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Electronic supplementary information *for*

Diketopyrrolopyrrole-based conjugated polymers synthesized by direct arylation polycondensation for anisole-processed high mobility organic thin-film transistors

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General methods

^{1}H NMR and ^{13}C NMR spectra were recorded using a Bruker AVANCE III (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR) spectrometer in chloroform-*d* ($CDCl_3$) at 25 ^{o}C. High resolution matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a Bruker/AutoflexIII Smartbean MALDI mass spectrometer using 2-[(2*E*)-3-(4-*t*-buthylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) as the matrix in a reflection mode. Elemental analysis was performed on a FlashEA1112 elemental analyser. High temperature gel permeation chromatography (HT-GPC) analysis was conducted on a PL-GPC 220 system at 150 ^{o}C with 1,2,4-trichlorobenzene as the eluent and polystyrene as the standard. Thermogravimetric analysis (TGA) was conducted on a TA Q50 thermogravimetric analyser under nitrogen flow with the heating rate of 10 ^{o}C min^{-1}. Differential scanning calorimetry (DSC) was carried out on a TA Q25 instrument with a heating/cooling rate of 10 ^{o}C min^{-1} under nitrogen flow. UV-*vis*-NIR absorption spectra were recorded by Shimadzu UV-3600Plus spectrometer. Solution spectra were measured in anisole, *o*-xylene or 1,2-dichlorobenzene (*o*-DCB) with a concentration of 1×10^{-5} mol L^{-1}, and films were prepared by spin-coating the anisole, *o*-xylene and *o*-DCB solutions on quartz substrates. Film cyclic voltammetry (CV) measurement was performed on a CHI660E electrochemical analyser with a three-electrode cell at a scan rate of 100 mV s^{-1} in anhydrous acetonitrile. A glassy carbon electrode with a diameter of 6 mm, a Pt wire, and a saturated calomel electrode (SCE) were used as the working, counter, and reference electrodes, respectively. Tetrabutylammonium hexafluorophosphate

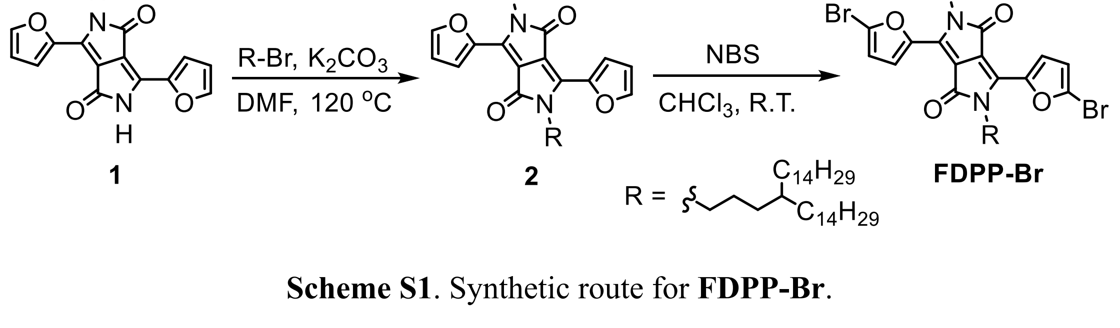
(Bu_4NPF_6, 0.1 mol L^{-1}) was used as the supporting electrolyte. In plane and out of plane X-ray diffraction (XRD) of the films were measured by a Rigaku Smart Lab with Cu $K_α$ source (λ = 1.54056 Å) in air. Atomic force microscopy (AFM) measurements were performed in tapping mode on a Bruker MultiMode 8 instrument.

Fabrication and characterization of organic thin-film transistors (OTFTs)

The silicon wafers with a 300 nm thick SiO_2 layer were washed by an ultrasonic cleaner with deionized water, acetone and isopropanol, then dried under a nitrogen flow and heated at 120 °C for 10 min. Au (30 nm) was vacuum-evaporated on the substrate as the source and drain electrodes with an interdigitated electrode pattern (W/L = 70, W = 5600 μm, L = 80 μm). For PEIE-modified OTFTs, the pre-patterned substrates were treated with UV-zone for 15 min, and 0.08 wt% PEIE solution (prepared by diluting 37 wt% PEIE water solution with 2-methoxyethanol) was spin-coated at 5000 rpm for 60 s, followed by thermal annealing at 100 °C for 10 min. Subsequently, the semiconductor films were prepared by spin-coating at 1000 rpm or bar-coating on the hot stage of 100 °C from polymer solutions (3.0 mg mL^{-1}) with anisole, *o*-xylene and *o*-DCB as solvent, respectively, followed by thermal annealing at 200 °C for 10 min. During bar-coating, the conjugated polymer solution with a confined volume was spread over the substrate with a coating speed of 40 mm s^{-1}. The term "parallel" is defined as when the bar-coating direction is parallel to the source-drain field. After that, poly(methyl methacrylate) (PMMA, M_w = 120 kDa) solution (80 mg mL^{-1}, butyl acetate) was spin-coated on the top of semiconductor layer as the dielectric layer (~600 nm) at 1300 rpm, then annealed at 100 °C for 40 min. Finally, Al (80 nm) was vacuum-evaporated as gate electrode. All the spin-coating and bar-coating processes were conducted in a glovebox and OTFTs were measured under ambient conditions with Keysight B1500A semiconductor analyser. Field-effect mobility in saturation regime was calculated by using the equation: $I_{DS}^{sat} = (\mu C_i W/2L)(V_{GS}-V_T)^2$, in which I_{DS} is the drain-source current, μ is the field-effect mobility, C_i (4.6 nF cm^{-2}) is the capacitance per unit area of the dielectric layer, V_{GS}, V_{DS} and V_T are the gate voltage, drain voltage and threshold voltage, respectively.

Synthesis procedure

N, *N*-Dimethylformamide (DMF) was dried over CaH_2 and distilled under reduced pressure. Toluene was dried over sodium with benzophenone as an indicator. 3,6-difuranyl-2,5-diketopyrrolo[3,4-*c*]pyrrole (**1**), **4FTVT** and **4ClTVT** were synthesized according to previously reported procedures.[1-3] Other chemical reagents were purchased from Sigma-Aldrich, Alfa-Aesar Energy Chemical and J&K Scientific and used as received.



Scheme S1. Synthetic route for **FDPP-Br**.

2,5-Bis(4-tetradecyloctadecyl)-3,6-difuran-2-yl-pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**2**): **1** (885.2 mg, 3.3 mmol), 15-(3-iodopropyl)nonacosane (4.47 g, 7.8 mmol), anhydrous potassium carbonate (K_2CO_3) (1.37 g, 9.9 mmol) and 18-crown-6-ether (10.0 mg, 37.8 μmol) were dissolved in anhydrous DMF (40 mL) in a threenecked flask. The mixture was stirred at 120 °C for 12 h. After removal of the solvent, the residue was dissolved in dichloromethane, and washed with brine. The combined organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by chromatography (silica gel, dichloromethane: petroleum ether = 1:1) to give compound **2** as a dark red solid (3.47 g, yield: 90%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.31 (d, J = 3.6 Hz, 2H), 7.62 (d, J = 1.6 Hz, 2H), 6.70 (dd, J = 3.6, 1.6 Hz, 2H), 4.08 (t, J = 7.6 Hz, 4H), 1.71-1.60 (m, 4H), 1.45-1.06 (m, 110H), 0.88 (t, J = 6.8 Hz, 12H). Elemental Anal. calcd. for $C_{78}H_{136}N_2O_4$: C 80.35, H 11.76, N 2.40; Found: C 81.16, H 11.08, N 2.46; HRMS (MALDI-TOF) *m/z*: calcd. for $C_{78}H_{136}N_2O_4$: 1165.0500; Found.1165.0501.

3,6-Bis(5-bromofuran-2-yl)-2,5-bis(4-tetradecyloctadecyl)-pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**FDPP-Br**): To a solution of compound **2** (1.55 g, 1.3 mmol) in chloroform (50 mL), *N*-bromosuccinimide (NBS) (521.3 mg, 2.9 mmol) was added slowly at 0 °C. The mixture was stirred at room temperature for 6 h in the absence of light. After removal of the solvent, the residue was purified by chromatography (silica gel, dichloromethane: petroleum ether = 1:1) to give **FDPP-Br** as a dark red solid (1.20 g, yield: 68%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.26 (d, J = 3.6 Hz, 2H), 6.63 (d, J = 3.6 Hz, 2H), 4.02 (t, J = 7.6 Hz, 4H), 1.71-1.60 (m, 4H), 1.45-1.06 (m, 110H), 0.88 (t, J = 6.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 160.48, 146.18, 132.52, 126.44, 122.13, 115.53, 106.27, 42.89, 37.21, 33.60, 31.95, 30.63, 30.12, 29.73, 29.69, 29.40, 27.44, 26.69, 22.72, 14.15. Elemental Anal. calcd. for $C_{78}H_{134}Br_2N_2O_4$: C 70.77, H 10.20, N 2.12; Found: C 71.63, H 9.69, N 2.13; HRMS (MALDI-TOF) *m/z*: calcd. for $C_{78}H_{134}Br_2N_2O_4$: 1322.8690; Found.1322.8708.

Fu-F: **FDPP-Br** (154.3 mg, 116.6 μmol, 1 eq.), **4FTVT** (30.8 mg, 116.6 μmol, 1 eq.), Herrmann′s catalyst (2.2 mg, 2.3 μmol, 2 mol%), P(*o*-MeOPh)$_3$ (1.6 mg, 4.6 μmol, 4 mol%), PivOH (11.9 mg, 116.6 μmol, 1 eq.) and Cs_2CO_3 (113.9 mg, 349.7 μmol, 3 eq.) were added into a pressure-proof-tube. The tube was sealed with a cap after anhydrous toluene (11.7 mL) was added in a glovebox. The mixture was stirred at 120 °C for 24 h. After cooling to room temperature, the mixture was precipitated in methanol. The precipitate was collected by filtration and purified by Soxhlet extraction with ethanol, acetone and hexane in succession. The remaining solid dissolved in *o*-DCB, and filtered by 0.45 μm filter. **Fu-F** was obtained as a black solid by precipitating the *o*-DCB solution in methanol, filtrated, and then dried in a vacuum (90%). GPC: M_n = 37.2 kDa, $Đ$ = 2.1. Elemental Anal. Calcd. for $(C_{88}H_{138}F_4N_2O_4S_4)_n$: C 74.01, H 9.74, N 1.96, S 4.49; Found: C 73.54, H 9.88, N 2.07, S 4.35.

Fu-Cl: **Fu-Cl** was obtained as a black solid (171.8 mg, yield 82%) from **FDPP-Br** (185.7 mg, 140.3 μmol, 1 eq.), **4ClTVT** (46.3 mg, 140.3 μmol, 1 eq.), Herrmann′s catalyst (2.6 mg, 2.8 μmol, 2 mol%), P(*o*-MeOPh)$_3$ (2.0 mg, 5.6 μmol, 4 mol%), PivOH (14.3 mg, 140.3 μmol, 1 eq.) and Cs_2CO_3 (137.1 mg, 420.8 μmol, 3 eq.) in toluene (7.0 mL) following the same procedure for the synthesis of **Fu-F**. GPC: M_n = 63.0 kDa, $Đ$ = 2.3. Elemental Anal. Calcd. for $(C_{88}H_{138}Cl_4N_2O_4S_2)_n$: C 70.75, H 9.31, N 1.88, S 4.29; Found: C 69.38, H 9.47, N 2.02, S 4.35.

Supplementary data

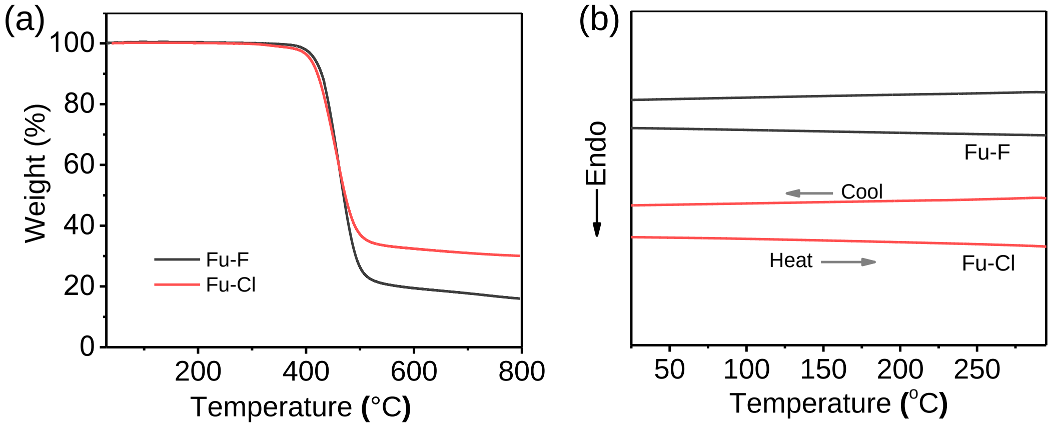
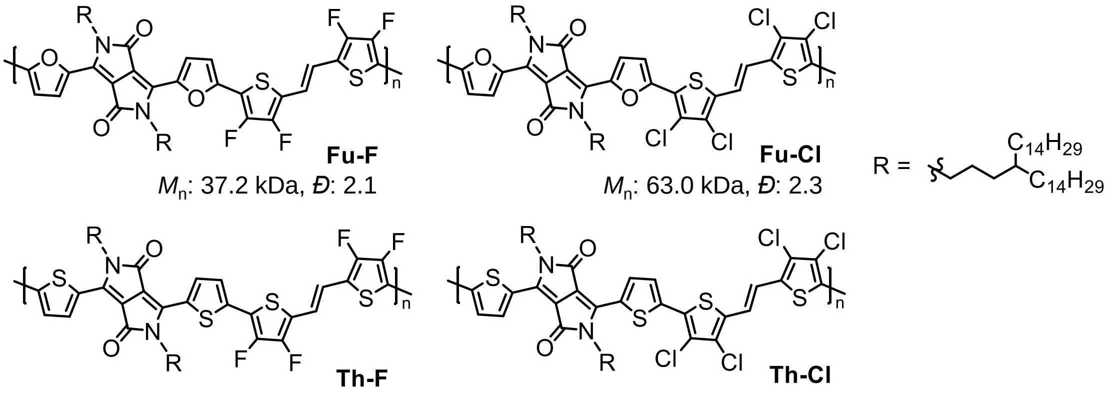


Figure S1. TGA (a) and DSC (b) curves of the polymers.

Table S1. Solubility of the polymers.



M_n: 37.2 kDa, $Đ$: 2.1

M_n: 63.0 kDa, $Đ$: 2.3

M_n: 30.1 kDa, $Đ$: 2.9

M_n: 70.6 kDa, $Đ$: 2.0

solvent		anisole				*o*-xylene				*o*-DCB			
conc. (mg mL^{-1})	temp. (^{o}C)	**Fu-F**	**Fu-Cl**	**Th-F**	**Th-Cl**	**Fu-F**	**Fu-Cl**	**Th-F**	**Th-Cl**	**Fu-F**	**Fu-Cl**	**Th-F**	**Th-Cl**
10	100	+	+	-	-	+	+	+	+	+	+	+	+
	70	+	-	-	-	+	+	+	+	+	+	+	+
	25	-	-	-	-	+	+	-	-	+	+	+	+
5	100	+	+	-	-	+	+	+	+	+	+	+	+
	70	+	+	-	-	+	+	+	+	+	+	+	+
	25	-	-	-	-	+	+	+	+	+	+	+	+

+ Soluble; - unsoluble.

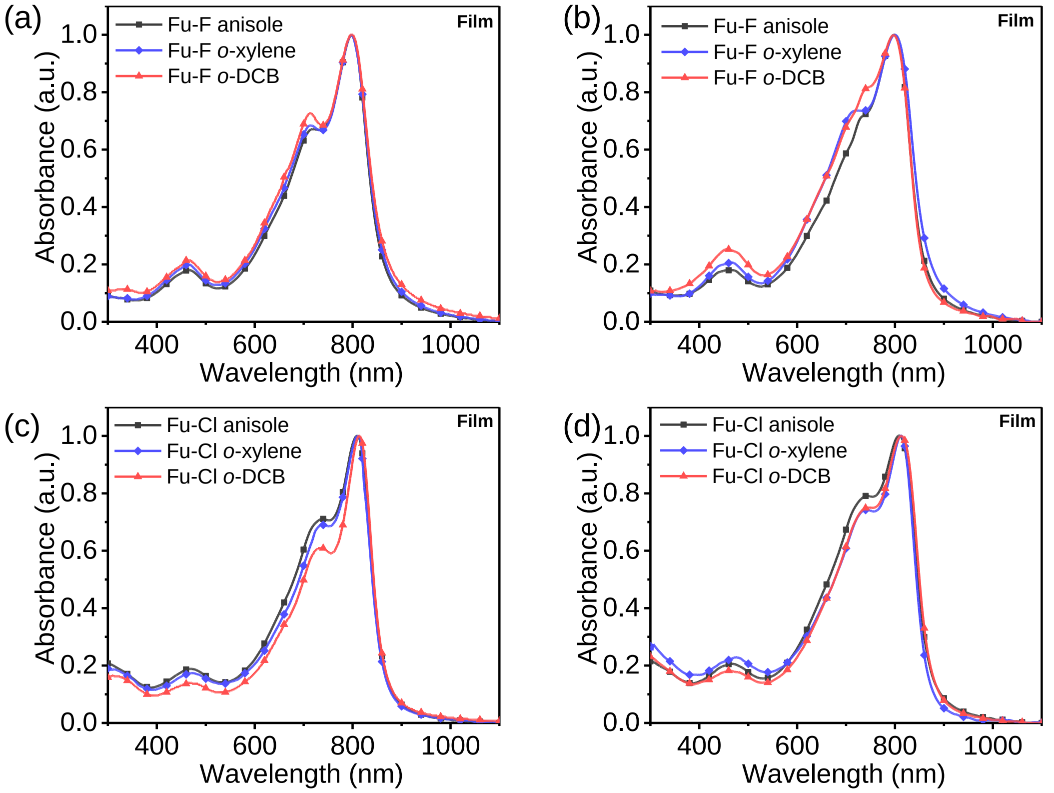


Figure S2. Film UV-vis-NIR absorption spectra of **Fu-F** (a, b) and **Fu-Cl** (c, d). Films were prepared by spin-coating the anisole, *o*-xylene and *o*-DCB solutions on quartz substrates with (b, d) and without (a, c) thermal annealing at 200 ºC.

Table S2. Optical properties of the polymer films.

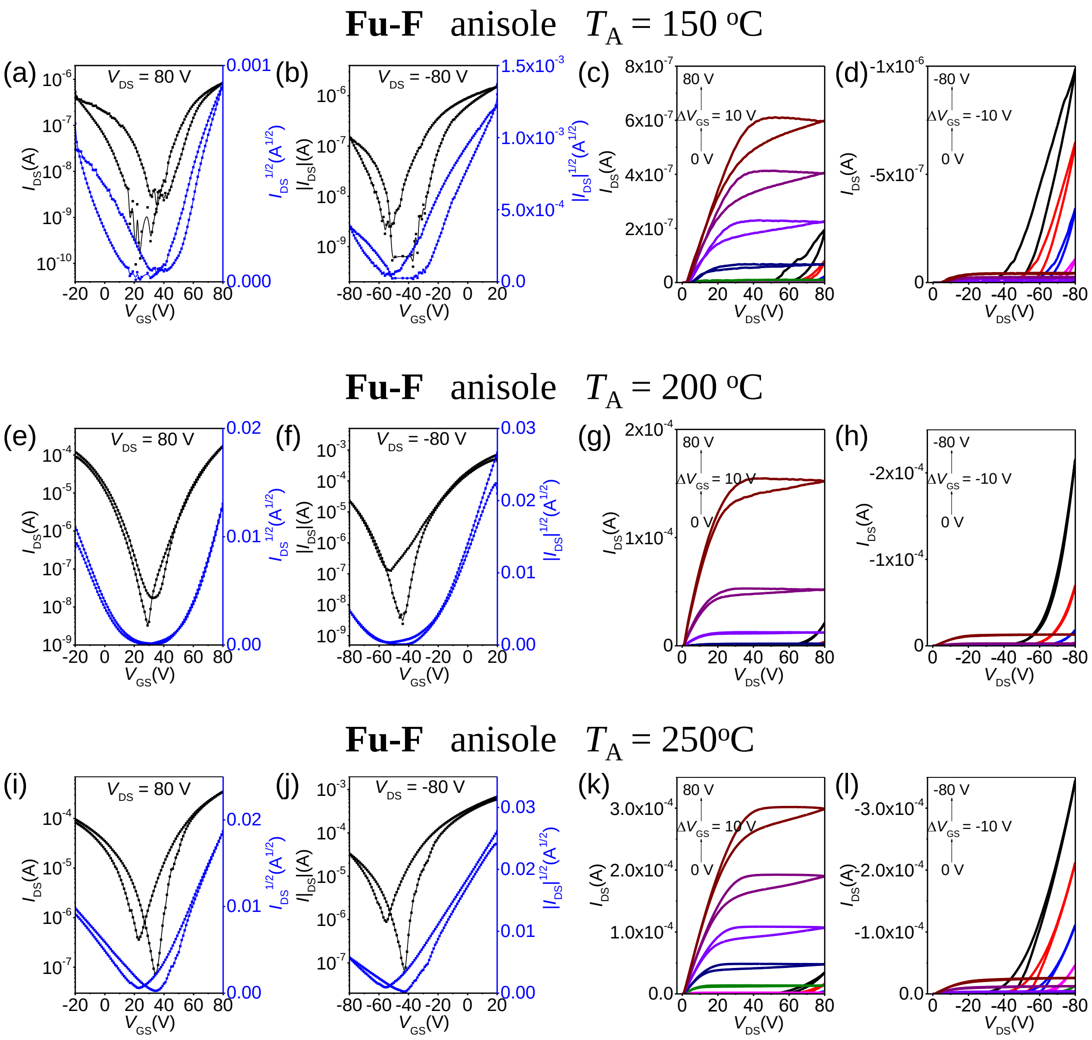
	anisole		*o*-xylene		*o*-DCB	
polymer	$\lambda_{\max}^{\text{film a}}$ (nm)	$\lambda_{\max}^{\text{film b}}$ (nm)	$\lambda_{\max}^{\text{film a}}$ (nm)	$\lambda_{\max}^{\text{film b}}$ (nm)	$\lambda_{\max}^{\text{film a}}$ (nm)	$\lambda_{\max}^{\text{film b}}$ (nm)
Fu-F	719,799	731, 799	713, 797	718, 799	713,799	740, 798
Fu-Cl	735, 810	742, 810	737, 811	740, 812	733, 814	743, 813

[a] The absorption maxima of the pristine films. [b] The absorption maxima of the films after thermal annealing at 200 °C for 10 min.

Table S3. The performance of spin-coated OTFT devices of the polymers[a].

		without modification						with PEIE modification		
		n-channel			p-channel			n-channel		
polymer	T_A[b] (°C)	$\mu_{e,max}$[c] ($\mu_{e,avg}$[d]) ($cm^2V^{-1}s^{-1}$)	V_T[e] (V)	I_{on}/I_{off}[f]	$\mu_{h,max}$[g] ($\mu_{h,avg}$[h]) ($cm^2V^{-1}s^{-1}$)	V_T[e] (V)	I_{on}/I_{off}[f]	$\mu_{e,max}$[c] ($\mu_{e,avg}$[d]) ($cm^2V^{-1}s^{-1}$) r[i] (%)	V_T[e] (V)	I_{on}/I_{off}[f]
Fu-F	150	2.8×10^{-3} (1.7×10^{-3})	33~39	10^2~10^3	7.1×10^{-4} (6.2×10^{-4})	-42~-47	10^2~10^3	1.26 (1.12) 83%	7~10	10^5~10^6
	200	1.30 (1.15)	50~55	10^4~10^5	0.36 (0.32)	-58~-62	10^3~10^4			
	250	0.94 (0.81)	28~32	10^3~10^4	0.17 (0.13)	-44~-47	10^2~10^3			
Fu-Cl	150	1.0×10^{-2} (9.2×10^{-3})	44~48	10^2~10^3	2.0×10^{-3} (1.6×10^{-3})	-40~-45	10^2~10^3	1.2×10^{-2} (9.3×10^{-3}) 76%	10~15	10^3~10^4
	200	1.1×10^{-2} (8.9×10^{-3})	29~34	10^4~10^5	2.7×10^{-3} (2.2×10^{-3})	-39~-44	10^2~10^3			
	250	5.2×10^{-3} (4.6×10^{-3})	27~32	10^3~10^4	1.7×10^{-3} (1.0×10^{-3})	-33~-39	10^2~10^3			

[a]The devices were measured under ambient conditions. [b]Thermal annealing temperature. [c]Maximum electron mobility calculated from the saturation regime. [d]Average electron mobility calculated from at least 15 devices. [e]Threshold voltage. [f]Current on/off ratio. [g]Maximum hole mobility calculated from the saturation regime. [h]Average hole mobility calculated from at least 15 devices. [i]Reliability factor.



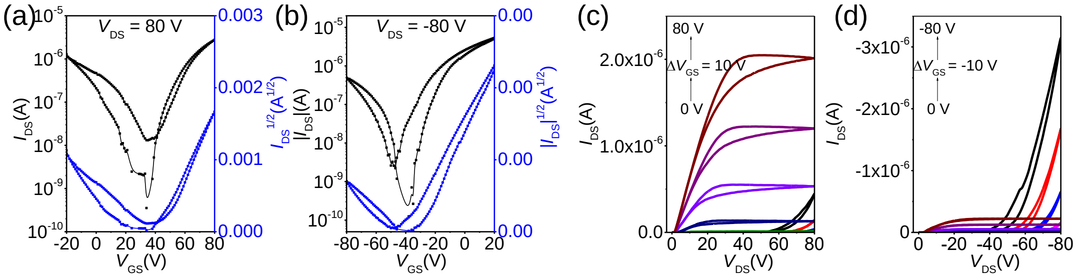
Fu-F anisole T_A = 150 °C

Fu-F anisole T_A = 200 °C

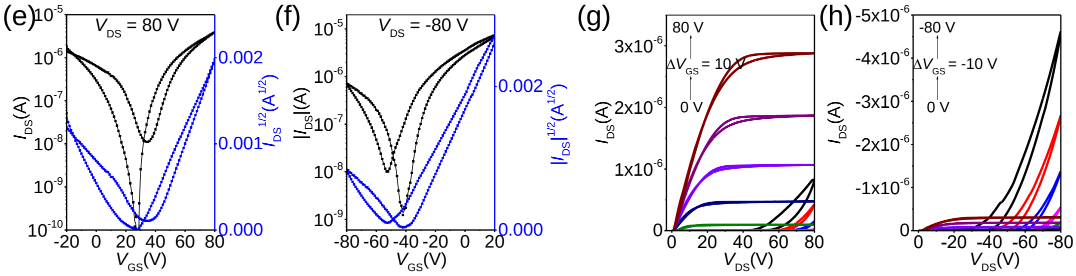
Fu-F anisole T_A = 250°C

Figure S3. Typical transfer (a, b, e, f, i, j) and output (c, d, g, h, k, l) curves of the spin-coated OTFTs based on **Fu-F**. Polymer films were prepared from anisole solution on bare Si/SiO2 substrates and annealed at 150, 200 or 250 °C for 10 min under an inert atmosphere.

Fu-Cl anisole T_A = 150 °C



Fu-Cl anisole T_A = 200 °C



Fu-Cl anisole T_A = 250°C

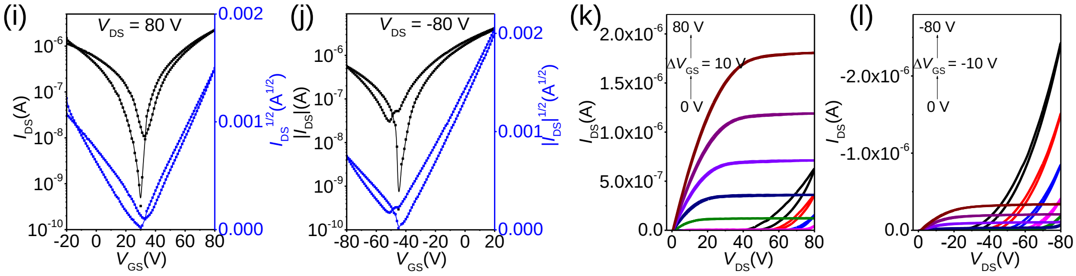
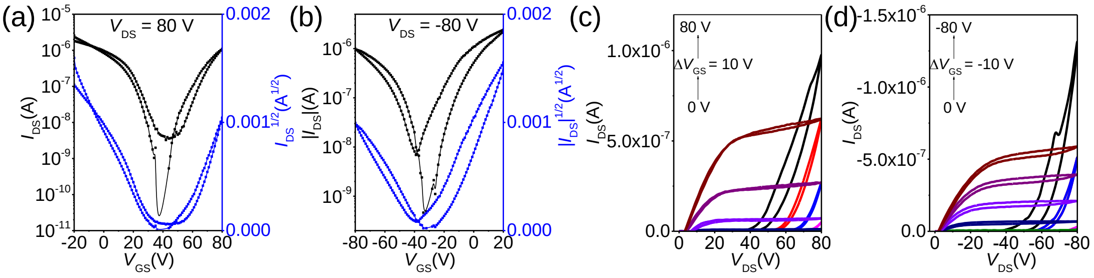
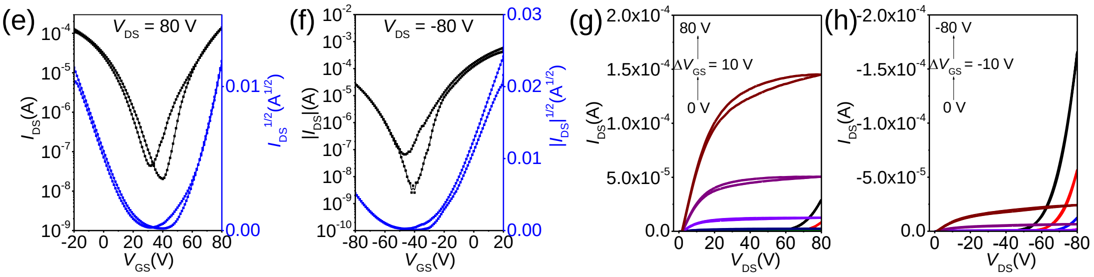


Figure S4. Typical transfer (a, b, e, f, i, j) and output (c, d, g, h, k, l) curves of the spin-coated OTFTs based on **Fu-Cl**. Polymer films were prepared from anisole solution on bare Si/SiO_2 substrates and annealed at 150, 200 or 250 °C for 10 min under an inert atmosphere.

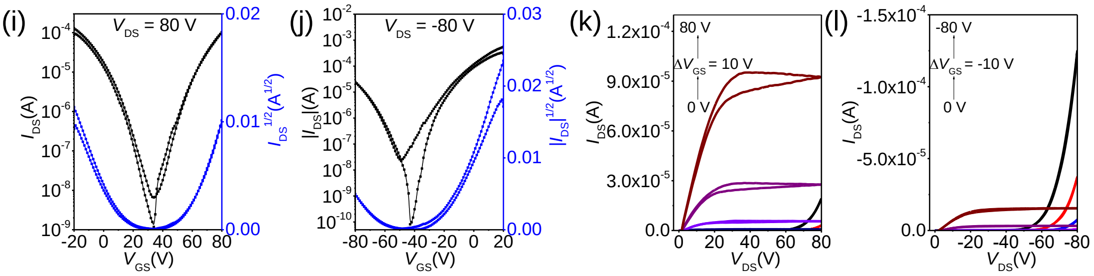
Fu-F anisole T_A = 150 °C



Fu-F anisole T_A = 250 °C



Fu-F *o*-xylene T_A = 200°C



Fu-F *o*-DCB T_A = 200°C

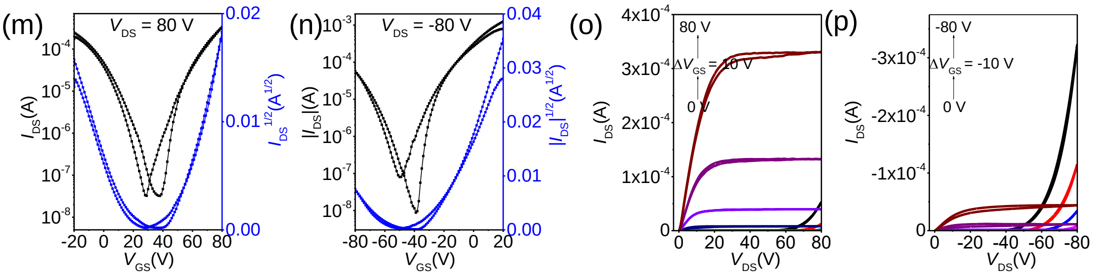


Figure S5. Typical transfer (a, b, e, f, i, j, m, n) and output (c, d, g, h, k, l, o, p) curves of the bar-coated OTFTs based on **Fu-F**. Polymer films were prepared from anisole, *o*-xylene or *o*-DCB solution on bare Si/SiO_2 substrates and annealed at 150, 200 or 250 °C for 10 min under an inert atmosphere.

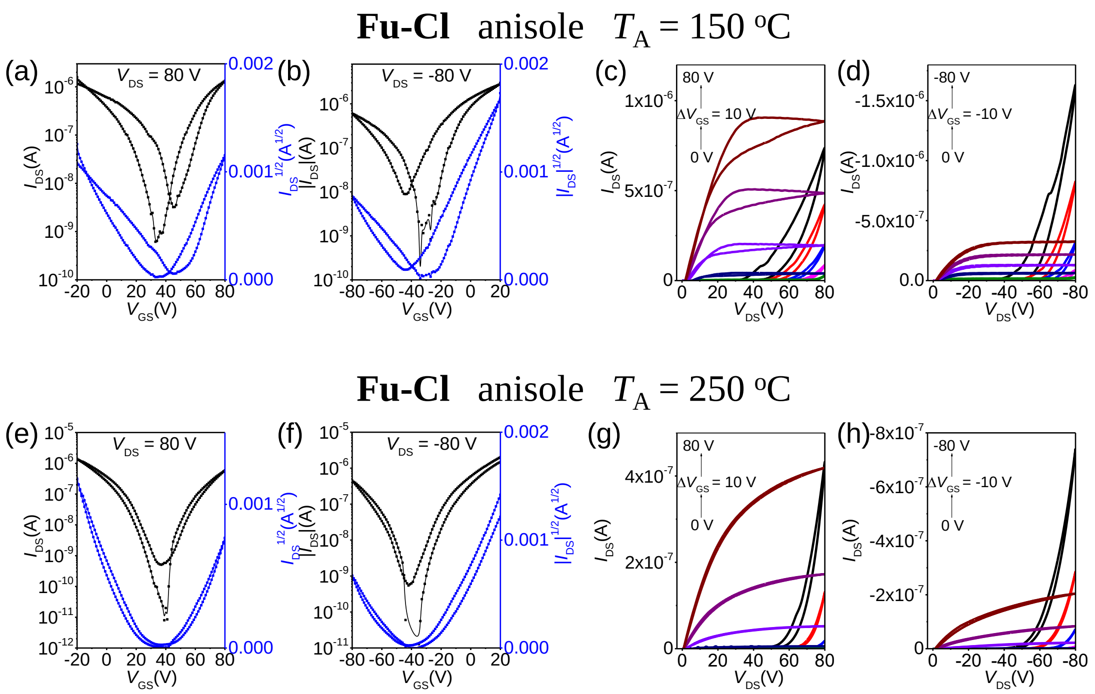


Figure S6. Typical transfer (a, b, e, f) and output (c, d, g, h,) curves of the bar-coated OTFTs based on **Fu-Cl**. Polymer films were prepared from anisole solution on Si/SiO2 substrates and annealed at 150 °C or 250 °C for 10 min under an inert atmosphere.

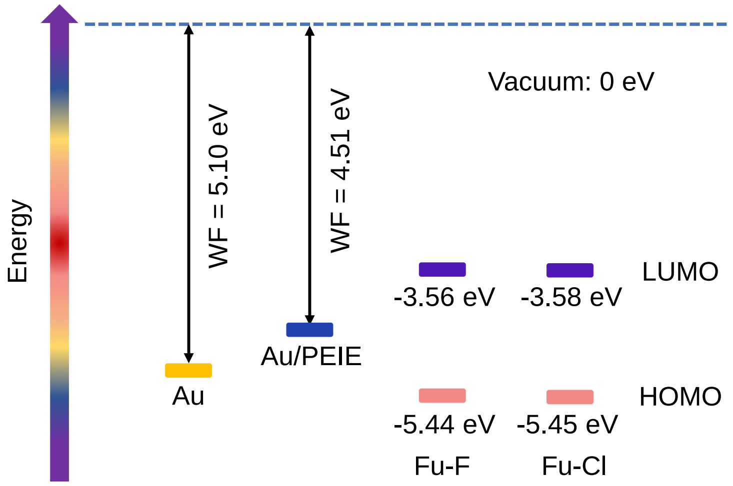
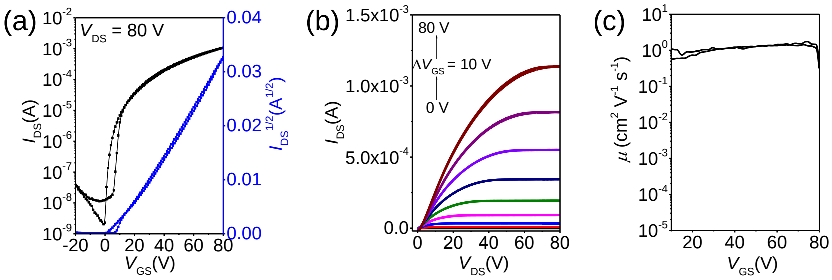


Figure S7. Energy level diagrams of Au, Au modified with PEIE, and the thin films of **Fu-F** and **Fu-Cl**. The work function of Au and Au modified with PEIE were measured by Kelvin probe microscopy.[4]

Fu-F anisole T_A = 200 °C



Fu-Cl anisole T_A = 200 °C

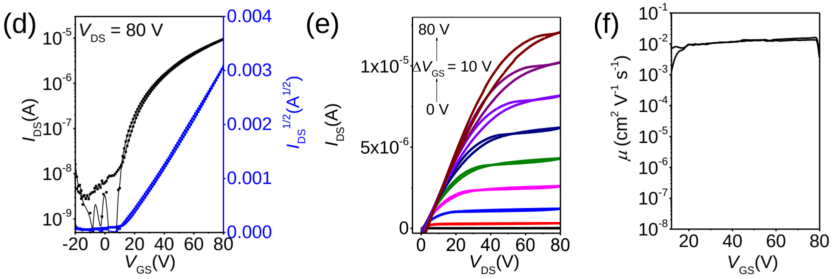
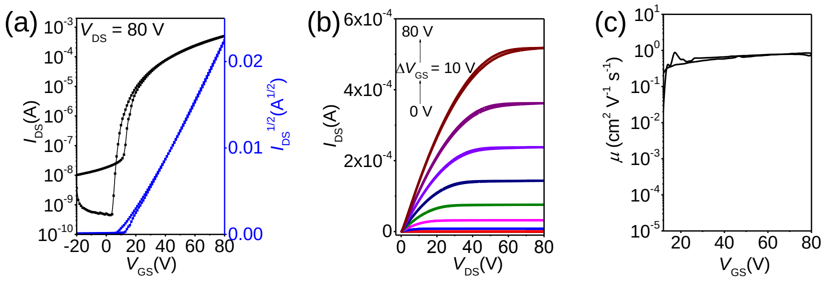


Figure S8. Typical transfer (a, d), output (b, e) curves and saturation mobility versus V_{GS} (c, f) of the spin-coated OTFTs based on **Fu-F** (a, b, c) and **Fu-Cl** (d, e, f). Polymer films were prepared from anisole solution on 0.08wt% PEIE-modified substrates and annealed at 200°C for 10 min under an inert atmosphere.

Fu-F *o*-xylene T_A = 200 ^{o}C



Fu-F *o*-DCB T_A = 200 ^{o}C

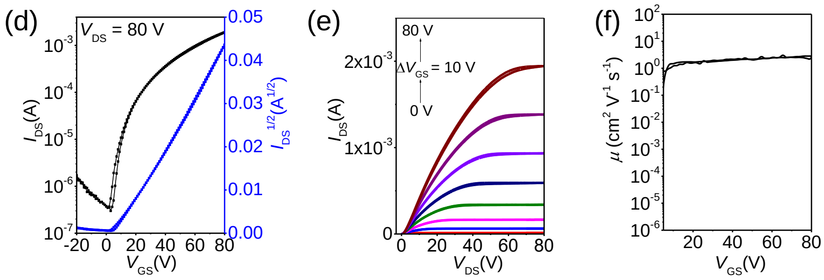


Figure S9. Typical transfer (a, d), output (b, e) curves and saturation mobility versus V_{GS} (c, f) of the bar-coated OTFTs based on **Fu-F**. Polymer films were prepared from *o*-xylene (a, b, c) or *o*-DCB (d, e, f) solution on 0.08wt% PEIE-modified substrates and annealed at 200ºC for 10 min under an inert atmosphere.

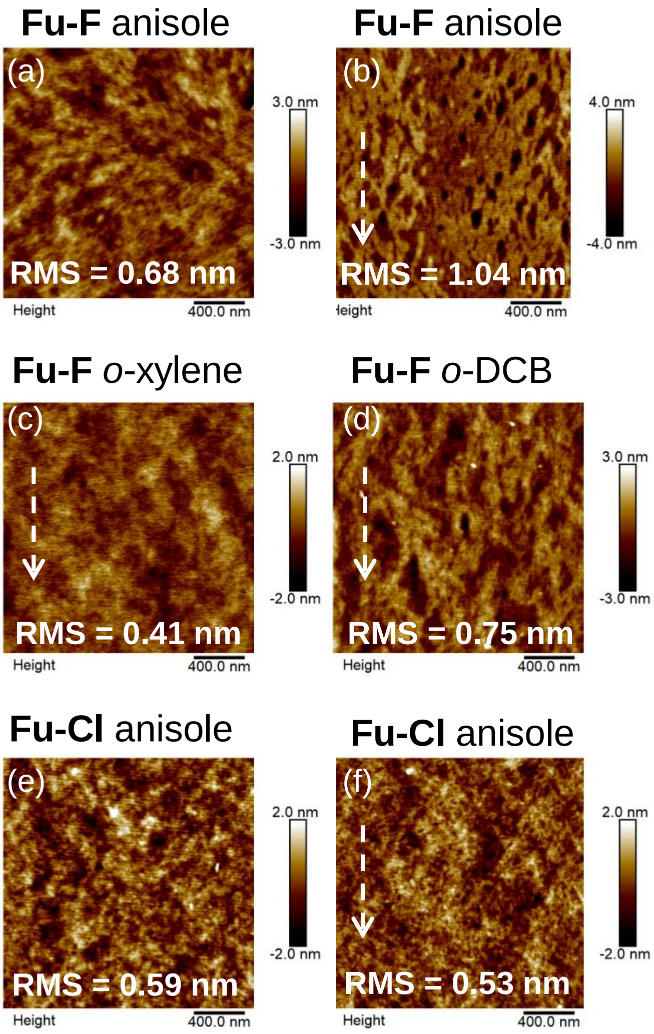


Figure S10. AFM height images (2 μm × 2 μm) of the spin-coated (a, e) and bar-coated (b, c, d, f) polymer films from anisole, *o*-xylene and *o*-DCB solutions. Thin films were prepared on 0.08wt% PEIE-modified Si/SiO_2 substrates and annealed at 200 °C for 10 min under an inert atmosphere. The arrows in the images denote bar-coating direction.

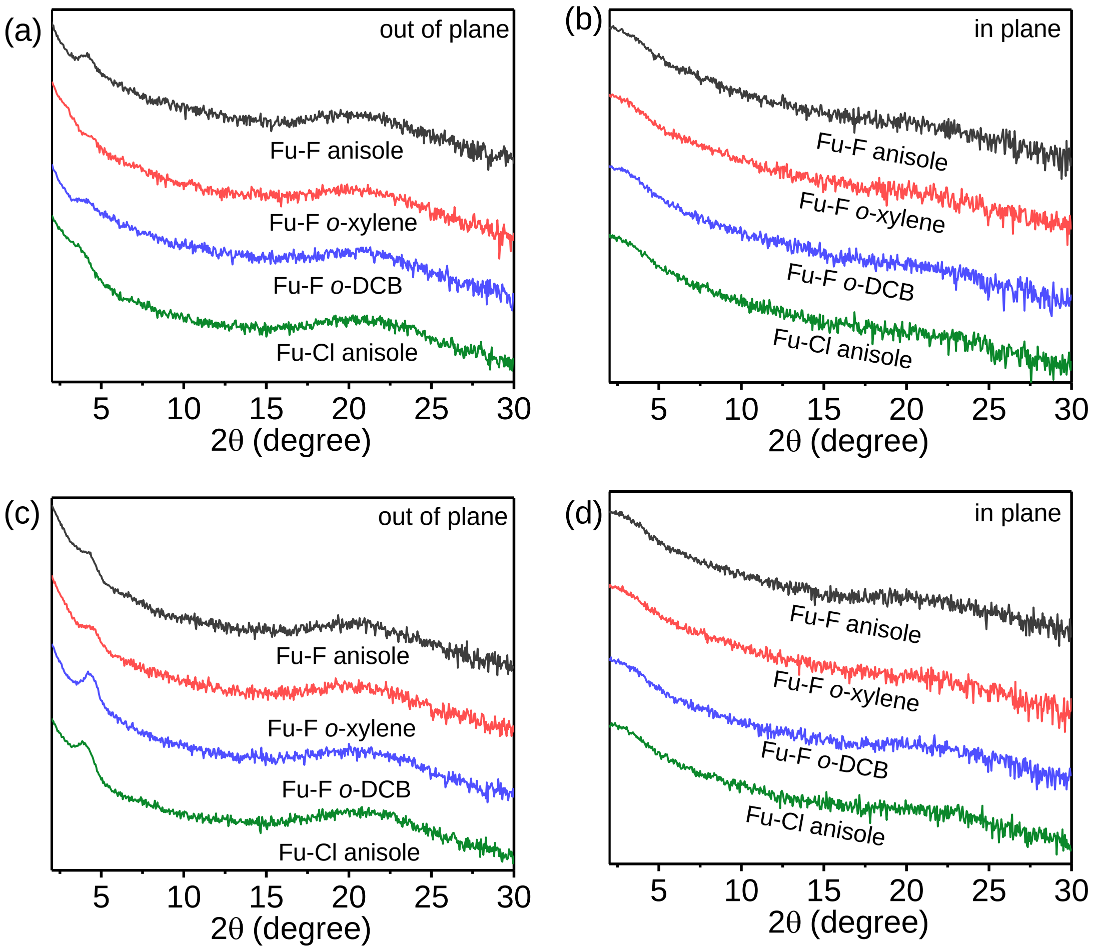


Figure S11. Out-of-plane (a, c) and in-plane (b, d) XRD spectra of the bar-coated polymer films from anisole, *o*-xylene and *o*-DCB solutions. The coating direction of the film is parallel to the incident light. Thin films were prepared on bare Si/SiO_2 substrates (a, b) and 0.08wt% PEIE-modified substrates (c, d), and thermally annealed at 200°C for 10 min under an inert atmosphere.

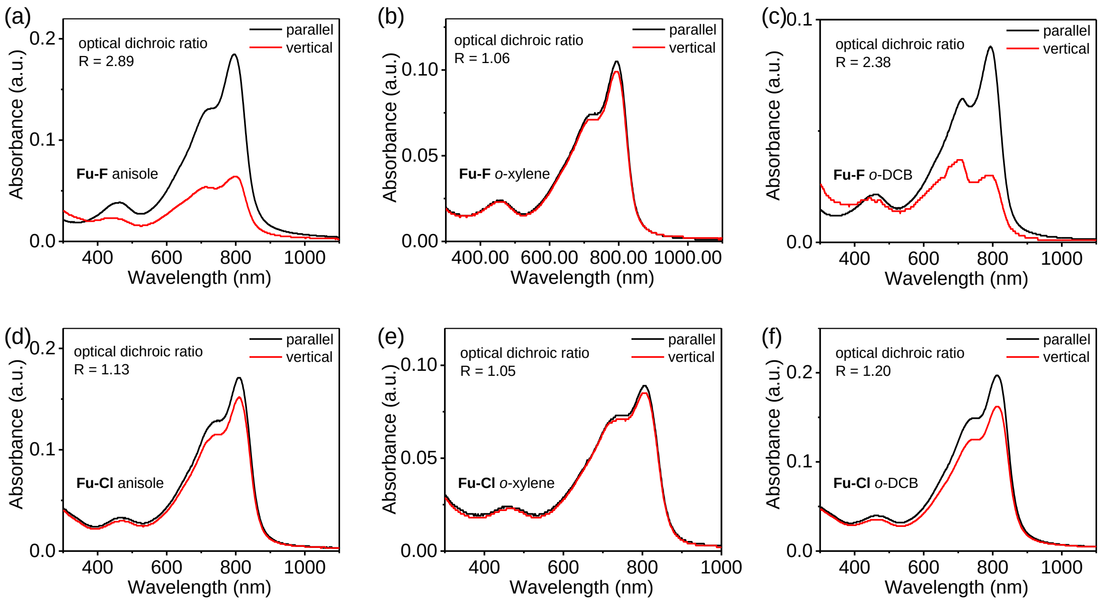


Figure S12. Linearly polarized absorption spectra of bar-coated films of **Fu-F** (a, b, c) and **Fu-Cl** (d, e, f) in parallel direction (black line) and vertical direction (red line) prepared from anisole (a, d), *o*-xylene (b, e) and *o*-DCB (c, f) solutions.

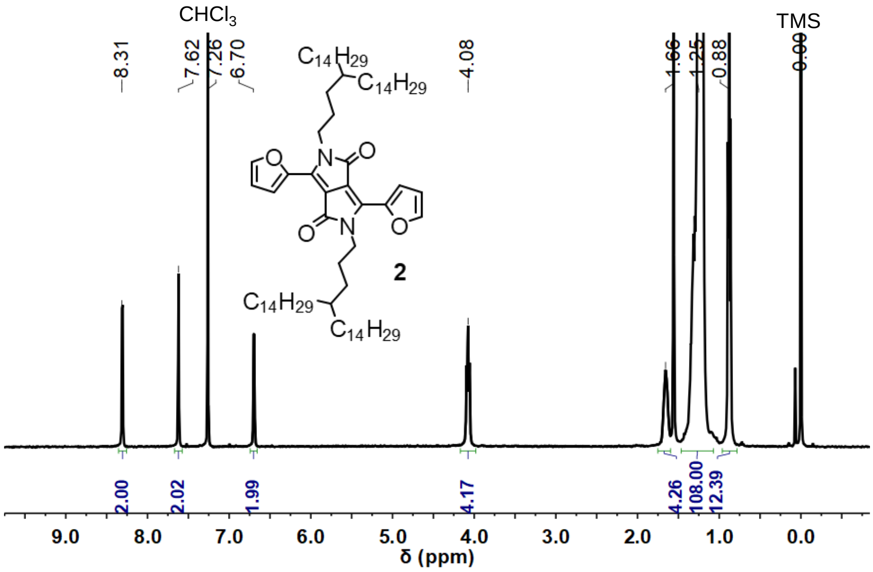


Figure S13. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of compound **2**.

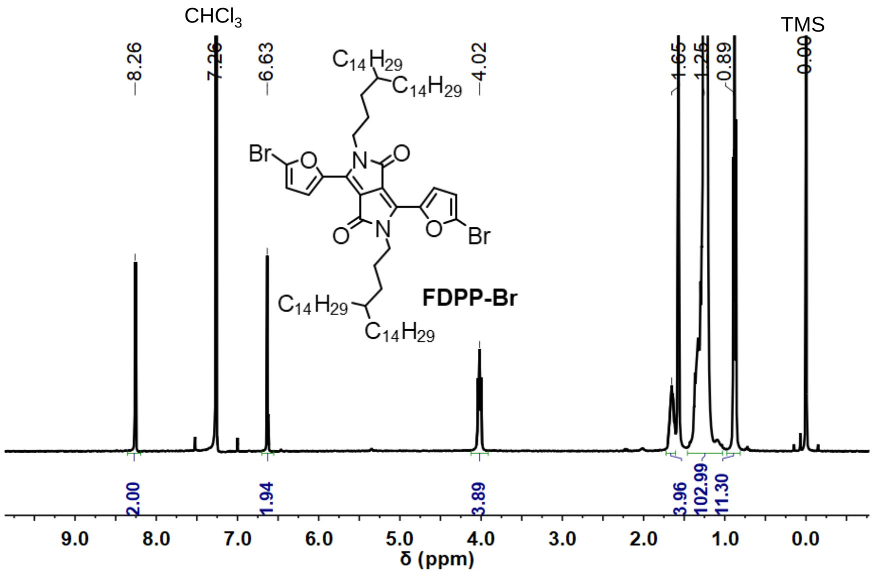


Figure S14. ^{1}H NMR spectrum (400 MHz, CDCl3, 25 °C) of **FDPP-Br**.

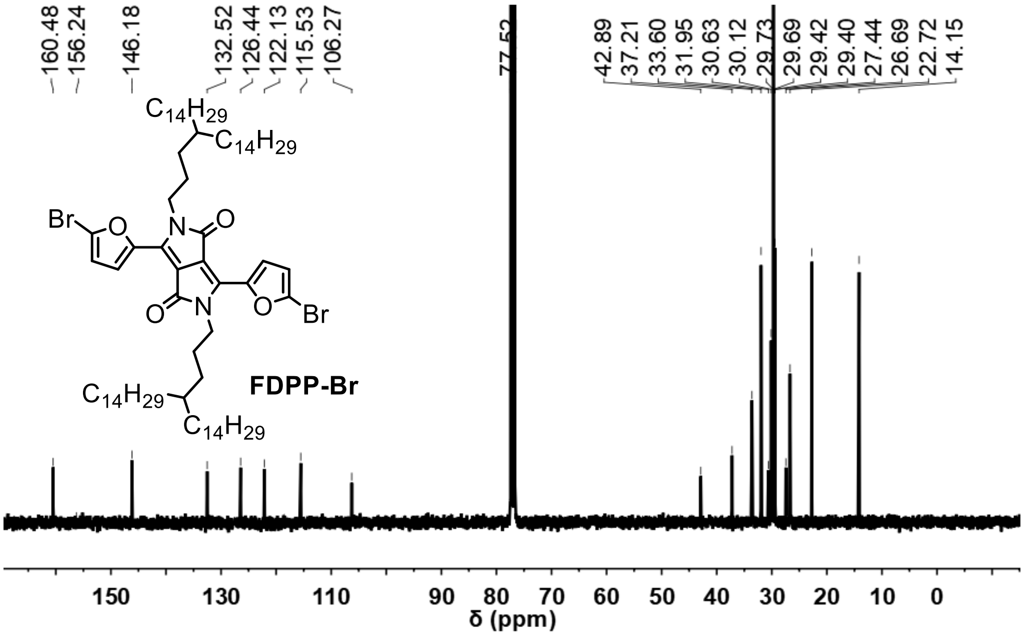


Figure S15. ^{13}C NMR spectrum (100 MHz, CDCl3, 25 °C) of **FDPP-Br**.

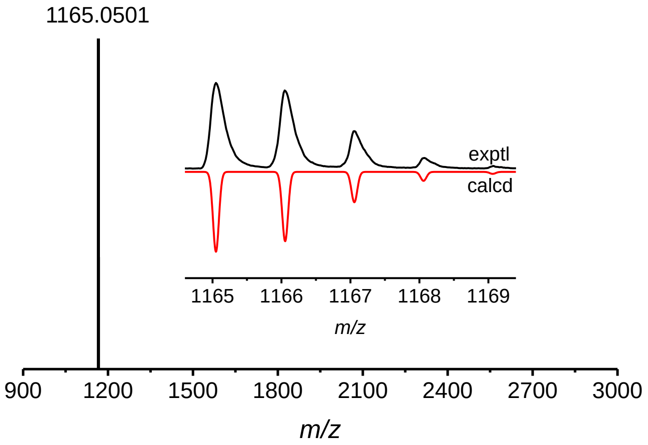


Figure S16. High-resolution MALDI-TOF mass spectrum of compound **2**.

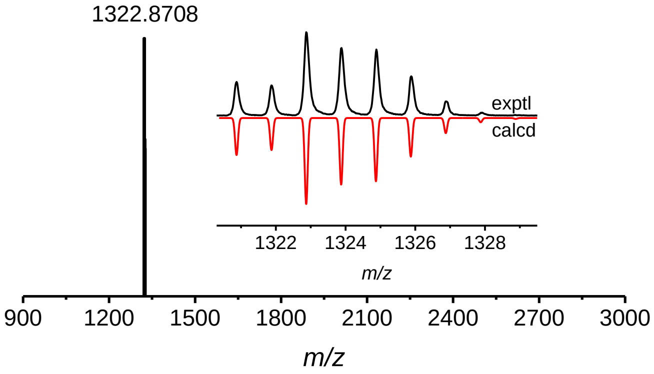


Figure S17. High-resolution MALDI-TOF mass spectrum of **FDPP-Br**.

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