

Supporting Information

Effect of Fluorination on Molecular Orientation of Conjugated Polymers in High Performance Field-Effect Transistors

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1. Materials and measurements

The synthesis of the monomer **6** and **9**, and the DPP polymers is shown in Scheme 1. All synthetic procedures were performed under argon atmosphere. Commercial chemicals were used as received. THF and toluene were distilled from sodium under an N₂ atmosphere. The monomer 3,6-bis(5-bromothiophen-2-yl)-2-(2-decyltetradecyl)-5-(tricosan-11-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (**1**),^{S 1} 3,6-Bis(4-methylthiophene-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**4**),^{S 2} 3-(4-methylthiophen-2-yl)-6-(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (**7**)^{S3} and the polymer **PDPP4T**^{S4} were synthesized according to literature procedures. (3,3'-difluoro-[2,2'-bithiophene]-5,5'-diyl)bis(trimethylstannane) (**2**) and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (**3**) were purchased from SunaTech Inc. ¹H-NMR and ¹³C-NMR spectra were recorded at 400 MHz and 100 MHz on a Bruker AVANCE spectrometer with CDCl₃ as the solvent and tetramethylsilane (TMS) as the internal standard. Molecular weight was determined with GPC at 140 °C on a PL-GPC 220 system using a PL-GEL 10 µm MIXED-B column and *o*-DCB as the eluent against polystyrene standards. Low concentration of 0.1 mg mL⁻¹ polymer in *o*-DCB was applied to reduce aggregation. Optical absorption spectra were recorded on a

JASCO V-570 spectrometer with a slit width of 2.0 nm and a scan speed of 1000 nm min⁻¹. Cyclic voltammetry was performed under an inert atmosphere at a scan rate of 0.1 V s⁻¹ and 1 M tetrabutylammonium hexafluorophosphate in acetonitrile as the electrolyte, a glassy-carbon working electrode coated with samples, a platinum-wire auxiliary electrode, and an Ag/AgCl as a reference electrode. The counter and reference electrodes were a Pt wire and Ag/AgCl, respectively.

The organic field-effect transistors were fabricated on a commercial Si/SiO₂/Au substrate purchased from First MEMS Co. Ltd. A heavily N-doped Si wafer with a SiO₂ layer of 300 nm served as the gate electrode and dielectric layer, respectively. The Ti (2 nm)/Au (28 nm) source–drain electrodes were sputtered and patterned by a lift-off technique. Before deposition of the organic semiconductor, the gate dielectrics were treated with octadecyltrichlorosilane (OTS) in a vacuum oven at a temperature of 120 °C, forming an OTS self-assembled monolayers. The treated substrates were rinsed successively with hexane, chloroform, and isopropyl alcohol. Polymer thin films were spin coated on the substrate from solution with a thickness of around 30 – 50 nm. The devices were thermally annealed at the corresponding temperature in air for 10 min, cooled down and then moved into a glovebox filled with N₂. The devices were measured on an Keithley 4200 SCS semiconductor parameter analyzer at room temperature. The mobilities were calculated from the saturation region with the following equation: $I_{DS} = (W/2L)C_i\mu(V_G - V_T)^2$, where I_{SD} is the drain–source current, W is the channel width (1400 μ m), L is the channel length (50 μ m), μ is the field-effect mobility, C_i is the capacitance per unit area of the gate dielectric layer, and V_G and V_T are the gate voltage and threshold voltage, respectively. This equation defines the important characteristics of electron mobility (μ), on/off ratio (I_{on}/I_{off}), and threshold voltage (V_T), which could be deduced by the equation from the plot of current–voltage. Linear mobility was calculated according to the equation: $I_{DS} = (W/L)C_i\mu(V_{GS} - V_T)V_{DS}$ $V_{DS} \ll V_{GS} - V_T$.

Differential scanning calorimetry (DSC) was performed on a TA instruments calorimeter (Perkin Elmer Corp DSC8000) at a heating rate of 10 °C min⁻¹. The second heating DSC scans are reported for all DPP polymers. 2D-GIWAXS measurements were performed at beamline 7.3.3 at the Advanced Light Source. Samples were prepared on Si substrates using blend solutions identical to those used in devices.^{S5} The 10 keV X-ray beam was incident at a grazing angle of 0.13° - 0.17°, which maximized the scattering intensity from the samples. The scattered X-rays were detected using a Dectris Pilatus 2M photon counting detector.

2. Synthesis of the monomers and polymers

2,5-bis(2-decyltetradecyl)-3-(4-methylthiophen-2-yl)-6-(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (5). To a solution of **4** (3.0 g, 9.5 mmol), potassium carbonate (3.8 g, 27.5 mmol) and 18-crown-6 (10 mg) in DMF (30 mL) was added 2-decyltetradecyl bromide (9.5 g, 22.8 mmol). The reaction mixture was stirred at 130 °C for 10 h and then cooled to room temperature. After reaction, dichloromethane (100 mL) and water (100 mL) were added and the layers were separated. The organic layer was washed with brine. Then the solution was dried with anhydrous sodium sulfate and the solvent evaporated. The resulting solid was subjected to column chromatography (silica, eluent petroleum ether/dichloromethane, v/v = 4/1) to afford **5** (2.7 g, 29%) as red solid. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.85 (d, 1H), 8.70 (s, 1H), 7.60 (d, 1H), 7.24 (m, 1H), 7.21 (s, 1H), 4.01 (m, 4H), 2.37 (s, 3H), 1.91 (br, 2H), 1.21 (m, 80H), 0.88 (t, 12H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 161.82, 161.72, 140.67, 140.05, 139.17, 137.23, 134.99, 130.21, 129.93, 129.54, 128.33, 126.60, 108.08, 107.71, 46.25, 37.74, 31.92, 31.26, 30.02, 29.65, 29.55, 29.35, 26.26, 22.68, 15.60, 14.09. MS (MALDI): calculated: 987.7, found: 987.9 (M⁺).

3-(5-bromo-4-methylthiophen-2-yl)-6-(5-bromothiophen-2-yl)-2,5-bis(2-decyltetradecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (6). To a solution of **5** (0.30 g, 0.30 mmol), Cs₂CO₃ (0.30 g, 0.92 mmol) in CHCl₃ (30 mL) was added dropwise bromine

solution (0.22 g, 1.38 mmol) in CHCl_3 (5 mL) at 0 °C in dark. The reaction mixture was stirred at room temperature for 3 min. Sodium sulfite solution (5.0 g, 20 mL H_2O) was added into reaction mixture and stirred for 30 min to remove bromine. The mixture was washed with brine and the layers were separated. The resulting solid was subjected to column chromatography (silica, eluent petroleum ether/dichloromethane, v/v = 4/1) to afford **6** as crude product. The solid was recrystallized from ethanol to afford pure **6** (0.27 g, 78 %) as a red solid. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.60 (m, 2H), 7.21, (d, 1H), 3.91 (m, 4H), 2.29 (s, 3H), 1.88 (br, 2H), 1.22 (m, 80H), 0.86 (t, 12H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 161.40, 161.35, 139.76, 139.11, 139.00, 136.65, 135.10, 131.38, 131.26, 128.94, 118.70, 116.88, 108.16, 107.78, 99.99, 46.35, 37.76, 31.93, 31.25, 29.99, 29.69, 29.64, 29.56, 29.36, 26.24, 22.68, 15.17, 14.10. MS (MALDI): calculated: 1145.5, found: 1144.8 (M^+).

2,5-bis(2-decyltetradecyl)-3,6-bis(4-methylthiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (8). To a solution of **7** (3.0 g, 9.1 mmol), potassium carbonate (3.8 g, 27.5 mmol) and 18-crown-6 (10 mg) in DMF (30 mL) was added 2-decyltetradecyl bromide (9.5 g, 22.8 mmol). The reaction mixture was stirred at 130 °C for 10 h and then cooled to room temperature. After reaction, dichloromethane (100 mL) and water (100 mL) were added and the layers were separated. The organic layer was washed with brine. Then the solution was dried with anhydrous sodium sulfate and the solvent evaporated. The resulting solid was subjected to column chromatography (silica, eluent petroleum ether/dichloromethane, v/v = 4/1) to afford **8** (3.0 g, 33%) as red solid. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.68 (s, 2H), 7.20 (s, 2H), 4.00 (m, 4H), 2.37 (s, 6H), 1.91 (br, 2H), 1.21 (m, 80H), 0.85 (t, 12H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 161.78, 140.30, 139.13, 137.08, 129.59, 126.42, 107.79, 46.22, 37.71, 31.92, 31.28, 30.03, 29.70, 29.68, 29.65, 29.63, 29.56, 29.35, 26.29, 22.67, 15.60, 14.08. MS (MALDI): calculated: 1001.7, found: 1001.8 (M^+).

3,6-bis(5-bromo-4-methylthiophen-2-yl)-2,5-bis(2-decyltetradecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (9). To a solution of **8** (0.30 g, 0.30 mmol), Cs_2CO_3

(0.30 g, 0.92 mmol) in CHCl_3 (30 mL) was added dropwise bromine solution (0.22 g, 1.38 mmol) in CHCl_3 (5 mL) at 0 °C in dark. The reaction mixture was stirred at room temperature for 3 min. Sodium sulfite solution (5.0 g, 20 mL H_2O) was added into reaction mixture and stirred for 30 min to remove bromine. The mixture was washed with brine and the layers were separated. The resulting solid was subjected to column chromatography (silica, eluent petroleum ether/dichloromethane, v/v = 4/1) to afford **9** as crude product. The solid was recrystallized from ethanol to afford pure **9** (0.30 g, 86 %) as a red solid. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 8.56 (s, 2H), 3.91 (m, 4H), 2.29 (s, 6H), 1.88 (br, 2H), 1.22 (m, 80H), 0.87 (t, 12H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 161.48, 139.39, 139.08, 136.45, 129.01, 116.67, 107.89, 46.35, 37.76, 31.92, 31.29, 30.00, 29.69, 29.64, 29.56, 29.35, 26.28, 22.68, 15.16, 14.09. MS (MALDI): calculated: 1159.5, found: 1158.8 (M^+).

PFDPP4T. To a degassed solution of the **1** (64.50 mg, 0.057 mmol), **3** (30.09 mg, 0.057 mmol) in toluene (2 mL) and DMF (0.2 mL), tris(dibenzylideneacetene)dipalladium(0) (1.50 mg, 1.6 μmol) and triphenylphosphine (1.72 mg, 6.6 μmol) were added. The mixture was stirred at 115 °C for 24 h, after which it was precipitated in methanol and filter through a Soxhlet thimble. The polymer was extracted with acetone, hexane, dichloromethane and then dissolved in 1,1,2,2-tetrachloroethane (TCE) (80 mL) at 140 °C, which was then precipitated into acetone. Finally the resulting polymer can be solubilized in CHCl_3 for device fabrication. Yield: 59.09 mg (88%) as a dark solid. GPC (*o*-DCB, 140 °C): $M_n = 116.7 \text{ kg mol}^{-1}$, $M_w = 326.6 \text{ kg mol}^{-1}$ and PDI = 2.80.

PDPP4T-M. Same procedure as for **PFDPP4T** but now **9** (87.55 mg, 0.076 mmol) and **2** (37.59 mg, 0.076 mmol) were used as the monomers. Yield: 84.3 mg (96%). GPC (*o*-DCB, 140 °C): $M_n = 64.6 \text{ kg mol}^{-1}$, $M_w = 151.0 \text{ kg mol}^{-1}$ and PDI = 2.34.

PFDPP4T-M. Same procedure as for **PFDPP4T** but now **8** (87.55 mg, 0.076 mmol) and **3** (40.35 mg, 0.076 mmol) were used as the monomers. Yield: 72.4 mg (85%). GPC (*o*-DCB, 140 °C): $M_n = 69.8 \text{ kg mol}^{-1}$, $M_w = 148.2 \text{ kg mol}^{-1}$ and PDI = 2.12.

PDPP4T-2M. Same procedure as for **PFDP4T** but now **6** (70.85 mg, 0.061 mmol) and **2** (30.06 mg, 0.061 mmol) were used as the monomers. Yield: 68.6 mg (96%). GPC (*o*-DCB, 140 °C): $M_n = 40.4 \text{ kg mol}^{-1}$, $M_w = 90.3 \text{ kg mol}^{-1}$ and PDI = 2.23.

PFDP4T-2M. Same procedure as for **PFDP4T** but now **6** (66.27 mg, 0.057 mmol) and **3** (30.17 mg, 0.057 mmol) were used as the monomers. Yield: 63.9 mg (93%). GPC (*o*-DCB, 140 °C): $M_n = 86.1 \text{ kg mol}^{-1}$, $M_w = 331.8 \text{ kg mol}^{-1}$ and PDI = 3.85.

3. Literature examples of fluorinated polymers for FETs

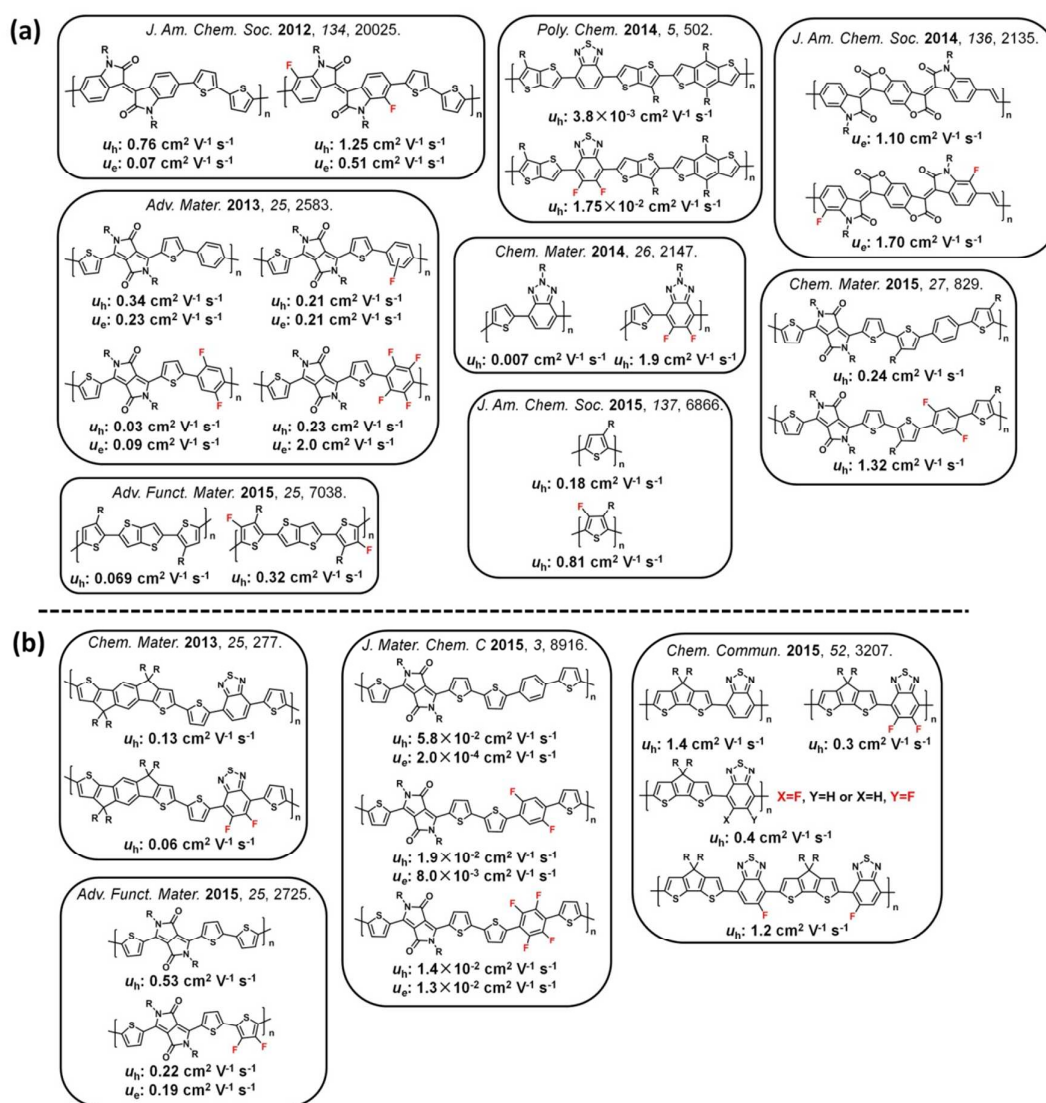


Figure S1. Literature examples of fluorinated conjugated polymers and their performance in FETs. (a) high mobility and (b) low mobility for fluorinated polymers compared to non-fluorinated polymers.

4. The chemical structures of PDPP4T-M and PFDPP4T-M

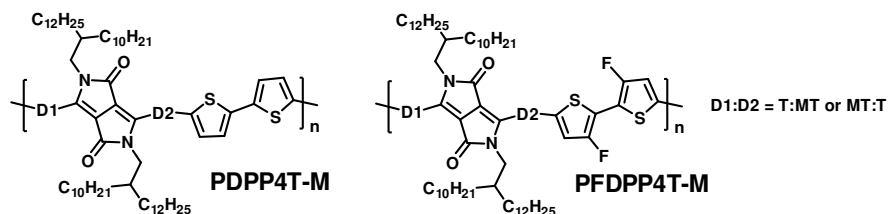


Figure S2. Chemical structures of the DPP polymers PDPP4T-M and PFDPP4T-M. T, thiophene; MT, methylthiophene.

5. DFT Calculations

Density functional theory (DFT) calculations were performed at the B3LYP/6-31G* level of theory by using the Gaussian 09 program package.

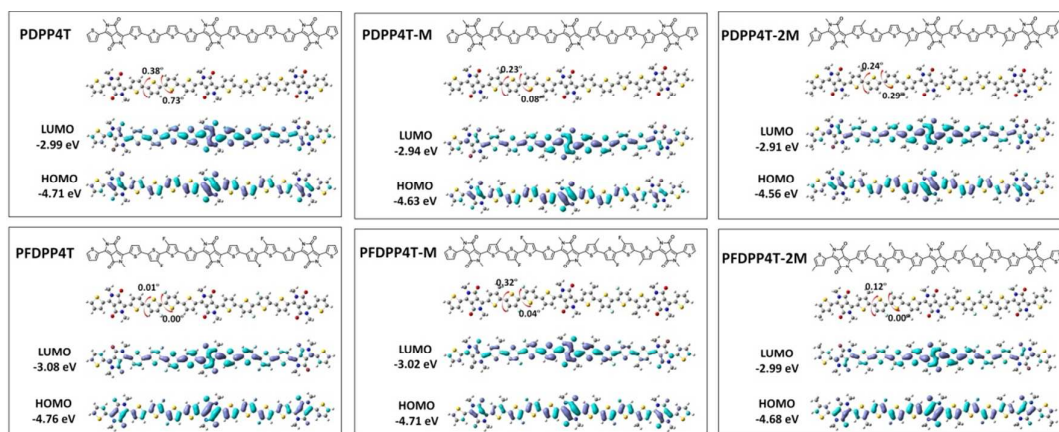


Figure S3. DFT frontier molecular orbitals and dihedral angle for the DPP polymers segment.

6. CV of the polymers

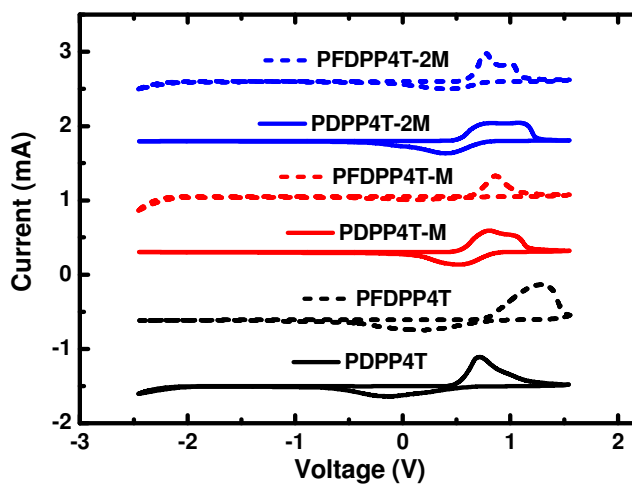


Figure S4. Cyclic voltammogram of the DPP polymer thin films. Potential vs. Fc/Fc⁺.

7. FETs

Table S1. Field effect hole mobilities of the DPP polymers in a BGBC configuration. The polymer thin films were thermally annealed (TA) for 10 min before measurement.

Polymer	TA	μ_h	V_T	I_{on}/I_{off}
	[°C]	[cm ² V ⁻¹ s ⁻¹]	[V]	
PDPP4T	RT ^a	1.4	7.1	1×10 ⁵
	90	1.5	-1.6	3×10 ⁴
	120	6.2	0.5	1×10 ⁶
	150	3.0	2.6	9×10 ⁴
	180	2.8	0.1	1×10 ⁶
	220	2.6	-4.1	1×10 ⁶
PFDPP4T	RT ^a	0.6	-19.9	2×10 ⁵
	90	1.8	-10.1	2×10 ⁵
	120	1.1	-24.7	9×10 ⁴
	150	1.4	-10.5	1×10 ⁵
	180	1.1	-9.4	5×10 ⁴
	220	1.5	-11.4	1×10 ⁶
PDPP4T-M	RT	3.6	1.6	3×10 ⁵
	90	4.2	-0.3	7×10 ⁴
	120	10.6	5.7	4×10 ⁴
	150	3.0	-0.5	9×10 ⁷
	180	3.1	-1.3	1×10 ⁷
	220	2.5	-5.1	2×10 ⁷
PFDPP4T-M	RT ^a	0.4	-7.7	1×10 ⁵
	90	1.2	-4.0	6×10 ⁴
	120	1.7	-21.7	1×10 ⁵
	150	0.8	-14.3	2×10 ⁷
	180	0.7	-15.7	7×10 ⁷
	220	0.6	-11.9	7×10 ⁵

PDPP4T-2M	RT ^a	1.3	-2.4	3×10^4
	90	3.6	-13.4	8×10^3
	120	11.2	0.3	7×10^5
	150	4.3	0.9	1×10^7
	180	3.2	-8.8	6×10^7
	220	3.8	-3.3	9×10^7
PFDPP4T-2M	RT ^a	0.5	-4.1	7×10^3
	90	0.9	-12.4	5×10^3
	120	0.9	-5.2	8×10^3
	150	0.7	-5.9	2×10^5
	180	0.6	-7.5	3×10^5
	220	0.7	-6.6	3×10^5

^aWithout thermal annealing.

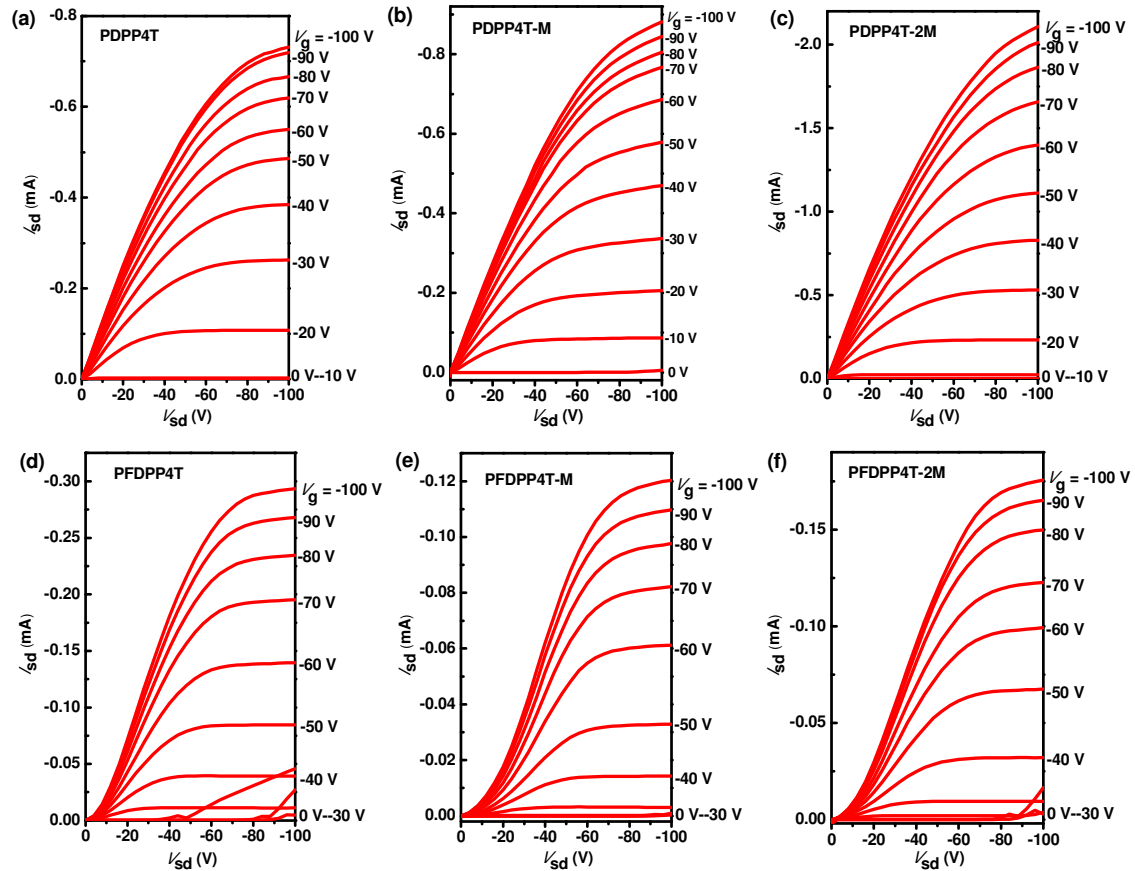


Figure S5. Output curves obtained from BGBC FET devices with DPP polymer thin films fabricated from CHCl_3 with 10% *o*-DCB. (a) PDPP4T. (b) PDPP4T-M. (c) PDPP4T-2M. (d)

PFDPP4T. (e) PFDPP4T-M. (f) PFDPP4T-2M. (d) and (f) Thin films were annealed at 90 °C for 10 min. (a) – (c) and (e) Thin films were annealed at 120 °C for 10 min.

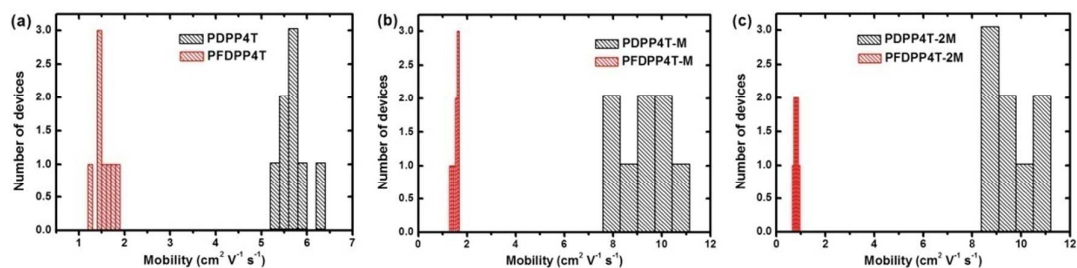


Figure S6. The mobility distribution for 8 FET devices based on the DPP polymers thin films spin coated from CHCl_3 with 10% *o*-DCB.

8. AFM

Atomic force microscopy (AFM) images were recorded using a Digital Instruments Nanoscope IIIa multimode atomic force microscope in tapping mode under ambient conditions.

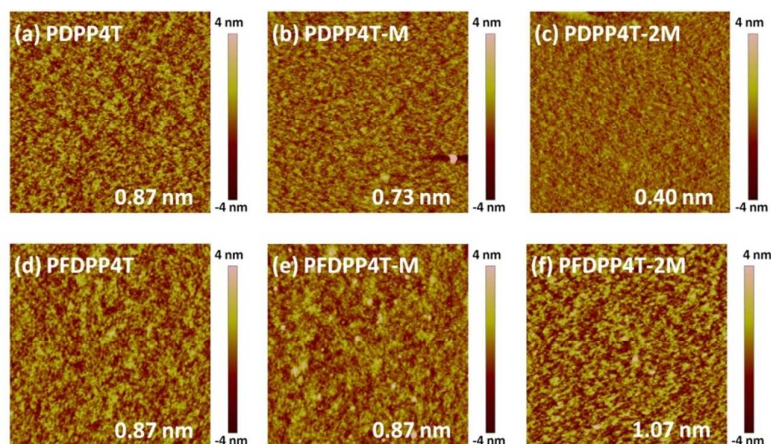


Figure S7. AFM height images ($3 \times 3 \mu\text{m}^2$) of the DPP polymer thin films spin coated from CHCl_3 with 10% *o*-DCB. (d), (f) Thermal annealed at 90 °C for 10 min. (a) – (c) and (e) Thermal annealed at 120 °C for 10 min. The root-mean-square (RMS) roughness is included in the images.

9. TGA of the DPP polymers

TGA measurement was performed on a Perkin-Elmer TGA-7 apparatus.

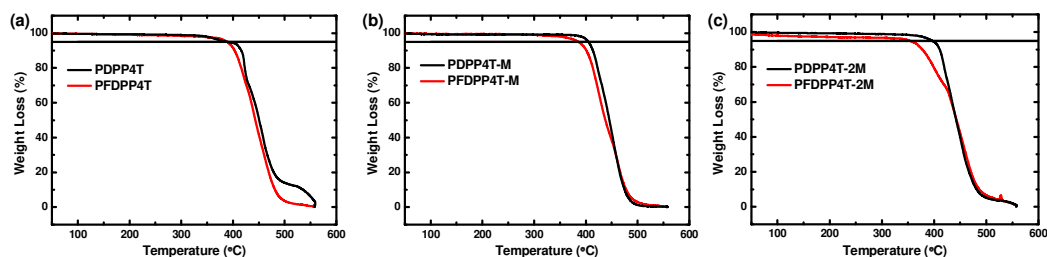


Figure S8. TGA plots of the DPP polymers with a heating rate of 10 °C/min under N₂ atmosphere. (a) PDPP4T and PFDPP4T. (b) PDPP4T-M and PFDPP4T-M. (c) PDPP4T-2M and PFDPP4T-2M. Temperatures with 5% weight loss for PDPP4T, PFDPP4T, PDPP4T-M, PFDPP4T-M, PDPP4T-2M and PFDPP4T-2M are 389, 389, 405, 386, 396 and 353 °C.

10. NMR spectra of the monomers and polymers

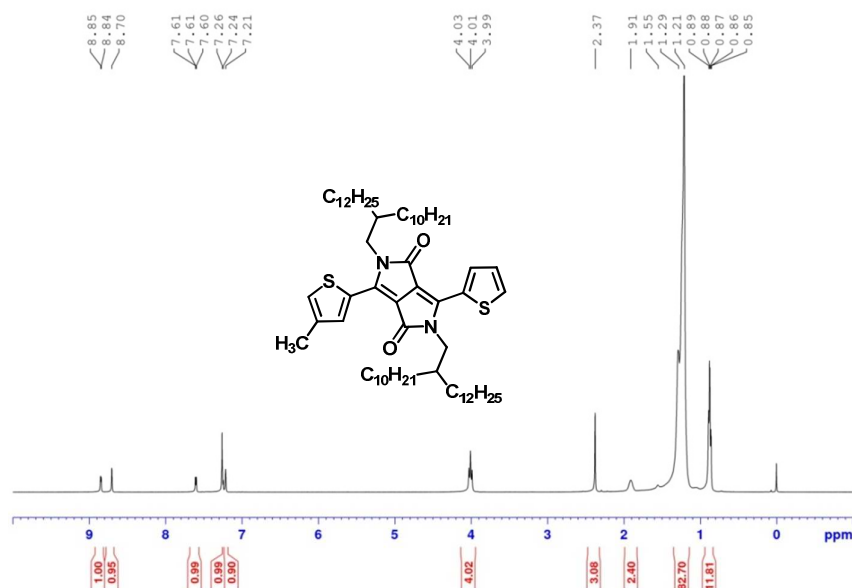


Figure S9. ¹H-NMR of the compound **5** recorded in CDCl₃.

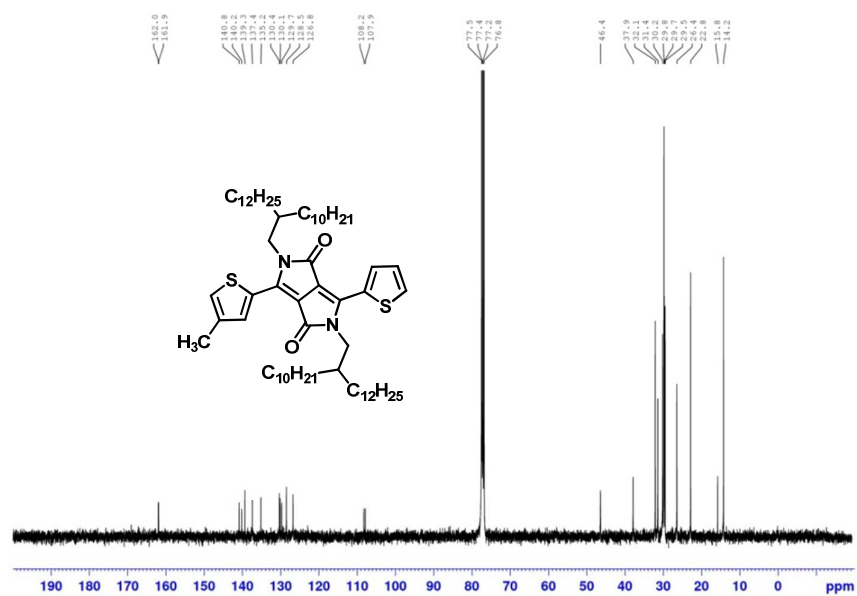


Figure S10. ^{13}C -NMR of the compound **5** recorded in CDCl_3 .

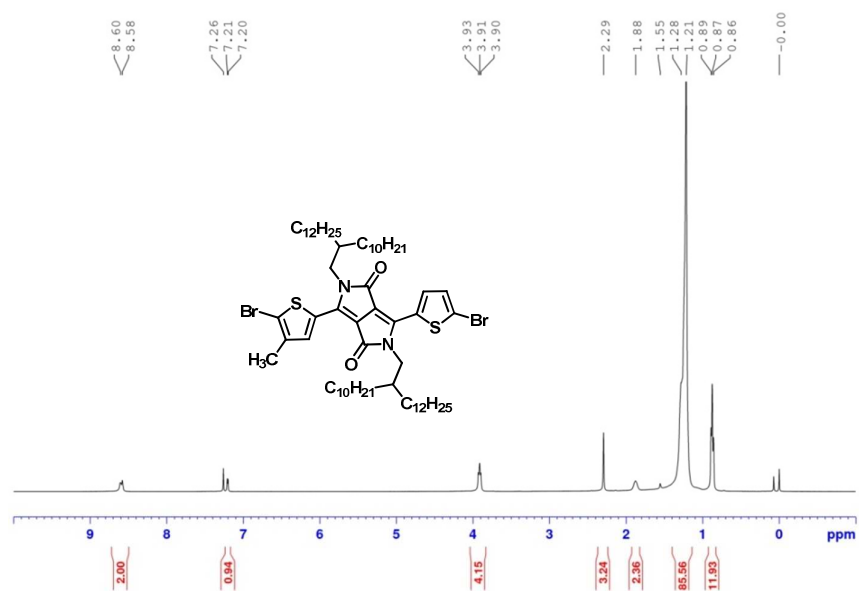


Figure S11. ^1H -NMR of the compound **6** recorded in CDCl_3 .

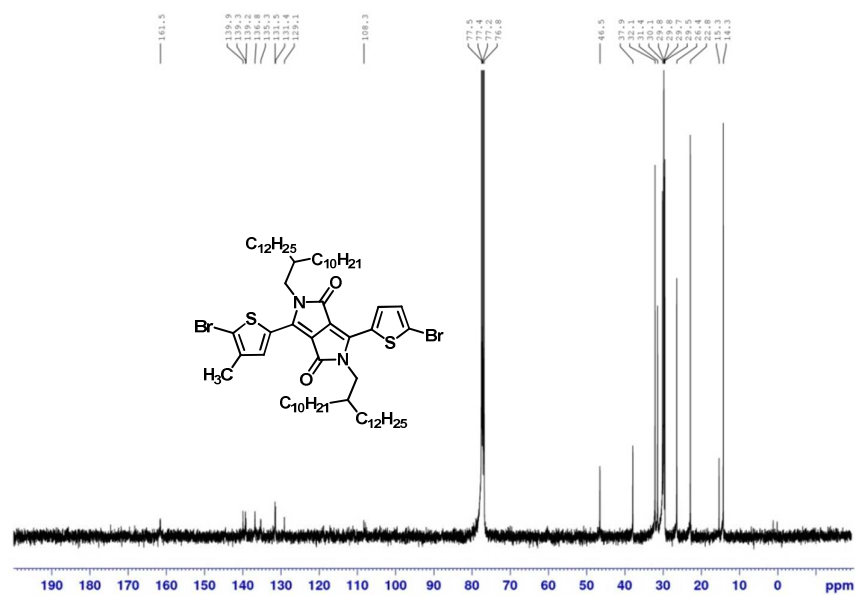


Figure S12. ¹³C-NMR of the compound **6** recorded in CDCl₃.

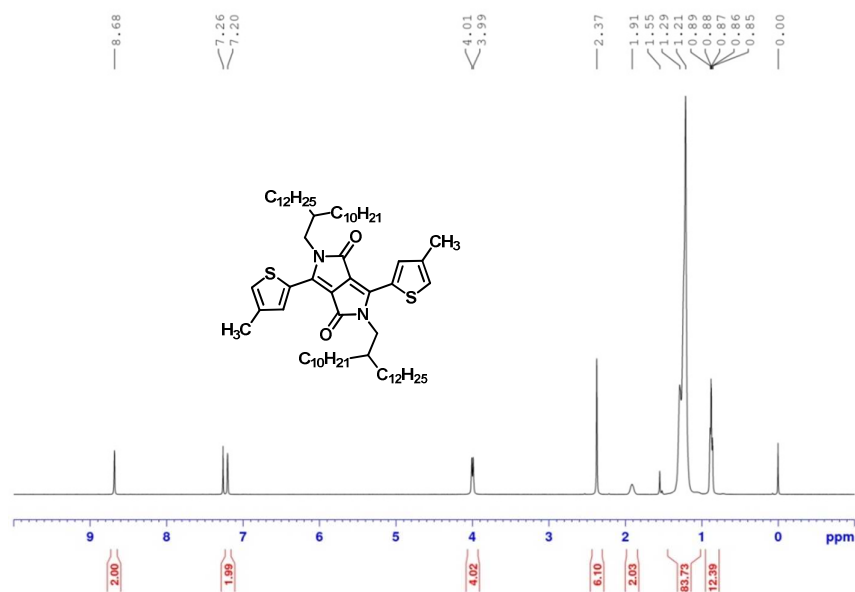


Figure S13. ¹H-NMR of the compound **8** recorded in CDCl₃.

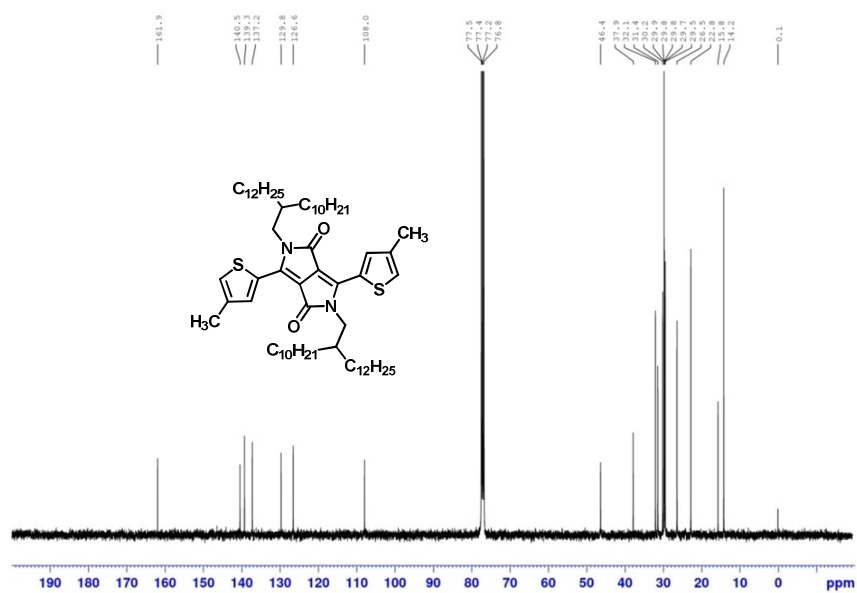


Figure S14. ^{13}C -NMR of the compound **8** recorded in CDCl_3 .

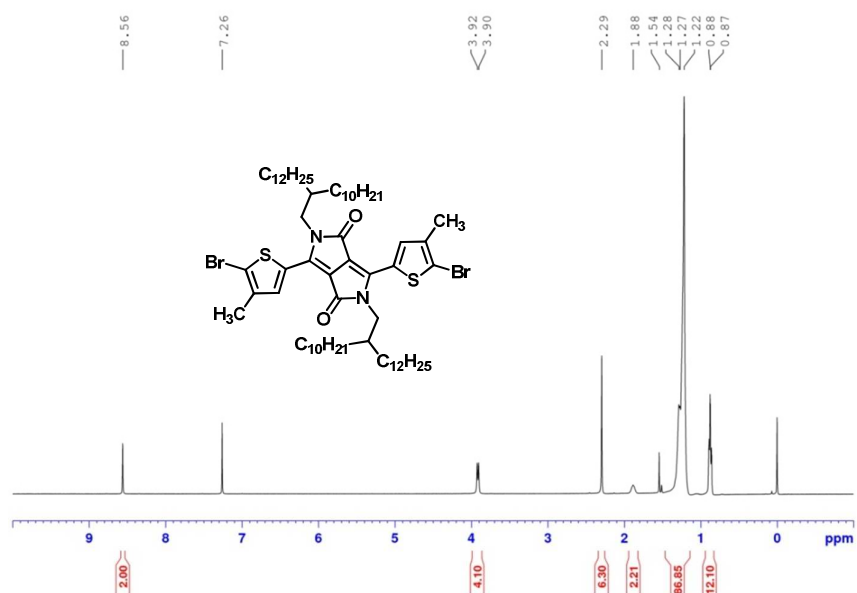


Figure S15. ^1H -NMR of the compound **9** recorded in CDCl_3 .

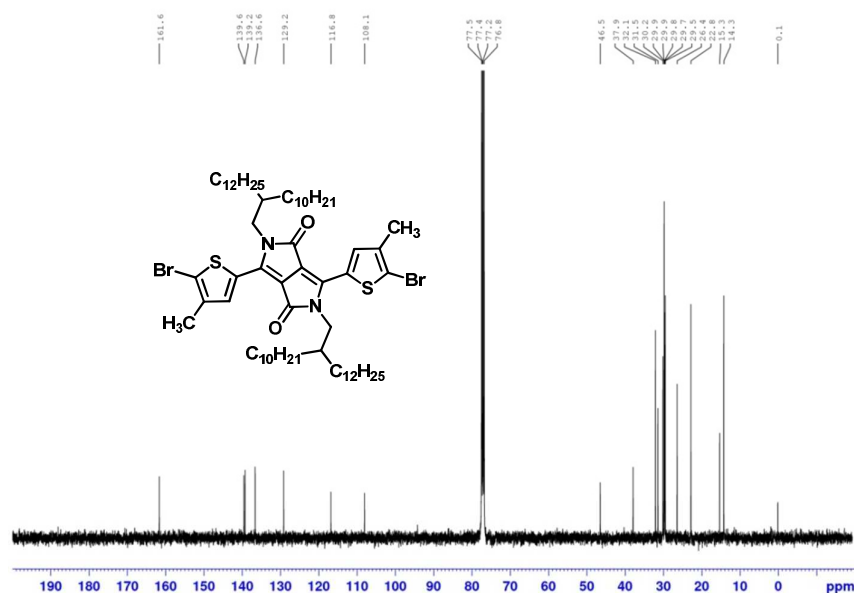


Figure S16. ¹³C-NMR of the compound **9** recorded in CDCl₃.

11. References

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