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Fluorine Substitution Influence on Benzo[2,1,3]thiadiazole Based Polymers for Field-Effect Transistor Applications

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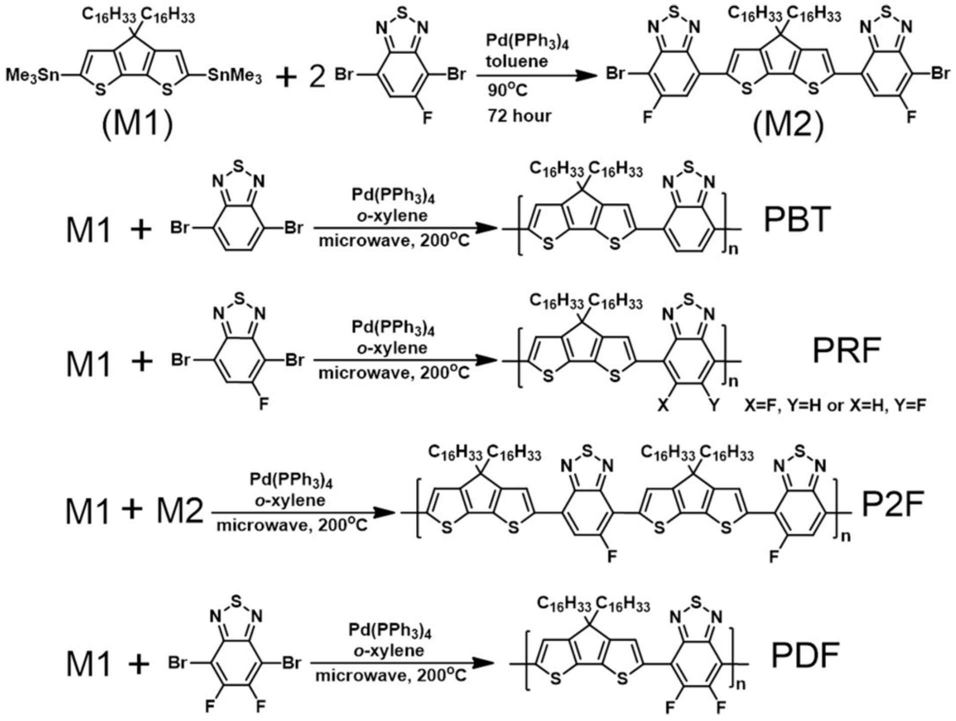
Supporting Information

Content

1. General methods

Microwave reactions were performed using a Biotage microwave reactor. Ultraviolet-Visible (UV-Vis) absorption spectra were recorded on a Perkin Elmer Lambda 750 spectrophotometer. Nuclear magnetic resonance (NMR) spectra were obtained on Varian 500 MHz spectrometer. Gel permeation chromatography (GPC) was performed in chloroform ($CHCl_3$) on a Waters 2690 Separation Module equipped with a Waters 2414 Refractive Index Detector and a Waters 2996 Photodiode Array Detector. Molecular weights were calculated relative to linear PS standards. Differential scanning calorimetry (DSC) was determined by a TA Instruments DSC (Model Q-20) with about 3 mg polymers samples at a rate of 10 °C / min in the temperature range of 50 to 350 °C. Cyclic voltammetry (CV) measurements were tested on a CHI-730B electrochemistry workstation. OFET Devices were measured under nitrogen in a glovebox using a Signatone 1160 probe station and Keithley 4200 semiconductor parametric analyzer. Mobility values calculated from a gate voltage range of -30 V to -50 V at a source-drain voltage of -80 V. Tapping-mode atomic force microscopy (AFM) images were obtained in air using an Innova AFM. Grazing incidence wide angle X-ray scattering (GIWAXS) measurements were performed at beamline 7.3.3 at the Advanced Light Source (ALS) Berkeley Lab with an X-ray wavelength of 0.124 nm. Samples were scanned in a He environment at an incident angle of 0.12^{o}.

2. Synthesis



Scheme S1. Synthesis of polymers

(4,4-Dihexadecyl-4H-cyclopenta[1,2-b:5,4-b']dithiophene-2,6-diyl)bis(trimethylstannane) (**M1**) was synthesized according to the reported procedure. 4,7-Dibromo-benzo[*c*][1,2,5]thiadiazole (**BT**) was purchased from Sigma-Aldrich Co. and purified via flash column using silica gel and chloroform and hexane mixture as the eluent. 4,7-Dibromo-5-fluoro-benzo[*c*][1,2,5]thiadiazole (**FBT**) and 4,7-Dibromo-5,6-difluoro-benzo[*c*][1,2,5]thiadiazole (**DFBT**)was purchased from Lumtec Co. and used as received. $Pd(PPh_3)_4$ was purchased from Strem Co. Anhydrous *o*-xylene was purchased from Acros Co.

5,5'-bis{(4-(6-fluoro-7-bromo-[1,2,5]thiadiazolobenzene)}-{4,4-bis(hexadecyl)cyclopenta-[2,1-b: 3,4-b']-dithiophene} (**M2**):

A 25 mL microwave reaction vial was charged with **M1** (952 mg, 1 mmol, 1.0 eq), **FBT** (780 mg, 2.5 mmol, 2.5 eq), $Pd(PPh_3)_4$ (60 mg, 0.05 mmol, 0.05 eq), and dry toluene (15 mL) inside the glovebox box. The reaction vial was then sealed using a Teflon®cap and moved out of the dry box. The reaction mixture was stirred at 90°C in a conventional oil bath for 72 hours. Then the product was purified via silica-gel

(200 mesh) column chromatography (20-33% chloroform in hexanes gradient, usually 1/4, 1/3, 1/2, chloroform/ hexane, v/v). The yield is about 650 mg ~ 60%, dark solid. ^{1}H NMR ($CDCl_3$, 500 MHz, δ) 8.06 (s, 2H), 7.73 (d, 2H), 1.98 (m, 4H), 1.00-1.30 (m, 56H), 0.87 (t, 6H). C^{13} NMR ($CDCl_3$, 125 MHz, δ) 161.81, 160.22, 159.81, 154.37, 154.31, 148.76, 139.99, 138.97, 128.13, 128.05, 123.36, 114.58, 114.44, 95.43, 95.23, 54.52, 37.78, 31.90, 29.96, 29.66, 29.65, 29.63, 29.62, 29.58, 29.57, 29.33, 24.65, 22.67, 14.10

PBT: **M1** (200 mg, 0.21 mmol), **BT** (59 mg, 0.20 mmol), $Pd(PPh_3)_4$ (11 mg, 0.01 mmol), anhydrous *o*-xylene (2 mL) and DMF (0.4 mL) were added to a 2-5 mL microwave tube in the nitrogen atmosphere glovebox. The tube was and subjected to the following reaction conditions in the microwave reactor: 80 °C for 2 min, 130 °C for 2 min, 160 °C for 2 min, and 200 °C for 40 min. The reaction was allowed to cool to room temperature, and then the vail was transferred to the glovebox. The vail was opened to add $Pd(PPh_3)_4$ (3 mg), 2-bromothiophene (0.1 mL) and xylene (2 mL) for end-capping reaction. Then the vail was sealed again and subjected to the microwave reactor under the conditions of 80 °C for 2 min, 130 °C for 2 min, 160 °C for 20 min. The reaction was allowed to cool to room temperature and the polymer was precipitated in methanol. The precipitates were collected by filter paper and extracted with methanol, dichloromethane and chloroform respectively via a Soxhlet extractor. The chloroform solution was concentrated under vacuum. Then concentrated polymer solution was passed through a short silica-gel (60-100 mesh) column. Then it was concentrated again and was dropwise to the methanol under stirring. The polymer was precipitated and collected via filter paper, dried over in the vacuum to provide dark solid 130 mg, yield 85%.

PRF (M_n = 53 kDa): **M1** (209 mg, 0.22 mmol), **FBT** (62 mg, 0.20 mmol), $Pd(PPh_3)_4$ (11 mg, 0.01 mmol), anhydrous *o*-xylene (3 mL) were added to a 2-5 mL microwave tube in the nitrogen atmosphere glovebox. Further synthesis procedure is similar to the synthesis of PBT to provide dark solid 137 mg, yield 88%.

PRF (M_n = 128 kDa): **M1** (200 mg, 0.21 mmol), **FBT** (62 mg, 0.20 mmol), $Pd(PPh_3)_4$ (11 mg, 0.01 mmol), anhydrous *o*-xylene (3 mL) were added to a 2-5 mL microwave tube in the nitrogen atmosphere glovebox. The microwave-assist polymerization and end-capping procedures are similar to the synthesis of PBT. The reaction was allowed to cool to room temperature and the polymer was precipitated in methanol. The precipitates were collected by filter paper and extracted with methanol, dichloromethane, chloroform and toluene respectively via a Soxhlet extractor. The toluene solution was concentrated under vacuum. Then concentrated polymer solution was passed through a short silica-gel (60-100 mesh) column. Then it was concentrated again and was dropwise to the methanol under stirring. The polymer was precipitated and collected via filter paper, to provide dark solid 147 mg, yield 94%.

P2F: **M1** (110 mg, 0.115 mmol), **M2** (109 mg, 0.10 mmol), $Pd(PPh_3)_4$ (6 mg, 0.005 mmol), anhydrous *o*-xylene (3 mL) were added to a 2-5 mL microwave tube in the nitrogen atmosphere glovebox. Further synthesis procedure is similar to the synthesis of PBT to provide dark solid 140 mg, yield 90%.

PDF: **M1** (209 mg, 0.115 mmol), **DFBT** (66 mg, 0.20 mmol), $Pd(PPh_3)_4$ (11 mg, 0.01 mmol), anhydrous *o*-xylene (3 mL) were added to a 2-5 mL microwave tube in the nitrogen atmosphere glovebox. Further synthesis procedure is similar to the synthesis of PBT to provide dark solid 140 mg, yield 88%.

3. Differential scanning calorimetry

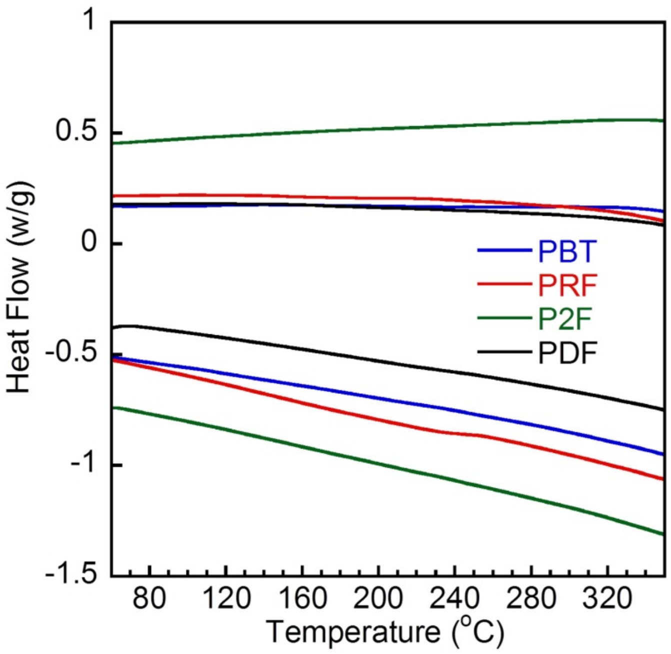


Figure S1. Differential scanning calorimetry measurements of polymers.

4. Cyclic voltammetry

Cyclic voltammetry (CV) measurements were conducted using a standard three-electrode configuration under an argon atmosphere. A three-electrode cell equipped with a glassy carbon working electrode, an Ag wire reference electrode and a Pt wire counter-electrode. The measurements were performed in absolute acetonitrile with tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte at a scan rate of 50 mV/s. Polymer films for CV test were drop-casted onto the glassy carbon working electrode from their chlorobenzene solution at a concentrations of 5 mg/mL. The absolute energy level of ferrocene/ferrocenium (Fc/Fc$^+$) was set to be 4.8 eV below vacuum. The HOMO level was calculated from the equation: $E_{HOMO} = -4.8\,\text{eV} - E_{onset}^{ox}$, and the LUMO level was calculated from: $E_{LUMO} = E_{HOMO} + E_g^{opt}$.

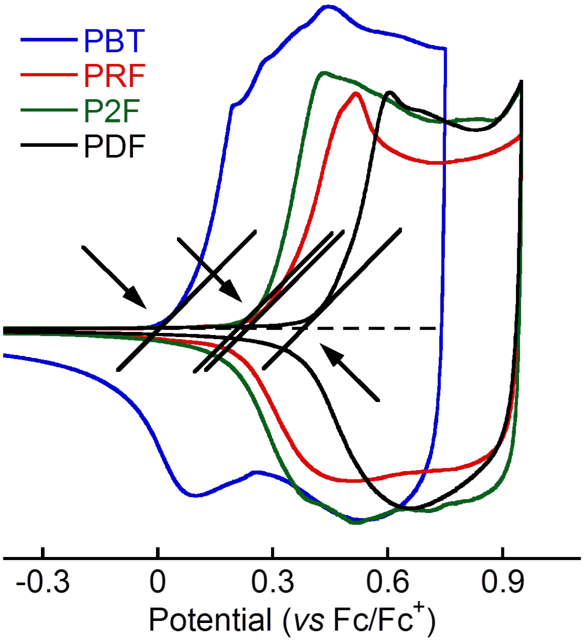


Figure S2. Cyclic voltammetry measurements of polymers.

5. AMF images

Tapping-mode atomic force microscopy (AFM) images were obtained in air using an Innova AFM.

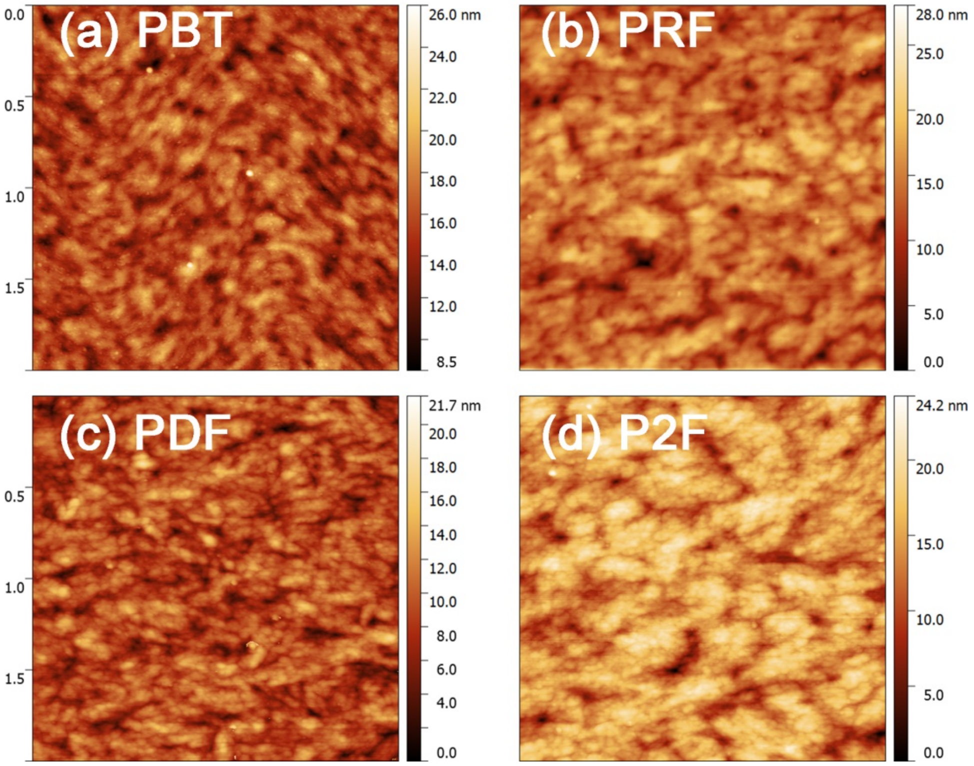


Figure S3. AFM images of OFET devices surface.

6. GIWAXS

Grazing incidence wide angle X-ray scattering (GIWAXS) measurements were performed at beamline 7.3.3 at the Advanced Light Source (ALS) with an X-ray wavelength of 1.2398 Å at a 300 mm sample detector distance. Samples were scanned in a He environment at an incident angle of 0.12°. The measurements were calibrated using an AgB Standard.

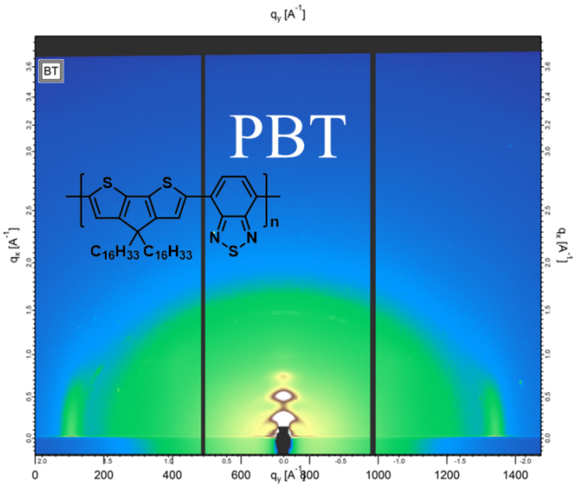


Figure S4. GIWAXS RAW image of polymers PBT film.

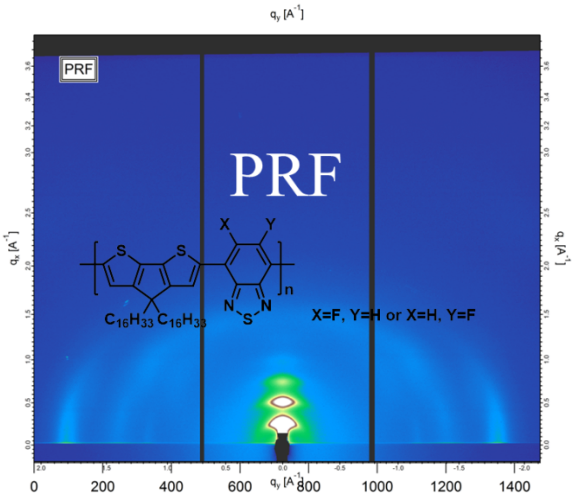


Figure S5. GIWAXS RAW image of polymers PRF (53 kDa) film.

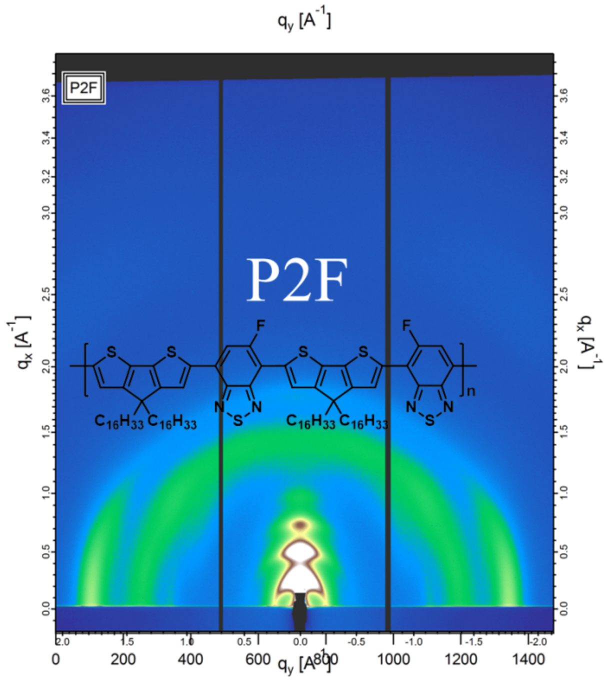


Figure S6. GIWAXS RAW image of polymers P2F film.

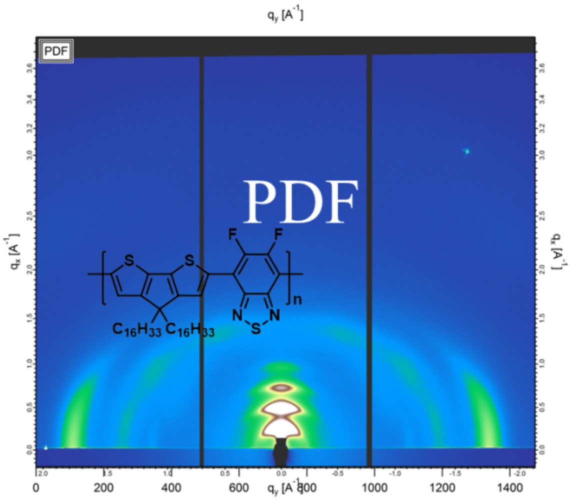


Figure S7. GIWAXS RAW image of polymers PDF film.

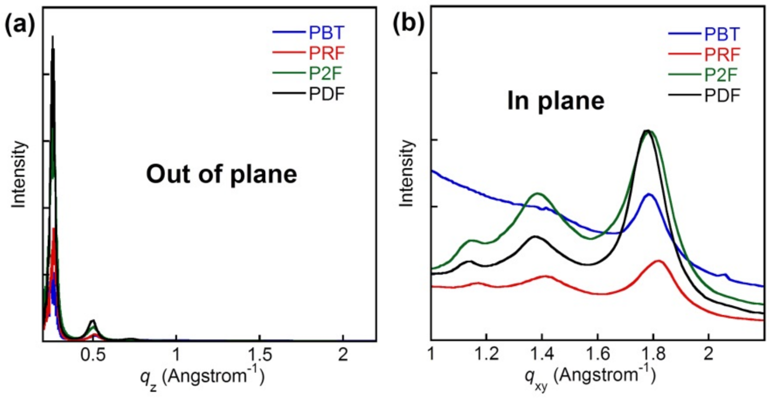


Figure S8. GIWAXS measurement line-cut profiles.

7. OFET measurements

The channel length was 80 µm or 160 µm and the width was 1000 µm or 2000µm. Thin films were prepared via doctor-blading at a speed of 1.2 mm/s at 100 ^{o}C, similar to previous conditions for the P2 polymer[1]. The films were thermally annealed at 200 ^{o}C before measuring the current-voltage characteristics in a nitrogen atmosphere glovebox. Hole mobilities in the saturation regime (drain-source voltage V_{DS} = -80 V) were calculated using the slope of root drain-source current $I_{DS}^{1/2}$ vs. gate voltage V_{GS} by the equation of $I_{DS}=(W/2L)\, C_i\mu(V_{GS}-V_{th})^2$, where W/L is the channel width/length, C_i is the gate dielectric layer capacitance per unit area, and V_{th} is the threshold voltage. No differences in mobility were observed with the device channel parallel or perpendicular to the blading direction. Average mobilities were calculated from eight devices.

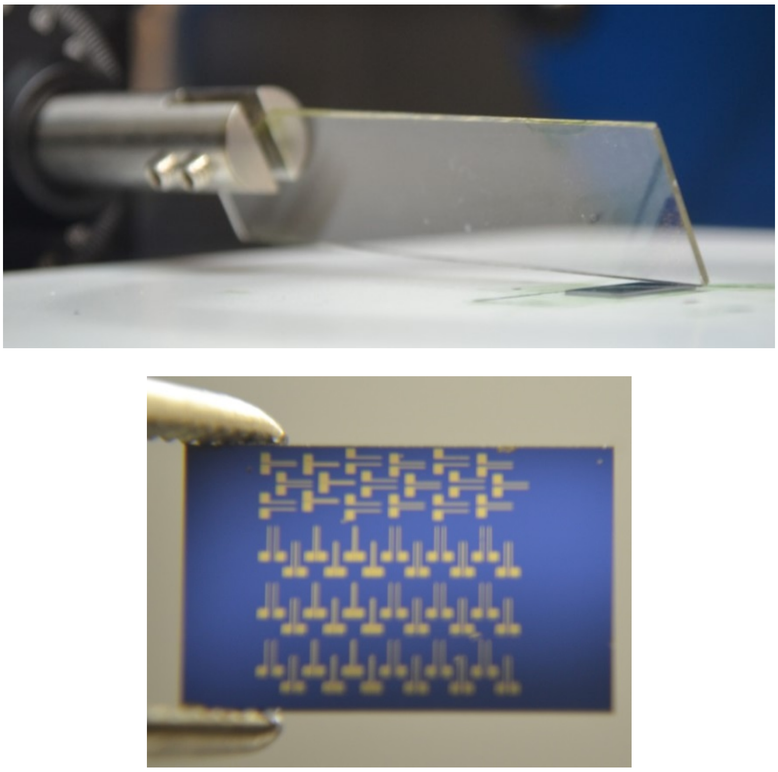


Figure S9. Doctor-blading set-up and the OFET substrate.

Table S1. PBT OFET devices data in nitrogen glovebox

No.	1	2	3	4	5	6	7	8
μ (cm^{2}V^{-1}s^{-1})	1.242	1.387	1.079	1.150	0.885	1.043	0.989	1.154
On/off	376	63.1	399	702	49.9	70.1	293	194
V_{th} (V)	16.72	10.11	16.10	20.65	15.81	12.23	16.53	16.44

Table S2. PRF OFET devices data in nitrogen glovebox (M_n=53 kDa)

No.	1	2	3	4	5	6	7	8
μ (cm^{2}V^{-1}s^{-1})	0.277	0.4	0.263	0.309	0.296	0.334	0.276	0.261
On/off	47	54.8	36.1	149	107	245	52	58.6
V_{th} (V)	9	16.36	9.01	12.99	12.28	14.09	9.42	7.59

Table S3. PRF OFET devices data in nitrogen glovebox (M_n=128 kDa)

No.	1	2	3	4	5	6	7	8
μ (cm^{2}V^{-1}s^{-1})	0.244	0.207	0.247	0.223	0.22	0.254	0.273	0.224
On/off(*10^3)	176	8.19	25.7	-	7.63	26	11.2	21.4
V_{th} (V)	5.2	-2.69	10.8	3.19	2.22	13.03	8.14	11.25

Table S4. P2F OFET devices data in nitrogen glovebox

No.	1	2	3	4	5	6	7	8
μ (cm^{2}V^{-1}s^{-1})	0.879	1.17	1.05	1.12	0.399	0.986	0.957	0.944
On/off	24.6	54.5	34.8	136	23.5	110	29	-
V_{th} (V)	7.9	14.56	15.3	17.17	24.94	17.88	9.23	33.48

Table S5. PDF OFET devices data in nitrogen glovebox

No.	1	2	3	4	5	6	7	8
μ (cm^{2}V^{-1}s^{-1})	0.297	0.301	0.297	0.304	0.295	0.305	0.314	0.260
On/off	36	25	18	24	22	23	23	32
V_{th} (V)	1.25	1.02	3.45	5.86	4.13	11.06	9.63	1.21

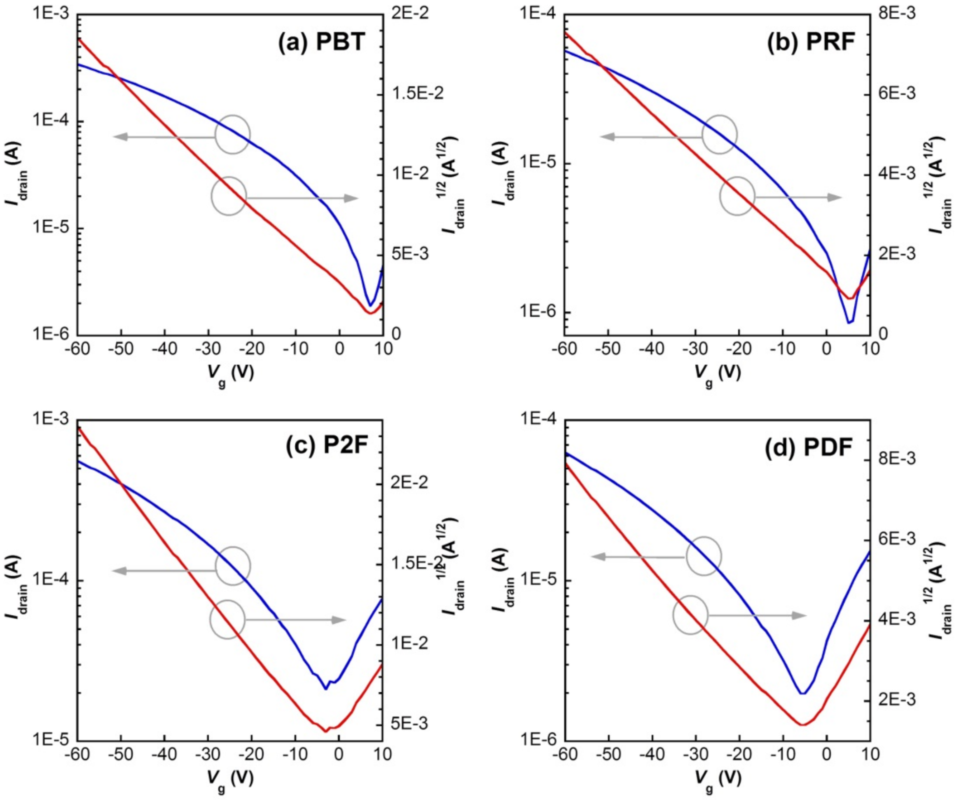


Figure S10. Transfer curves of OFET devices measured in nitrogen.

For the air stability test, devices were stored in air and the current-voltage characteristics measurements were performed in ambient condition. Average mobilities were calculated from four devices and shown in Table S-6.

Table S6. PBT and PDF OFET devices data in nitrogen glovebox (day 0) and in ambient condition (from day 1 to day 5). On/off ratios are calculated from the $I_{drain}^{max}/I_{drain}^{min}$ since a well-defined OFF state was not always clear under the scanning conditions.

day	PBT			PDF		
	μ (cm^{2}V^{-1}s^{-1})	V_t (V)	on/off	μ (cm^{2}V^{-1}s^{-1})	V_t (V)	on/off
0	1.1	16	2.2E+02	0.3	8	4.5E+01
1	0.1	4	9.4E+01	0.3	-1	7.3E+03
2	0.006	1	9.6E+01	0.1	-6	1.4E+04
3	0.002	-5	1.2E+02	0.07	-13	2.9E+05
4	0.004	-4	1.0E+02	0.07	-12	2.3E+05
5	0.002	-3	1.6E+02	0.07	-14	1.2E+05

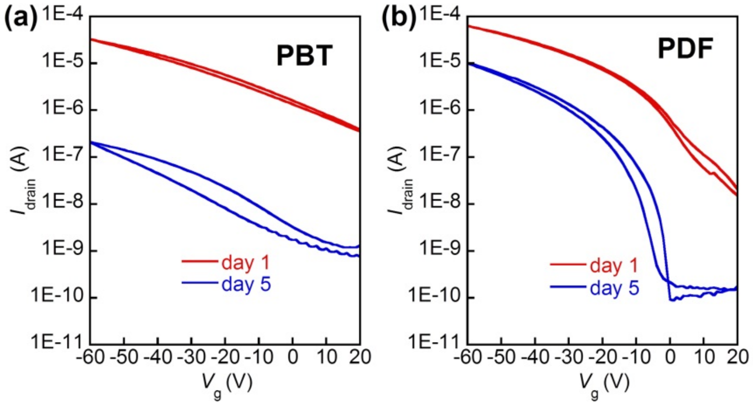


Figure S11. Transfer curves of PBT and PDF OFETs after 1 day and 5 days in ambient condition.

Reference

1. S. N. Patel, G. M. Su, C. Luo, M. Wang, L. A. Perez, D. A. Fischer, D. Prendergast, G. C. Bazan, A. J. Heeger, M. L. Chabinyc and E. J. Kramer, *Macromolecules*, 2015, **48**, 6606.