BPTs: thiophene-flanked benzodipyrrolidone conjugated polymers for ambipolar organic transistors

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Supporting Information

General Experimental

Experimental Procedures & NMR Spectra

Additional Schemes, Figures & Spectra

Instrumental

Microwave chemistry was performed in a Biotage initiator v.2.3. NMR spectra were recorded on a Bruker DPX0 400 MHz spectrometer using an internal deuterium lock at ambient probe temperatures unless stated otherwise. Chemical shifts (δ) are quoted in ppm relative to the solvent residual peak, with peak multiplicity (bs, broad singlet; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), integration and coupling constants (J) quoted in Hz (uncorrected) as appropriate. CDCl₃ was used as the solvent for all spectra unless stated otherwise. Proton solvent residual peaks are taken as: 7.26 for CDCl₃, 7.15 for C₆D₆, 3.34 for methanol- d_4 , 2.52 for DMSO- d_6 ; and carbon solvent residual peaks as: 77.16 for CDCl₃, 128.6 for C₆D₆, 49.9 for methanol-d₄, 39.7 for DMSO-d₆. Mass spectra: low resolution and high resolution mass spectra were obtained using positive or negative electrospray ionisation (ES) unless otherwise stated. Infrared spectra were recorded using an FTIR spectrometer as evaporated films or neat using sodium chloride windows. *Melting points* are uncorrected. UV-Vis detection was performed using a UV-1601 Shimadzu UV-Vis spectrometer; solutions are dilute in chlorobenzene and thin-films prepared by spin-coating from 1 mg/mL hot chlorobenzene solutions on glass substrates. UV-Vis-NIR detection was performed using a Perkin Elmer Lambda 950 UV/VIS Spectrometer; polymer thin-films were prepared by dropcasting from 1 mg/mL hot chlorobenzene solutions on glass substrates. Molecular weights (Number-average $[M_n]$ and weight-average $[M_w]$) were recorded on an Agilent Technologies 1200 series GPC in chlorobenzene at 80°C, using two PL mixed B columns in series, calibrated against narrow polydispersity polystyrene standards. Ionisation potentials were evaluated by Photo-electron Spectroscopy in Air (PESA) on a Riken Keiki AC-2 PESA spectrometer. PESA samples were prepared by spin-coating polymer thin-films on glass substrates from 1 mg/mL solutions in chlorobenzene and were run with a light intensity of 5 nW and data processed with a power number of 0.5. *Differential scanning calorimetry* (DSC) experiments were carried out on a TA Instruments DSC Tzero Q20 instrument. Thermal gravimetric analysis (TGA) plots were obtained with a Perkin Elmer Pyris 1 TGA. X-ray diffraction (XRD) measurements were carried out with a PANALYTICAL X'PERT-PRO MRD diffractometer equipped with a nickel-filtered Cu K α 1 beam and a X' CELERATOR detector, using a current of 40 mA and an accelerating voltage of 40 kV; films were drop-cast from polymer solution (10 mg/mL in hot chlorobenzene) onto an Si substrate and allowed to dry in air for 24 h. Field-effect transistor (FET) device fabrication: top gate

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devices: top-gate, bottom-contact devices were fabricated on 2x2 cm glass substrates under an inert atmosphere. Glass slides are cleaned in a DECON90 DI-Water solution in an ultrasonic bath twice for 10 min and then rinsed with DI-Water. To help with the adhesion of the gold 2 nm of chromium are evaporated before putting 25 nm of gold down. Chlorobenzene solution and substrates were heated to processing temperature. Polymer thinfilms (5 mg/mL) were spin-coated at 2000 rpm for 30-60 s then dried at 150 °C for 10 min to remove residual solvent and then further annealed at 175 °C. A perfluorinated polymer (commercial name CYTOP from Ashani Glass) is used as the gate dielectric and applied via spin-coating at 2000 rpm for 60 s and curing at 100 °C for 30 min. 50 nm Aluminium is evaporated on top of the dielectric as the gate electrode. Bottom gate devices: standard silicon bottom gate bottom contact (400 nm SiO₂ over Si⁺⁺) substrates with gold electrodes are used. The substrates are cleaned in an ultrasonic bath (acetone 10 min, isopropanol 10 min) and then treated with an OTS SAM before contact evaporation. The devices are spun from the same solution, with identical processing parameters as above. Atomic force microscopy (AFM) was performed on an Agilent 5500 instrument in tapping mode; polymer thin films were prepared by spin-coating from polymer solution (5 mg/mL hot chlorobenzene) on OTSmodified SiO₂ substrates and then annealed at 300 °C under an inert atmosphere.

Detailed experimental procedures are described below. All solvents, reagents and other chemicals were used as received from commercial sources, or purified using standard procedures unless stated otherwise. The use of anhydrous chemicals, intuitive from the reaction, infers anhydrous conditions under an argon or nitrogen atmosphere. Glassware for inert atmosphere reactions was oven dried and cooled under a flow of nitrogen. All temperatures – other than room temperature – are recorded as bath temperatures of the reaction, unless stated otherwise. Merck aluminium backed precoated silica gel (50 F254) plates were used for thin-layer chromatography (TLC). Visualisation was by ultraviolet light (254 nm) and/or either potassium permanganate(VII), vanillin, iodine or Molybdate staining with heating as appropriate. Column chromatography was performed on Merck silia gel (Merck 9385 Kieselgel 60, 230-400 mesh) under a positive air pressure using reagent or GR (guaranteed reagent) grade solvent as received.

PE refers to petroleum spirit 60-80 °C; Hex refers to hexane; DMSO refers to dimethyl sulfoxide; TFAA refers to trifluoroacetic acid; CAN refers to cerium(IV) ammonium nitrate; NBS refers to *N*-bromosuccinimide; DDQ refers to 2,3-dichloro-5,6-dicyanobenzoquinone; EtOAc refers to ethyl acetate.

1,5-bis(2-Octyldodecyl)pyrrolo[2,3-f]indole-2,3,6,7(1H,5H)-tetraone (3)



To a solution of oxalyl chloride (0.85 ml, 9.76 mmol) in CH₂Cl₂ (30 ml) at -78 °C was added DMSO (1.26 ml, 17.8 mmol) in CH₂Cl₂ (10 mL) dropwise via cannula addition. After stirring for 30 min a solution of *N*,*N*'-(1,4-phenylene)bis(2-hydroxy-*N*-(2-octyldodecyl)acetamide)¹ (3.48 g, 4.43 mmol) in CH₂Cl₂ (10 mL) was added dropwise via cannula addition. The solution was stirred for a further 1 h at -78 °C, then NEt₃ (6.2 ml, 44 mmol) was added, and the solution allowed to warm to room temperature and stirred for 1.5 h. CH₂Cl₂ (75 mL) and a saturated aqueous solution of NaHCO₃ (100 mL) were then added, and the organic layer was separated and washed with a saturated aqueous solution of NaHCO₃ (2 × 100 mL), dried (MgSO₄) and concentrated *in vacuo* to yield the intermediate glyoxamide as a green oil, which was used immediately without further purification.

To a solution of the crude glyoxamide in CH₂Cl₂ (50 mL) was added thiophenol (0.91 g, 8.9 mmol). The resulting solution was stirred for 15 h at 20 °C. TFAA (5.5 mL, 40 mmol) was then added, the solution stirred for 1 h, then BF₃·OEt₂ (2.8 mL, 22 mmol) was added. After 6 h, the solution was cooled to 0 °C and carefully quenched with a saturated aqueous solution of NaHCO₃ (100 mL), then washed with a saturated aqueous solution of NaHCO₃ (3 × 50 mL), dried (MgSO₄) and concentrated *in vacuo* to yield **2** as a deep red oil (crude mass, 4.13 g), which was used without further purification. ¹H NMR (400 MHz, CDCl₃): 0.92 (m, 12H; $4 \times$ CH₃), 1.33 (m, 64 H; 32 × CH₂), 1.77 (m, 2 H; 2 × CHS [one diastereoisomer]), 6.74 (s, 2 H; 2 × ArH), 7.26 (m, 4 H; 4 × ArH), 7.33 (m, 2 × ArH, 2H), 7.46 (m, 4 H; 4 × ArH). ¹³C NMR (100 MHz, CDCl₃): 14.0 (8 × CH₃ [both diastereoisomers]), 22.5, 26.08, 26.11, 26.14,

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26.18, 29.20, 29.45, 29.50, 29.53, 29.87, 29.91, 31.1, 31.2, 31.8 ($64 \times CH_2$ [both diastereoisomers]), 35.94 (2 × CH [one diastereoisomer]), 35.99 (2 × CH [one diastereoisomer]), 44.8 (4 × NCH₂ [both diastereoisomers]), 49.3 (4 × CHS [both diastereoisomer]), 106.3 (4 × ArCH [both diastereoisomers]), 126.7 (2 × ArC [one diastereoisomer]), 126.8 (2 × ArC [one diastereoisomer]), 128.48 (2 × ArCH [one diastereoisomer]), 128.53 (2 × ArCH [one diastereoisomer]), 128.58 (4 × ArCH [one diastereoisomer]), 128.62 (4 × ArCH [one diastereoisomer]), 131.0 (2 × ArC [one diastereoisomer]), 131.1 (2 × ArC [one diastereoisomer]), 133.9 (4 × ArCH [one diastereoisomer]), 134.0 (4 × ArCH [one diastereoisomer]), 139.07 (2 × ArC [one diastereoisomer]), 139.14 (2 × ArC [one diastereoisomer]), 173.3 (2 × C=O [one diastereoisomer]); IR (ATR): $v_{max}/(cm^{-1})$: 2922, 2852,

1699, 1470, 1346, 1159, 872, 738, 689, 649. MS m/z (ES+): 964 (100 %, M⁺). HRMS (ES⁺): C₆₂H₉₅N₂O₂S₂ requires 963.6840, found 963.6825.

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¹H NMR (400 MHz, CDCl₃)





¹³C NMR (100 MHz, CDCl₃)



To a portion of the crude intermediate (2) (1.66 g) was added THF (44 mL), H₂O (7.4 mL), followed by CAN (7.53 g, 13.7 mmol). The solution was stirred for 24 h at room temperature then concentrated *in vacuo*. Purification by flash column chromatography on silica gel eluting with 10% EtOAc in hexane yielded the pure product (**3**) (0.96 g, 1.2 mmol, 69 % for 3 steps) as a blue oil; ¹H NMR (400 MHz, CDCl₃) 0.79 - 0.95 (m, 12 H; $4 \times CH_3$), 1.15 - 1.45 (m, 62 H; $30 \times CH_2$ and $2 \times CH$), 1.55 - 2.17 (m, 4 H; $2 \times CH_2$), 3.62 (d, J = 7.6 Hz, 4 H; $2 \times NCH_2$), 7.13 (s, 2 H; $2 \times ArCH$); ¹³C NMR (101 MHz, CDCl₃) 14.1 (4 × CH₃), 22.6, 22.7, 26.2, 29.2, 29.3, 29.5, 29.6, 29.9, 31.3, 31.8, 31.9, 35.9 (32 × CH₂ and $2 \times CH$), 45.3 (2 × NCH₂), 106.9 (2 × ArCH), 123.1 (2 × ArC), 147.7 (2 × ArC), 157.0 (C=O), 183.2 (C=O); IR(ATR): v_{max} / cm^{-1} : 2921, 2852, 1729 (C=O), 1465, 1159. MS *m*/*z* (APCI⁺): 778 (100 %, [M+H]⁺).

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¹H NMR (400 MHz, CDCl₃)

MTL-1.esp



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1,5-bis(2-Octyldodecyl)-3,7-di(thiophen-2-yl)pyrrolo[2,3-f]indole-2,6(1H,5H)-dione (4)



To a solution of 3 (0.956 g, 1.23 mmol) in THF (26 ml) under N₂ at -78 °C was added dropwise thienyl magnesiumbromide (3.69 mL, 1 M, 3.69 mmol). The resulting solution was stirred at -78 °C for 5 h, and quenched with H₂O (10 mL). The mixture was then allowed to warm to room temperature and hexane (50 mL) added. The solution was washed with a saturated aqueous solution of NaHCO₃ (3 \times 20 mL), dried (Na₂SO₄), and concentrated in *vacuo*. To a suspension of the crude intermediate (1.05 g) in AcOH (100 mL) was added NaI (2.34 g, 15.6 mmol), and NaPO₂H₂ (1.65 g, 15.6 mmol), then the suspension refluxed for 3 h under N₂ in the absence of light. The solution was then cooled to room temperature and hexane (100 mL) added. The solution was washed with H_2O (5 × 100 mL), dried (Na₂SO₄) and concentrated in vacuo. To a solution of the crude intermediate (1.09 g) in CH₂Cl₂ (20 ml), was added DDQ (0.30 g, 1.3 mmol), followed by stirring at room temperature for 2 h. Hexane (100 mL) was then added and the solution washed with a saturated aqueous solution of NaHCO₃ (3 \times 40 mL), dried (Na₂SO₄), and concentrated *in vacuo* to yield the crude product. Purification by flash column chromatography on silica gel eluting with 40 % toluene in hexane gave pure 4 (0.392 g, 0.430 mmol, 35 %) as an amorphous magenta solid; ¹H NMR (400 MHz, C_6D_6) 0.84 - 1.01 (m, 12 H; 4 × CH₃), 1.21 - 1.56 (m, 64 H; 32 × CH₂), 1.87 - 2.07 (m, 2 H; $2 \times CH$), 3.53 (d, J = 7.0 Hz, 4 H; $2 \times NCH_2$), 6.61 (s, 2 H; $2 \times C=CH$), 6.82 (dd, J = 5.1, 3.8 Hz, 2 H; 2× C=CH), 7.01 (dd, J = 5.1, 1.0 Hz, 2 H; 2 × C=CH), 8.40 (dd, J = 3.8, 1.0 Hz, 2 H; 2 × C=CH); ¹³C NMR (126 MHz, CDCl₃): 14.1 (4 × CH₃), 22.7, 26.8, 29.3, 29.3, 29.6, 29.7, 29.7, 30.0, 31.8, 31.9 (32 × CH₂), 37.2 (2 × CH), 44.1 (2 × NCH₂), 98.4 (2 × C=*C*H), 121.0 (2 × C=*C*), 128.3 (2 × C=*C*H), 128.9 (2 × C=*C*H), 129.8 (2 × C=CH), 129.9 (2 × C=C), 134.5 (2 × C=C), 143.6 (2 × C=C), 169.1 (2 × C=O); IR (ATR): $v_{max}/(cm^{-1})$: 2924, 2854, 1694 (C=O), 1424, 697; MS (APCI⁺): 912 ([M+H]⁺, 100%).

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¹³C NMR (126 MHz, CDCl₃)

SDY.esp



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3,7-*bis*(5-Bromothiophen-2-yl)-1,5-*bis*(2-octyldodecyl)pyrrolo[2,3-*f*]indole-2,6(1H,5H)dione (M1)



To a solution of **4** (0.152 g, 0.167 mmol) in THF (2 mL) at 0 °C, in the absence of light, was added NBS (0.065 g, 0.367 mmol). After stirring for 16 h at room temperature, the solvent was removed *in vacuo*. Purification by flash column chromatography on silica gel eluting with 30-50 % toluene in hexane gave the desired product (0.170 g, 0.159 mmol, 95 %) as an amorphous waxy purple solid; ¹H NMR (400 MHz, C₆D₆) 0.90-0.94 (m, 12 H; 4 × CH₃), 1.36 (m, 64 H; 32 × CH₂), 1.90 (m, 2 H; 2 × CH), 3.48 (d, *J* = 7.3 Hz, 4 H; 2 × NCH₂), 6.37 (s, 2 H; 2 × C=CH), 6.75 (d, *J* = 4.2 Hz, 2 H; 2 × C=CH), 7.92 (d, *J* = 4.2 Hz, 2 H; 2 × C=CH); ¹³C NMR (101 MHz, C₆D₆) 14.8 (4 × CH₃), 23.5, 27.6, 30.2, 30.46, 30.51, 30.52, 30.6, 30.9, 32.70, 32.73 (32 × CH₂), 38.0 (2 × CH), 44.2 (2 × NCH₂), 98.4 (2 × C=CH), 118.1 (2 × C=C), 120.4 (2 × C=C), 130.6 (2 × C=CH), 131.1 (2 × C=CH), 132.0 (2 × C=C), 137.5 (2 × C=C), 144.6 (2 × C=C), 169.1 (2 × C=O); IR (ATR): $v_{max}/(cm^{-1})$: 2922, 2852, 1694 (C=O), 1411. MS (MALDI-Dithranol): 1071 (M⁺, 100%).

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¹H NMR (400 MHz, C₆D₆)





¹³C NMR (101 MHz, C₆D₆)



BPT-T

[BPT-T: Poly-benzodipyrrolidonedithiophenyl-thiophene]



Α microwave vial charged with **M1** 0.20 mmol), 2,5was (217)mg, bis(trimethylstannyl)thiophene (83 0.20 mmol), 2.2 mol% of mg, tris(dibenzylideneacetone)dipalladium and 8.8 mol% of tri(o-tolyl)phosphine. The vial was then sealed, chlorobenzene added (2 mL), the mixture degassed for approximately 40 minutes and submitted to the microwave reactor for: 3 minutes at each of 100 °C, 120 °C, 140 °C, 160 °C and finally 50 minutes at 180 °C. The crude polymer was precipitated in methanol and then purified by Soxhlet extraction with acetone, hexane, chloroform and chlorobenzene. Remaining palladium residues were removed by vigorously stirring the latter fraction with aqueous sodium diethyldithiocarbamate for 3 hours at 55 °C. The organic phase was then separated, washed (water), concentrated in vacuo and again precipitated in methanol, filtered off and dried under high vacuum to afford the title compound as a dark purple solid (118 mg, 56 % yield; chloroform and chlorobenzene fractions). $M_n = 34$ kDa, $M_w = 57$ kDa, PDI = 1.67 (chloroform fraction).

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[BPT-2T: Poly-benzodipyrrolidonedithiophenyl-bithiophene]



A microwave vial was charged with M1 (139 mg, 0.13 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (64 mg, 0.13 mmol), 2.2 mol% of tris(dibenzylideneacetone)dipalladium and 8.8 mol% of tri(o-tolyl)phosphine. The vial was then sealed, chlorobenzene added (2mL), the mixture degassed for approximately 40 minutes and submitted to the microwave reactor for: 3 minutes at each of 100 °C, 120 °C, 140 °C, 160 °C and finally 50 minutes at 180 °C. The crude polymer was precipitated in methanol and then purified by Soxhlet extraction with acetone, hexane, chloroform and chlorobenzene. Remaining palladium residues were removed by vigorously stirring the latter fraction with aqueous sodium diethyldithiocarbamate for 3 hours at 55 °C. The organic phase was then separated, washed (water), concentrated in vacuo and again precipitated in methanol, filtered off and dried under high vacuum to afford the title compound as a dark purple solid (49 mg, 35 % yield; chloroform and chlorobenzene fractions). $M_n = 5 \text{ kDa}$, $M_w = 17 \text{ kDa}$, PDI = 3.30 (chloroform fraction).

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Figure S1. GPC trace of BPT-T, $M_n = 34$ kDa, $M_w = 57$ kDa, PDI = 1.67.



Figure S2. GPC trace of BPT-2T, $M_n = 5 \text{ kDa}$, $M_w = 17 \text{ kDa}$, PDI = 3.29.

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Figure S3. (*Top*) TGA curve of the **BPT-T** polymer (under a nitrogen atmosphere with a heating rate of 10 °C/min).; and, (*bottom*) DSC (differential scanning calorimetry) scans of the **BPT**-based polymers (-30 to 350 °C, heating at 10 °C/min under a nitrogen atmosphere).



Figure S4. X-ray diffraction (XRD) diagram of the BPT-T and BPT-2T polymer thin-film on Si substrates as cast.

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Figure S5. Normalized UV-Vis absorption spectra of monomer M1 and polymers BPT-T and BPT-2T; solutions are in (dilute) chlorobenzene and thin-films spin-coated on glass substrates.

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Figure S6. (*Top*) transfer curves for a **BPT-2T** field-effect transistor device annealed at various temperatures (150-300 °C); (bottom gate/bottom contact architecture; channel width 1500 μ m and channel length 20 μ m); and (*bottom*) output curves for a **BPT-2T** field-effect transistor device after annealing at 175 °C; (bottom gate/bottom contact architecture; channel width 1500 μ m and channel length 20 μ m). Large hysteresis occurs due to charge trapping at the interface.

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Figure S7. Output curves for a **BPT-2T** field-effect transistor device after annealing at 175 °C; (bottom gate/bottom contact architecture; channel width 1500 μ m and channel length 20 μ m). Large hysteresis occurs due to charge trapping at the interface.



Figure S8. Microscopy images of BPT-2T polymer films on OTS treated SiO₂: (left) as cast and (right) after annealing at 300 °C.

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Figure S9. Atomic force microscopy (AFM) phase images of (*left*) **BPT-T** and (*right*) **BPT-2T** polymer films on OTS treated SiO₂: (*top*) after annealing at 175 °C and (*bottom*) after annealing at 300 °C.

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Figure S10. Energy minimized structures (B3LYP/6-31G*) of **BPT-T** and **BPT-2T** tetramers with N-methyl substitution, with visualisation of the HOMO (bottom) and LUMO (top) energy distributions and calculated bandgap beneath each structure; the total energy of the alternative configuration of the **BPT-T** tetramer (*Alt***BPT-T**) is also shown for comparison.