

Supporting Information
for
Ambipolar Polymer Field-Effect Transistors Based on Fluorinated Isoindigo:
High Performance and Improved Ambient Stability

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Table of Contents

1. General procedures and experimental details	S2
2. Figures S1-S8 and Table S1	S4
3. Synthetic procedures and characterization	S9
4. ¹ H and ¹³ C NMR spectra of new compounds	S13

1. General procedures and experimental details

Chemical reagents and CYTOP were purchased and used as received. All air and water sensitive reactions were performed under nitrogen atmosphere. Toluene was distilled from sodium prior to use. ^1H and ^{13}C NMR spectra were recorded on Bruker ARX-400 (400 MHz). All chemical shifts were reported in parts per million (ppm). ^1H NMR chemical shifts were referenced to TMS (0 ppm), and ^{13}C NMR chemical shifts were referenced to CDCl_3 (77.00 ppm). HR ESI-MS were recorded on a Bruker BIFLEX III mass spectrometer (Bruker Daltonics, Billerica, MA, USA). Absorption spectra were recorded on PerkinElmer Lambda 750 UV-*vis* spectrometer. Cyclic voltammetry was performed using BASI Epsilon workstation and measurements were carried out in acetonitrile containing 0.1 M $n\text{Bu}_4\text{NPF}_6$ as a supporting electrolyte. Carbon electrode was used as a working electrode and a platinum wire as a counter electrode, all potentials were recorded versus Ag/AgCl (saturated) as a reference electrode. The scan rate was 50 mV s^{-1} . Elemental analyses were performed using a German Vario EL III elemental analyzer. Thermal gravity analyses (TGA) were carried out on a TA Instrument Q600 analyzer, and differential scanning calorimetry (DSC) analyses were performed on a METTLER TOLEDO Instrument DSC822 calorimeter. Gel permeation chromatography (GPC) was performed on Polymer Laboratories PL-GPC220 at $150\text{ }^\circ\text{C}$ using 1,2,4-trichlorobenzene (TCB) as eluent. Atomic force microscopy studies were performed with a Nanoscope IIIa microscope (Extended Multimode, Digital Instruments, Santa Barbara, CA). All experiments were carried out in tapping mode at ambient condition. A silicon nitride cantilever (Budget Sensors Tap300Al) was used with a resonant frequency around 300 kHz. The X-ray diffraction data were obtained at beamline BL14B1 of the Shanghai Synchrotron Radiation Facility (SSRF) at a wavelength of 1.2398 \AA . BL14B1 is a beamline based on bending magnet and a Si (111) double crystal monochromator was employed to monochromatize the beam. The size of the focus spot is about 0.5 mm and the end station is equipped with a Huber 5021 diffractometer. NaI scintillation detector was used for data collection.

Device fabrication and characterization. Top-gate/bottom-contact OFET devices were fabricated using $n^{++}\text{-Si/SiO}_2$ (300 nm) substrates. The gold source and drain bottom electrodes (with Ti as the adhesion layer) were patterned by photolithography on the SiO_2 surface. The substrates were subjected to cleaning using ultrasonication in acetone, cleaning agent, deionized water (twice), and *iso*-propanol. The cleaned substrates were dried under vacuum at $80\text{ }^\circ\text{C}$. The substrates were used directly in ambient condition or transfer into a glove box. A thin film of the polymer was deposited on the treated substrates by spin-coating using a polymer solution (6 mg/mL) at 1500 rpm for 40 s, optionally followed by thermal annealing at $140\text{ }^\circ\text{C}$, $160\text{ }^\circ\text{C}$, $180\text{ }^\circ\text{C}$ or $200\text{ }^\circ\text{C}$ under ambient condition or in a glove box for 10 min. After polymer thin film deposition, a CYTOP solution (CYTOP CTL809M:CT-solv180 = 3:1) was spin-coated onto the semiconducting layer at 2000 rpm for 60 s resulting in a dielectric layer of 500 nm

thick. The CYTOP layer was then baked at 100 °C for 1 h in ambient condition or in a glove box. Gate electrodes comprising a layer of Al (50 nm) were then evaporated through a shadow mask onto the dielectric layer by thermal evaporation. The OTFT devices had a channel length (L) of 50 μm and a channel width (W) of 1000 μm .

The evaluations of the OTFTs were carried out in atmosphere (humidity 50-60%) using a Keithley 4200 parameter analyzer on a probe stage. The carrier mobility, μ , was calculated from the data in the saturated regime according to the equation $I_{\text{SD}} = (W / 2L)C_i\mu(V_G - V_T)^2$, where I_{SD} is the drain current in the saturated regime. W and L are, respectively, the semiconductor channel width and length, C_i ($C_i = 3.7$ nF) is the capacitance per unit area of the gate dielectric layer, and V_G and V_T are the gate voltage and threshold voltage. $V_G - V_T$ of the device was determined from the relationship between the square root of I_{SD} at the saturated regime.

2. Figure S1-S8 and Table S1

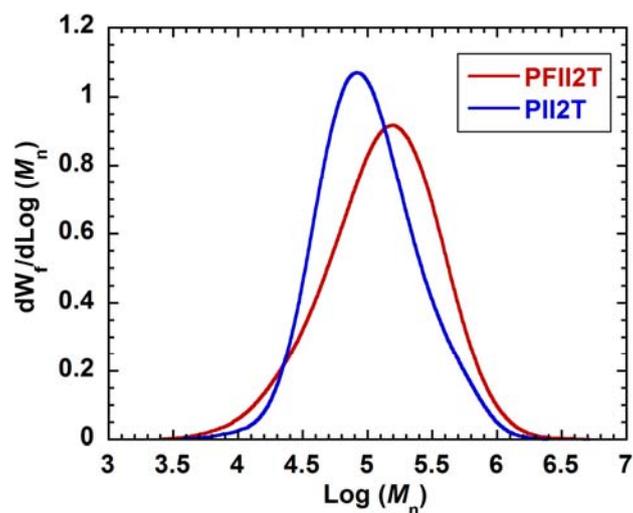


Figure S1. Gel permeation chromatography (GPC) traces of both polymers. Molecular weight of polymers were evaluated using high temperature GPC with 1,2,4-trichlorobenzene (TCB) as eluent at 140 °C.

Table S1. Thermal, Optical and Electrochemical Properties of Both Polymers

Polymers	T_d (°C)	$\lambda_{\max}^{\text{sol}}$ (nm) ^a	$\lambda_{\max}^{\text{film}}$ (nm)	E_g^{opt} (eV) ^b	$E_{\text{HOMO}}^{\text{CV}}$ (eV) ^c	$E_{\text{LUMO}}^{\text{CV}}$ (eV) ^c	$E_{\text{HOMO}}^{\text{PES}}$ (eV) ^d	$E_{\text{LUMO}}^{\text{PES}}$ (eV) ^e
PFII2T	411	728, 682	734, 667	1.50	-5.60	-3.88	-5.46	-3.96
PII2T	416	714, 667	718, 652	1.57	-5.42	-3.70	-5.31	-3.74

^a 10^{-5} M in chloroform. ^b Estimated from the onset of thin-film absorption. ^c Cyclic voltammetry determined with Fc/Fc⁺ ($E_{\text{HOMO}} = -4.80$ eV) as external reference. ^d Determined by UV-PES. ^e $E_{\text{LUMO}}^{\text{PES}} = E_{\text{HOMO}}^{\text{PES}} - E_g^{\text{opt}}$.

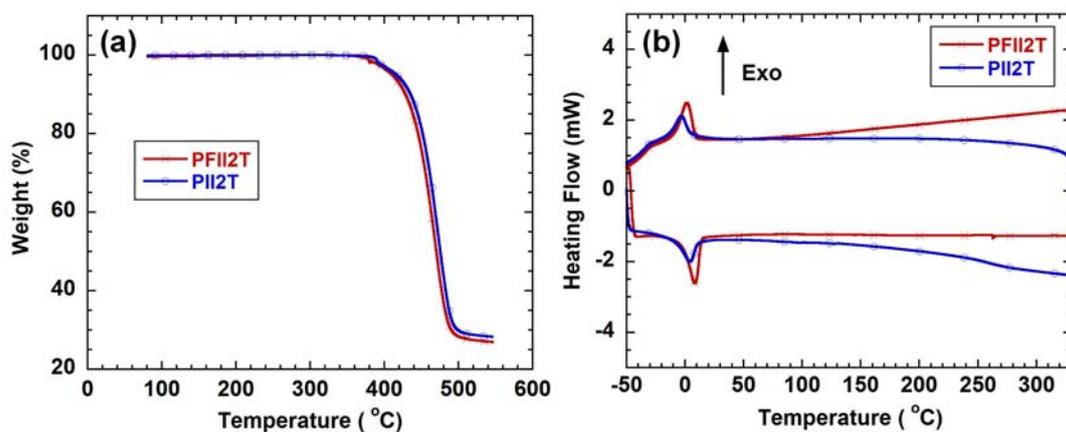


Figure S2. (a) Thermal gravity analyses (TGA) of **PFII2T** (5% loss, 411 °C) and **PII2T** (5% loss, 416 °C). (b) Differential scanning calorimetry (DSC) traces of **PFII2T** ($T = 8$ °C) and **PII2T** ($T = 4$ °C) (scan rate: 10 °C/min).

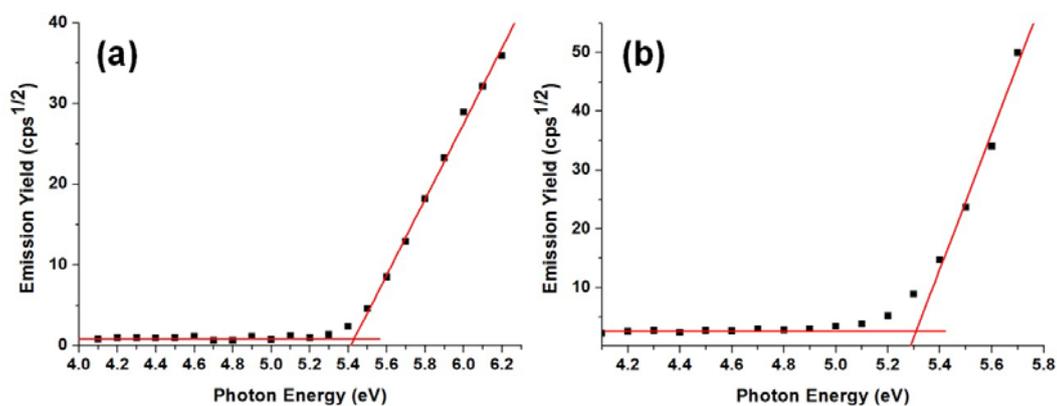


Figure S3. Photo-electron spectra (PES) of (a) **PFII2T** and (b) **PII2T** in thin films.

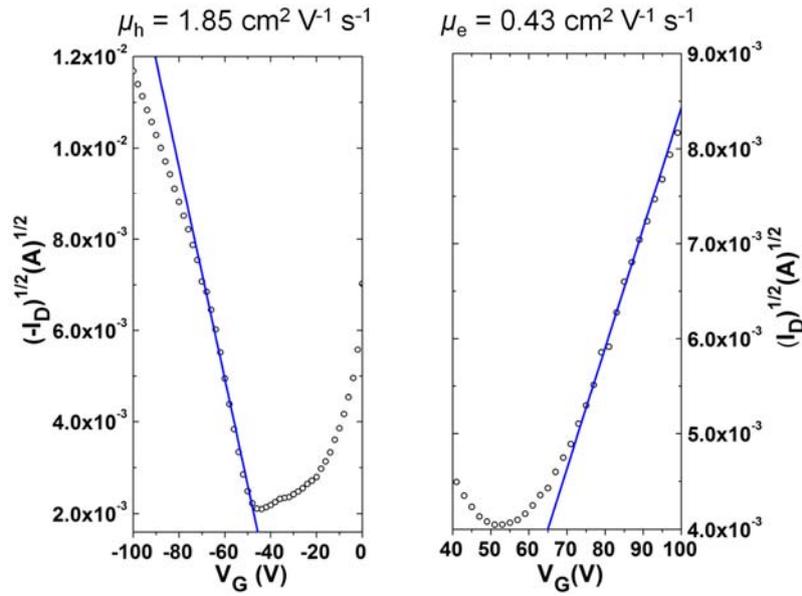


Figure S4. The effective hole and electron mobilities of **PFII2T** device fabricated under ambient conditions, which were calculated by using the slope obtained from the linear fitting of the square root of the drain current ($V_D = 100$ V). The effective hole mobility is $1.85 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and the electron mobility is $0.43 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. OFET devices ($L = 50 \text{ }\mu\text{m}$, $W = 1000 \text{ }\mu\text{m}$) were fabricated with CYTOP around 500 nm thick (capacitance $C_i = 3.7 \text{ nF cm}^{-2}$).

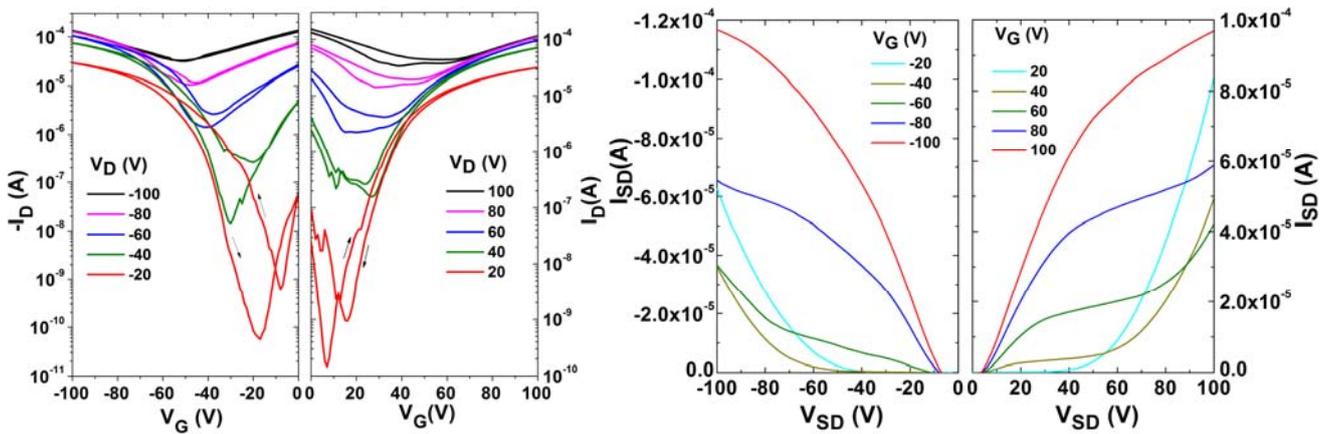


Figure S5. The transfer and output characteristics of **PFII2T** devices fabricated in glove box and tested in ambient conditions. OFET devices ($L = 50 \text{ }\mu\text{m}$, $W = 1000 \text{ }\mu\text{m}$) were fabricated with CYTOP around 500 nm thick (capacitance $C_i = 3.7 \text{ nF cm}^{-2}$).

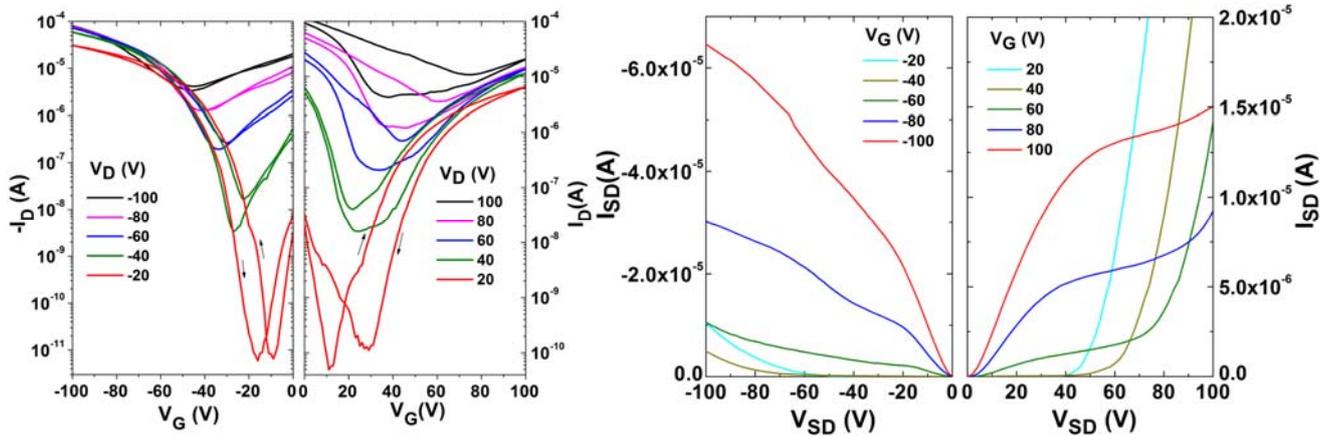


Figure S6. The transfer and output characteristics of **PII2T** devices fabricated in glove box and tested in ambient conditions. OFET devices ($L = 50 \mu\text{m}$, $W = 1000 \mu\text{m}$) were fabricated with CYTOP around 500 nm thick (capacitance $C_i = 3.7 \text{ nF cm}^{-2}$).

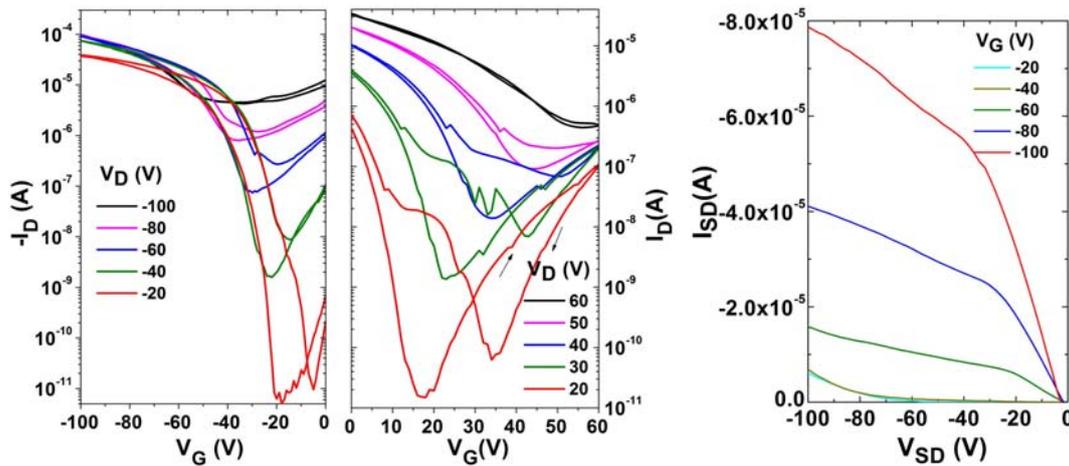


Figure S7. The transfer and output characteristics of **PII2T** devices fabricated and tested under ambient conditions. n-Type output characteristics were not shown because of the low electron mobilities. OFET devices ($L = 50 \mu\text{m}$, $W = 1000 \mu\text{m}$) were fabricated with CYTOP around 500 nm thick (capacitance $C_i = 3.7 \text{ nF cm}^{-2}$).

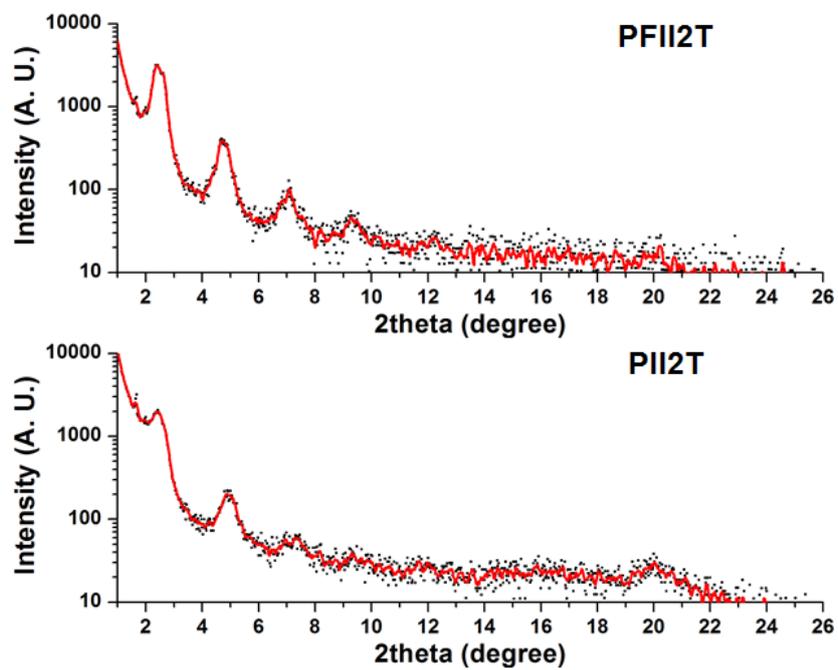
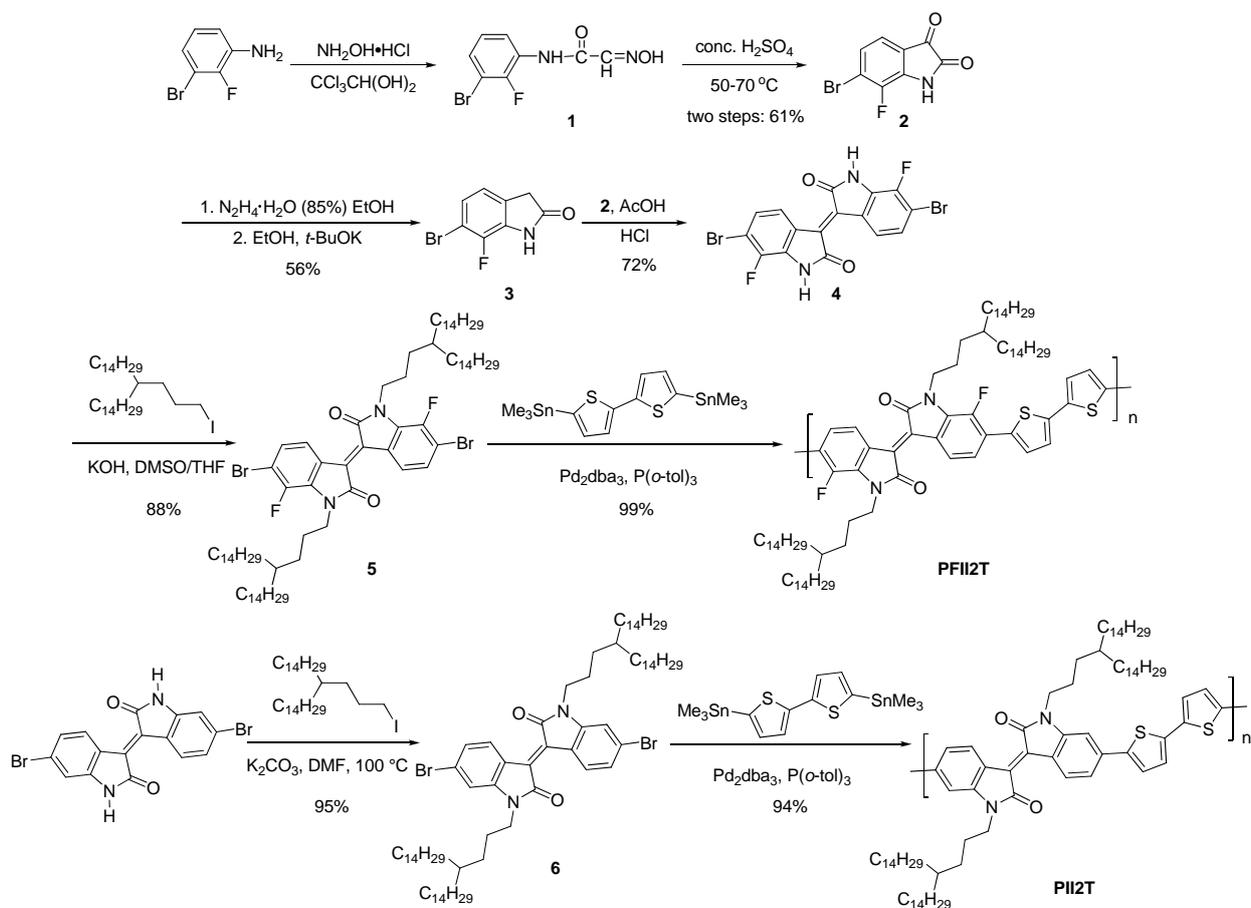
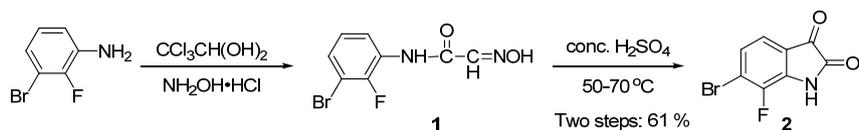


Figure S8. Out-of-plane GIXD plots of **PFII2T** and **PII2T** films obtained from a point detector in beamline BL14B1 (SSRF). **PFII2T** show much stronger ($h00$) peaks compared with **PII2T**.

3、Synthetic procedures and characterization



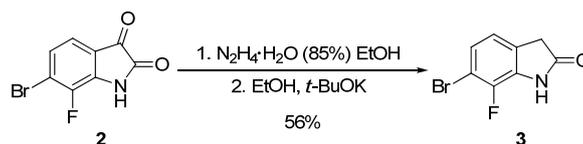
6,6'-Dibromoisindigo, and compound **6** were synthesized according to our previous report.^{1,2}



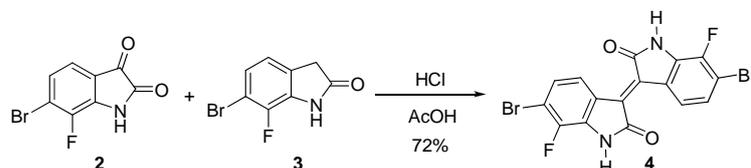
6-Bromo-7-fluoroisatin (2). To a solution of chloral hydrate (9.55 g, 57.89 mmol) in deionized water (150 mL), Na_2SO_4 (100 g, 684.19 mmol), 3-bromo-2-fluoroaniline (10 g, 52.63 mmol), H_2SO_4 (40 mL, 1 M) and hydroxylamine hydrochloride (10.97 g, 157.89 mmol) was added. The mixture was heated to 130°C and refluxed for 30 min. The mixture was then cooled to 80°C and filtered to collect the product. The product was washed with deionized water and dried under reduced pressure to afford **1** as a yellowish solid, which was directly used for the next step without further purification.

To a concentrated H_2SO_4 (100 mL) in 250 mL round-bottom flask kept at 50°C , compound **1** was added portionwise with stirring. The mixture was heated to 70°C for 1 h before pouring into ice water. The precipitate was collected by filtration and the filtrate was extract with ethyl acetate (EA). The precipitate and the extraction were combined and subject to column chromatography (silica gel; eluent: PE:EA = 8:1) to afforded **2** as an orange solid (7.80 g, 61%). ^1H NMR (DMSO-d_6 , 400 MHz, ppm): δ

11.74 (s, 1H), 7.40–7.37 (dd, $J_{\text{H-H}} = 8.0$ Hz, $J_{\text{H-F}} = 5.6$ Hz, 1H), 7.32–7.30 (d, $J_{\text{H-H}} = 8.0$ Hz, 1H). ^{13}C NMR (DMSO- d_6 , 100 MHz, ppm): δ 182.29–182.25 (d, $J_{\text{F-C}^4} = 3.9$ Hz), 159.17, 145.23–142.78 (d, $J_{\text{F-C}^1} = 246$ Hz), 138.19–138.05 (d, $J_{\text{F-C}^2} = 14.0$ Hz), 126.47–126.45 (d, $J_{\text{F-C}^4} = 1.7$ Hz), 121.38–121.34 (d, $J_{\text{F-C}^3} = 3.8$ Hz), 119.89–119.85 (d, $J_{\text{F-C}^3} = 3.7$ Hz), 118.42–118.25 (d, $J_{\text{F-C}^2} = 17.3$ Hz). EI-MS calcd. for $[\text{M}+\text{H}]^+$: 243. Found: 243. Elemental Anal. calcd. for $\text{C}_8\text{H}_3\text{BrFNO}_2$: C, 39.38; H, 1.24; N, 5.74. Found: C, 39.39; H, 1.40; N, 5.74.

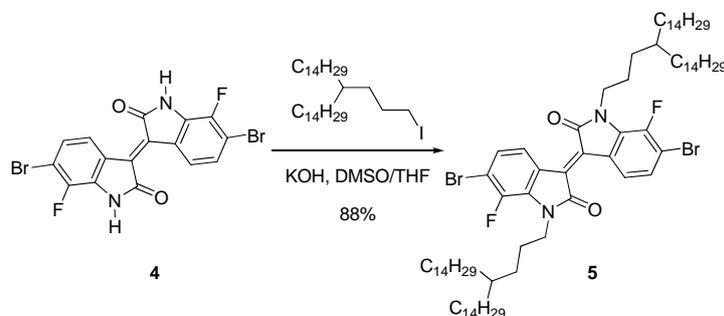


6-Bromo-7-fluoroindolin-2-one (3). To a solution of **2** (2.80 g, 11.48 mmol) in ethanol (50 mL), hydrazine hydrate (85%, 0.5 mL) was added under nitrogen. After the mixture was refluxed for 30 min, a yellow particulate was formed and collected by filtration. The yellow precipitate was then dissolved in anhydrous ethanol (50 mL), and *t*-BuOK (4.03 g, 35.90 mmol) was added. The mixture was refluxed under nitrogen for 2 h before pouring into water. The mixture was acidified with dilute HCl to pH = 2 and extracted with EA. The combined organic phase was washed with water, brine, dried with Na_2SO_4 , and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel; eluent: PE:EA = 5:1) to provide **3** as a light-yellow solid (1.49 g, 56%). ^1H NMR (DMSO- d_6 , 400 MHz, ppm): δ 11.04 (s, 1H), 7.26–7.15 (dd, $J_{\text{H-H}} = 7.9$ Hz, $J_{\text{F-H}} = 6.2$ Hz, 1H), 7.06–6.95 (d, $J = 7.9$ Hz, 1H), 3.54 (s, 1H). ^{13}C NMR (DMSO- d_6 , 100 MHz, ppm): δ 175.95, 143.82–141.41 (d, $J_{\text{F-C}^1} = 242$ Hz), 131.97–131.85 (d, $J_{\text{F-C}^2} = 12.6$ Hz), 128.55–128.51 (d, $J_{\text{F-C}^3} = 4.1$ Hz), 124.74, 121.69–121.65 (d, $J_{\text{F-C}^3} = 3.6$ Hz), 106.70–106.53 (d, $J_{\text{F-C}^2} = 17.0$ Hz), 35.89–35.87 (d, $J_{\text{F-C}^4} = 2.4$ Hz). EI-MS: calcd. for $[\text{M}+\text{H}]^+$: 229. Found: 229. Elemental Anal. calcd. for $\text{C}_8\text{H}_3\text{BrFNO}$: C, 41.77; H, 2.19; N, 6.09. Found: C, 41.52; H, 2.27; N, 6.22.



6,6'-Dibromo-7,7'-difluoroisoidigo (4). To a suspension of **2** (1.58 g, 6.48 mmol) and **3** (1.49 g, 6.48 mmol) in AcOH (75 mL) was added conc. HCl (37%) solution (0.4 mL). The mixture was refluxed for 24 h. The mixture was allowed to cool and filtered. The solid material was washed with water, ethanol, and ether. After drying under vacuum, deep red 6,6'-Dibromo-7,7'-difluoroisoidigo (2.13 g, 72%) was obtained. ^1H NMR (DMSO- d_6 , 400 MHz, ppm): δ 11.68 (s, 2H), 8.83–8.81 (d, $J_{\text{H-H}} = 8.7$ Hz, 2H), 7.31–7.27 (dd, $J = 8.7$ Hz, $J_{\text{F-H}} = 6.7$ Hz, 2H). ^{13}C NMR (DMSO- d_6 , 100 MHz, ppm): δ 68.46, 151.66,

143.98–141.58 (d, $J_{F-C}^1 = 242$ Hz), 133.13–133.09 (d, $J_{F-C}^3 = 3.9$ Hz), 132.62–132.49 (d, $J_{F-C}^2 = 13.6$ Hz), 126.33, 124.50, 123.41–123.36 (d, $J_{F-C}^3 = 4.6$ Hz), 112.47–112.30 (d, $J_{F-C}^2 = 16.8$ Hz). EI-MS: calcd. for $[M+H]^+$: 456. Found: 456. Elemental Anal. calcd. for $C_{16}H_6Br_2F_2N_2O_2$: C, 42.14; H, 1.33; N, 6.14. Found: C, 42.13; H, 1.40; N, 6.15.



Compound **5**. To a solution of 6,6'-dibromo-7,7'-difluoroisoidindigo (**4**) (150 mg, 0.33 mmol) and freshly powered KOH (1.68 g, 12.1 mmol) in dimethyl sulfoxide (DMSO) (20 mL), 15-(3-iodopropyl)nonacosane (478 mg, 0.83 mmol) in THF (20 mL) was added under nitrogen. The mixture was stirred for 24 h at 25 °C before pouring into water. The residues were dissolved in $CHCl_3$ (100 mL) and washed with water (3×50 mL). The combined organic phase was washed with brine and dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by silica gel chromatography with eluting (PE: $CH_2Cl_2 = 5:1$) to give **5** as a deep-red solid. (390 mg, 88 %). 1H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.90-8.88 (d, $J = 8.7$ Hz, 2H), 7.26-7.17 (dd, $J_{H-H} = 8.7$ Hz, $J_{F-H} = 6.3$ Hz, 2H), 3.91-3.88 (t, $J = 7.4$ Hz 4H), 1.68-1.65 (m, 4H), 1.33-1.21 (m, 110H), 0.89-0.86 (t, $J = 6.8$ Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 167.05, 144.88–142.46 (d, $J_{F-C}^1 = 243$ Hz), 133.19–133.16 (d, $J_{F-C}^3 = 3.3$ Hz), 132.44–132.34 (d, $J_{F-C}^2 = 9.5$ Hz), 126.46–126.43 (d, $J_{F-C}^3 = 3.4$ Hz), 125.82, 123.21–123.17 (d, $J_{F-C}^3 = 3.3$ Hz), 114.91–114.72 (d, $J_{F-C}^2 = 19.4$ Hz), 42.79, 42.73, 37.08, 33.52, 31.94, 30.52, 30.10, 29.72, 29.68, 29.38, 26.64, 26.06, 22.70, 14.12. Elemental Anal. calcd. for $C_{80}H_{134}Br_2F_2N_2O_2$: C, 70.98; H, 9.98; N, 2.07. Found: C, 70.90; H, 9.61; N, 2.06. ESI-HRMS: calcd. for $[M+H]^+$: 1351.88529. Found: 1351.88157.

General Procedures for Stille Polymerization and Polymer Purification.

PFII2T. 5 (100 mg, 0.0739 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (36.3 mg, 0.0739 mmol), $Pd_2(dba)_3$ (1.4 mg, 2 mol%), $P(o-tol)_3$ (1.8 mg, 8 mol%), and 10 mL of toluene were added to a Schlenk tube. The tube was charge with nitrogen through a *freeze-pump-thaw* cycle for three times. The mixture was stirred for 48 h at 120 °C. *N,N'*-Diethylphenylazothioformamide (10 mg) was then added and then the mixture was stirred for 1 h to remove any residual catalyst before being precipitated into methanol (200 mL). The precipitate was filtered through a nylon filter and purified via Soxhlet extraction for 8 h

with acetone, 12 h with hexane, and finally was collected with chloroform. The chloroform solution was then concentrated by evaporation and precipitated into methanol (200 mL) and filtered off to afford a dark brown solid (99.1 mg, yield 99%). Elemental Anal. calcd: for $(C_{88}H_{138}F_2N_2O_2S_2)_n$: C, 77.82; H, 10.24; N, 2.06. Found: C, 76.92; H, 9.79; N, 2.02.

PII2T. The synthetic procedure is similar as described for **PFII2T** (yield 94%). Elemental Anal. calcd. for $(C_{88}H_{140}N_2O_2S_2)_n$: C, 79.94; H, 10.67; N, 2.12. Found: C, 78.88; H, 10.12; N, 2.07.

References:

1. Lei, T.; Cao, Y.; Fan, Y.; Liu C.-J.; Yuan, S.-C.; Pei, J. *J. Am. Chem. Soc.* **2011**, *133*, 6099.
2. Lei, T.; Dou, J.-H.; Pei, J. *Adv. Mater.* **2012**, DOI: 10.1002/adma.201202689.

4. ^1H and ^{13}C NMR spectra

