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Supporting Information

A simple strategy to the side chain functionalization on the quinoxaline unit for efficient polymer solar cell

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1. Characterization

^{1}HNMR spectra were recorded using a Bruker AV-500 spectrometer in deuterated chloroform solution at 298 K, unless specified otherwise. Chemical shifts were reported as δ values (ppm) with tetramethylsilane (TMS) as the internal reference. Mass spectroscopy was obtained from Agilent mass spectrometer. Molecular weight and polydispersity index of the polymer were determined by gel permeation chromatography(GPC) analysis with polystyrene as standard (Waters 515 HPLC pump, a Waters 2414 differential refractometer, and three Waters Styragel columns(HT2, HT3 and HT4)using THF(HPLC grade) as eluent at a flow rate of 1.0 mL/min at 35 °C. Thermogravimetric analysis (TGA) was conducted on a Perkin-Elmer TGA-7 with a heating rate of 20 K/min under nitrogen. UV-Vis absorption spectra were recorded on the SHIMADZU UV-2450 spectrophotometer. For the solid state measurements, polymer solution in chloroform was spin-coated on quartz plates. The cyclic voltammetry was recorded with a computer controlled Zahner IM6e electrochemical workstation using polymer films on platinum electrode (1.0 cm^2) as the working electrode, a platinum wire as the counter electrode and Ag/AgCl (0.1 M) as the reference electrode in an anhydrous and argon-saturated solution of 0.1 M of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile at a scanning rate of 50 mV·s^{-1}. Electrochemical onsets were determined at the position where the current starts to differ from the baseline. The morphologies of the polymer/$PC_{71}BM$ blend films were investigated by atomic force microscopy (AFM, Agilent Technologies, 5500 AFM/SPM System, USA) in contacting mode 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. Patterned 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 treatment in detergent, deionized water, acetone and isopropanol, and then treated in an ultraviolet-ozone chamber (Ultraviolet Ozone Cleaner, Jelight Company, USA) for 20 min. Then PEDOT:PSS (poly(3,4-ethylene dioxythiophene): poly(styrene sulfonate)) (Baytron PVP Al 4083, Germany) was filtered through a 0.45 μm 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 ºC for 15 min in the air, and the thickness of the PEDOT:PSS layer is about 40 nm. The polymer and $PC_{71}BM$ (10 mg/mL for polymer) were dissolved in ODCB and 3% volume ratio of 1,8-diiodooctane (DIO, Sigma Aldrich) overnight and spin-cast at 1700 rpm for 90 s onto the PEDOT:PSS layer. The thickness of the photoactive layer is about 110 nm measured by Ambios Technology XP-2 profilometer. A bilayer cathode consisting of ETLs (~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 mm^2.

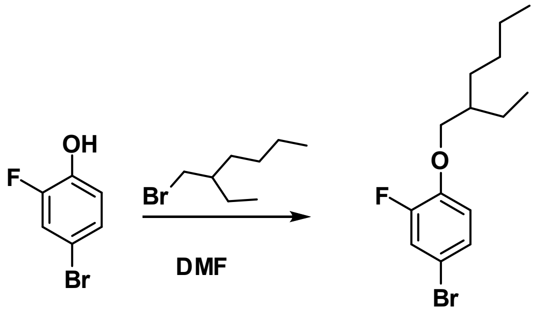
Device characterization was carried out under AM 1.5G irradiation with the intensity of 100 mW cm^{-2} (Oriel 67005, 500 W), calibrating by a standard silicon cell. *J-V* curves were recorded with a Keithley 236 digital source meter. A xenon lamp with AM 1.5 filter was used as the white light source 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 of these fabrications and characterizations after cleaning of ITO substrates were conducted in a glove box.

3. Materials

Lithium diisopropylamide (LDA), n-butyllithium(n-BuLi), $Sn(CH_3)_3Cl$, tetrakis(triphenylphosphine)palladium(0)($Pd(PPh_3)_4$) and Bis(triphenylphosphine)palladium(II) dichloride($PdCl_2(PPh_3)_2$) were obtained from Acros Organics, and they were used as received. Toluene was dried over P_2O_5 and freshly distilled prior to use. 4-Bromo-2-fluorophenol, 3,6-dibromo-4,5-difluorobenzene-1,2-diamine and other solvents were purchased from Aldrich and TCI Chemical Co. respectively. 3,6-Dibromo-4,5-difluorobenzene-1,2-diamine and 2,6-bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophene-2-yl)benzo[1,2-b:4,5-b']dithiophene (M2) were prepared according to literatures.

4. Synthesis

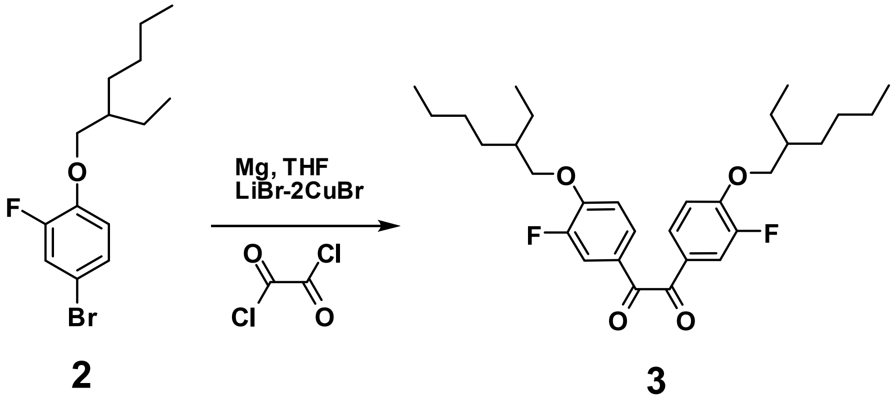
4-Bromo-1-(2′-ethylhexyloxy)-2-fluorobenzene (2)



1 2

4-Bromo-2-fluorophenol (1) (15 g, 75mmol), K_2CO_3 (11 g, 80mmol) were put into a three-neck round-bottom flask, and then added 100 mL DMF. Under the argon atmosphere, 1-bromo-2-ethylhexane (15 g, 75mmol) was added and the reaction mixture was stirred for 10h at 150°C. And then cooled to room temperature and the reaction mixture was poured into 200 mL water and then extracted three times with dichloromethane. The organic extraction was washed successively with saturated potassium hydroxide and water for twice, respectively. The combined organic phases were dried over magnesium sulfate. After filtration, the solvents were evaporated under vacuum and the crude product was purified on a silica gel column eluting with petroleum ether. Colorless oil was obtained (18.5 g, 82% yield). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ: 7.24 (dd, 1H), 7.19 (dd, 1H), 6.86 (t, 1H), 3.91 (d, 2H), 1.78 (m, 1H), 1.59 – 1.32 (m, 8H), 0.95 (m, 6H). MS: m/z=302 (M^+)

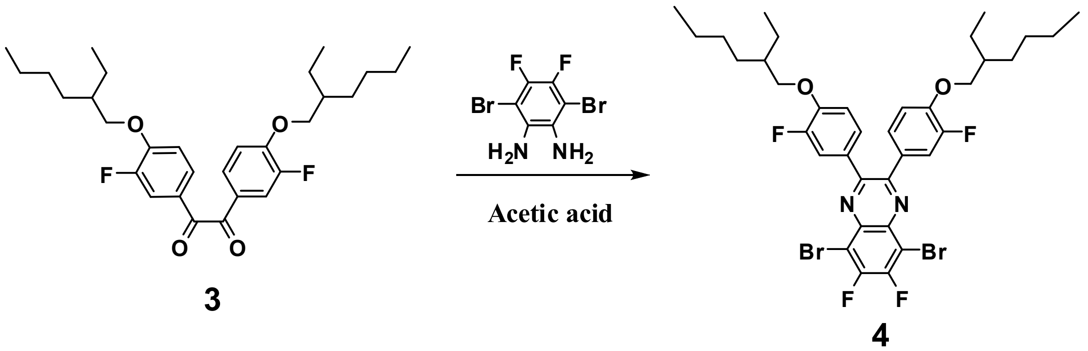
1,2-bis(4-(2-ethylhexyloxy)-3-fluorophenyl)ethane-1,2-dione (3)



Under vigorous stirring, 4-bromo-1-(2′-ethylhexyloxy)-2-fluorobenzene (11 g, 36.8 mmol) was added dropwisely to magnesium turnings (1 g, 44 mmol) in anhydrous THF (45 mL) which was protected by Ar. During the process, I_2 (10 mg) was added as catalyst in the reaction. The solution was refluxed for 5h until the magnesium was consumed. The mixture was refluxed for one more hour and then was cooled down. The solution system was added slowly to lithium bromide (6.75 g, 77.6 mmol) and cuprous bromide (5.58 g, 38.8 mmol) dispersed in 60 mL THF under 0°C. Oxalyl chloride (2.14 g, 46.4 mmol) was dissolved in 10% aqueous HCl (12.4 mL) and then added dropwisely into the above reaction mixture.

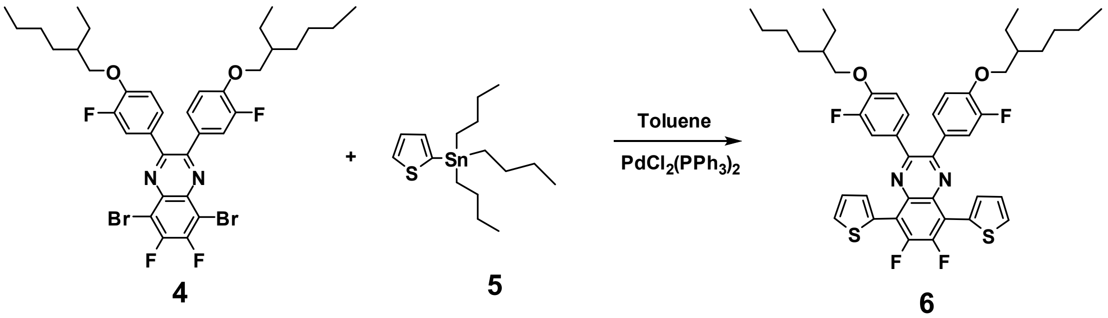
The solution was stirred for another 1 h at 50 °C. After cooling to room temperature, the mixture was poured into water and extracted with dichloromethane, the organic extraction was washed successively with water and sodium bicarbonate solution twice and the combined organic phase was dried over magnesium sulfate and evaporated to afford the crude product. The crude product was purified on a silica gel column, eluting with pure hexane. Light yellow viscous liquid were obtained (5.1 g, 28 % yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 – 7.44 (m, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 6.97 (t, 2H), 4.04 – 3.89 (m, 4H), 1.82 (dq, 2H), 1.70 – 1.24 (m, 16H), 1.08 – 0.86 (m, 12H). MS: m/z= 504 (M^+)

5,8-dibromo-2,3-bis(4-(2-ethylhexyloxy)-3-fluorophenyl-6,7-difluoroquinoxaline (4)



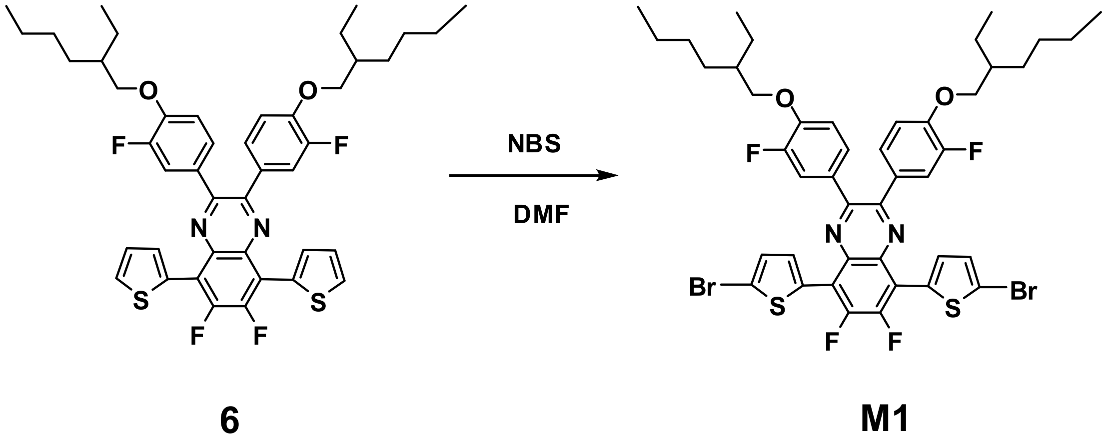
3,6-Dibromo-4,5-difluorobenzene-1,2-diamine (1.26 g, 4.2 mmol) was suspended in 80 mL acetic acid and compound 3 (1.8 g, 3.6 mmol) dissolved in 30 mL acetic acid was added. The suspension was heated to 60 °C for 1 h and then the temperature was raised to 120 °C for 3h. The solution was stirred for another 10 h at 80 °C. After cooling to room temperature, the mixture was poured into water and extracted with dichloromethane, the organic extraction was washed successively with water and sodium bicarbonate solution twice, the combined organic phase was dried over magnesium sulfate and evaporated to afford the crude product. The crude product was purified on a silica gel column, eluting with dichloromethane/hexane=1/7. Brown yellow viscous liquid were obtained (2.2 g, 79 % yield).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 – 7.46 (m, 2H), 7.38 (d, 2H), 6.97 (t, 2H), 4.06 – 3.88 (m, 4H), 1.82 (dq, 2H), 1.66 – 1.26 (m, 16H), 1.11 – 0.86 (m, 12H). MS: m/z= 768 (M^+)

2,3-bis(4-(2-ethylhexyloxy)-3-fluorophenyl)-6,7-difluoro-5,8-di(thiophen-2-yl)quinoxaline (6)



To a solution of compound 4 (1 g, 1.3 mmol), tributyl(thiophene-2-yl)-stannane (0.97 g, 2.6 mmol) and $PdCl_2(PPh_3)_2$ (22 g, 0.032 mmol) in dry toluene (25 ml) and the reaction mixture was heated to reflux for 48 h under an argon atmosphere. The reaction mixture was allowed to cool to room temperature and then concentrated under reduced pressure. The crude product was chromatographically purified on a silica gel column eluting with dichloromethane/hexane (1:6, v/v) to afford compound 6 as an orange solid (0.9 g, 90 % yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, 2H), 7.78 – 7.62 (m, 2H), 7.56 (ddd, 2H), 7.44 (ddd, 2H), 7.08 – 6.90 (m, 2H), 4.07 – 3.93 (m, 4H), 1.92 – 1.73 (m, 2H), 1.67 – 1.22 (m, 16H), 0.95 (ddd, 12H). MS: m/z= 775 (M^+)

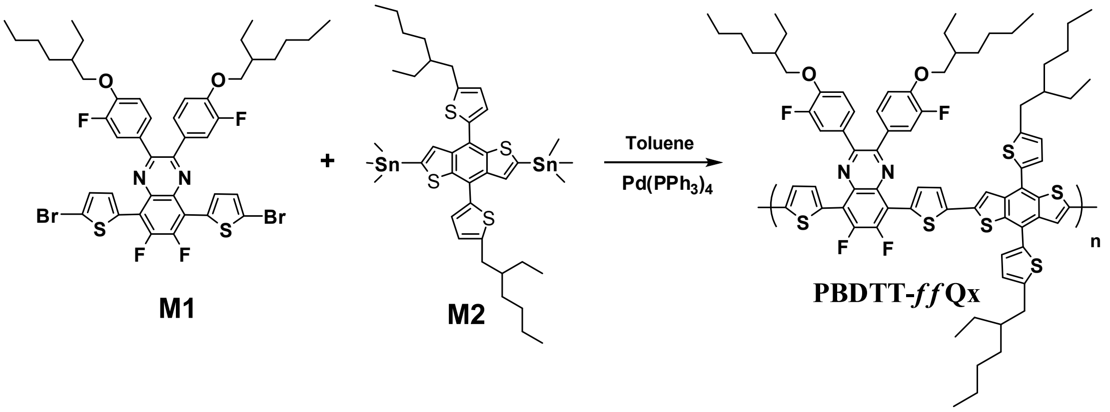
5,8-bis(5-bromothiophen-2-yl)-2,3-bis(4-(2-ethylhexyloxy)-3-fluorophenyl)-6,7-difluoroquinoxaline (M1)



6 **M1**

To a solution of compound 6 (0.9 g, 1.16 mmol) in dimethyl formamide (20 mL) was added *N*-bromosuccinimide (NBS) (0.41 g, 2.32 mmol) in one portion. The mixture was stirred at room temperature in the dark for 24 h. The solution was concentrated in vacuum and the residue was chromatographically purified on a silica gel column eluting with dichloromethane/hexane (1:8, v/v) to afford **M1** as an orange solid (0.72 g, 78 % yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, 2H), 7.50 (dd, 2H), 7.44 (d, 2H), 7.24 – 7.18 (m, 2H), 7.02 (t, 2H), 4.05 – 3.97 (m, 4H), 1.84 (dt, 2H), 1.66 – 1.22 (m, 16H), 0.95 (ddd, 12H). MS: m/z= 930 (M^+).

Synthesis of PBDTT-*ff*Qx



M1 (0.18 g, 0.2 mmol), M2 (0.19 g, 0.2 mmol) and 15 mL of dry toluene were put into a two-necked flask. The solution was flushed with Ar for 20 min, then Pd(PPh$_3$)$_4$ (15 mg) was added into the flask. The solution was flushed with Ar again for 20 min. The oil bath was heated to 110 °C carefully, and the reactant was stirred for 24 h at this temperature under argon atmosphere. Then the reaction mixture was cooled to room temperature and then poured into methanol (100 mL) slowly. The resulting precipitate was filtered through a Soxhlet thimble, which was then subjected to Soxhlet extractions with methanol, hexane and chloroform. Finally the polymer was recovered as a solid from the chloroform fraction by rotary evaporation. Finally, the blue-black solid was obtained (0.21 g, yield: 77%). ^{1}H NMR (500 MHz, CDCl$_3$, ppm) δ 8.03 (s, 2H), 7.54 (s, 4H), 7.02 (s, 4H), 8.21-6.67 (br, 6H), 4.29-3.86 (br, 4H), 3.17-2.75 (br, 4H), 2.32–2.21 (m, 2H), 1.98–1.85 (m, 2H), 1.54-0.89 (m, 56H).

5. ^{1}H NMR

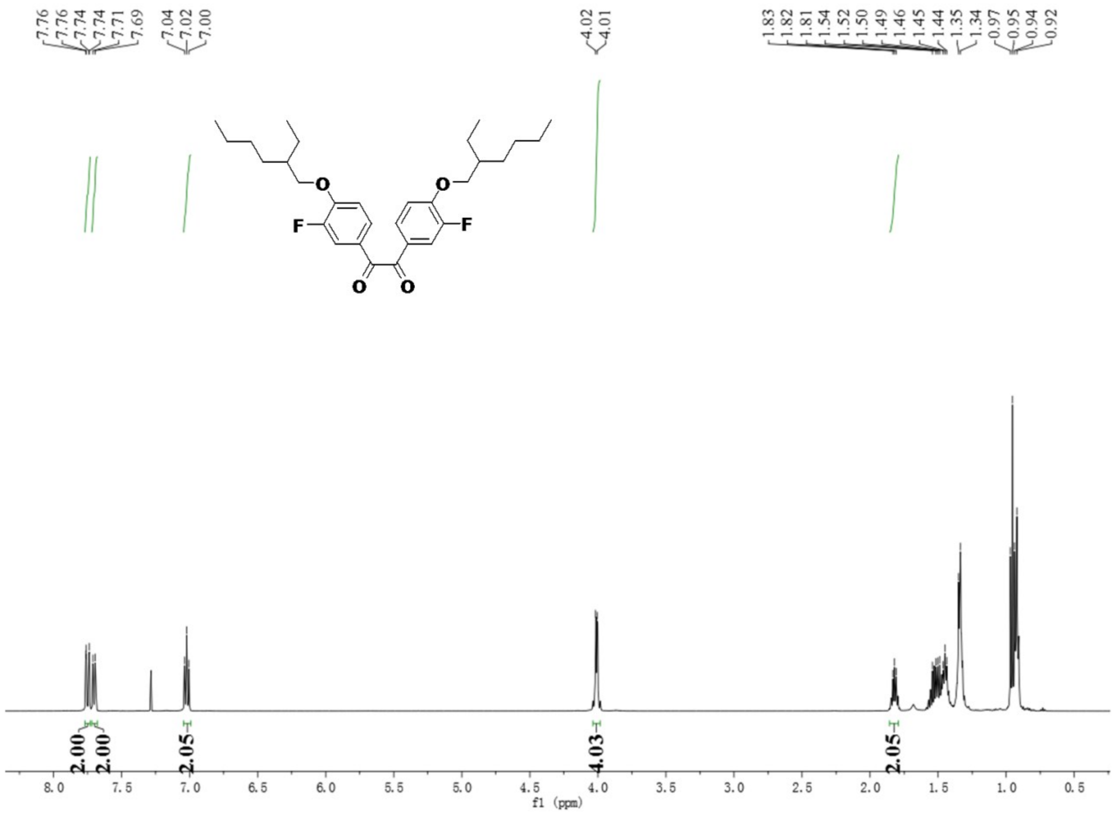


Figure S1. ^{1}H NMR spectrum of 1,2-bis(4-(2-ethylhexyloxy)-3-fluorophenyl)ethane-1,2-dione (3).

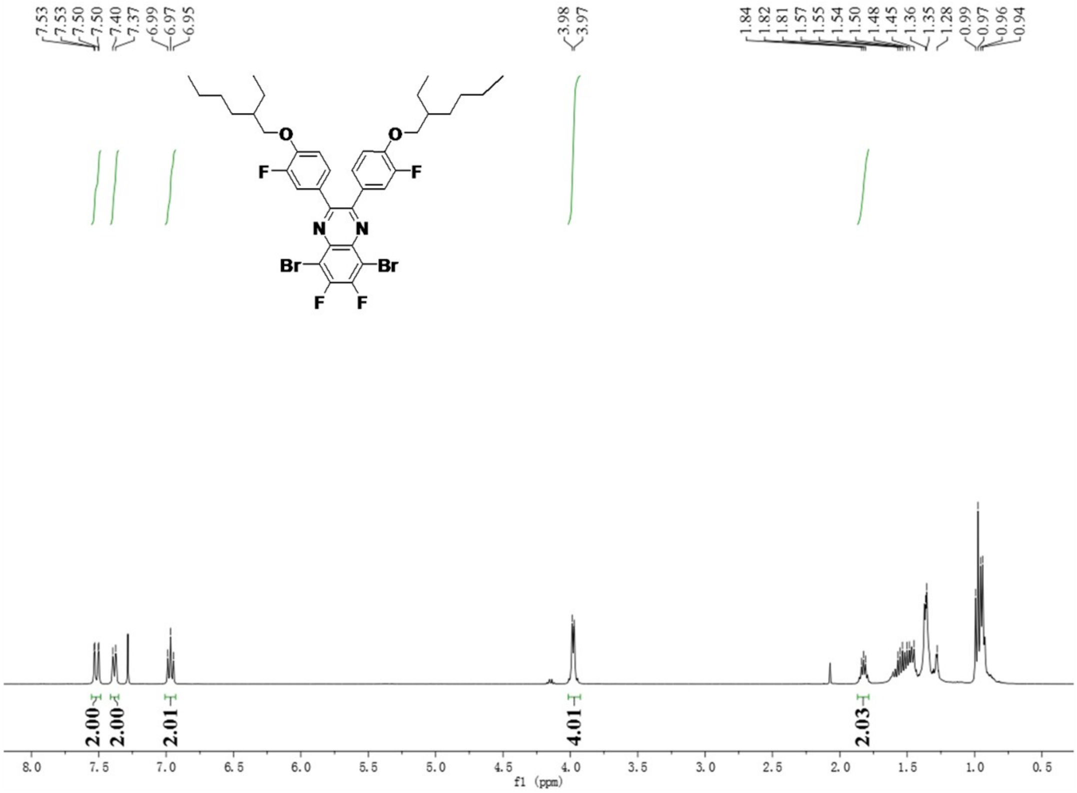


Figure S2. ^{1}H NMR spectrum of 5,8-dibromo-2,3-bis(4-(2-ethylhexyloxy) -3-fluorophenyl-6,7-difluoroquinoxaline (4).

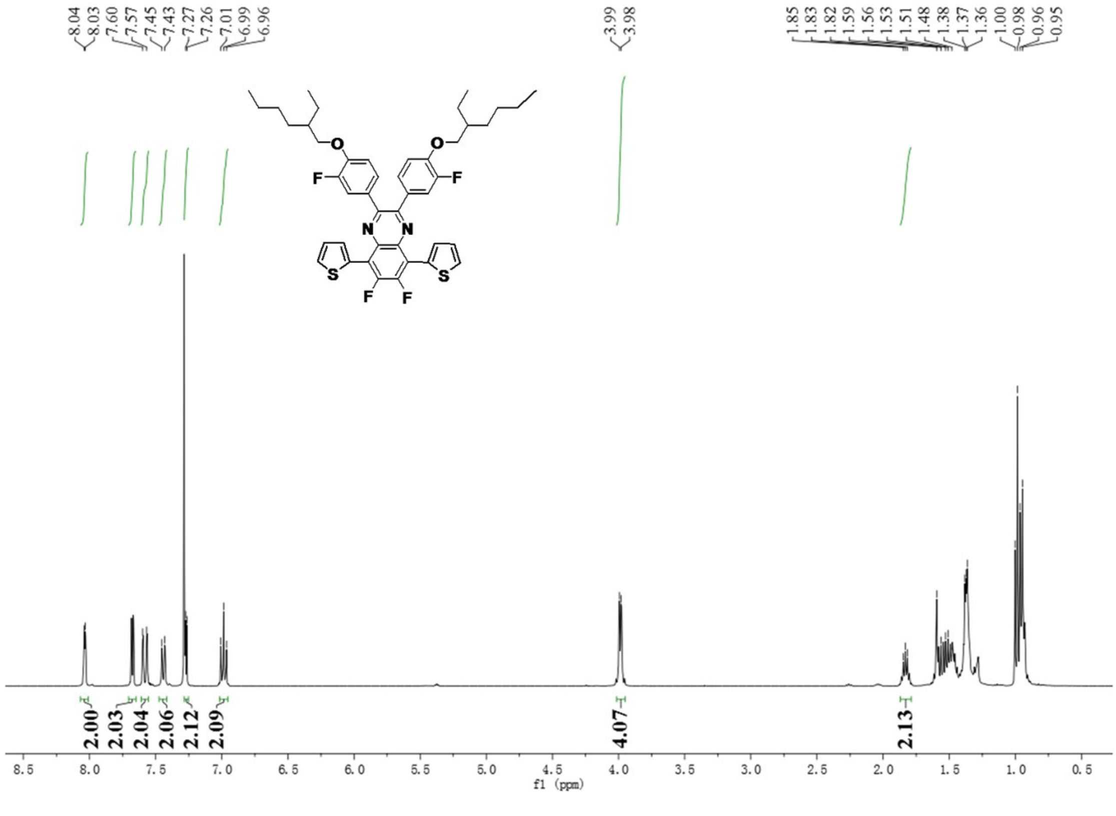


Figure S3.^{1}H NMR spectrum of2,3-bis(4-(2-ethylhexyloxy)-3-fluorophenyl)-6,7-difluoro-5,8- di(thiophen-2-yl)quinoxaline (6).

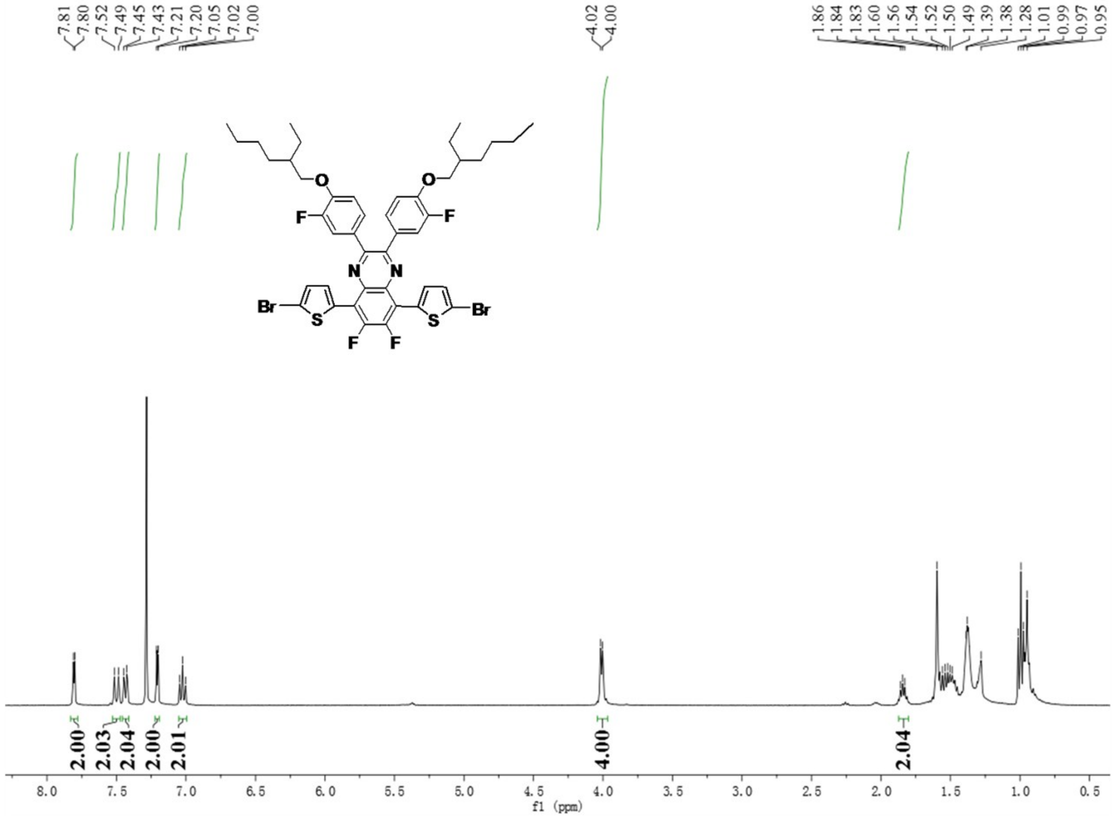


Figure S4. ^{1}H NMR spectrum of 5,8-bis(5-bromothiophen-2-yl)-2,3-bis (4-(2-ethylhexyloxy)-3-fluorophenyl)-6,7-difluoroquinoxaline (M1).

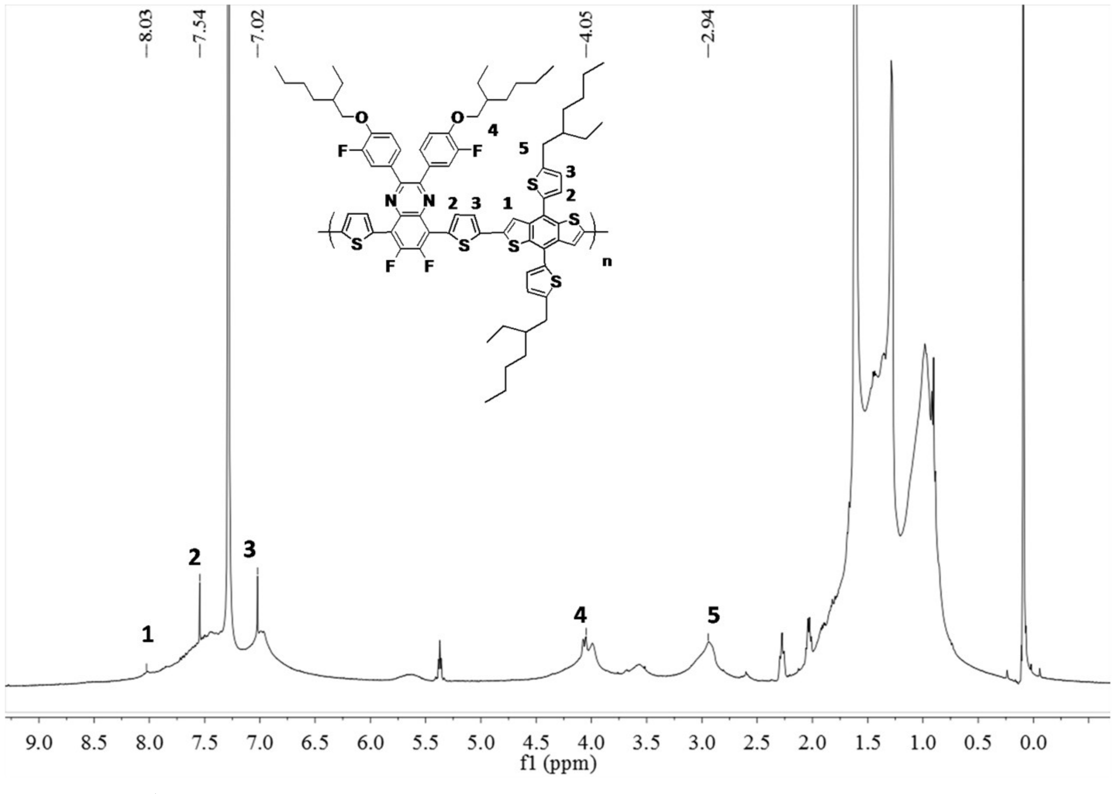


Figure S5. ^{1}H NMR spectrum of PBDTT-*ff*Qx

6. TGA

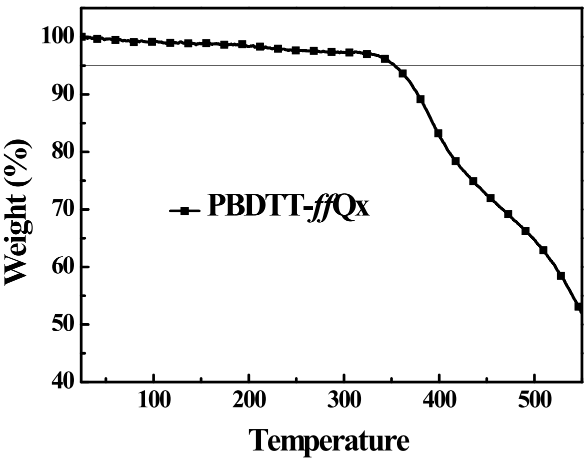


Figure S6. TGA curves for the PBDTT-*ff*Qx

7. Space charge limited current (SCLC) measurements

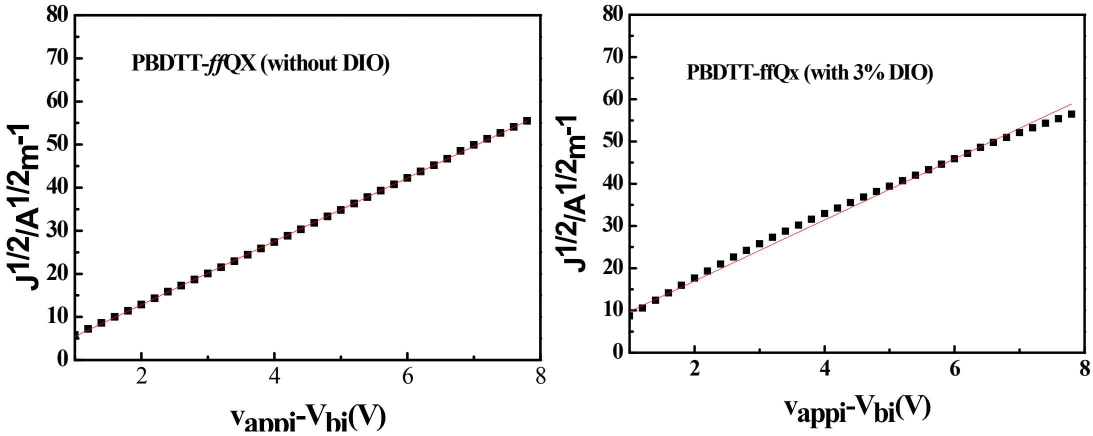


Figure S7. *J-V* curves of the PBDTT-*ff*Qx/PC$_{71}$BM blend with or without DIO for hole mobility measurement by SCLC method.

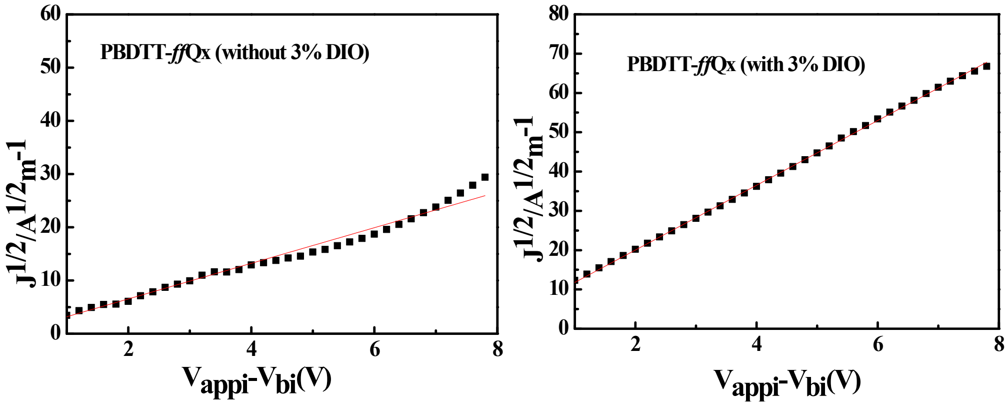


Figure S8. *J*-*V* curves of the PBDTT-ffQx/PC$_{71}$BM blend with or without DIO for electron mobility measurement by SCLC method.

8. Stability measurement

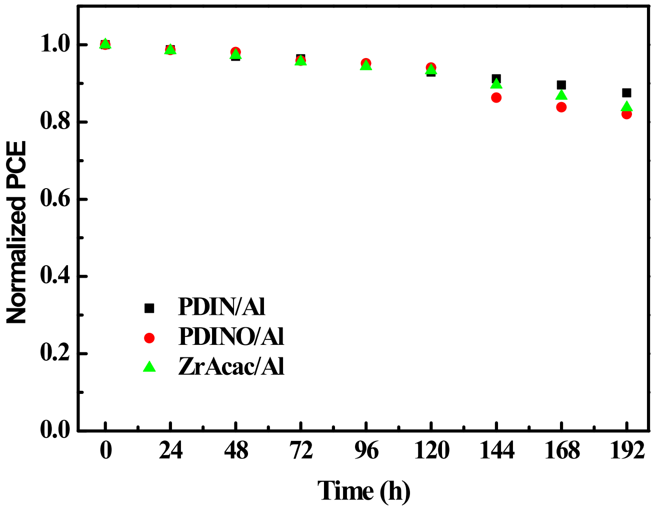


Figure S9. Normalized PCEs under ambient conditions for PBDTT-*ff*Qx/PC$_{71}$BM based PSCs with PDIN/Al, PDINO/Al and ZrAcac/Al.

9. Molecular weight and Thermal data

Table S1 Molecular weights and thermal property of the copolymer.

Polymer	M_n (kDa)	M_w (kDa)	PDI	Yield (%)	T_d (ºC)
PBDTT-*ff*Qx	23.5	37.6	1.6	87	351

10. Optical and Electrochemical data

Table S2: Optical and Electrochemical Properties of PBDTT-*ff*Qx

Polymer	Absorption spectra				Cyclic voltammetry		
	Sol[a]	Film[b]			*p*-doping	*n*-doping	
	λ_{max} (nm)	λ_{max} (nm)	λ_{onset} (nm)	E_g^{opt} [c] (eV)	E_{on}^{ox} /HOMO[d] (V)/(eV)	E_{on}^{red} /LUMO[d] (V)/(eV)	E_g^{EC} (eV)
PBDTT-*ff*Qx	583	638	729	1.7	0.96/-5.36	-0.84/-3.56	1.8

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_{on}^{ox} +4.4) (eV); LUMO= -e (E_{on}^{red} +4.4) (eV) using (eV) using Ag/AgCl as the reference electrode.

11. All detailed photovoltaic data

Table S3. The device parameters of PSCs based on PBDTT-*ff*Qx:$PC_{71}BM$ with different cathode and DIO ratio under illumination of AM 1.5G,100 mW cm^{-2}.

Active layer	**V_{oc} (V)**	**J_{sc} (mA cm^{-2})**	***FF* (%)**	**PCE (%)**
PBDTT-*ff*Qx:$PC_{71}BM$=1:1[c]	0.91	11.6	53	5.6
PBDTT-*ff*Qx: $PC_{71}BM$=1:2[c]	0.91	8.3	49	3.6
PBDTT-*ff*Qx: $PC_{71}BM$=1:1[b]	0.91	11.7	58	6.2
PBDTT-*ff*Qx $PC_{71}BM$=1:1[a]	0.91	11.3	57	5.9
PBDTT-*ff*Qx $PC_{71}BM$=1:1[c] (1%DIO)	0.87	12.2	65	6.9
PBDTT-*ff*Qx: $PC_{71}BM$=1:1[c] (3%DIO)	0.86	14.5	70	8.6
PBDTT-*ff*Qx: $PC_{71}BM$=1:1[c] (5%DIO)	0.87	11.7	69	7.0
PBDTT-*ff*Qx: $PC_{71}BM$=1:1[b] (3%DIO)	0.86	13.7	71	8.3
PBDTT-*ff*Qx: $PC_{71}BM$=1:1[a] (3%DIO)	0.85	13.3	70	8.0

[a]The cathode interlayer is PDIN. [b]The cathode interlayer is PDINO [c]The cathode interlayer is ZrAcac.