

Supporting Information

A New Fluoropyrido[3,4-b]pyrazine Based Polymer for Efficient Photovoltaics

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1. Characterization

¹H, ¹³C NMR spectra were collected on a Bruker AV-400 or AV-500 spectrometer using tetramethylsilane (TMS) as a reference in deuterated chloroform solution at 298 K, Chemical shifts were reported as δ values (ppm) with tetramethylsilane (TMS) as the internal reference. Molecular weight and polydispersity of the polymer were determined by high-temperature gel permeation chromatography (HT-GPC) analysis with polystyrene as the standard (Waters 515 HPLC) pump, a Waters 2414 differential refractometer, and three Waters Styragel columns (HT2, HT3,

HT4) using 1,2,4-trichlorobenzene (HPLC grade) as eluent at a flow rate of 1.0 mL min⁻¹ at 150 °C. Thermogravimetric analysis (TGA) was conducted on a Perkin-Elmer TGA-7 with a heating rate of 20 K min⁻¹ under nitrogen atmosphere. Ultraviolet-visible absorption spectra were carried out on the SHIMADZU UV-2600 spectrophotometer. For the solid state measurements, polymer solution in chloroform was spin-coated on quartz plates. The cyclic voltammograms (CV) were conducted by CHI660D electrochemical station to determine the energy level of the target polymer by casting thin film on platinum electrode (1.0 cm²) as working electrode, a platinum wire and Ag/AgCl electrode were used as counter electrode and reference electrode, respectively. The three electrode electrochemical cell in an anhydrous and argon-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in acetonitrile (CH₃CN) with a scan rate of 50 mV·s⁻¹ at room temperature. Electrochemical onsets were determined at the position where the current starts to differ from the baseline. Photoluminescence (PL) spectra of the polymer and the polymer blends were measured on a Hitachi F-4600 fluorescence spectrophotometer with 620 nm as the excitation wavelength. The surface morphology of BDT-S-*f*PP/PC₇₁BM blend films were investigated by atomic force microscopy (AFM, Agilent Technologies, 5500 AFM/SPM System, USA) in contacting under normal air conditions at room temperature with a 5 μm scanner.

Transmission electron microscope (TEM) measurements were performed in a JEM-2100F.

2. Fabrication and characterization of polymer solar cells.

The PSCs were fabricated in the configuration of the traditional sandwich structure with an indium tin oxide (ITO) glass positive electrode and a ETL/Al negative electrode. Platterned ITO glass with a sheet resistance of 10 Ω /sq was purchased from CSG HOLDING Co. LTD. (China). The ITO glass was cleaned by sequential ultrasonic treatments in detergent, deionized water, actone and isopropanol and then treated in an ultraviolet-ozone chamber (Ultraviolet Ozone Cleaner, Jelight Company, USA) for 20 minutes. The PEDOT: PSS (poly(3,4-ethylene dioxythiophene): poly(styrene sulfonate)) (Baytron PVP Al 4083, Germany) was filtered through a 0.45 μ m poly(tetrafluoroethylene) (PTFE) filter and spin coated at 3000 rpm for 40 s on the ITO substrate. Subsequently, PEDOT: PSS film was baked at 150 $^{\circ}$ C for 15 minutes in the air to give a thin film, and the thickness of the PEDOT: PSS layer is about 40 nm. The polymer and PC₇₁BM (10 mg mL⁻¹ for polymer) were dissolved in CF and 1.2% volume ratio of 1,8-diiodooctane (DIO, Sigma Aldrich) overnight and spin-cast at 2000 rpm for 45 s on the PEDOT: PSS layer. The thickness of the photoactive layer is about 100-110 nm measured by Ambios Technology XP-2 profilometer. The ZrAcac was simply prepared by spin-coating its ethanol solution (1 mg mL⁻¹) on a

photoactive layer at 3000 rpm for 30 s at room temperature. A bilayer cathode consisting of ZrAcac (~15 nm) capping with Al (~40 nm) was thermal evaporated under a shadow mask with a base pressure of ca. 10^{-5} Pa. The active area of the PSCs is 5 mm².

Device characterization was carried out under AM 1.5G irradiation with the intensity of 100 mW cm⁻² (Oriel 67005, 500 W), calibrating by a standard silicon cell. *J-V* curves were recorded with a Keithley 236 digital source meter. A xenon lamp with AM 1.5G filter was used as the white light source and the optical power was 100 mW cm⁻². The EQE measurements of PSCs were performed by Stanford Systems model SR830 DSP lock-in amplifier coupled with WDG3 monochromator and 500 W xenon lamp. A calibrated silicon detector was used to determine the absolute photosensitivity at different wavelengths. All the fabrications and characterizations after cleaning of ITO substrates were conducted in a glove box.

3. Materials

4-bromo-2-fluorophenol,

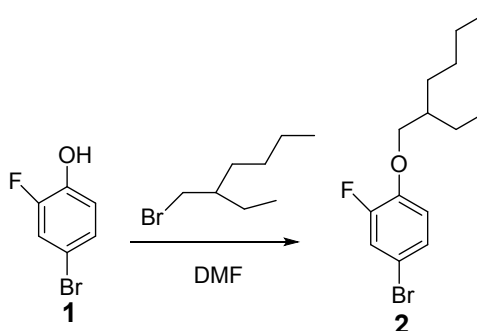
Tetrakis(triphenylphosphine)palladium(0)(Pd(PPh₃)₄),

Tetrahydrofuran(THF), pyridine-3,4-diamine were obtained from Aladdin and Sun Chemical Technology(Shanghai) Co., LTD. Toluene was dried over molecular sieves and freshly distilled prior to use. The other reagents and chemicals were purchased from commercial sources (TCI), and they

were used without any further purification. Compound **2**, **3**, **4**, **5**, **7**, **fPP**, **BDT-S** were synthesized according to the reported literatures¹⁻³. **5**, **7**, **fPP** and the corresponding polymer were well characterized by ¹H NMR and ¹³C NMR.

4. Synthesis of the intermediates and polymer

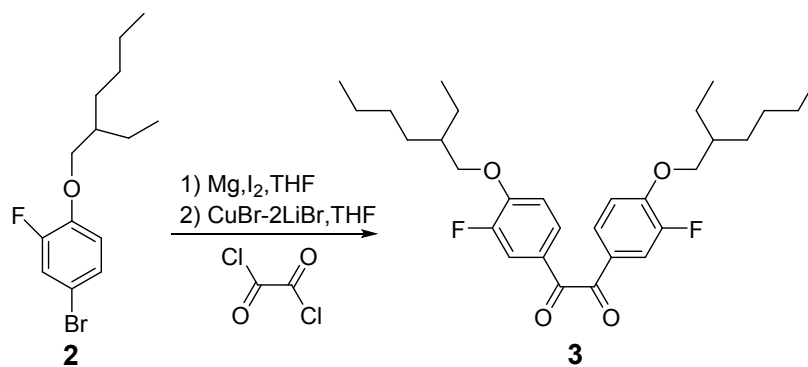
4-Bromo-1-((2-ethylhexyl)oxy)-2-fluorobenzene(**2**)



4-Bromo-2-fluorophenol (**1**) (15 g, 75 mmol) and potassium carbonate (11 g, 80 mmol) were mixed with N,N-dimethylformamide (DMF, 100 mL), and stirred for 30 minutes at 60 °C under nitrogen atmosphere. Then 3-(bromomethyl)heptane (15 g, 75 mmol) was added dropwise and the mixture was stirred for 10 hours at 150 °C. After cooling to room temperature, it was poured into water (200 mL) and extracted with dichloromethane (DCM) (70 mL × 3). The organic layer was washed with water and saturated sodium bicarbonate solution successively for twice, respectively. The organic phase were dried with anhydrous MgSO₄, filtered and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether) to give compound **2** as a colorless liquid (19.3 g, 85%).

¹HNMR (400 MHz, CDCl₃, ppm: δ: 7.30-7.40 (m, 2H) , 6.80-6.85 (t, 1H) , 3.98-3.86 (m, 2H), 1.86-1.72 (m, 1H), 1.57-1.30 (m, 8H), 1.02-0.88 (m, 6H). MS: m/z = 302 (M⁺).

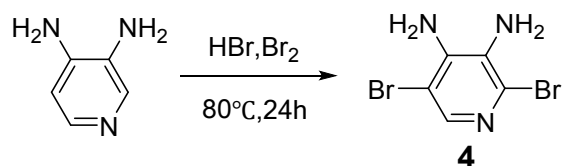
1,2-Bis(4-((2-ethylhexyl)oxy)-3-fluorophenyl)ethane-1,2-dione(3)



Magnesium turnings (1.06 g, 44 mmol) and a grain of iodine were puted into 250 mL three flasks (a). Compound **2** (11.15 g, 36.8 mmol) dispersed in anhydrous tetrahydrofuran (60 mL) and then were added to the flask appropriately under nitrogen atmosphere. A large number of air bubbles were released. When the solution became colorless, the remaining compound **2** with anhydrous tetrahydrofuran were added in potions. The reaction mixture was stirred at 60 °C for 3.5 hours until the magnesium was consumed. In another flask (b), cuprous bromide (CuBr, 5.28 g, 36.8 mmol) and lithium bromide (6.39 g, 73.6 mmol) were dispersed in anhydrous tetrahydrofuran (50 mL) at 0 °C under nitrogen atmosphere. As the resulting mixture became homogeneous, the fresh Grignard was added slowly to the stirred solution by syringe. After the reaction mixture was stirred at 0 °C for 2 hours, oxalyl chloride (2.14 g, 16.85 mmol) was added quickly and the mixture was stirred at 0 °C for 1 hour. The solution

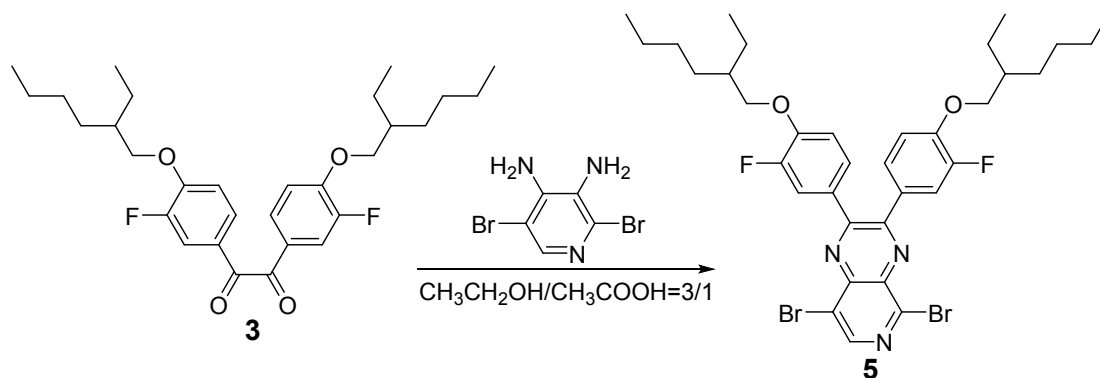
was then stirred at room temperature overnight. The mixture was poured into saturated aqueous NH_4Cl , extracted with DCM, the organic phase washed with water three times. After drying over anhydrous MgSO_4 , it was filtered and the solvent was removed. Then the crude product was purified with column chromatography using petroleum ether and ethyl acetate ($V : V = 40 : 1$) as eluent to get yellow viscous liquid (2.5 g, 29%). $^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm): δ : 7.55-7.45 (m, 2H), 7.40-7.32 (m, 2H), 7.00-6.90 (m, 2H), 4.02-3.90 (m, 4H), 1.87-1.70 (m, 2H), 1.58-1.25 (m, 16H), 1.03-0.83 (m, 12H). MS: $m/z = 504$ (M^+).

2,5-Dibromopyridine-3,4-diamine (**4**)



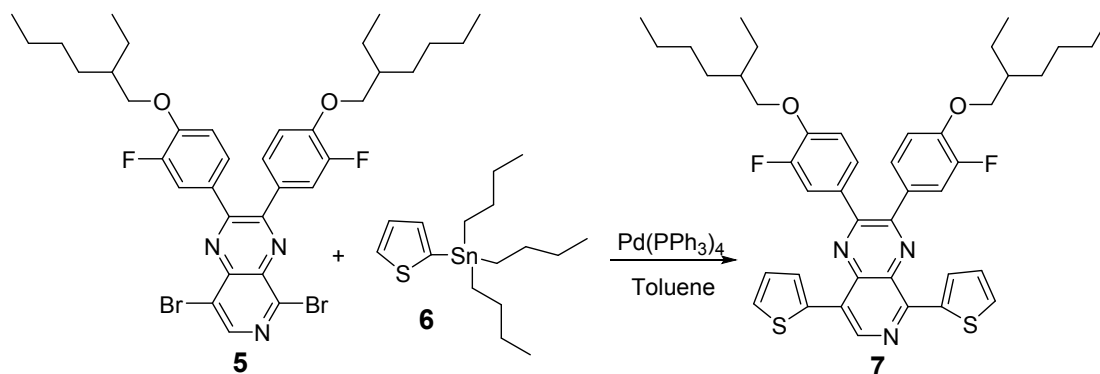
Pyridine-3,4-diamine (2.18 g, 20 mmol) and 48% HBr (16 mL) were added into 50 mL three necked flask. Then Br_2 (3.2 mL) was added dropwisely. The solution was then stirred at 80 °C for 24 hours. After cooling down to the room temperature, the resultant precipitate was collected by filtration and washed sequentially with saturated aqueous sodium thiosulfate, saturated aqueous sodium bicarbonate and water. The product was directly used for the next reaction without any purification (3.3 g, 62%).

5,8-Dibromo-2,3-bis(4-((2-ethylhexyl)oxy)-3-fluorophenyl)pyrido[3,4-b]pyrazine (**5**)



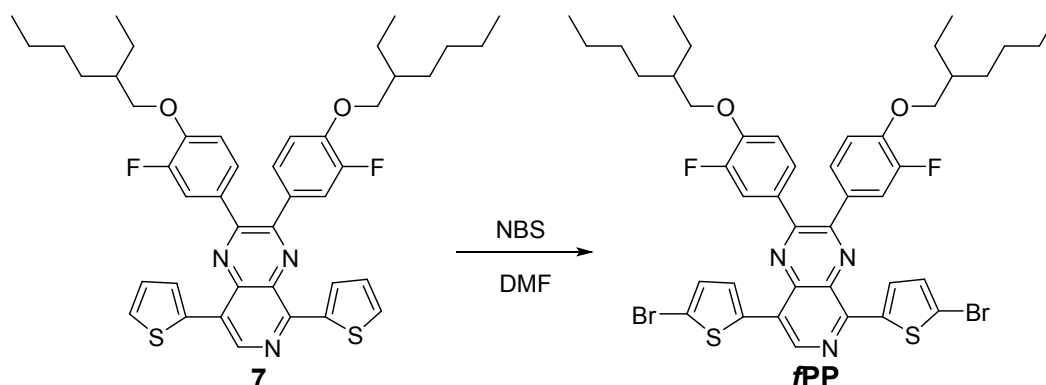
2,5-Dibromopyridine-3,4-diamine (5) (2.67 g, 10 mmol) and 1,2-bis(4-((2-ethylhexyl)oxy)-3-fluorophenyl)ethane-1,2-dione (5.02 g, 10 mmol) were dissolved in a mixture of absolute alcohol (30 mL) and glacial acetic acid (10 mL) solution. The mixture then was stirred at 60 °C for 16 hours and cooled down to room temperature. Water was added to the solution and the mixture was extracted with DCM, then the combined organic layers were washed with water for twice. The crude product was further purified with silica column chromatography using petroleum ether and dichloromethane ($V : V = 2 : 1$) as eluent to get yellow liquid (3.2 g, 43%).
 $^1\text{H NMR}$ (500 MHz, CDCl_3 , ppm): δ : 8.72 (1 H, s), 7.57 – 7.47 (2 H, m), 7.41 (2 H, t, $J = 6.5$), 6.96 (2 H, dt, $J = 14.7, 7.4$), 3.99 – 3.93 (4 H, m), 1.80 (2 H, dt, $J = 12.3, 6.2$), 1.49 – 1.43 (5 H, m), 1.38 – 1.30 (9 H, m), 1.25 (2 H, s), 0.93 (14 H, dt, $J = 12, 7.2$). MS: $m/z = 731$ (M^+).

2,3-Bis(4-((2-ethylhexyl)oxy)-3-fluorophenyl)-5,8-di(thiophen-2-yl)pyrido[3,4-b]pyrazine (7)



5,8-Dibromo-2,3-bis(4-((2-ethylhexyl)oxy)-3-fluorophenyl)pyrido[3,4-b]pyrazine (0.73 g, 1 mmol) and tributyl(thiophen-2-yl)stannane (1.2 g, 3 mmol) were added into 10 mL dry toluene. Then tetrakis(triphenylphosphine)palladium (0.058 g, 0.05 mmol) was added quickly under nitrogen atmosphere. The reaction mixture was heated at reflux for 48 hours, cooled to room temperature and poured into water (200 mL). The solution was extracted with DCM for three times. The organic layer was washed sequentially with 10% aqueous HCl solution and saturated sodium bicarbonate solution, dried over anhydrous MgSO₄. The crude was further purified with silica column chromatography using petroleum ether and dichloromethane (*V* : *V* = 3 : 1) as eluent to get red viscous liquid (0.6 g, 82%). ¹H NMR (500 MHz, CDCl₃, ppm): δ: 9.05 (1 H, s), 8.55 (1 H, d, *J* = 3.1), 7.82 (1 H, d, *J* = 3.2), 7.58 – 7.48 (4 H, m), 7.44 – 7.38 (2 H, m), 7.19 (2 H, ddd, *J* = 8.6, 4.9, 3.9), 6.97 (2 H, dt, *J* = 15.3, 8.4), 3.98 (4 H, td, *J* = 6.2, 2.5), 1.82 (2 H, dd, *J* = 11.6, 5.9), 1.59 – 1.43 (8 H, m), 1.36 (8 H, dt, *J* = 7.2, 3.6), 1.00 – 0.92 (12 H, m). MS: *m/z* = 741 (M⁺).

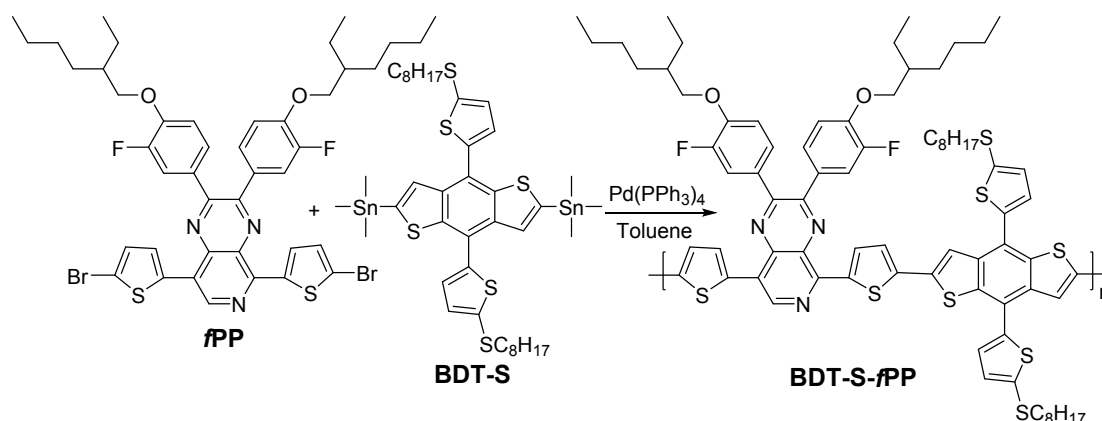
5,8-Bis(5-bromothiophen-2-yl)-2,3-bis(4-((2-ethylhexyl)oxy)-3-fluorophenyl)pyrido[3,4-b]pyrazine (fPP)



2,3-Bis(4-((2-ethylhexyl)oxy)-3-fluorophenyl)-5,8-di(thiophen-2-yl)pyrido[3,4-b]pyrazine (0.41 g, 0.55 mmol) was dissolved in 15 mL of DMF under nitrogen atmosphere and N-bromosuccinimide (0.23 g, 1.3 mmol) was added in one portion. Then the solution was stirred at 0 °C for 1 hour, the mixture was stirred at room temperature for 12 hours and then quenched with water (200 mL). The solution was extracted with chloroform and washed with water for three times, sequentially. Solvent was removed under reduced pressure and the residue was further purified with silica column chromatography using petroleum ether and dichloromethane ($V : V = 2 : 1$) as eluent to get orange solid (0.45 g, 90%). $^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm): δ : 8.98 (1 H, s), 8.26 (1 H, d, $J = 4.1$), 7.55 (1 H, d, $J = 4.0$), 7.51 – 7.39 (4 H, m), 7.15 (2 H, dd, $J = 7.3, 4.1$), 7.03 (2 H, td, $J = 8.3, 5.0$), 4.05 – 3.98 (4 H, m), 1.85 (2 H, ddd, $J = 12.2, 6.0, 3.8$), 1.63 (2 H, d, $J = 6.4$), 1.59 – 1.48 (6 H, m), 1.38 (8 H, dd, $J = 3.5, 1.7$), 1.02 – 0.93 (12 H, m). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) 154.13,

153.33, 151.75, 151.37, 149.88, 149.42, 149.08, 142.74, 142.03, 141.03, 139.39, 139.18, 134.99, 132.09, 131.82, 130.41, 130.09, 127.39, 126.92, 126.53, 123.59, 118.11, 118.05 – 117.56, 117.34, 114.66, 114.11, 77.28, 77.03, 76.77, 71.95, 40.07, 39.39, 33.81, 32.58, 30.43, 29.72, 29.08, 28.86, 25.72, 23.80, 23.17 – 22.96, 14.26 – 14.01, 11.12, 10.87, 1.04. MS: $m/z = 899 (M^+)$.

Synthesis of BDT-S-*f*PP.



In a dry 50 mL two-necked flask, **fPP** (0.134 g, 0.15 mmol) and **BDT-S** (0.147 g, 0.15 mmol) were dissolved in 13 mL dry toluene. After flushing with argon for 10 minutes, 13 mg of $\text{Pd}(\text{PPh}_3)_4$ was added into the flask quickly, the mixture was flushed with argon for another 15 minutes and stirred at 110 °C for 24 hours under argon. Then the reaction mixture was cooled down to room temperature and precipitated into 200 mL of methanol. The polymer was collected by filtration through a Soxhlet extractor, and then subjected to soxhlet extractions with methanol, hexane, acetone and chloroform each for 12 hours, respectively. Then the chloroform fraction was concentrated and precipitated with methanol, the

purple-black solid was obtained (0.205 g, 85%). Elemental analysis calculated for $C_{79}H_{91}F_2N_3O_2S_8$: C, 67.34; H, 6.51; F, 2.7; N, 2.98; S, 18.20. Actual analysis: C, 67.30; H, 6.49; F, 2.68; N, 2.99; S, 18.26. HT-GPC (THF): $M_n = 16.1$ kDa; $M_w = 57.9$ kDa; PDI = 3.59.

5. NMR spectra

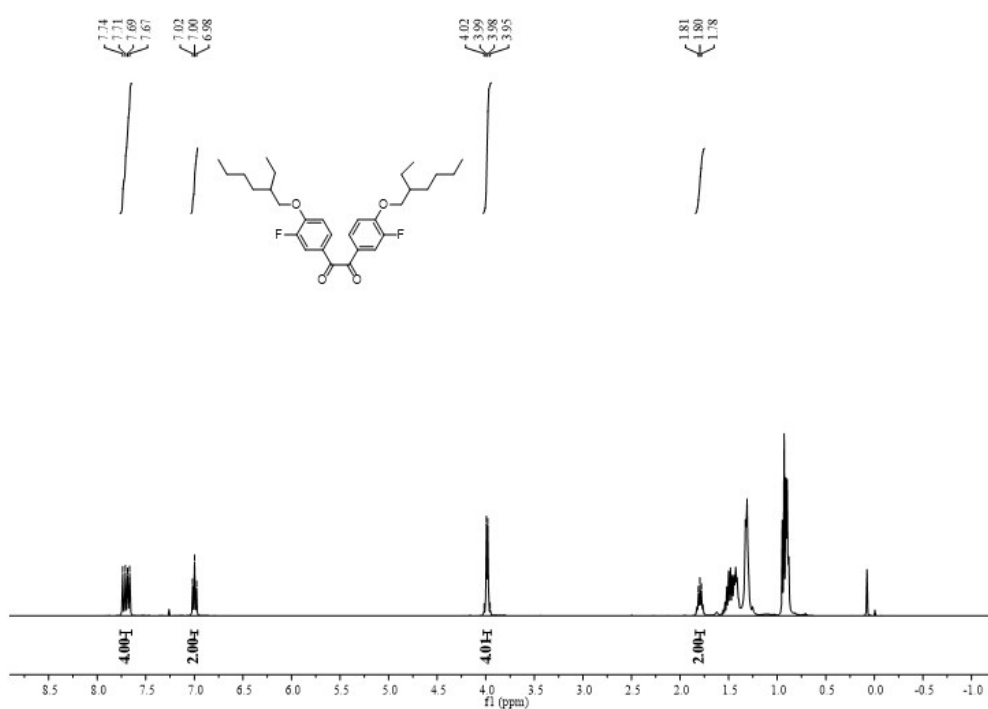


Figure S1. 1H NMR spectrum of 1,2-bis(4-((2-ethylhexyl)oxy)-3-fluorophenyl)ethane-1,2-dione

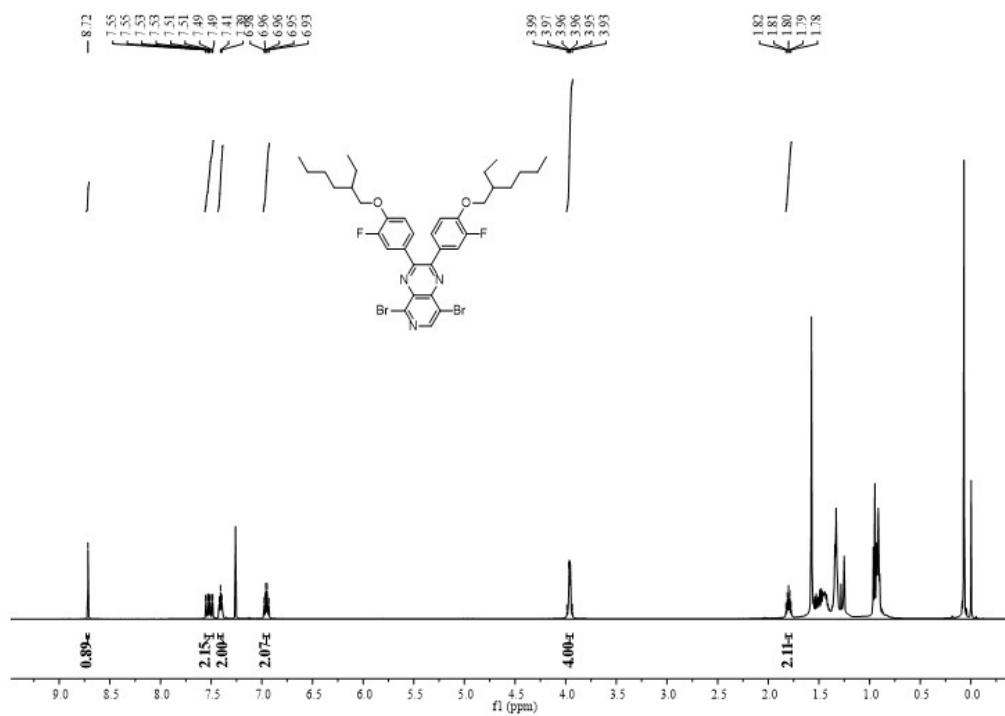


Figure S2. ^1H NMR spectrum of 5,8-dibromo-2,3-bis(4-((2-ethylhexyl)oxy)-3-fluorophenyl)pyrido[3,4-b]pyrazine (5)

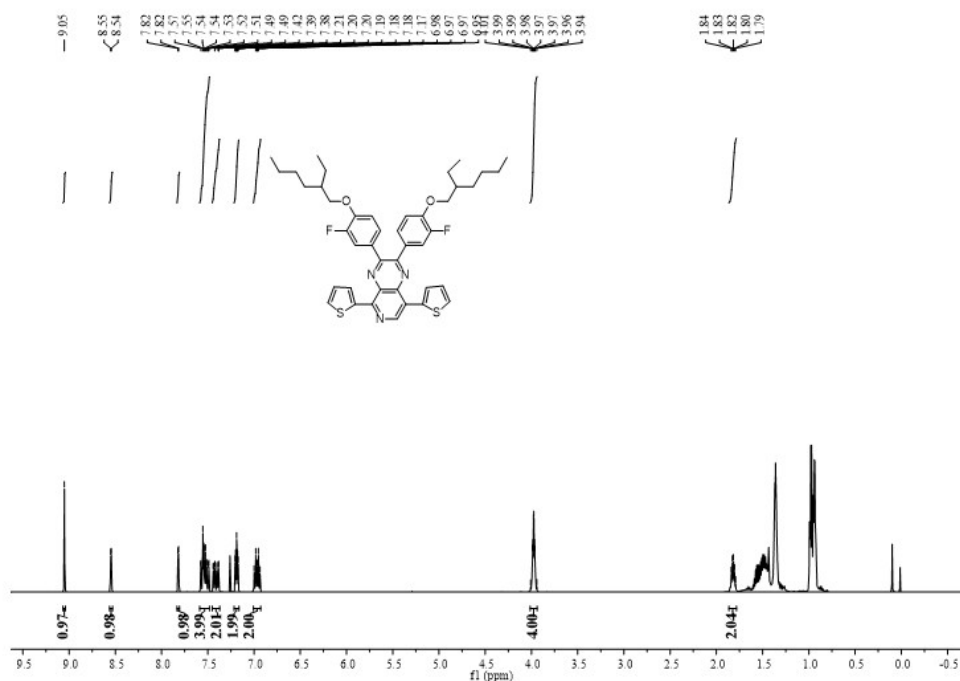


Figure S3. ^1H NMR spectrum of 2,3-bis(4-((2-ethylhexyl)oxy)-3-fluorophenyl)-5,8-di(thiophen-2-yl)pyrido[3,4-b]pyrazine (7)

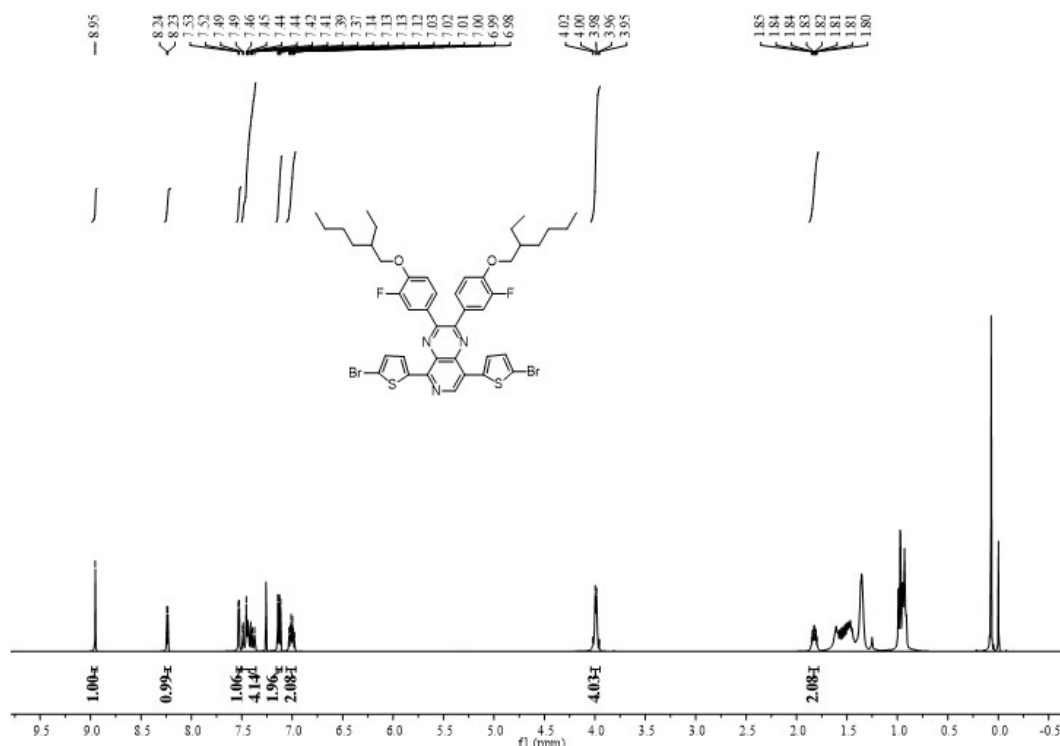


Figure S4. ^1H NMR spectrum of 5,8-bis(5-bromothiophen-2-yl)-2,3-bis(4-((2-ethylhexyl)oxy)-3-fluorophenyl)pyrido[3,4-b]pyrazine (fPP)

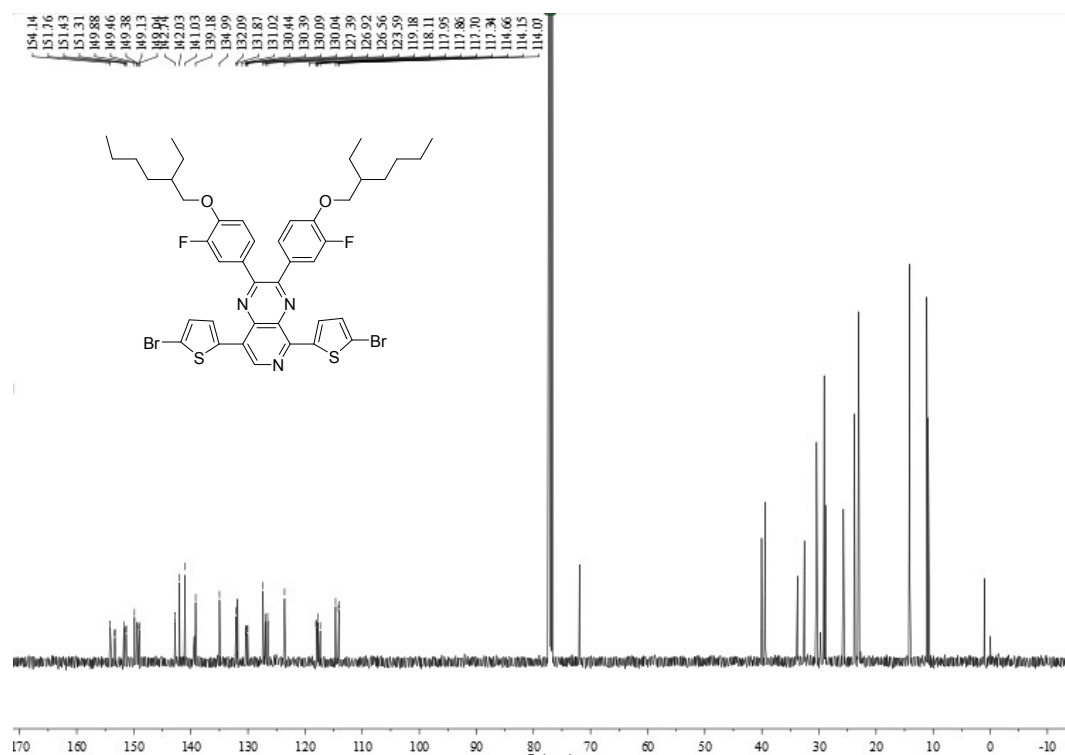


Figure S5. ^{13}C NMR spectrum of 5,8-bis(5-bromothiophen-2-yl)-2,3-bis(4-((2-ethylhexyl)oxy)-3-fluorophenyl)pyrido[3,4-b]pyrazine (fPP)

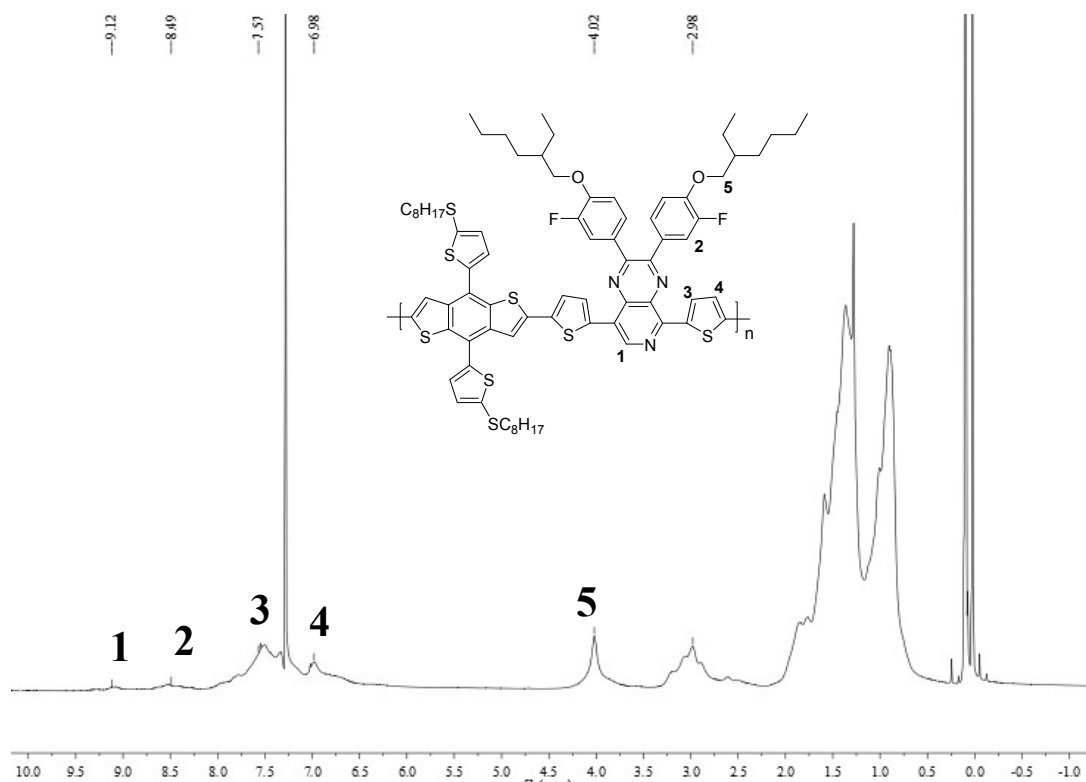


Figure S6. ¹H NMR spectrum of BDT-S-fPP

6. HT-GPC

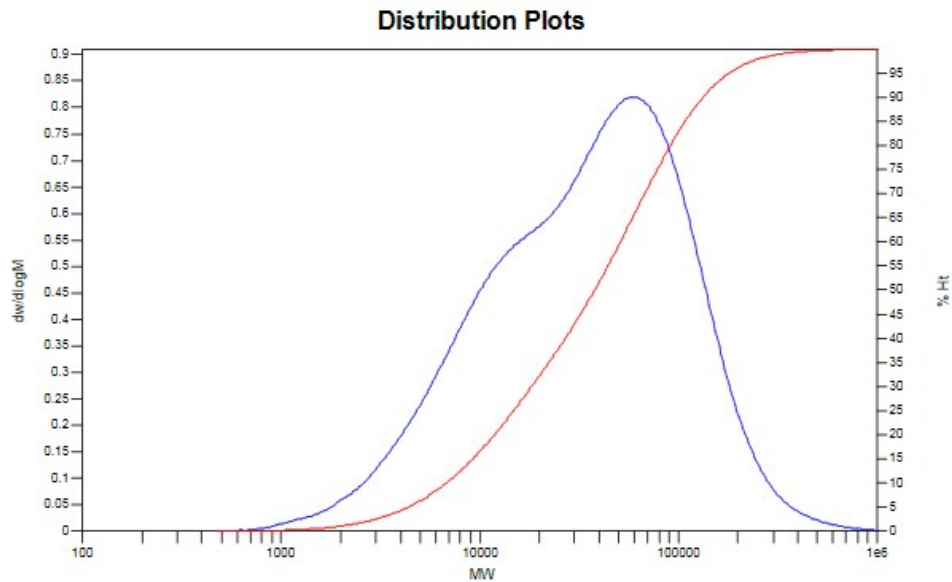


Figure S7. High-temperature gel permeation chromatography (HT-GPC) trace of BDT-S-fPP. The molecular weight was evaluated with 1,2,4-trichlorobenzene as eluent at 150 °C.

7. TGA

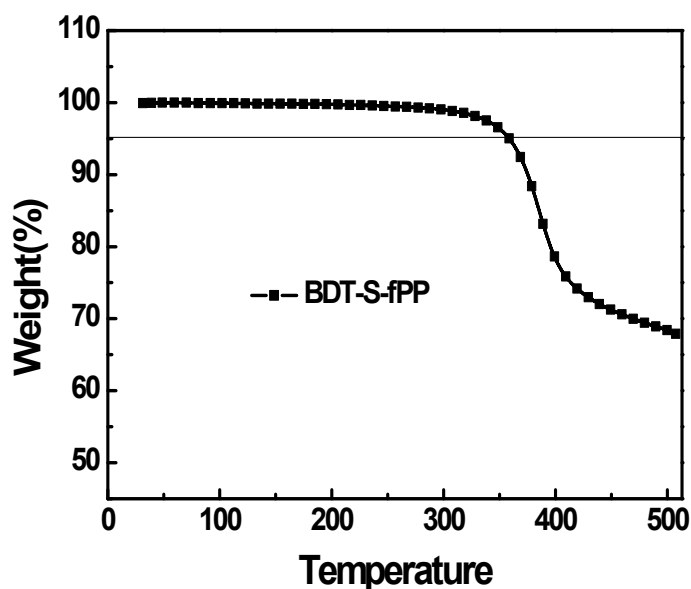


Figure S8. TGA curve of BDT-S-fPP at a heating rate of 20 K min⁻¹ under nitrogen.

8. Optical and electrochemical data

Table S1. Optical and electrochemical properties of BDT-S-fPP.

Polymer	Absorption spectra				Cyclic voltammetry	
	Sol ^a		Film ^b		p-doping	n-doping
	λ_{\max}	λ_{\max}	λ_{onset}	E_g^{opt} ^c	$E_{\text{on}}^{\text{ox}}/\text{HOMO}^{\text{d}}$	LUMO ^d
	(nm)	(nm)	(nm)	(eV)	(V)/(eV)	(eV)
BDT-S-fPP	442	633	748	1.66	0.92/-5.32	-3.66

^a Measured in chloroform solution. ^b Cast from chloroform solution. ^c Bandgap estimated from the onset wavelength of the optical absorption. ^d HOMO = $-e (E_{\text{on}}^{\text{ox}} + 4.4)$ (eV), LUMO = $E_g^{\text{opt}} + \text{HOMO}$ (eV) using Ag/AgCl electrode as the reference electrode.

9. Photovoltaic data

Table S2. Photovoltaic data and the device parameter standard deviation of PSCs based on BDT-S-*f*PP blended with PC₇₁BM^a under the illumination of AM 1.5G, 100 mW cm⁻².

Ratio	Additive	Annealing	FF	J_{sc} (mA cm⁻²)	V_{oc} (V)	PCE (%)
1 : 1	none	none	0.41	9.10	0.84	3.15
1 : 1	none	110 °C	0.45	10.51	0.83	3.88
1 : 1	none	130 °C	0.43	9.79	0.82	3.41
1 : 1	0.5	none	0.48	12.52	0.78	4.68
1 : 1	0.8	none	0.49	12.44	0.79	4.80
1 : 1	1.2	none	0.56	13.85	0.80	6.20
1 : 1	0.5 (CN)	none	0.56	8.83	0.81	3.91
1.5 : 1	0.5	none	0.48	12.35	0.80	4.76
1 : 1.5	0.5	none	0.58	10.56	0.78	4.83

^a Device structure of ITO/PEDOT:PSS/BDT-S-*f*PP:PC₇₁BM/ZrAcac/Al

10. Hole mobility

Table S3. The mobilities^a data of BDT-S-*f*PP.

polymer	Hole Mobility (μ_h) ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	Electron Mobility (μ_e) ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	μ_h/μ_e
BDT-S- <i>f</i> PP	1.1×10^{-5}	1.58×10^{-5}	0.73
BDT-S- <i>f</i> PP (1.2% DIO)	1.43×10^{-4}	1.85×10^{-4}	0.77

^a Measured by using the space-charge-limited current (SCLC) method.

Notes and References

1. C. Cui, W.-Y. Wong and Y. Li, *Energy Environ. Sci.*, 2014, 7, 2276-2284.
2. M.-C. Yuan, M.-Y. Chiu, C.-M. Chiang and K.-H. Wei, *Macromolecules*, 2010, 43, 6270-6277.
3. Y.-Q. Wu, H.-C. Chen, Y.-S. Yang, S. H. Chang, P.-J. Wu, Y.-Y. Chu and C.-G. Wu, *J. Polym. Sci. Part A: Polym. Chem.*, 2016, 54, 1822-1833.