

SUPPORTING INFORMATION

**Optimizing conjugated side chains on quinoxaline based polymers for nonfullerene
solar cells with 10.5% efficiency**

Shutao Xu^a, Xiaojing Wang^b, Liuliu Feng^a, Zhicai He^b, Hongjian Peng^a, Věra Cimrová^c, Jun Yuan^a,
Zhi-Guo Zhang^d, Yongfang Li^d, Yingping Zou^{a*}

^a College of Chemistry and Chemical Engineering, Central South University, Changsha 410083,
China. * E-mail: yingpingzou@csu.edu.cn(Y.Zou)

^b Institute of Polymer Optoelectronic Materials and Devices, State Key Laboratory of Luminescent
Materials and Devices, South China University of Technology, Guangzhou 510640, China.

^c Institute of Macromolecular Chemistry, The Czech Academy of Sciences, Heyrovský Sq. 2, 162
06 Prague 6, Czech Republic

^d Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of
Sciences, Beijing 100190, China.

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1. General measurement

^1H NMR, ^{13}C NMR spectra were recorded using a Bruker AV-400 and 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. Molecular weight and polydispersity index of the polymers were determined by high temperature 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 1,2,4-trichlorobenzene as eluent at a flow rate of 1.0 mL/min at 150°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-2600 spectrophotometer. Photoluminescence (PL) quenching measurements were recorded on the HITACHI F-4600 spectrophotometer. For the solid state measurements, a polymer solution in chloroform was spin-coated on quartz plate. The cyclic voltammetry was recorded with a computer controlled CHI660E electrochemical workstation using polymer films on platinum electrode (1.0 cm²) 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 (Bu₄NPF₆) 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:acceptor blend films were investigated by atomic force microscopy (AFM, Agilent Technologies, 5500 AFM/SPM System, USA) in contacting mode with a 3 μm scanner. Transmission

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

2. Fabrication and characterization of PSCS

PSCs were fabricated in the configuration of the traditional sandwich structure with an indium tin oxide (ITO) glass positive electrode and an 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 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 min in the air, and the thickness of the PEDOT:PSS layer was about 40 nm. The TTFQx-T1 and ITIC (10 mg/mL for polymer) were dissolved in CF and spin-cast at 2500 rpm for 90s onto the PEDOT:PSS layer. The TTFQx-T1 and PC₇₁BM (10 mg/mL for polymer) were dissolved in CF and spin-cast at 2800 rpm for 90s onto the PEDOT:PSS layer. Thermal annealing treatment under different temperatures is at 10 min. The TTFQx-T2 and ITIC (10 mg/mL for polymer) were dissolved in CF and spin-cast at 2500 rpm for 90s onto the PEDOT:PSS layer. The TTFQx-T2 and PC₇₁BM (10 mg/mL for polymer) were dissolved in CF and spin-cast at 2800 rpm for 90 s onto the PEDOT:PSS layer. Thermal annealing treatment was performed at different temperatures for 10 min. The thickness

of the photoactive layer was 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 was 4.5 mm².

Inverted PSCs were fabricated with the architecture of ITO/ZnO/ poly[9,9-dioctylfluorene-2,7-diyl-*alt*-9,9-bis(3-(*N,N*-dimethylamino)propyl)fluorene-2,7-diyl] (PFN)/TTFQx-T1:ITIC/MoO₃/Ag. Thin film of ZnO (about 30nm) was prepared on top of the cleared ITO by the ZnO precursor with solution zinc acetate dehydrate C₄H₆ O₄Zn·2(H₂O) (99.5%, Merck, 1g) and monoethanolamine (HOCH₂CH₂NH₂, 98%, Acros,0.28g) in 2-methoxyethanol (CH₃OCH₂CH₂OH, Aldrich, 99.8%,10 mL) and then heating at 200 °C for 30 minutes in air. On top of the ZnO layer, a thin film of poly[9,9-dioctylfluorene-2,7-diyl-*alt*-9,9-bis(3-(*N,N*-dimethylamino)propyl)fluorene-2,7-diyl] (PFN) (about 10nm) was deposited. The TTFQx-T1 and ITIC (10 mg/mL for polymer) were dissolved in CF and spin-cast at 2500 rpm for 90s onto the PFN layer. The device was completed by thermal evaporation of 10 nm MoO₃ and then 100 nm Ag electrode. The active area of the PSCs was 16 mm².

Device characterizations were 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 a 500 W xenon

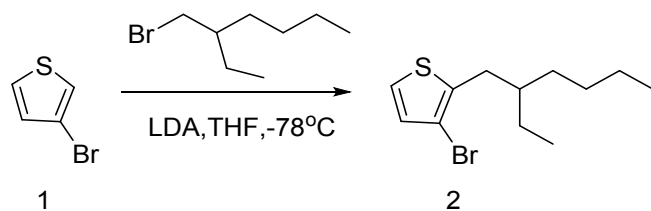
lamp. A calibrated silicon detector was used to determine the absolute photosensitivity at different wavelengths. All of these fabrications and characterizations after cleaning ITO substrates were conducted in a glove box.

3. Materials

n-Butyllithium (n-BuLi), Lithium diisopropylamide (LDA), Tetrabutylammonium fluoride (TBAF), trimethylchlorosilane (Me₃SiCl), tributylchlorostannane (SnCl(Bu)₃), tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄) and bis(triphenylphosphine)palladium(II)dichloride (PdCl₂(PPh₃)₂) were obtained from Acros Organics, and they were used as received. Toluene was dried over P₂O₅ and freshly distilled prior to use. 3-Bromothiophene, 4,7-dibromo-5,6-difluorobenzo[*c*][1,2,5]thiadiazole, sodium borohydride (NaBH₄), 2,6-bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophene-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene (M2), (4,8-bis(5-(2-butylloctyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(trimethylstannane) (M3) and other solvents were purchased from Aldrich and TCI Chemical Co, respectively.

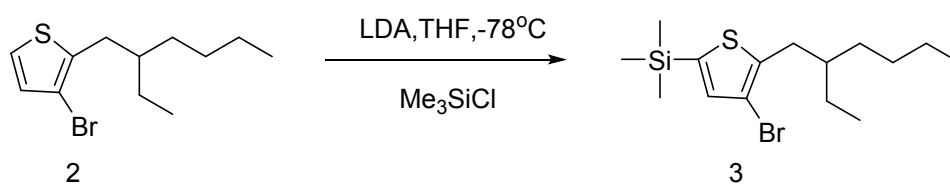
4. Synthesis

3-Bromo-2-(2-ethylhexyl)thiophene (2)



To 3-bromothiophene (1) (20 g, 122.7 mmol) in anhydrous THF (200 mL), the LDA (74.82 mL, 149.64 mmol) was added at -78°C under argon and the reaction mixture was stirred for 30 min, 1-bromo-2-ethylhexane (35.81 g, 185.54 mmol) was added and the mixing continued for another 30 min at -78°C . Then the reaction mixture was warmed to 70°C and stirred overnight. After cooling to room temperature, the mixture was poured into water and extracted with dichloromethane to afford the crude product. The crude product was purified by column chromatography on a silica gel using hexane as eluent. The pure product 2 was obtained as a colorless liquid (27 g, 80 % yield). ^1H NMR (400 MHz, CDCl_3): δ 7.11 (d, $J = 5.3$ Hz, 1H), 6.89 (d, $J = 5.3$ Hz, 1H), 2.72 (d, $J = 7.1$ Hz, 2H), 1.30 (t, $J = 6.4$ Hz, 7H), 0.89 (dd, $J = 7.5, 4.2$ Hz, 8H).

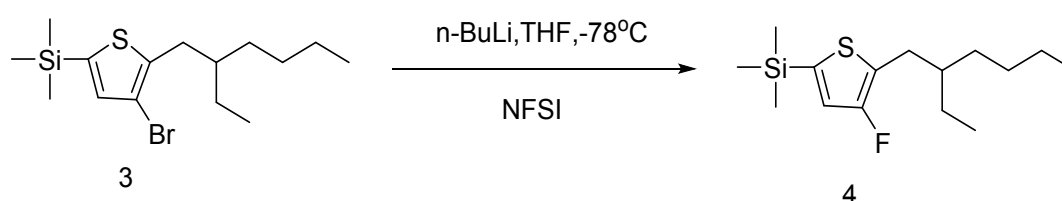
(4-Bromo-5-(2-ethylhexyl)thiophen-2-yl)trimethylsilane (3)



To 3-bromo-2-(2-ethylhexyl)thiophene (2) (33.23 g, 120.84 mmol) in anhydrous THF (250 mL), the LDA (108.75 mL, 217.51 mmol) was added at -78°C under argon and the reaction mixture was mixed for 1 h. Then the Me_3SiCl (23.49 g, 217.51 mmol) was added and the mixture was stirred for another 30 min at -78°C and 5h at room temperature. The mixture was poured into water and extracted with dichloromethane to

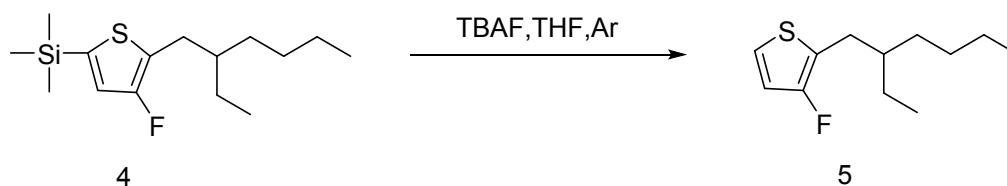
afford the crude product. The crude product was purified by column chromatography on a silica gel using hexane as eluent. The pure product 3 was obtained as a colorless liquid (35.64 g, 85 % yield). ¹H NMR (400 MHz, CDCl₃): δ 6.86 (s, 1H), 2.58 (d, J = 7.0 Hz, 2H), 0.77-0.73 (m, 7H), 0.14 (s, 8H).

(5-(2-Ethylhexyl)-4-fluorothiophen-2-yl)trimethylsilane (4)



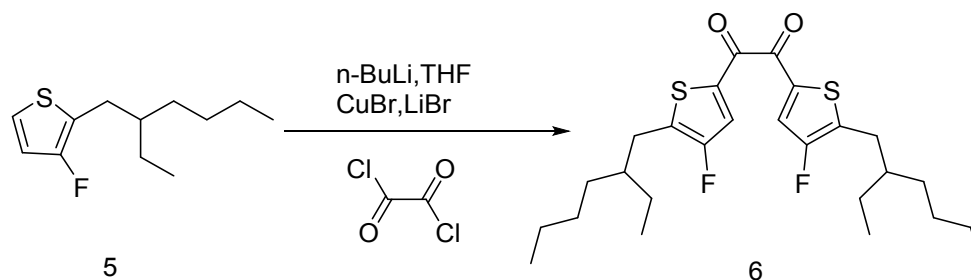
To the (4-bromo-5-(2-ethylhexyl)thiophen-2-yl)trimethylsilane (3) (34.71 g, 100 mmol) in anhydrous THF (200 mL), the *n*-BuLi (62.52 mL, 150 mmol) was added at -78°C under argon and the reaction mixture was stirred for 30 min. The NFSI (63 g, 200 mmol) in 60 mL THF was added and the mixture was stirred for another 30 min at -78°C and for 5h at room temperature. The mixture was poured into water and extracted with dichloromethane to afford the crude product. The crude product was purified by column chromatography on a silica gel using hexane as eluent. The product 4 was obtained as a colorless liquid (17.83 g, 62 % yield). ¹H NMR (400 MHz, CDCl₃): δ 6.74 (s, 1H), 2.60 (d, J = 6.7 Hz, 2H), 1.28 (s, 7H), 0.89 (d, J = 7.0 Hz, 8H).

2-(2-Ethylhexyl)-3-fluorothiophene (5)



(5-(2-Ethylhexyl)-4-fluorothiophen-2-yl)trimethylsilane (4) (17.83 g, 62.22 mmol) in THF (300 mL) was degassed in a three-neck round-bottom flask by stirring (20 min) under argon, TBAF (68.45 mL, 68.45 mmol) was added and the reaction mixture was stirred for 3h at room temperature. The mixture was poured into water and extracted with dichloromethane to afford the crude product. The crude product was purified by column chromatography on a silica gel using hexane as eluent. The product 5 was obtained as a colorless liquid (12.44 g, 93.3 % yield). ¹H NMR (400 MHz, CDCl₃): δ 6.97 (dd, J = 5.5, 3.8 Hz, 1H), 6.72 (dd, J = 5.5, 0.6 Hz, 1H), 2.67 (d, J = 0.8 Hz, 2H), 1.28 (d, J = 3.8 Hz, 7H), 0.88 (d, J = 7.3 Hz, 8H).

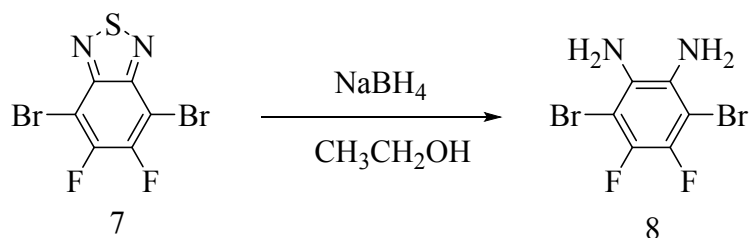
1,2-Bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)ethane-1,2-dione (6)



To the 5-(2-ethylhexyl)-4-fluorothiophene (5) (12.44 g, 58.04 mmol) in anhydrous THF (100 mL), the *n*-BuLi (24.2 mL, 58.04 mmol) was added at $-78\text{ }^{\circ}\text{C}$ under argon and the reaction mixture was stirred for 2h. Then the mixture was added slowly to lithium bromide (10.76 g, 123.7 mmol) and cuprous bromide (8.36 g, 58.04 mmol) dispersed in 200 mL THF at 0°C . After 1h of stirring, the oxalyl chloride (3.35

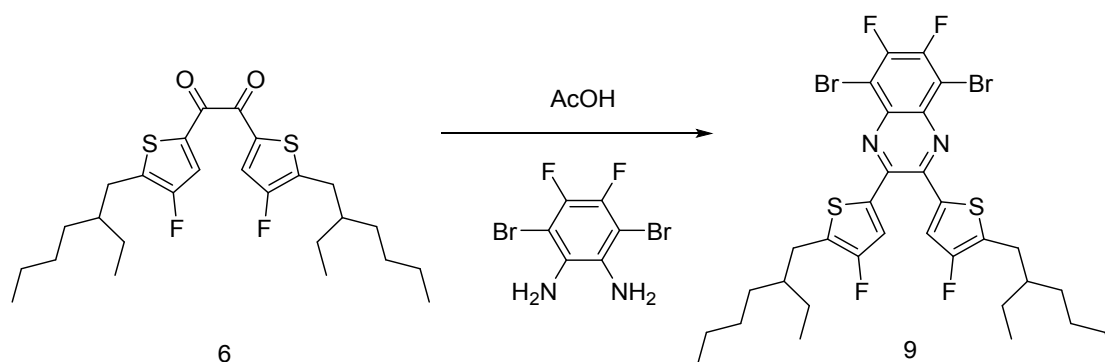
g, 26.32 mmol) was added and the reaction mixture was stirred for 30 min at 0 °C and for another 2 h at room temperature. Then the mixture was poured into water, extracted with dichloromethane, and the organic extraction was washed thoroughly with water and aqueous sodium bicarbonate. The organic phase was dried over magnesium sulfate and evaporated to afford the crude product. The crude product was purified by column chromatography on a silica gel using hexane as eluent. The product 6 was obtained as a light yellow viscous liquid (2.80 g, 22 % yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.74 (s, 2H), 2.76 (d, *J* = 6.8 Hz, 4H), 1.66 (s, 2H), 1.37 (d, *J* = 6.8 Hz, 18H), 0.89 (d, *J* = 2.4 Hz, 10H).

3,6-Dibromo-4,5-difluorobenzene-1,2-diamine (8)



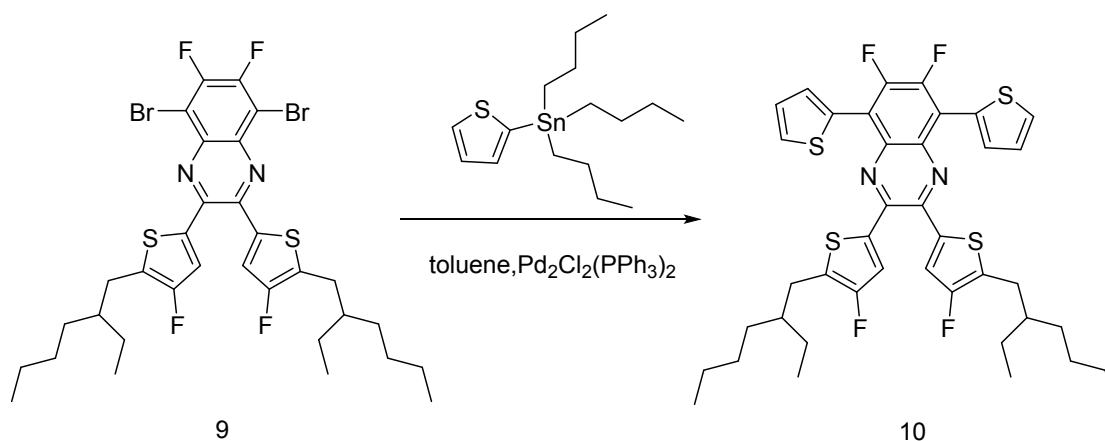
To the 4,7-dibromo-5,6-difluorobenzo[*c*][1,2,5]thiadiazole (7) (1.84 g, 5.8 mmol) in ethanol (60 mL), the NaBH₄ was added (2.26 g, 58 mmol) in one portion at 0 °C and the mixture was stirred at room temperature for 6 h. The reaction mixture was poured into water (200 mL) and then extracted with dichloromethane (3×) and water (3×). The combined organic extractions were dried over magnesium sulfate, solvent was evaporated under vacuum and the white crude product 8 was used without purification in the next step.

5,8-Dibromo-2,3-bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)-6,7-difluoroquinoxaline (9)



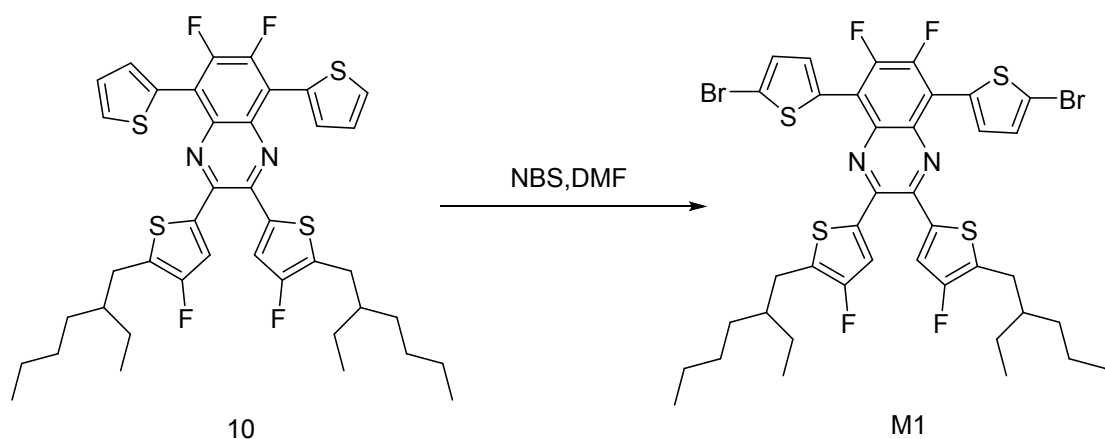
3,6-Dibromo-4,5-difluorobenzene-1,2-diamine (8) (1.397 g, 4.627 mmol) was suspended in acetic acid (100 mL) and compound (6) (1.92 g, 3.972 mmol) dissolved in acetic acid (60 mL) was added. The suspension was heated at 60 °C for 1 h and then the temperature was increased to 120 °C for 3h. The solution was stirred overnight at 90 °C. After cooling to room temperature, the mixture was poured into water and extracted with dichloromethane. The organic extraction was washed thoroughly with water and aqueous sodium bicarbonate, dried over magnesium sulfate and evaporated to afford the crude product. The crude product was purified by column chromatography on silica gel using dichloromethane/hexane = 1/9 (v/v) as eluent. The product 9 was obtained as a yellow viscous liquid (2.19 g, 73.7 % yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.24 (s, 2H), 2.76 (d, *J* = 6.8 Hz, 4H), 1.67 (dd, *J* = 11.9, 5.9 Hz, 2H), 1.54 (s, 2H), 1.36 (d, *J* = 22.6 Hz, 14H), 0.98 - 0.84 (m, 12H).

2,3-Bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)-6,7-difluoro-5,8-di(thiophen-2-yl)quinoxaline (10)



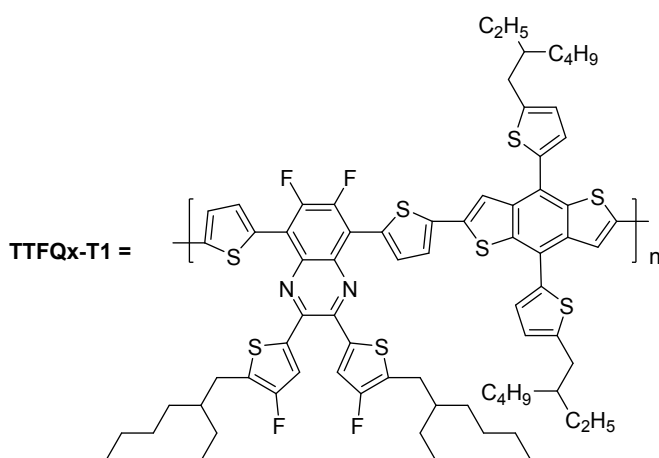
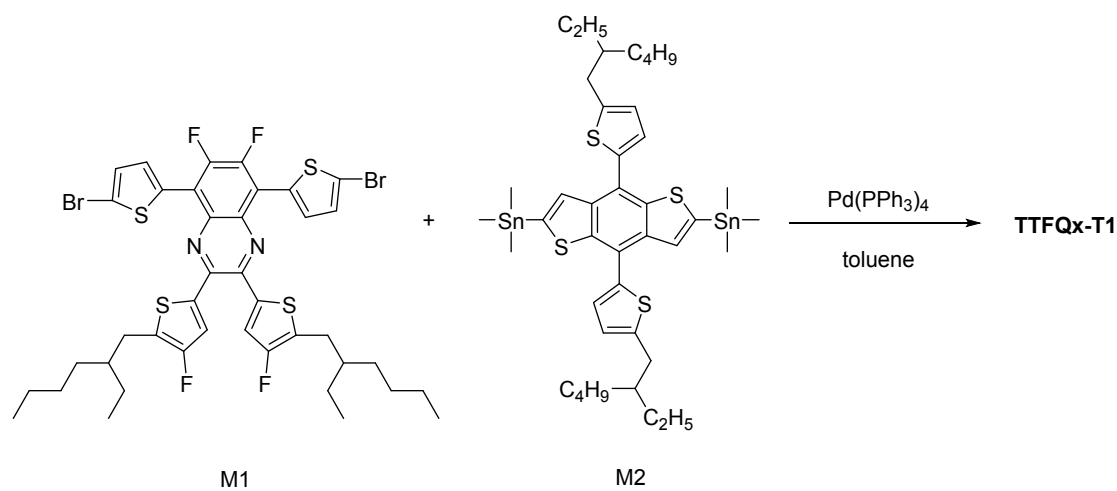
The mixture of compound 9 (2.19 g, 2.93 mmol), tributyl(thiophen-2-yl)- stannane (2.74 g, 7.31 mmol), and PdCl₂(PPh₃)₂ (82.26 mg, 0.12 mmol) in dry toluene (30 mL) was refluxed for 48 h under argon. The reaction mixture was allowed to cool to room temperature and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on a silica gel using dichloromethane/hexane (1:9, v/v) as eluent to afford compound 10 as an orange solid (1.29 g, 58.2 % yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.94 (d, *J* = 3.4 Hz, 2H), 7.60 (d, *J* = 5.1 Hz, 2H), 7.22 - 7.17 (m, 4H), 2.76 (d, *J* = 6.7 Hz, 4H), 1.70 - 1.63 (m, 2H), 1.44 - 1.31 (m, 18H), 0.98 - 0.91 (m, 10H).

5,8-Bis(5-bromothiophen-2-yl)-2,3-bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)-6,7-difluoroquinoxaline (M1)



To compound 10 (1.29 g, 1.71 mmol) in dimethyl formamide (60 mL), the N-bromosuccinimide (NBS) (0.76 g, 4.23 mmol) was added slowly (40 min) in several portions. The mixture was stirred for 24 h at room temperature in the dark. The solution was concentrated in vacuum and the residue was purified by column chromatography on a silica gel using dichloromethane/hexane (1:10, *v/v*) as eluent. The product M1 was obtained as a red solid (1.0 g, 64.5 % yield). ¹H NMR (400 MHz, CDCl₃): δ 7.71 (d, *J* = 4.1 Hz, 2H), 7.21 (s, 2H), 7.15 (d, *J* = 4.1 Hz, 2H), 2.80 (d, *J* = 6.6 Hz, 4H), 1.70 (dd, *J* = 12.2, 6.1 Hz, 2H), 1.49 - 1.42 (m, 4H), 1.36 (t, *J* = 9.4 Hz, 12H), 0.94 (dt, *J* = 13.9, 7.2 Hz, 12H). ¹³C NMR (101 MHz, CDCl₃): δ 155.38, 152.83, 150.86, 150.67, 148.28, 148.09, 143.67, 134.22, 134.14, 133.38, 131.94, 131.23, 131.12, 131.04, 130.96, 129.35, 127.43, 127.26, 119.81, 119.54, 118.79, 116.79, 77.34, 77.22, 77.02, 76.70, 40.84, 32.59, 31.94, 29.71, 29.26, 28.91, 25.79, 22.97, 14.14, 10.94.

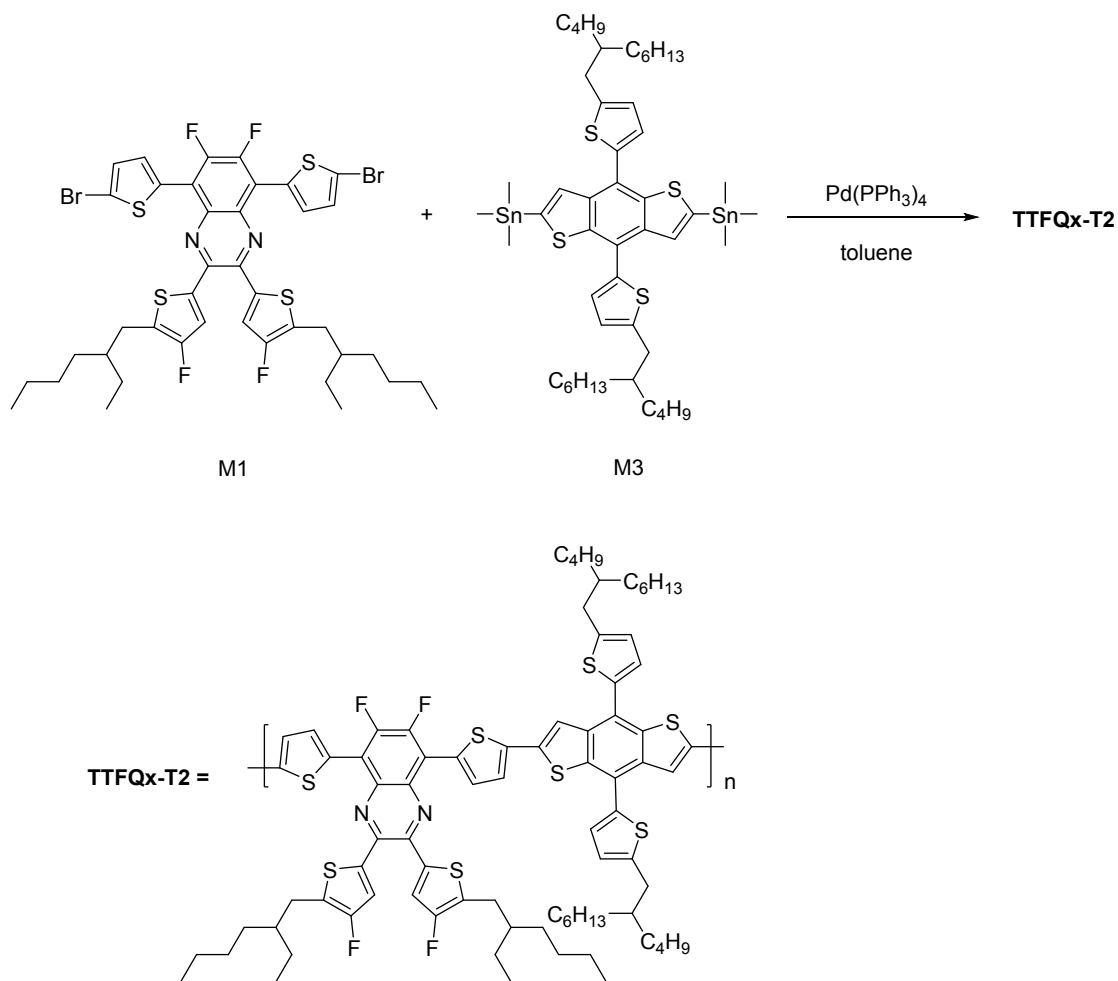
Polymer TTFQx-T1



In a 50 mL two-necked flask, M1 (0.14 g, 0.15 mmol) and M2 (0.14 g, 0.15 mmol) were dissolved in 10 mL anhydrous toluene. The reaction system was purged with argon for 10 min to remove the oxygen. The catalyst Pd(PPh₃)₄ (13 mg) was added quickly into the flask, which was flushed for 5 min with argon again, and the reaction mixture was heated to 110 °C for 24 h under vigorous stirring. The reaction mixture was cooled to room temperature, poured into 200 mL of methanol and the crude polymer precipitated out. After stirring for 30 min, the crude polymer was filtered off and purified by a Soxhlet extraction with methanol, n-hexane, acetone and chloroform successively. The chloroform fraction was collected and evaporated under vacuum to afford the target polymer TTFQx-T1 as deep green solid (185 mg, 68% yield). TTFQx-

T1 has a number average molecular weight (M_n) of 24.8 kDa with the dispersity (D : M_w/M_n) of 2.87.

Polymer TTFQx-T2



In a 50 mL two-necked flask, M1 (0.14 g, 0.15 mmol) and M3 (0.15 g, 0.15 mmol) were dissolved in 10 mL anhydrous toluene. The reaction system was purged with Ar for 10 min to remove the oxygen. The catalyst $\text{Pd}(\text{PPh}_3)_4$ (13 mg) was added quickly into the flask, then purged with Ar for 5 min again. The reaction mixture was heated to 110 °C and stirred for 24 h. After cooling, it was poured into 200 mL of methanol and stirred for 30 min to precipitate out the crude polymer, which was filtered off. The

polymer was purified by a Soxhlet extraction with methanol, n-hexane, acetone and chloroform. The chloroform fraction was collected and evaporated under vacuum to afford the target polymer TTFQx-T2 as deep green solid (145 mg, 50% yield). TTFQx-T2 has a number average molecular weight (M_n) of 13.7 kDa with a D of 2.31.

5. ^1H NMR

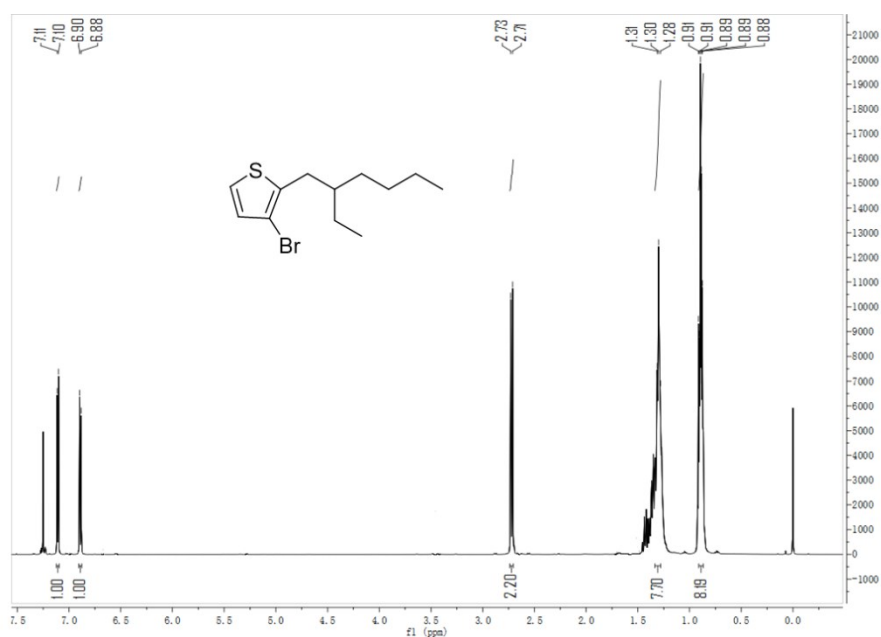


Figure S1. ^1H NMR spectrum of 3-bromo-2-(2-ethylhexyl)thiophene (2)

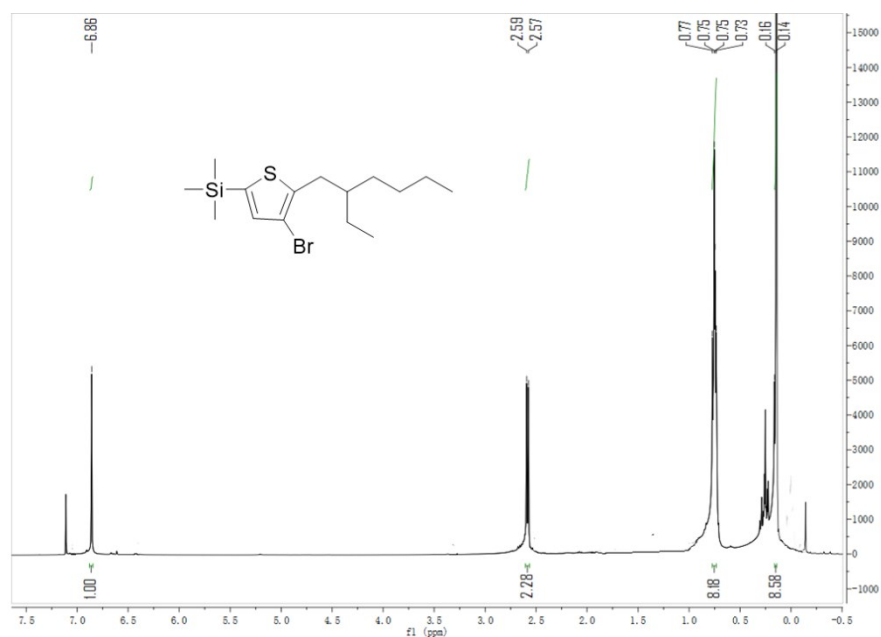


Figure S2. ^1H NMR spectrum of (4-bromo-5-(2-ethylhexyl)thiophen-2-yl)trimethylsilane (3)

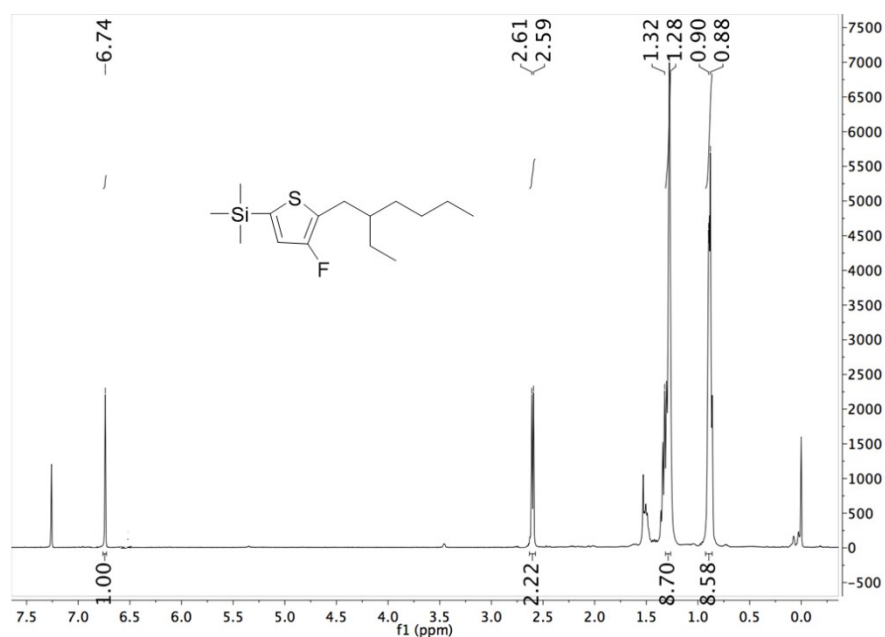


Figure S3. ^1H NMR spectrum of (5-(2-ethylhexyl)-4-fluorothiophen-2-yl)trimethylsilane (4)

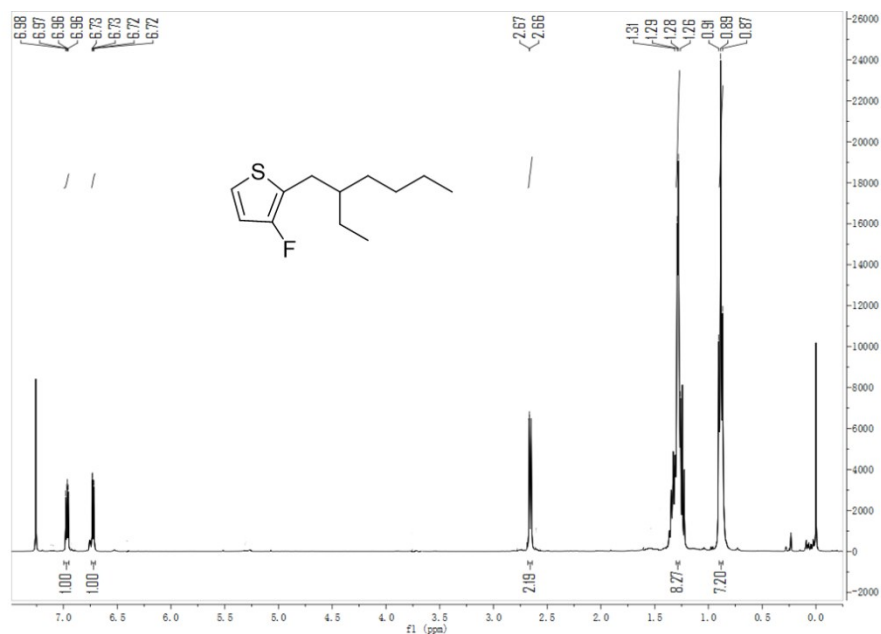


Figure S4. ^1H NMR spectrum of 2-(2-ethylhexyl)-3-fluorothiophene (5)

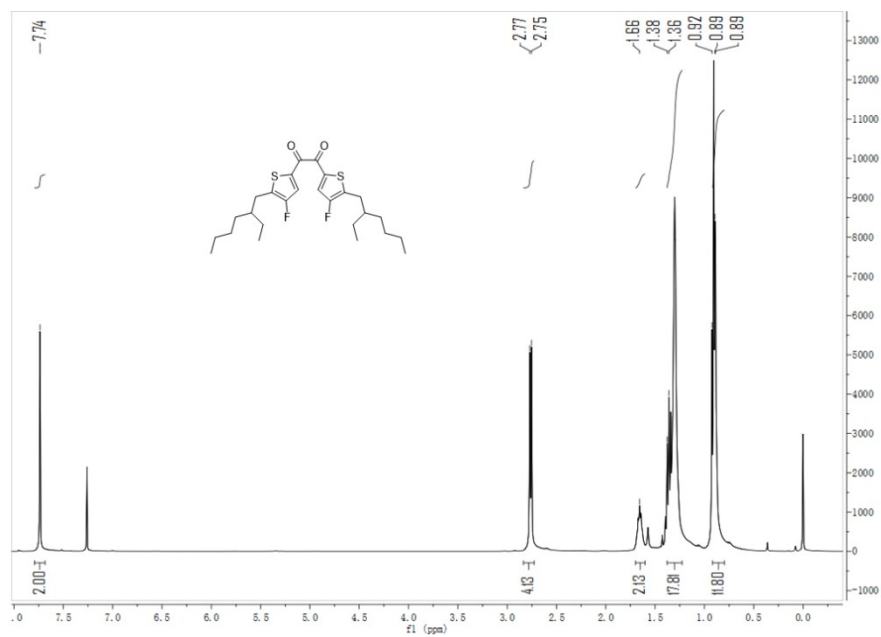


Figure S5. ¹H NMR spectrum of 1,2-bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)ethane-1,2-dione (6)

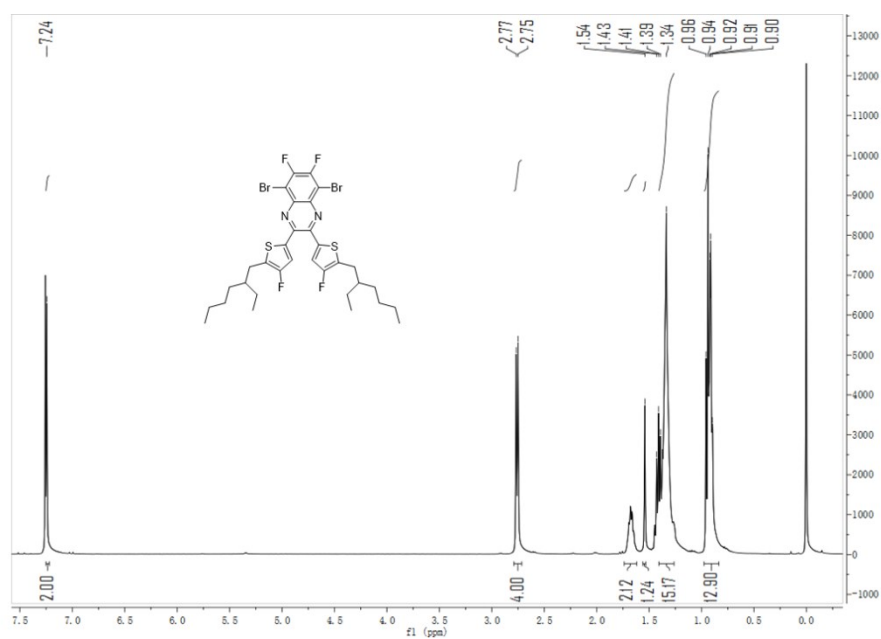


Figure S6. ¹H NMR spectrum of 5,8-dibromo-2,3-bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)-6,7-difluoroquinoxaline (9)

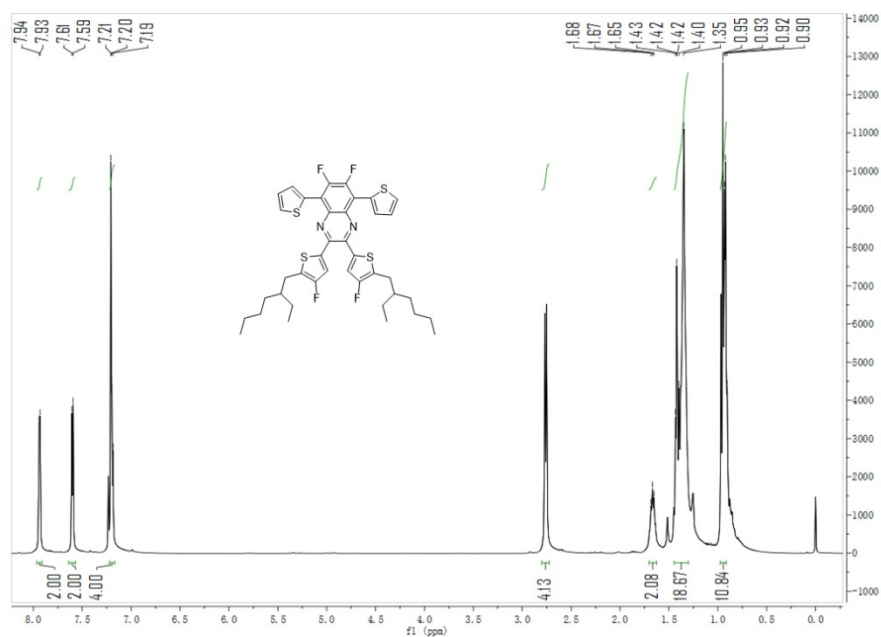


Figure S7. ¹H NMR spectrum of 2,3-bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)-6,7-difluoro-5,8-di(thiophen-2-yl)quinoxaline (10)

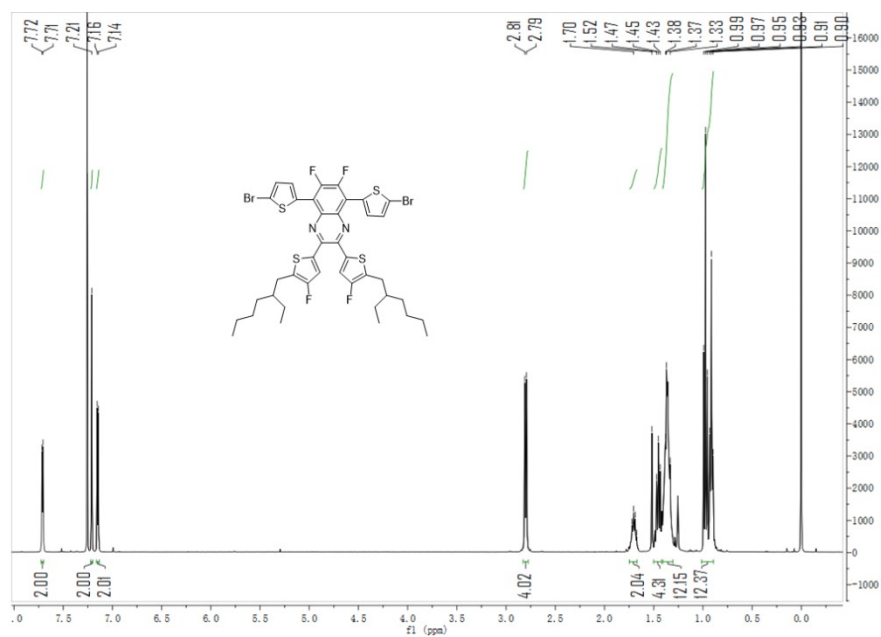


Figure S8. ¹H NMR spectrum of 5,8-bis(5-bromothiophen-2-yl)-2,3-bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)-6,7-difluoroquinoxaline (M1)

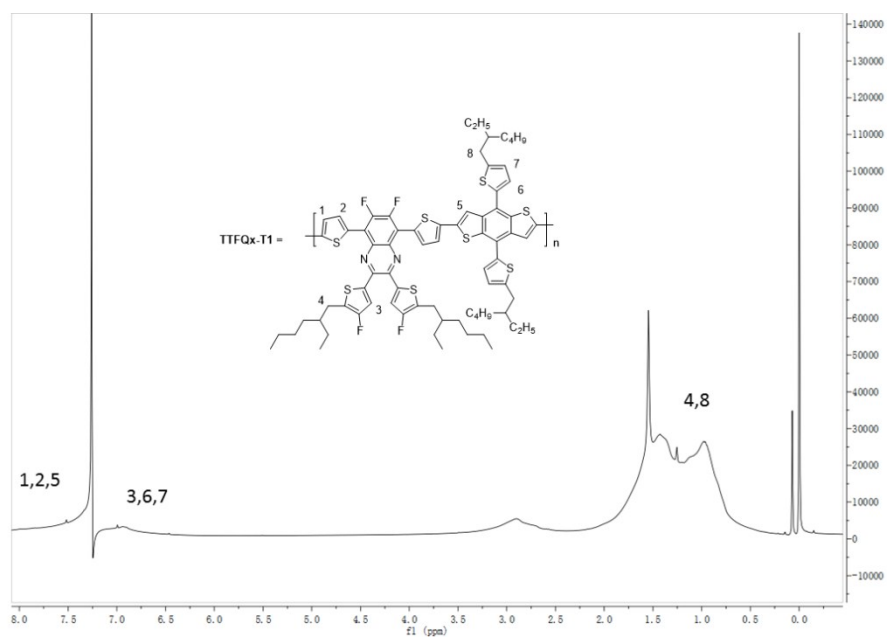


Figure S9. ^1H NMR spectrum of TTFQx-T1

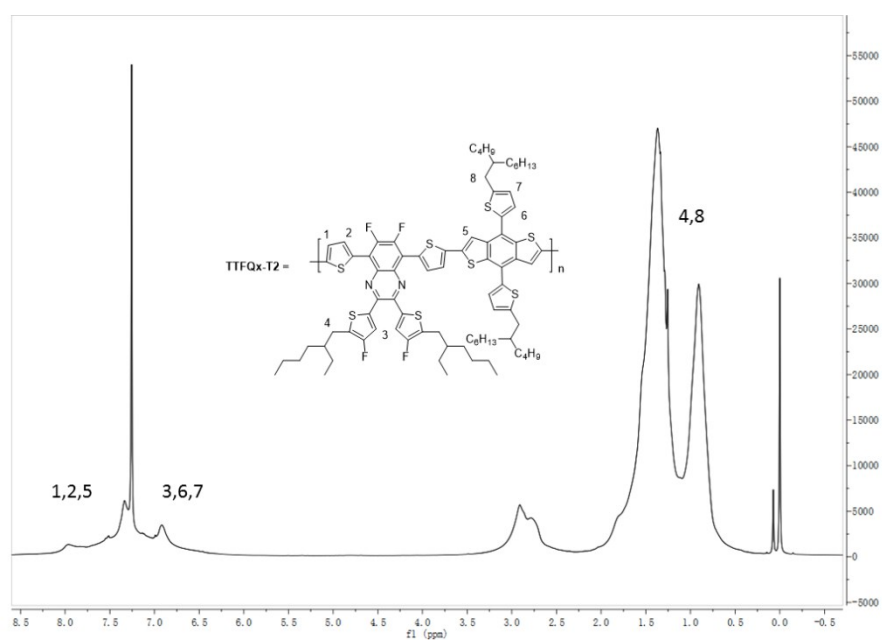


Figure S10. ^1H NMR spectrum of TTFQx-T2

6. ^{13}C HMR

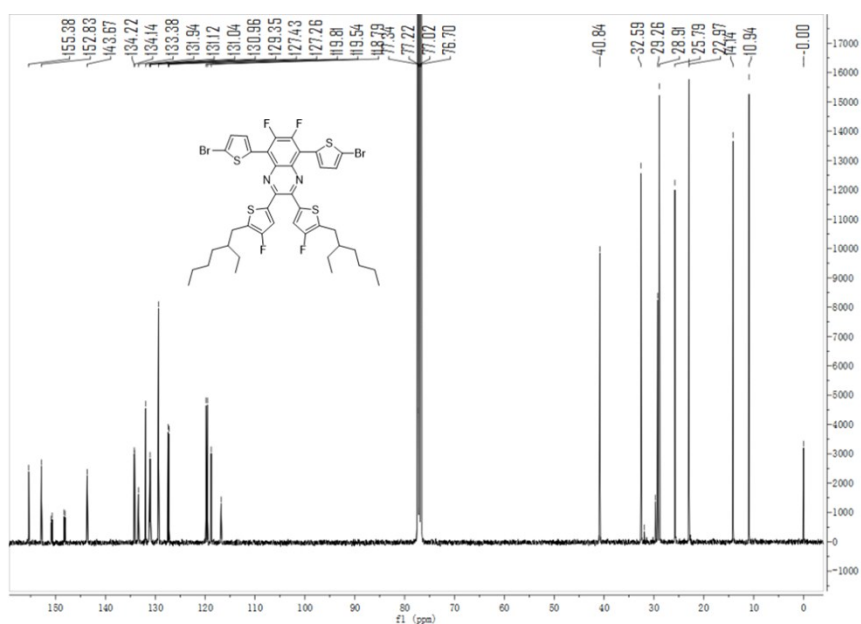


Figure S11. ^{13}C NMR spectrum of 5,8-bis(5-bromothiophen-2-yl)-2,3-bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)-6,7-difluoroquinoxaline (M1)

7. GPC, thermal, optical and photovoltaic data

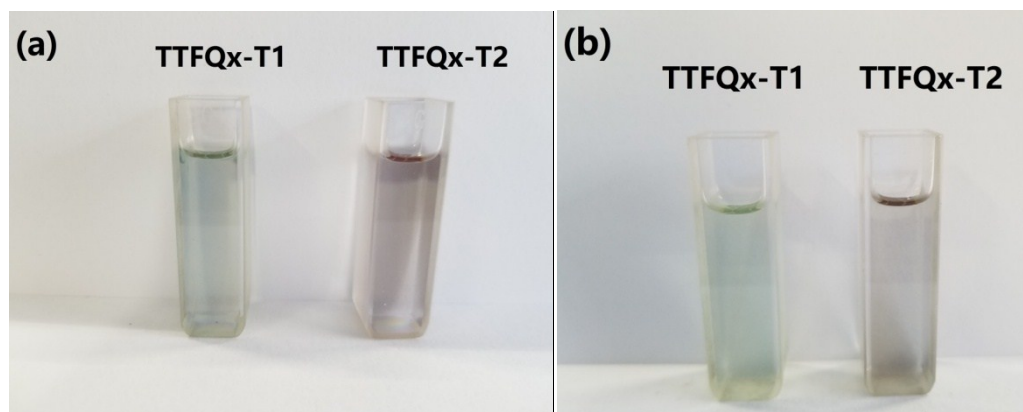
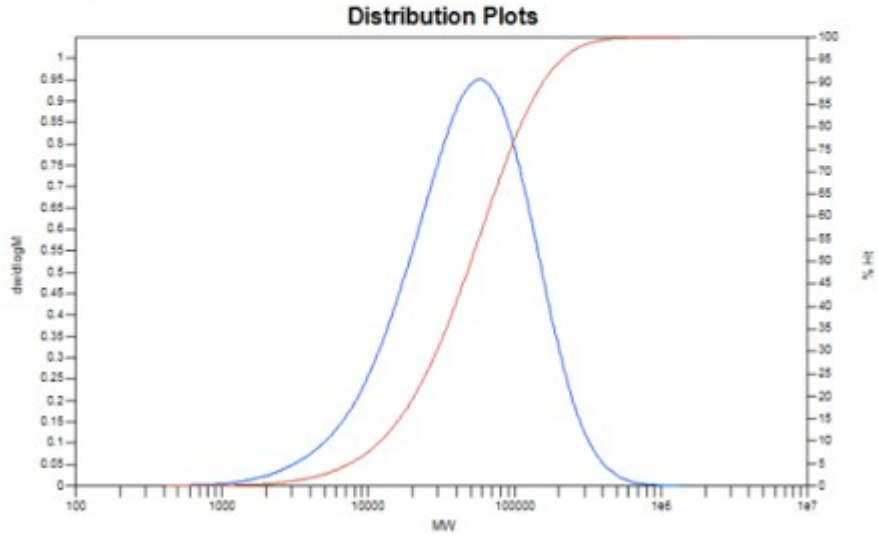


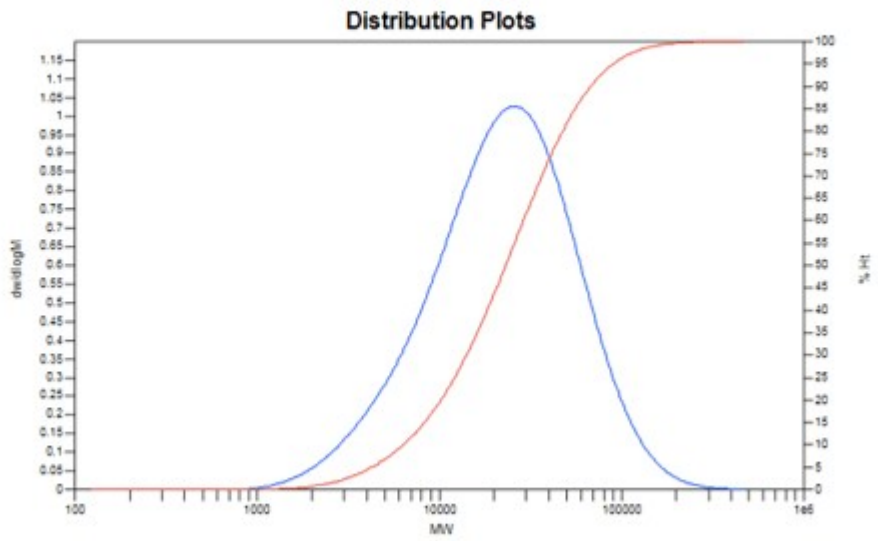
Figure S12. The images of TTFQx-T1 and TTFQx-T2 (a) in dilute chlorobenzene (polar solvents); (b) in dilute toluene solution (non-polar solvents).

(a)

TTFQx-T1 MW Averages
Mp: 58356 Mn: 24762 Mv: 63187 Mw: 71169
Mz: 145287 Mz+1: 253376 PD: 2.8741



TTFQx-T2 MW Averages
Mp: 25620 Mn: 13721 Mv: 28448 Mw: 31633
Mz: 60876 Mz+1: 102496 PD: 2.3054



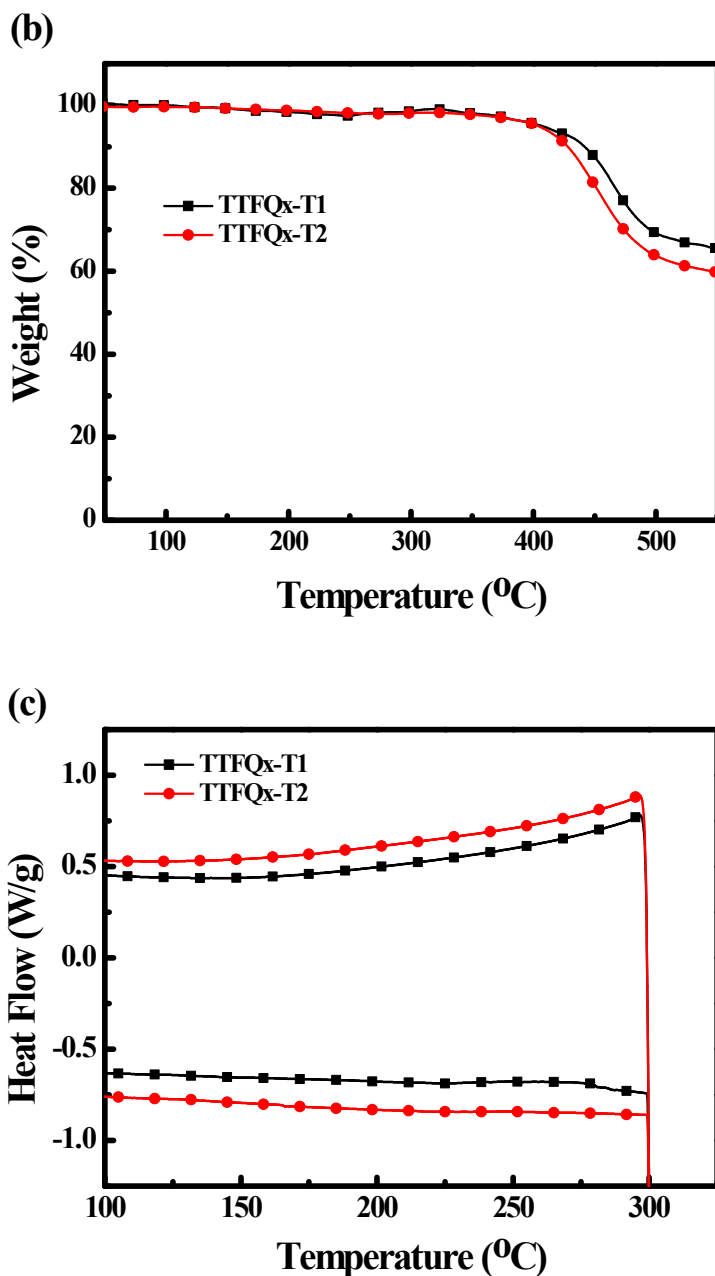


Figure S13. (a) GPC curves of TTQx-T1 and TTFQx-T2; (b) TGA curves of the TTQx-T1 and TTFQx-T2 measured with a heating rate of 20 K/min. (c) DSC thermograms of TTQx-T1 and TTFQx-T2 measured with a scan rate of 20 K/min under nitrogen atmosphere.

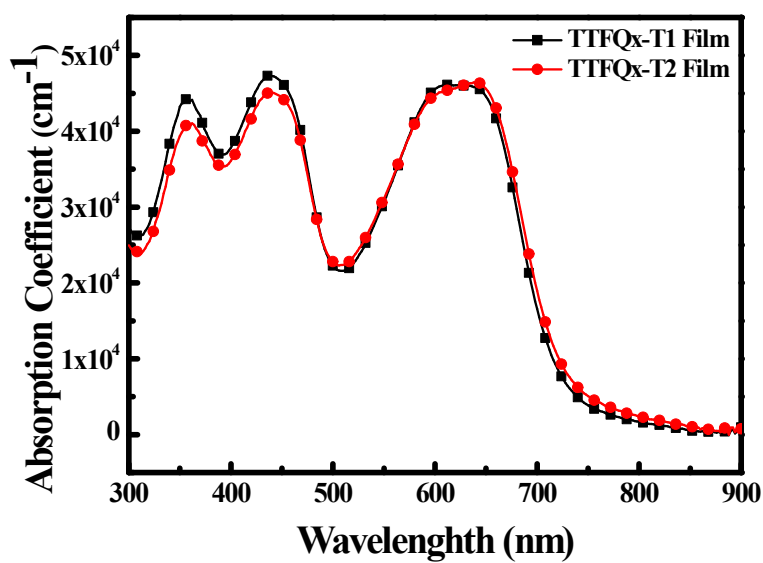
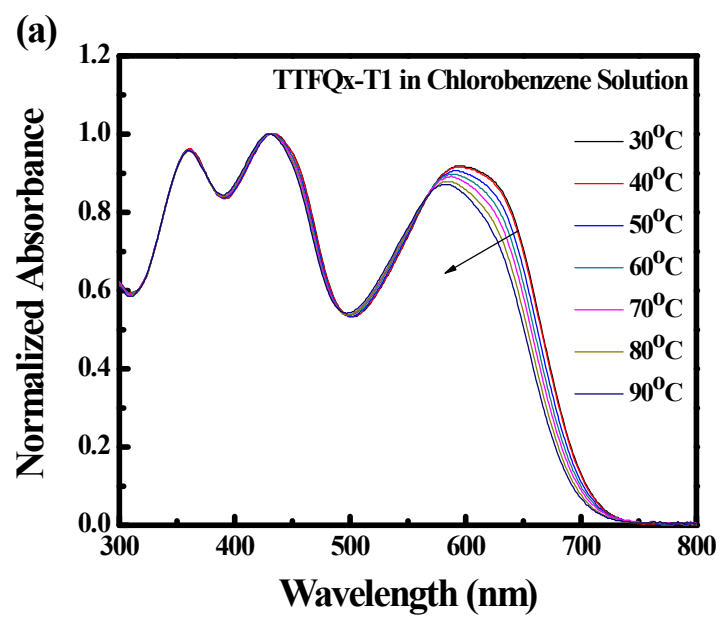
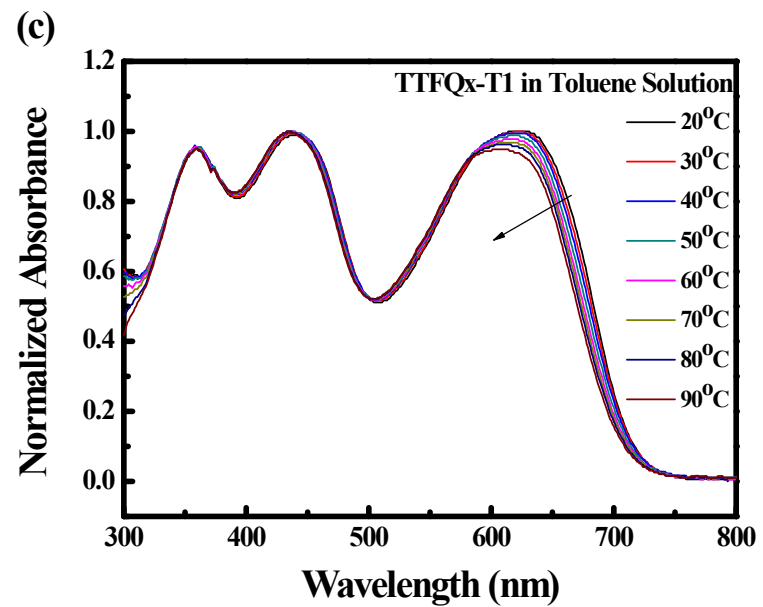
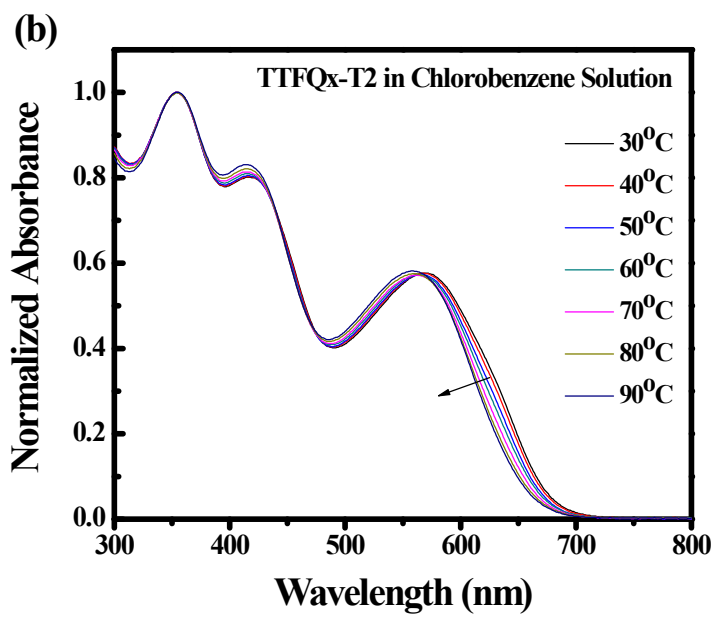


Figure S14. Absorption coefficients of TTFQx-T1 and TTFQx-T2 in films





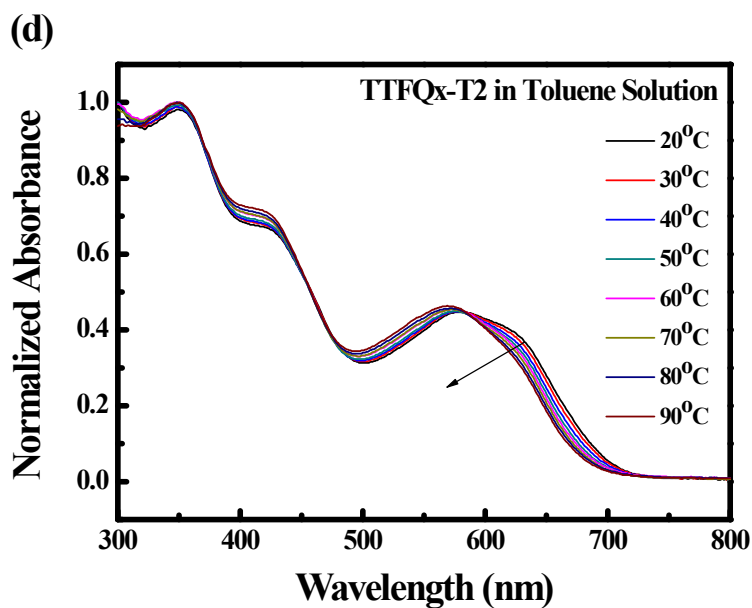


Figure S15. Normalized absorption spectra of TTFQx-T1 and TTFQx-T2 in dilute chlorobenzene (a, b) and toluene solution (c, d) at different temperatures .

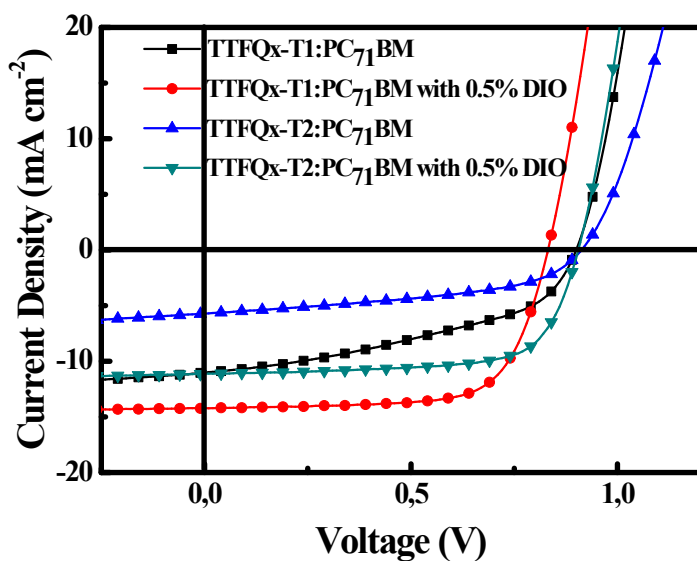


Figure S16. The J - V curves of PSCs based on TTFQx-T1:PC₇₁BM and TTFQx-T2:PC₇₁BM under the illumination of AM 1.5G, 100 mW/cm²

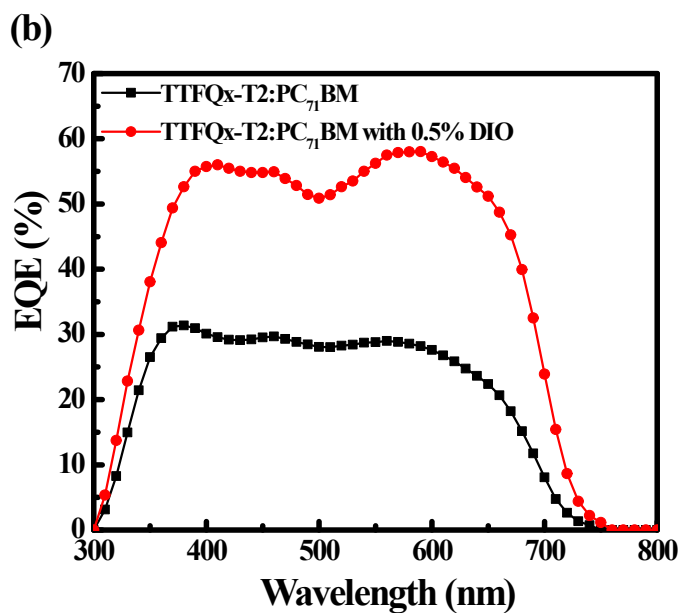
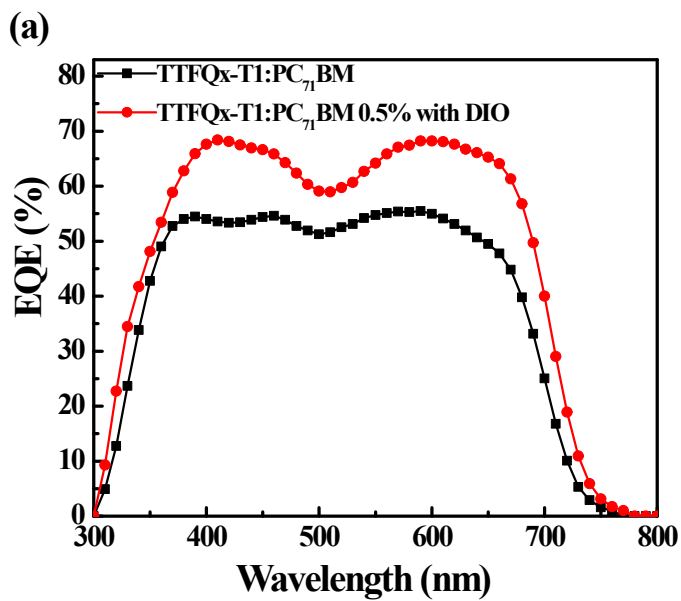
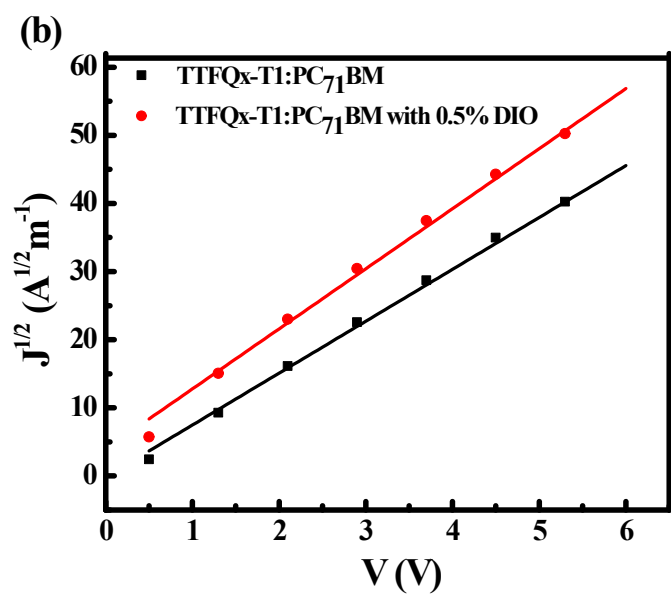
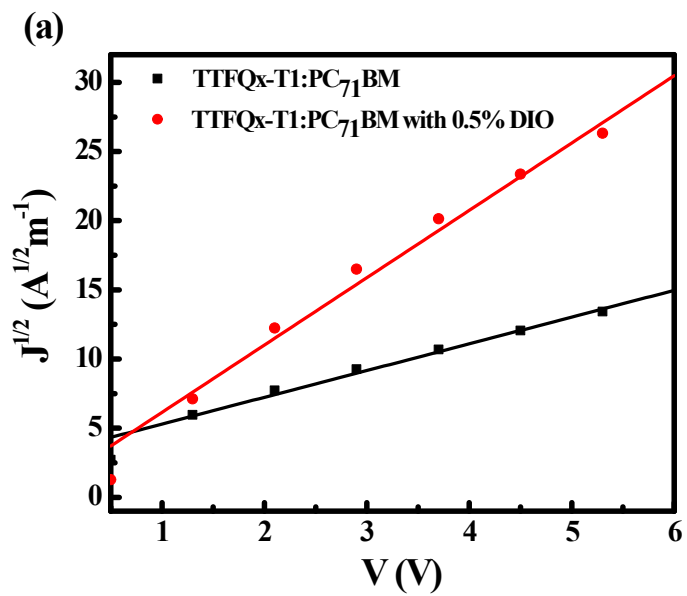


Figure S17. The *EQE* curves of the (a) TTFQx-T1:PC₇₁BM and (b) TTFQx-T2:PC₇₁BM based devices.



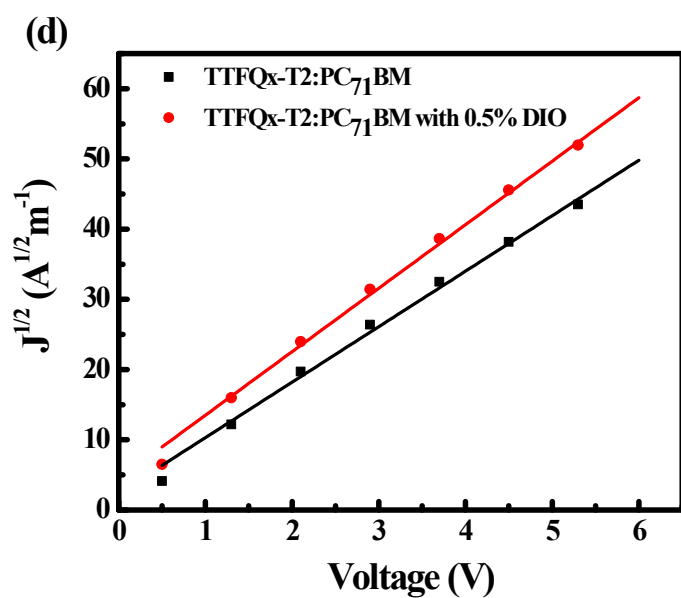
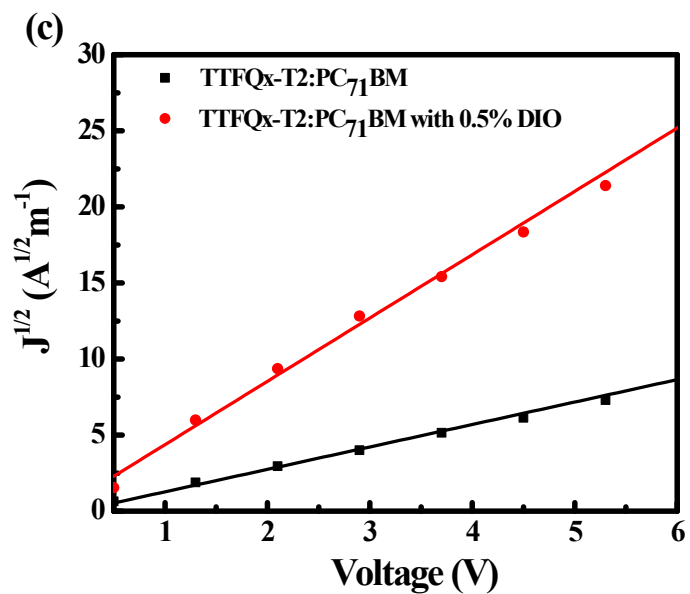


Figure S18. The dependence of square root of current density ($J^{1/2}$) on voltage for hole-only devices of ITO/PEDOT:PSS/active layer/Au and electron-only devices of ITO/ZnO/ active layer/ZrAcac/Al with active layers **(a)** and **(b)** TTFQx-T1:PC₇₁BM blends; **(c)** and **(d)** TTFQx-T2:PC₇₁BM blends.

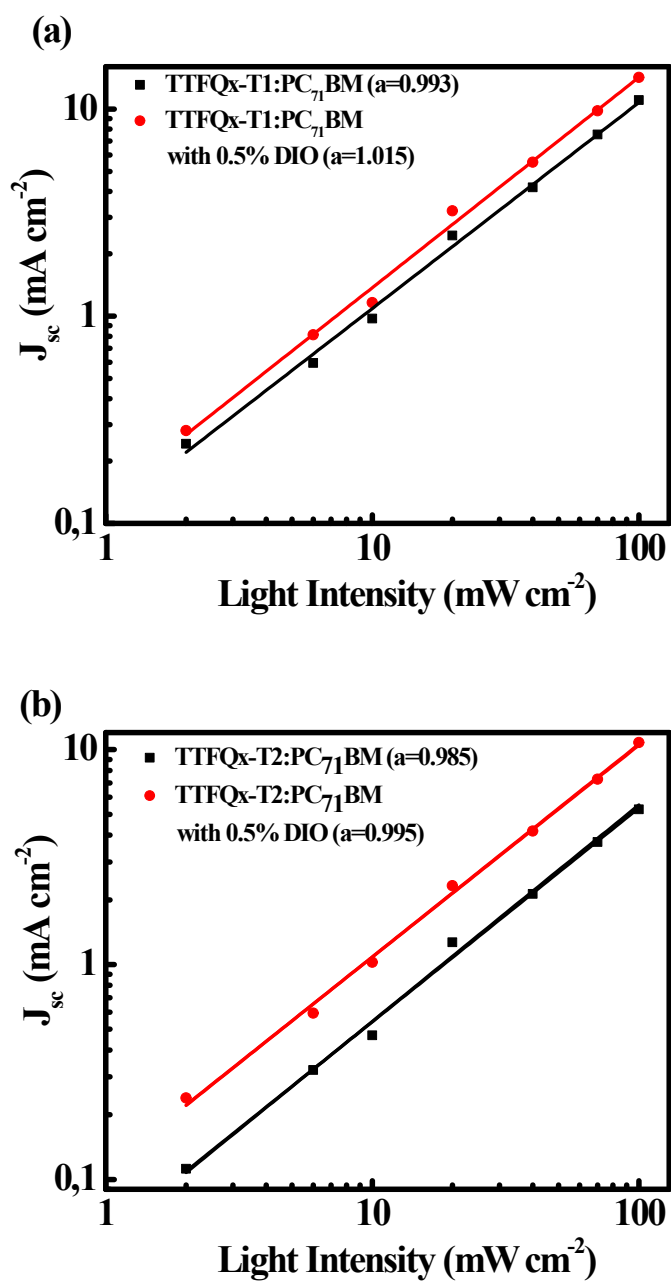


Figure S19. Light intensity dependence of the J_{sc} density of the PSCs based on **(a)** TTFQx-T1:PC₇₁BM and **(b)** TTFQx-T2: PC₇₁BM.

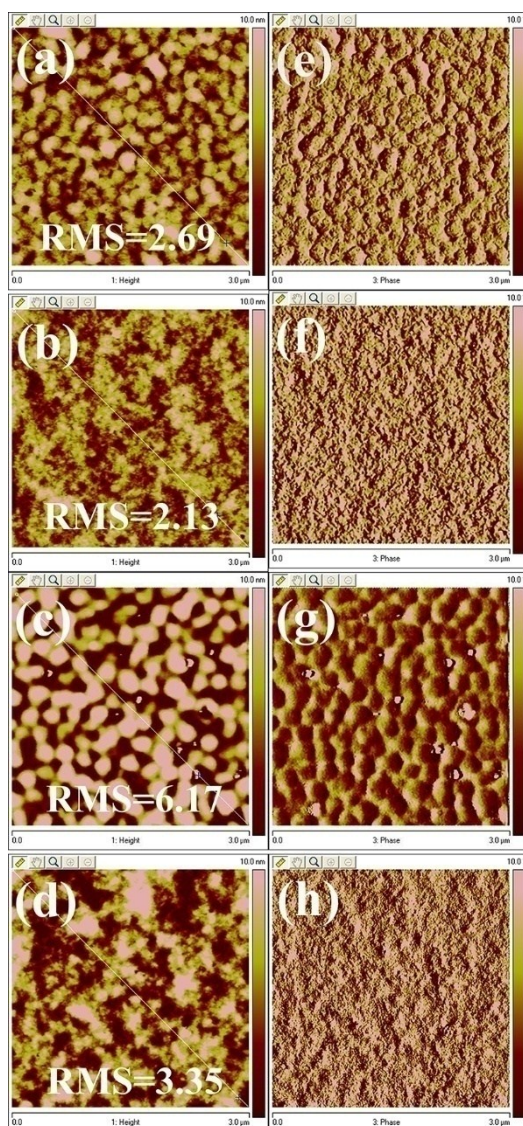


Figure S20. Topographic AFM images (a-d height and e-h phase): **(a)** and **(e)** TTFQx-T1:PC₇₁BM blend films (1:1.5, w:w); **(b)** and **(f)** with 0.5 vol% DIO (1:1.5, w:w); **(c)** and **(g)** TTFQx-T2:PC₇₁BM blend films (1:1.5, w:w); **(d)** and **(h)** with 0.5 vol% DIO (1:1.5, w:w). Dimension of images: 3x3 μm².

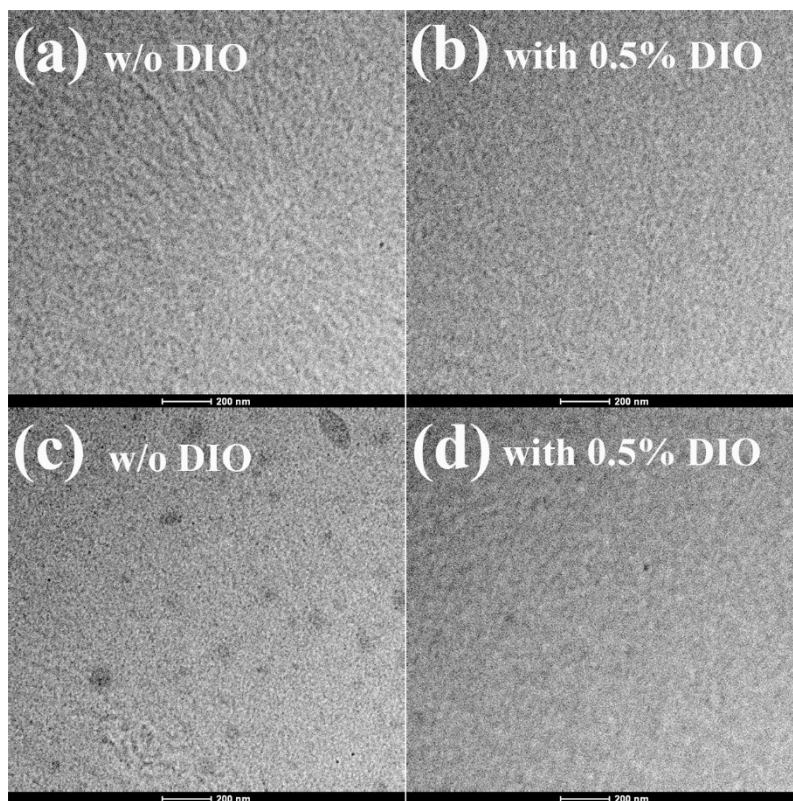


Figure S21. Topographic TEM images ($1 \times 1 \mu\text{m}^2$): **(a)** TTFQx-T1:PC₇₁BM blend films (1:1.5, *w:w*); **(b)** with 0.5 vol% DIO (1:1.5, *w:w*); **(c)** TTFQx-T2:PC₇₁BM blend films (1:1,5 *w:w*); **(d)** with 0.5 vol% DIO (1:1.5, *w:w*).

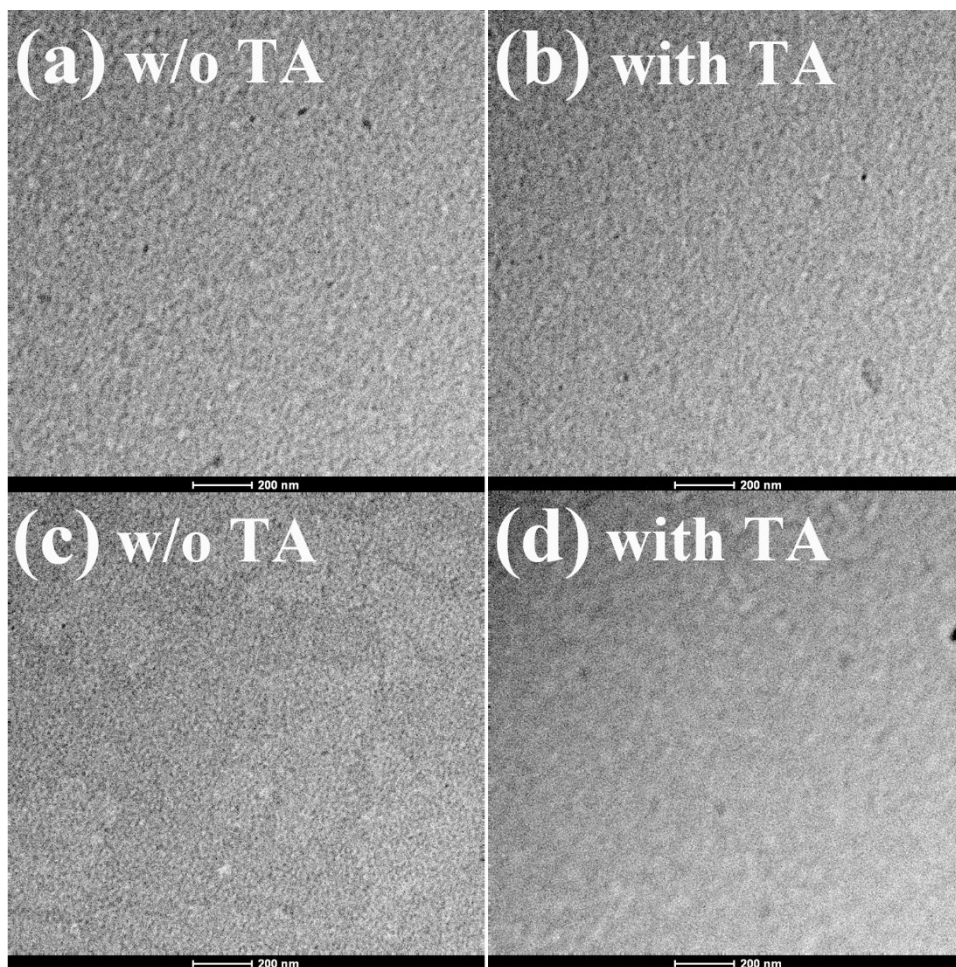


Figure S22. Topographic TEM images ($1 \times 1 \mu\text{m}^2$): **(a)** TTFQx-T1:ITIC blend films (1:1.5, $w:w$); **(b)** with TA treatment (1:1.5, $w:w$); **(c)** TTFQx-T2:ITIC blend films (1:1.5, $w:w$); **(d)** with TA treatment (1:1.5, $w:w$).

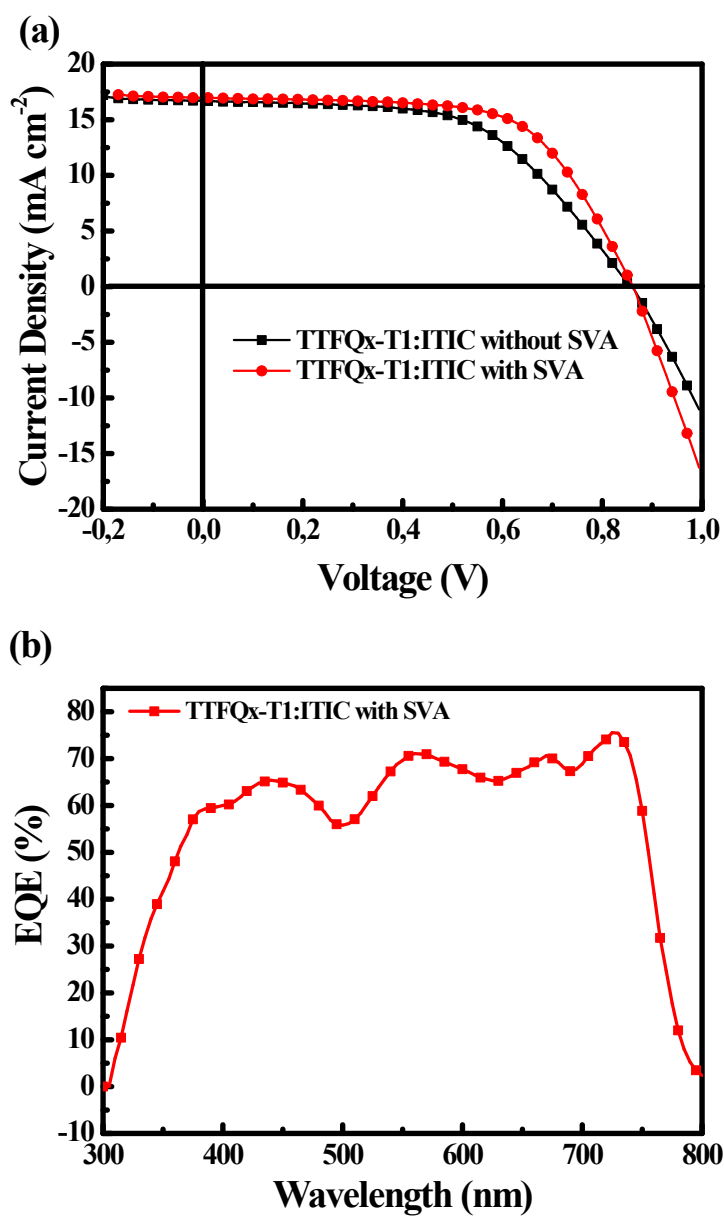


Figure S23. (a) The *J-V* curves of inverted PSCs based on TTFQx-T1:ITIC under the illumination of AM 1.5G, 100 mW/cm^2 (b) The *EQE* curves of the TTFQx-T1:ITIC based inverted devices.

Table S1. Summary of the photovoltaic data of the TTFQx-T1:PC₇₁BM/ITIC and TTFQx-T2:PC₇₁BM/ITIC blend films based devices

BHJ layer	Ratio	Additive ^a	Annealing	V_{oc}	J_{sc}	FF	PCE (%)	
		(%)	(°C)	(V)	(mA/cm ²)	(%)	Max ^b	Ave ^c
TTFQx-T1:PC ₇₁ BM	1:1.5	None	None	0.91 (0.90 ± 0.01)	11.02 (10.88 ± 0.35)	43.89 (42.80 ± 1.35)	4.35	4.18 ± 0.21
		0.5	None	0.84 (0.84 ± 0.01)	14.22 (13.98 ± 0.19)	70.18 (69.90 ± 0.39)	8.30	8.22 ± 0.07
TTFQx-T2:PC ₇₁ BM	1:1.5	None	None	0.91 (0.90 ± 0.01)	5.72 (5.53 ± 0.24)	47.68 (45.79 ± 1.76)	2.49	2.29 ± 0.18
		0.5	None	0.91 (0.90 ± 0.01)	11.83 (11.65 ± 0.15)	69.36 (69.58 ± 1.09)	7.74	7.23 ± 0.23
TTFQx-T1:ITIC	1:1.5	None	None	0.94 (0.94 ± 0.01)	14.58 (14.94 ± 0.07)	66.18 (64.88 ± 0.91)	9.24	9.09 ± 0.12
		None	110	0.93 (0.93 ± 0.01)	15.22 (15.19 ± 0.15)	67.18 (66.36 ± 0.70)	9.48	9.35 ± 0.13
		None	130	0.91 (0.91 ± 0.01)	16.19 (16.08 ± 0.23)	69.65 (68.62 ± 1.23)	10.24	10.00 ± 0.18
		None	150	0.90 (0.90 ± 0.01)	16.88 (16.80 ± 0.12)	69.24 (68.39 ± 0.76)	10.52	10.32 ± 0.09
TTFQx-T2:ITIC	1:1.5	None	None	0.97 (0.97 ± 0.01)	11.62 (11.47 ± 0.13)	51.10 (51.01 ± 0.13)	5.76	5.67 ± 0.08
		None	110	0.96 (0.96 ± 0.01)	12.83 (12.56 ± 0.19)	54.06 (54.18 ± 0.71)	6.65	6.53 ± 0.11
		None	130	0.95 (0.95 ± 0.01)	12.73 (12.76 ± 0.02)	56.09 (55.26 ± 0.68)	6.75	6.67 ± 0.06
		None	150	0.94 (0.93 ± 0.01)	13.75 (13.42 ± 0.27)	56.11 (56.56 ± 0.54)	7.22	7.07 ± 0.11

^aThe additive is 1,8-diiodooctane. ^bThe maximum PCE value of devices. ^cThe average PCE values of 10 devices.

Table S2. Summary of the hole and electron mobilities of TTFQx-T1:PC₇₁BM/ITIC and TTFQx-T2:PC₇₁BM/ITIC blend films determined by SCLC method

BHJ active layer	TTFQx-T1:PC ₇₁ BM		TTFQx-T2:PC ₇₁ BM		TTFQx-T1:ITIC		TTFQx-T2:ITIC	
D/A weight ratio	1:1.5							
DIO (vol%)	None	0.5	None	0.5	None	None	None	None
TA (°C)	None	None	None	None	None	150	None	150
Hole mobility (10 ⁻⁶ cm ² ·V ⁻¹ ·s ⁻¹)	6.41	40.7	2.5	19.9	31.9	113	7.55	13.9
Electron mobility (10 ⁻⁶ cm ² ·V ⁻¹ ·s ⁻¹)	99.5	134	71.7	93.9	176	160	53.6	68.0