Selenophene diketopyrrolopyrrole based polymers for High-Mobility Ambipolar Organic Thin-Film Transistors

Supporting information

S1 Experimental section

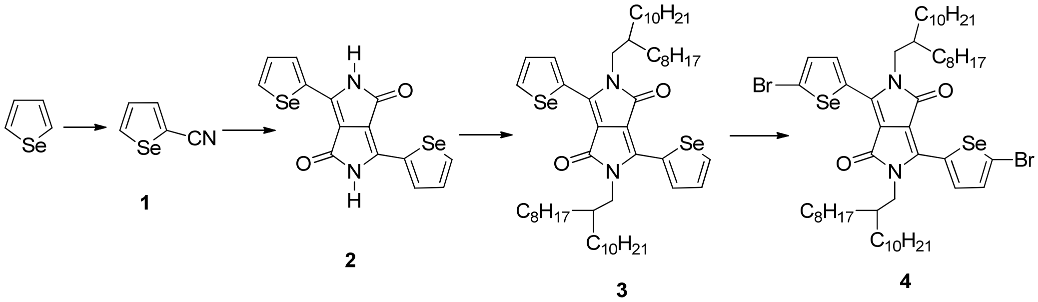
All other chemicals were purchased from Aldrich and used as received. All reactions were carried out in under Argon using solvents and reagents as commercially supplied, unless otherwise stated. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-400 (400 MHz), using the residual solvent resonance of CDCl3 or TMS as an internal reference and are given in ppm. Number average (Mn) and weight average (Mw) molecular weights 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 spectrometry was performed with a Thermo Electron Corporation DSQII mass spectrometer. UV-vis spectra were recorded on a UV-1601 Shimadzu S2 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 5mg mL^{-1}. Thermogravimetric analysis (TGA) was carried out using a Perkin Elmer Pyris 1 TGA machine, with heating from 50 to 800°C, in dry air, at a heating rate of 10°C/min. X-ray diffraction (XRD) measurements were carried out with a PANALYTICAL X' PERT-PRO

MRD diffractometer equipped with a nickel-filtered Cu-$K_{\alpha 1}$ beam and X' CELERATOR detector, using current I = 40 mA and accelerating voltage U = 40kv. Samples for X-ray diffraction were produced by preparing homogeneous solutions of 1 wt% total material content in chlorobenzene, followed by casting onto glass slides at room temperature. The solvent was evaporated at ambient pressure in air. AFM images were taken in close-contact mode using a Veeco Dimension 3100 SPM.

S2 Synthetic Procedures

Selenophene was purchased from Frontier Scientific, Inc. 1-iodo-2-octyldodecane[1], 2, 5-bis(trimethylstannyl) thieno[3,2-*b*]thiophen[2] and 2,5-bis(trimethylstannyl)selenophene[3] were prepared according to the literature procedures.

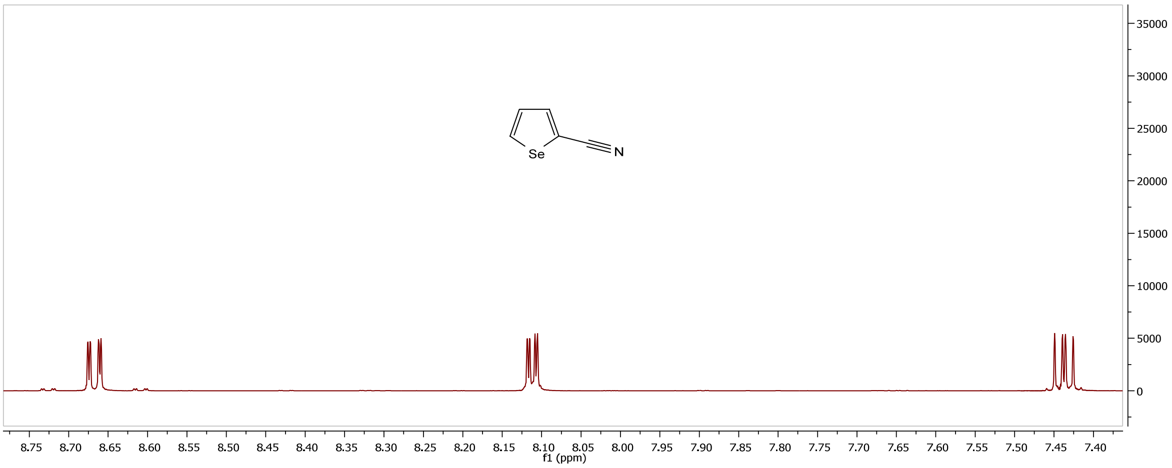
S3 Monomer Synthesis and characterization



Selenophene-2-carbonitrile (1)

To an ice cooled solution of selenophene (10 g, 76.3 mmol) in dry dichloromethane (50 mL) was added chlorosulfonyl isocyanate (11.38 g, 80.4 mmol) drop-wise. The reaction mixture was stirred at 10-15°C for 1 h and then at RT for another hour. The resulting green mixture was cooled to 0°C and dimethylformamide (11.71 g, 160.1 mmol) was added drop-wise over 20 minutes. After two hours at room temperature, the resulting brown mixture was poured onto ice and extracted with dichloromethane (3 x 30 mL). The organic layer was washed with distilled water, brine, and dried over magnesium sulphate. The solvent was removed under reduced pressure to afford a brown oil which was further purified by short path distillation (Kugel ruhr; 105°C, 4mbar) to afford **1** as a pale yellow liquid (9.09g, 75.8%).

^{1}H NMR (DMSO): 8.67 (dd excl. ^{77}Se satellites, J_1=1.21Hz, J_2=5.46Hz, 1H), 8.11 (dd, J_1=1.24Hz, J_2=3.90Hz, 1H), 7.44 (dd, J_1=3.93Hz, J_2=5.47Hz, 1H). ^{13}C NMR (DMSO): 142.27, 141.52, 129.94, 116.49, 111.85. ^{77}Se NMR: 726.5ppm (ddd, J_1=3.17Hz, J_2=8.07Hz, J_3=46.93Hz). IR (neat) 3107, 2214, 1425, 1373 cm^{-1}. *m/z*: (EI+) 157 $[M+H]^+$



3,6-Bis-(selenophenyl)-1,4-diketopyrrolo[3,4-*c*]pyrrole (2)

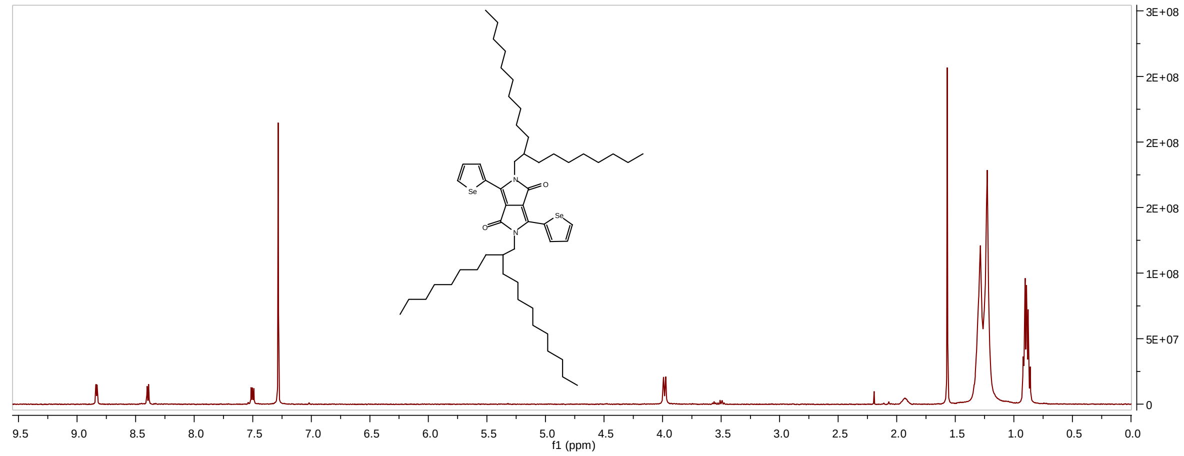
Sodium (2.01 g, 87 mmol) was added to a stirred solution of iron(III) chloride (10 mg) in 2-methylbutan-2-ol (50 mL) and heated to reflux until the complete consumption of sodium. The solution was cooled to 85°C and selenophene-2-carbonitrile **1** (9.09 g, 58 mmol) was added followed by diisopropyl succinate (5.27 g, 26 mmol). The resulting mixture was stirred at 85°C for 4 h and then cooled to 50°C. The reaction was quenched by the addition of glacial acetic acid (5 mL) in methanol (30 mL) and the mixture stirred at 50°C for 30 min. The resulting dark brown mixture was poured into methanol (100 mL). The precipitate was collected by filtration and washed with several portions of water and methanol and dried *in vacuo* overnight to yield **2** as a dark red/purple powder (5.49 g, 48 %). The crude product was used without further purification.

^{1}H NMR (DMSO-d_6): 11.21 (s, 1H), 8.60 (dd, J$_1$=1.05 Hz, J$_2$=5.48 Hz, 1H), 8.31 (dd, J$_1$=1.05 Hz, J$_2$=4.00 Hz, 1H), 7.49 (dd, J$_1$=3.97 Hz, J$_2$=5.49 Hz). ^{13}C NMR (DMSO-d_6): 161.72, 139.64, 137.85, 135.02, 133.22, 130.82, 109.20, ^{77}Se NMR (DMSO): 657.6 (dd, J$_1$=3.1Hz, J$_2$=44.7 Hz). *m/z*: (EI+) 397 [M+H]$^+$

2,5-Di(2-octyldodecyl)-3,6-bis-(selenophenyl)-1,4-diketopyrrolo[3,4-*c*]pyrrole (3)

1-Iodo-2-octyldodecane (12 g, 29.4 mmol) was added to a mixture of 2,5-di(2-octyldodecyl)-3,6-bis-(selenyl)-1,4-diketopyrrolo[3,4-*c*]pyrrole **2** (2.9 g, 7.35 mmol), potassium carbonate (4.57 g, 33.07 mmol) and 18-crown-6 (~30 mg) in dry DMF (60 mL) at 120°C. After 18 hrs the reaction mixture was cooled, poured into ice-water (200 mL) and extracted with chloroform (3 x 100 mL) The combined extracts were washed with water and brine and dried (MgSO$_4$). The solvent was then removed under reduced pressure and the crude product was purified by column chromatography on silica (eluent: chloroform: hexane 3:7 to 1:2; 1% added triethylamine) to give **3** as a deep red solid (2.2 g, 31%).

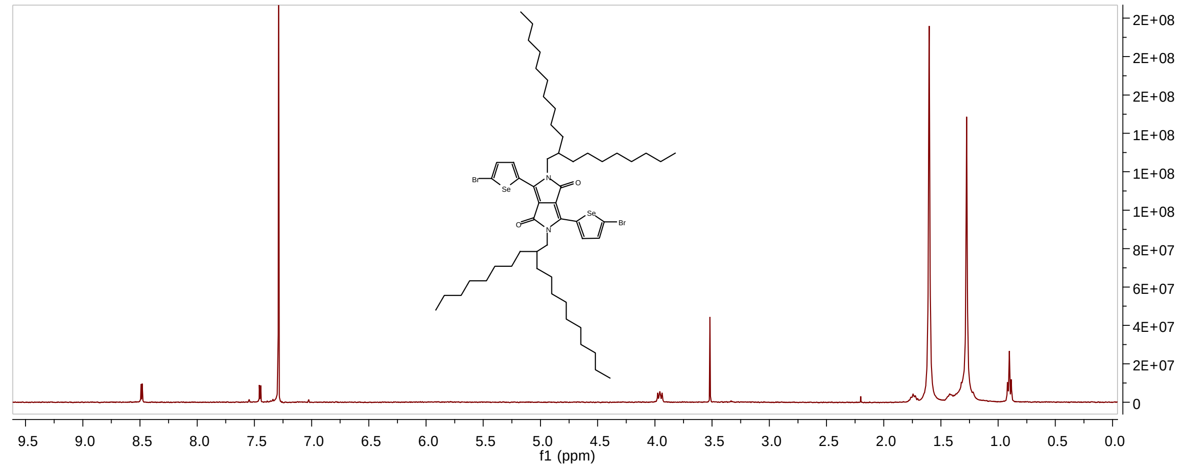
^{1}H NMR (CDCl$_3$): 8.81 (dd excl. Se satellites, J$_1$=1.04 Hz, J$_2$=4.08 Hz, 2H), 8.37 (dd, J$_1$=1.02 Hz, J$_2$=5.56 Hz, 2H), 7.48 (dd, J$_1$=4.10 Hz, J$_2$=5.56 Hz, 2H), 3.96 (d, J=7.74 Hz, 4H), 1.91 (m, 2H), 1.26 (m, 64H), 0.87 (m, 12H) . ^{13}C NMR (CDCl$_3$): 161.86, 142.18, 136.92, 136.46, 134.06, 108.04, 46.13, 37.65, 31.91, 31.86, 31.21, 29.99, 29.69, 29.62, 29.54, 29.48, 29.34, 29.27, 26.19, 22.67, 22.65, 14.10 , ^{77}Se NMR (CDCl$_3$): 645.86 (ddd, J$_1$=5.21 Hz, J$_2$=7.63 Hz, J$_3$=48.68 Hz). IR(amide at1671cm^{-1}). *m/z*: (EI+) 954 [M+H]$^+$



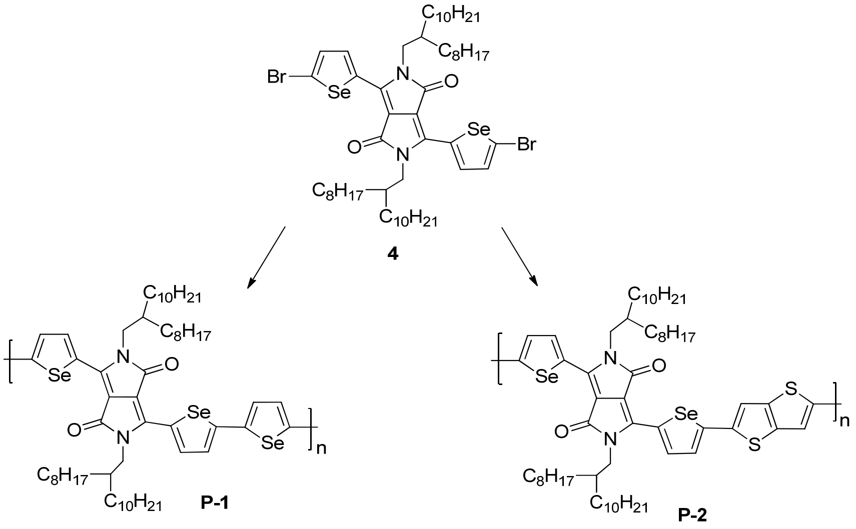
2,5-Di(2-octyldodecyl)-3,6-bis-(5-bromoselenophenyl)-1,4-diketopyrrolo[3,4-*c*]pyrrole (4)

To a stirred solution of **3** (1.25 g, 1.3 mmol) in chloroform (90 mL) under argon atmosphere, *N*-bromosuccinimide (0.51 g, 2.86 mmol) was added in small portions and the mixture stirred overnight at room temperature. The reaction mixture was poured into methanol (300 mL) and kept in refrigerator overnight. The resulting precipitates were filtered and washed with hot distilled water and methanol. The crude product was further purified by column chromatography on silica (eluent: chloroform: hexane 2:1) to obtain **5** as a dark purple solid (0.85 g, 58%).

^{1}H NMR ($CDCl_3$): 8.42 (d excl. Se satellites, J=4.42 Hz, 2H), 7.42 (d, J=4.42 Hz, 2H), 3.90 (d, J=7.69 Hz, 4H), 1.91 (m, 2H), 1.26 (m, 64H), 0.89 (m, 12H). ^{13}C NMR ($CDCl_3$): 161.56, 140.92, 136.07, 135.62, 134.23, 123.99, 108.34, 50.87, 46.33, 37.63, 31.92, 31.88, 31.17, 29.97, 29.69, 29.64, 29.54, 29.49, 29.36, 29.29, 26.14, 22.69, 22.67, 14.12, ^{77}Se NMR ($CDCl_3$): 707.75 (dd, J_1=1.39 Hz, J_2=2.38 Hz). *m/z* (EI+ HMRS) 1113.3495, calculated for $C_{54}H_{87}N_2O_2Se_2$: 1113.3465).



S4 Polymer synthesis and characterization



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-selenophene)bis-selenophene]-5,5'-diyl]])

PDPP3Se

To a 2 mL microwave vial was added 2,5-di(2-octyldodecyl)-3,6-bis-(5-bromoselenophenyl)-1,4-diketopyrrolo[3,4-*c*]pyrrole **4** (0.20 g, 0.17 mmol), 2,5-bis(trimethylstannyl)selenophene (0.082 g, 0.17 mmol). Chlorobenzene (1 mL) was added and the solution degassed before addition of Pd$_2$(dba)$_3$ (2.5 mg, 2.7 µmol, 1.5 mol%) and P(oTol)$_3$ (3.3 mg, 10 µmol, 6 mol%). 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) and hexane (24 hr). After cooling to room temperature, the polymer was dried *in vacuo* and dissolved in chloroform by heating and stirring. 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 washed with water (2 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 precipitates were filtered over a 4.5 µm PTFE filter and dried *in vacuo* to afford the desired polymer (155 mg, 80%)

GPC (chlorobenzene): Mn= 70000 g/mol Mw=210000 g/mol, PDI=3.0

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'-(2,5-selenophene)bis-thieno[3,2-*b*]thiophen]-5,5'-diyl]])

PSeDPPTT

The synthetic procedure was similar as described for **P-1**. Yield (93%)

GPC(PS): *Mn* = 100000 g/mol; *Mw* = 250000 g/mol; PDI = 2.5

S5 FET Device Fabrication and Characterization

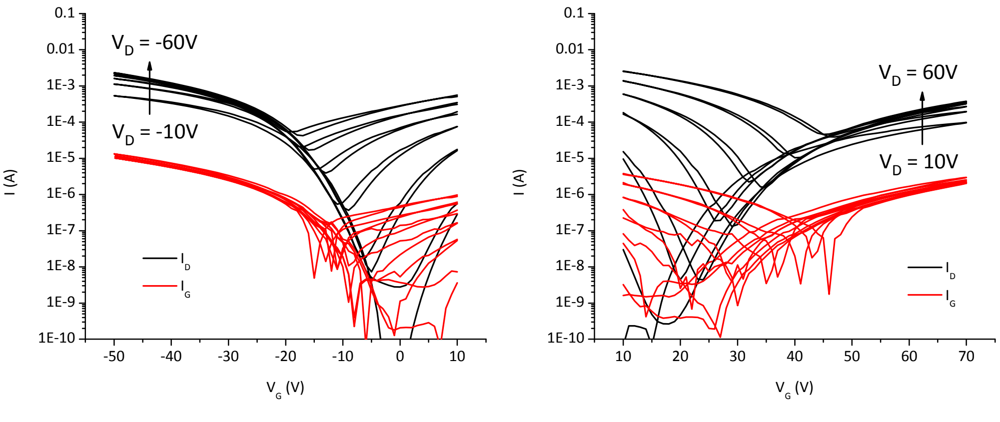
Bottom-gate, bottom-contact (BG, BC) organic field-effect transistors (OFETs) were fabricated on a highly-doped silicon substrate, which acted as a common gate electrode. A thermally grown 200 nm layer of silicon dioxide was then used as the gate dielectric. Gold source and drain electrodes were patterned using standard photolithography. The SiO2 layer was treated with the primer hexamethyldisilazane (HMDS) to passivate the surface. Solutions of polymers P1 and P2 were made in chlorobenzene with a concentration of 10 mg / ml, and then spin-cast onto the substrates under atmospheric-pressure N_2.

Bottom-gate, top-contact (BG, TC) OFETs were similarly fabricated on a highly-doped silicon substrate, which acted as a common gate electrode. A thermally grown 400 nm layer of silicon dioxide was used as the gate dielectric. The SiO2 layer was in this case treated with the primer octyltrichlorosilane (OTS). Solutions of **P1** and **P2** were then processed in a similar manner to that described above. Finally, 50nm gold source and drain electrodes were deposited via vacuum sublimation, through shadow masks.

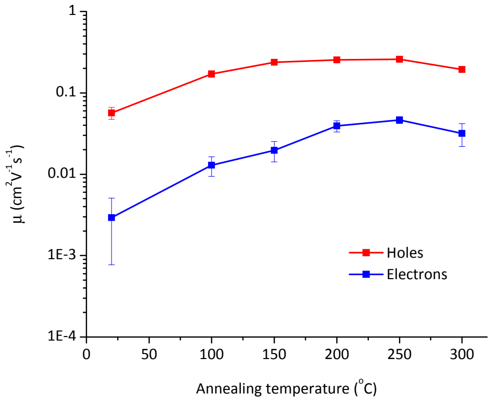
Electrical characterisation was carried out in N2 at atmospheric pressure using a Keithley 4200 semiconductor parameter analyser. Using standard semiconductor models,1 the field effect mobility was determined from transfer characteristics in the saturation regime using the following equation:

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

Here μ is the field-effect mobility, ID is the drain current in the saturation regime, VG is the voltage applied to the gate terminal of the OFET, L and W are the OFET channel length and width respectively and Ci is the geometrical capacitance of the gate dielectric.



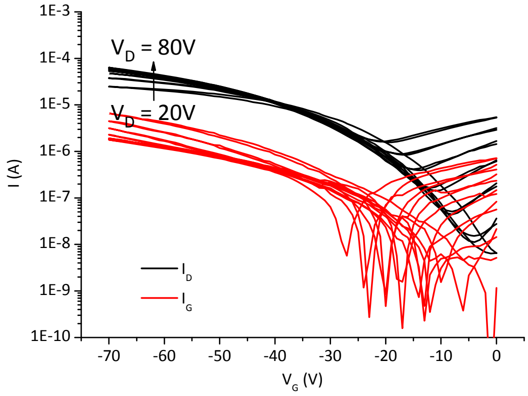
(A)

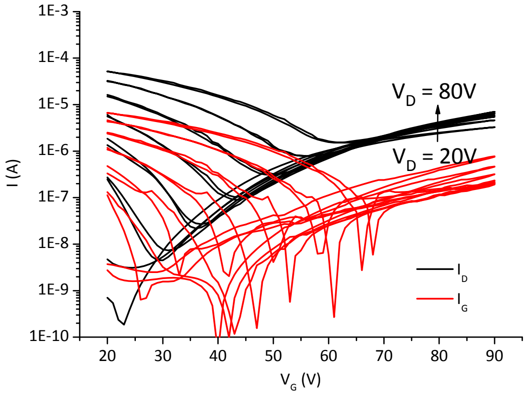


(B)

Figure S5.1. Transfer characteristics of bottom-gate, bottom contact (BG, BC) organic field-effect transistor (OFET) with channel length = 10 µm and channel width = 10 mm based on polymer **P2**. (A) Transfer characteristics measured at VD = -10 V and VD = -60 V (left), and VD = 10 V and VD = 60 V (right) at room temperature under N2. Gate leakage current shown in red. (B) Average saturation-regime field-effect mobility of holes and electrons measured in 5 BG, BC OFETs, at room temperature ,after annealing for 30 minutes at temperatures between 50 - 200˚C.

Transfer characteristics:





Output characteristics:

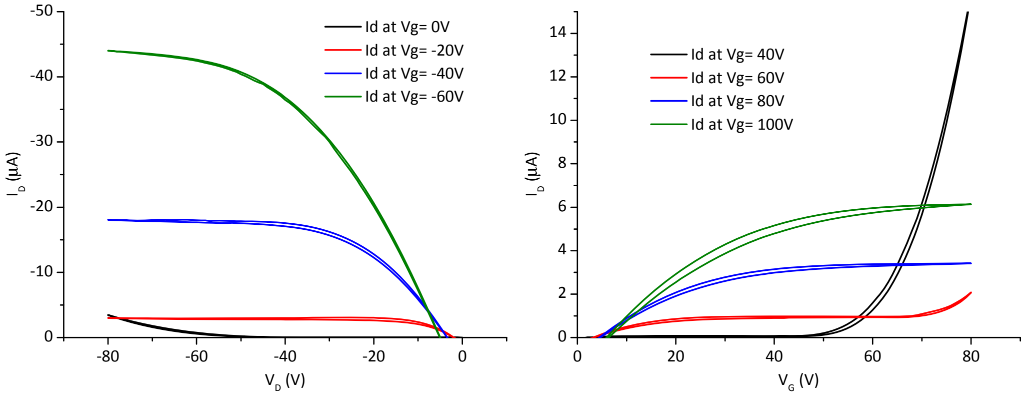


Figure S6 Transfer (top) and output (bottom) characteristics for **P2** for top contact devices, channel length = 30 μm and channel width = 0.5 mm.

S7. UV-VIS Spectroscopy

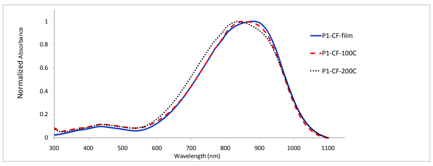


Fig S7.1 UV-VIS Film of P1: As-spun from chloroform, and after annealing at 100 and 200C.

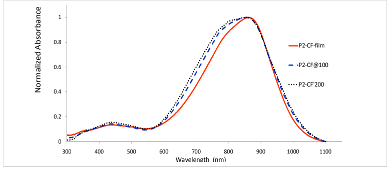


Fig S7.2 UV-VIS Film of P2: As-spun from chloroform, and after annealing at 100 and 200C.

S8 TGA

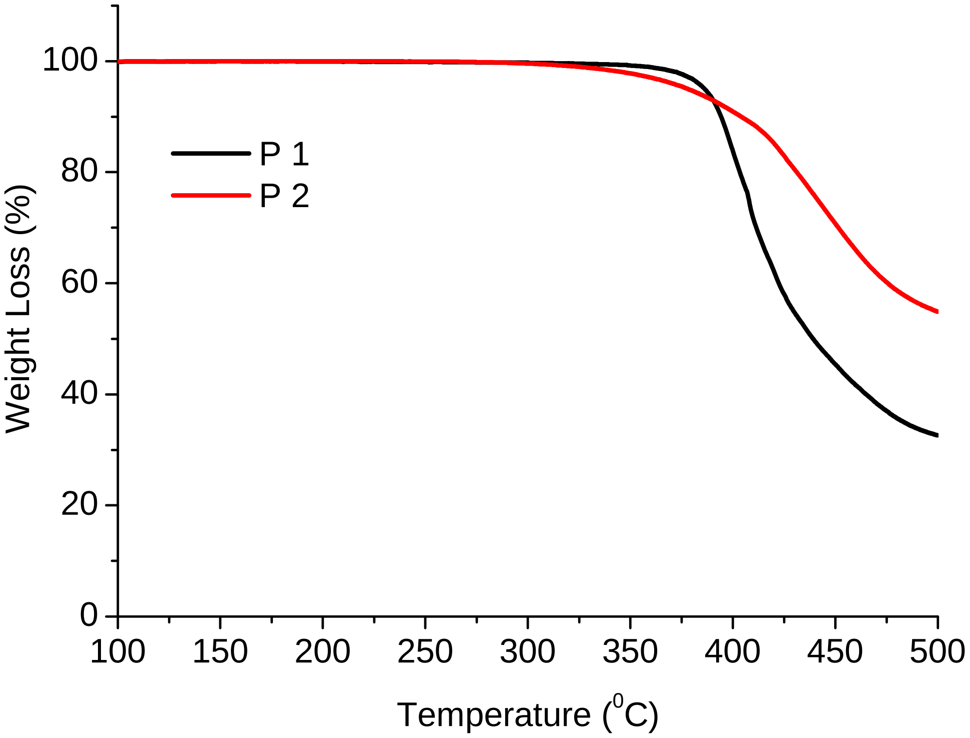


Figure S8. Thermogravimetric traces in air of **P1** and **P2.**

S9 References

1) Letizia, J. A.; Salata, M. R.; Tribout, C. M.; Facchetti, A; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc*. **2008**, 130, 9679.

2) McCulloch, I.; Heeney, M.; Bailey, C.; Genevicius, K.; MacDonald, I.; Shkunov, M.; Sparrowe, D.; Tierney, S.; Wagner, R.; Zhang, W.; Chabinyc, M. L.; Kline, R. J.; McGehee, M. D.; Toney, M. F. *Nat. Mater*. **2006**, *5*, 328-333.

3) Seitz, D. E.; Lee, S. H.; Hanson, R. N.; Bottaro, J. C. *Synth. Commun.* **1983**, *13*, 121.