₂), 1.45 – 0.94 (m, 64H, C*H*₂), 0.97 – 0.74 (m, 12H, C*H*₃).¹³C NMR (101 MHz, CDCl₃) δ 161.7, 143.3, 140.6, 140.3, 132.0, 131.2, 127.5, 119.3, 46.6, 37.9, 31.9, 31.2, 30.0, 29.6, 29.6, 29.5, 29.4, 29.3, 26.2, 22.7, 14.1.

m/z: (EI+) 972 [M+H]⁺



3,6-Bis(2-bromothieno[3,2-*b*]thiophen-5-yl)-2,5-bis(2-octyldodecyl)pyrrolo[3,4*c*]pyrrole-1,4(2*H*,5*H*)-dione 4

To a suspension of 2,5-bis(2-octyldodecyl)-3,6-di(thieno[3,2-*b*]thiophen-2yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione **3** (0.67 g, 0.69 mmol) in chloroform (10 mL) was added a solution of bromine (0.22 g, 1.37 mmol) in chloroform (5 mL) dropwise. The reaction mixture was refluxed for 2 hr and then cooled to 0 °C, filtered and washed with aqueous Na₂SO₃ solution (10% w/v, 2 x 25 ml) and water (2 x 25 mL). The crude product was purified *via* column chromatography on silica gel using Hexanes:Chloroform (3:1) as eluent to afford the product as a dark solid (0.67 g, 86%).

¹H NMR (400 MHz, CDCl₃) δ : 9.14 (s, 2 H, Ar*H*), 7.24 (s, 2 H, Ar*H*), 3.98 (d, *J* = 7.7 Hz, 4 H, NC*H*₂), 1.98-1.84 (m, 2H, NCH2C*H*(CH₂R)₂), 1.35-1.10 (m, 64H, C*H*₂) 0.90-0.78 (m, 12H, C*H*₃). ¹³C NMR (101 MHz, CDCl₃) δ : 161.4, 142.0, 140.3, 140.1, 130.4, 126.8, 122.0, 119.0, 108.3, 46.6, 37.8, 31.9, 31.9, 31.2, 30.0, 29.7, 29.6, 29.5, 29.4, 29.3, 26.2, 22.7, 14.1.

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m/z: (EI+) 1130 [M+H]⁺

S3 Polymer Synthesis



P1

(Poly[[2,5-bis(2-octyldodecyl)-2,3,5,6-tetrahydro-3,6-dioxopyrrolo[3,4-*c*]pyrrole-1,4-diyl]- *alt* –[[2,2'-(2,5-thiophene)bis-thieno[3,2-*b*]thiophen]-5,5'-diyl]])

PDPP-TT-T-TT

To a microwave vial was added 3,6-bis(2-bromothieno[3,2-*b*]thiophen-5-yl)-2,5-bis(2-octyldodecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione **4** (0.25 g, 0.22 mmol), 2,5-bis(trimethylstannyl)thiophene (0.10 g, 0.24 mmol). Chlorobenzene (3.5 mL) was added and the solution degassed before addition of $Pd_2(dba)_3$ (4 mg, 0.0044 mmol) and $P(oTol)_3$ (5 mg, 0.0176 mmol). The reaction mixture was further degassed and subsequently sealed. The vial was heated in a microwave reactor at 100 °C (2 min), 140 °C (2 min), 170 °C (2 min) and 200 °C (30 min). After cooling to room temperature, the mixture was added to vigorously stirred methanol (200 mL), filtered and washed with methanol (2 x 25 mL). The polymeric material was purified by Soxhlet extraction with acetone (24 hr), hexane (24 hr) and finally chloroform (12 hr). To the chloroform extract was added an aqueous solution of sodium diethyldithiocarbamate (~1 g/100mL) and the mixture was heated to 60 °C with vigorous stirring for 2 hr. After cooling to room temperature, the layers were

separated and the organic fraction was extracted with water (4 x 250 mL), and concentrated *in vacuo*. The resulting residue was dissolved in a minimum amount of chloroform and added dropwise to a vigorously stirred methanol (250 mL). The resulting precipitate was isolated by filtration and dried *in vacuo* to afford the desired polymer (220 mg, 95%)

GPC(PS):
$$M_n = 13,998$$
 g/mol; $M_w = 75,416$ g/mol; PDI = 5.4



P2

(Poly[[2,5-bis(2-octyldodecyl)-2,3,5,6-tetrahydro-3,6-dioxopyrrolo[3,4-*c*]pyrrole-1,4-diyl]- *alt* –[[2,2'-bis-thieno[3,2-*b*]thiophen]-5,5'-diyl]])

PDPP-TT-TT

To a thoroughly degassed solution of hexamethylditin (0.076 g, 0.23 mmol) and 3,6bis(2-bromothieno[3,2-b]thiophen-5-yl)-2,5-bis(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione 4 (0.25 g, 0.22 mmol) in THF (7.5 mL) and NMP (3.75 mL) was added tetrakis(triphenylphosphine)palladium(0) (0.013 g, 0.01 mmol) and copper(I)iodide (1 mg, 0.004 mmol). The reaction mixture was further degassed and subsequently sealed and heated to reflux for 3 days. After cooling to room temperature, the mixture was added to vigorously stirred methanol (200 mL), filtered and washed with methanol (2 x 25 mL). The polymeric material was purified by Soxhlet extraction with acetone (24 hr), hexane (24 hr) and finally chloroform (12 hr). To the chloroform extract was added an aqueous solution of sodium diethyldithiocarbamate (~1 g/100mL) and the mixture was heated to 60 °C with vigorous stirring for 2 hr. After cooling to room temperature, the layers were separated and the organic fraction was extracted with water (4 x 250 mL), and concentrated in vacuo. The resulting residue was dissolved in a minimum amount of chloroform and added dropwise to a vigorously stirred methanol (250 mL). The resulting precipitate was isolated by filtration and dried in vacuo to afford the desired polymer (192 mg, 89%)

GPC(PS): $M_n = 15,749$ g/mol; $M_w = 77,595$ g/mol; PDI = 4.9



¹H NMR (400 MHz, $CDCl_3$)



S4 FET Device preparation and characterization

The gold source and drain bottom electrodes (with Cr as the adhesion layer) were patterned by photolithography on clean low-sodium glass substrates. A layer of polymer was then spin cast from 1,2-dichlorobenzene solutions (10 mg/mL) at a speed of 1500 rpm for 60 s. For as-spun OFETs, solvent drying was performed at 100 °C for more than two hours. For annealed OFETs, after solvent drying samples were further placed on a hotplate (preheated to the annealing temperature) for 30 minutes

before cooling down to room temperature. Subsequently, the PMMA dielectric layer was spin cast from anhydrous *n*-butyl acetate solution (45 mg/mL) was then spincoated onto the semiconducting polymer at a speed of 1000 rpm for 45 s. 10-nm-thick gold gate electrodes were evaporated through a shadow mask onto the dielectric layer by thermal evaporation under high vacuum (10^{-6} mbar). Except for the photolithography step, all procedures/measurements were carried out inside a dry nitrogen glovebox.



Figure S4.1 Square-root of the drain current of the transfer characteristics shown in figure 2 (a) of the manuscript. The arrows show the gate-voltage sweep directions.



Figure S4.2 Effect of annealing temperature on the saturation hole and electron mobility of **P1** (a) and **P2** (b) OFETs. 100°C corresponds to as-spun conditions. Each data point was averaged on 4 to 7 devices (channel length $L = 20 \mu m$, channel width W = 1 or 2 cm).

O2 Plasma treatment of contacts



Figure S4.3: Comparison of out-put characteristics on P1-based FETs fabricated using identical device structure and fabrication conditions except the cleaning procedure of gold contacts. The two left characteristics were measured on devices based on gold contacts cleaned using solvent cleaning and O2 plasma treatment. The two right characteristics were measured on devices based on gold contacts without O2 plasma treatment.

S5 OPV Device preparation and characterization. Photovoltaic devices were made by spin coating PEDOT:PSS (Clevios P, VP Al4083) onto pre-cleaned, patterned indium tin oxide (ITO) substrates (14 Ω per square) (Naranjo Substrates). The photoactive layer was deposited by spin coating from the appropriate solvent. The counter electrode of LiF (1 nm) and aluminum (100 nm) was deposited by vacuum evaporation at 3×10^{-7} mbar. The active area of the cells was 0.091 cm². J-V characteristics were measured under ~100 mW/cm² white light from a tungstenhalogen lamp filtered by a Schott GG385 UV filter and a Hoya LB120 daylight filter, using a Keithley 2400 source meter. Short circuit currents under AM1.5G conditions were obtained from the spectral response and convolution with the solar spectrum. Spectral response was measured under operation conditions using bias light from a 532 nm solid state laser (Edmund Optics). Monochromatic light from a 50 W tungsten halogen lamp (Philips focusline) in combination with monochromator (Oriel, Cornerstone 130) was modulated with a mechanical chopper. The response was recorded as the voltage over a 50 Ω resistance, using a lock-in amplifier (Stanford research Systems SR830). A calibrated Si cell was used as reference. The device was kept behind a quartz window in a nitrogen filled container.

Initial devices were spun from a mixture of Polymer (5 mg/mL) : [70]PCBM (10 mg/mL) in a 1:2 ratio of Chloroform:ODCB (4:1), spin speed ~750 RPM.

The optimized P1 device was prepared from a mixture of **P1**:[70]PCBM (1:2) (total concentration 20 mg/mL) from 1: Chloroform:ODCB (4:1), with a spin speed of 2500 RPM.

S6 References

(1) Chang, H. C.; Shiozaki, T.; Kamata, A.; Kishida, K.; Ohmori, T.; Kiriya, D.; Yamauchi, T.; Furukawa, H.; Kitagawa, S. *Journal of Materials Chemistry* **2007**, *17*, 4136-4138.