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Electronic Supplementary Information (ESI)

Asymmetric Fluorine and Chlorine Side-Chains Engineered Quinoxaline-Based D-A Copolymer for Both Fullerene and Nonfullerene Polymer Solar Cells

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1. Materials and Instruments.

All reagents and chemicals were purchased commercially and used directly without further purification unless otherwise stated. Unless otherwise stated, all reactions were carried out under inert atmosphere using standard Schlenk-line techniques. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Ascend 400 MHz spectrometer using $CDCl_3$ as the deuterium solvent. Mass spectra (MS) were measured on a Bruker Daltonics BIFLEX Ш MALDITOF analyzer. Polymer molecular weights were evaluated by gel permeation chromatography (GPC) using $CHCl_3$ as the eluent and polystyrenes as the standards. UV-vis absorption spectra of polymer solutions and films were recorded on a Shimadzu HP-453 UV spectrophotometer. Cyclic voltammetry (CV) was conducted on a CHI620 voltammetric analyzer under argon atmosphere in an anhydrous acetonitrile solution of tetra(n-butyl) ammonium hexafluorophosphate (Bu_4NPF_6, 0.1 M) at a scan rate of

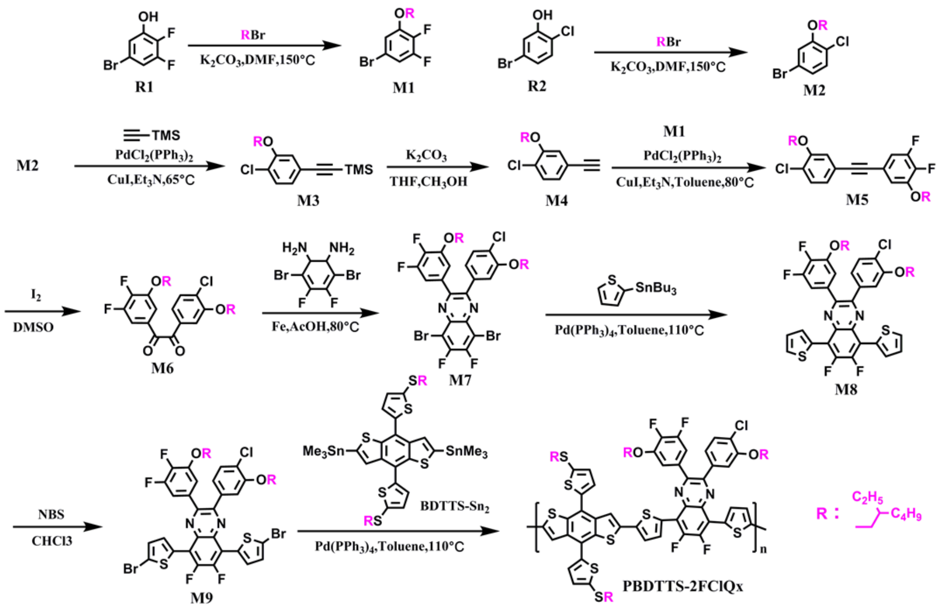
50 mV/s. A platinum disk working electrode, a platinum wire counter electrode and an Ag/AgCl electrode were used as working electrode, counter electrode, reference electrode, respectively, and the ferrocene/ferrocenium (Fc/Fc^+) redox couple was used as the reference for all measurements with a scanning rate of 50 mV s^{-1}. Thermogravimetric analysis (TGA) was measured on a Perkin-Elmer Diamond TG/DTA thermal analyzer at a scan rate of 10 °C/min under nitrogen atmosphere. The external quantum efficiency (EQE) spectra of solar cells were recorded by a QE-R3011 measurement system (Enli Technology, Inc.). AFM and TEM measurements were obtained by using a Dimension Icon AFM (Bruker) in a tapping mode (5 × 5 μm^2). The molecular packing was investigated by grazing incidence X-ray diffffraction (GI-XRD) and in-plane X-ray diffffraction (IP-XRD). GI-XRD data were obtained on a Bruker D8 Discover reflector (Cu Ka, l = 1.54056 Å) under 40 kV and 40 mA tube current. The electron and hole mobility were measured by using the method of space-charge limited current (SCLC) for electron-only devices with the structure of ITO/ZnO/active layer/PNDIT-F3N/Ag and hole-only devices with the structure of ITO/PEDOT:PSS/active layer/MoO_3/Ag. The charge carrier mobility was determined by fitting the dark current to the model of a single carrier SCLC according to the equation: $J = 9\varepsilon_0\varepsilon_r\mu V^2/8d^3$, where J is the current density, d is the film thickness of the active layer, μ is the charge carrier mobility, ε_r is the relative dielectric constant of the transport medium, and ε_0 is the permittivity of free space. $V = V_{app} - V_{bi}$, where V_{app} is the applied voltage, V_{bi} is the offset voltage. The carrier mobility can be calculated from the slope of the $J^{1/2} \sim V$ curves.

2. Fabrication of organic solar cells

Solar cells were fabricated in a conventional device configuration of ITO/PEDOT:PSS(40 nm)/PBDTTS-2FClQx:Y6:$PC_{71}BM$/PDIN (5 nm)/Ag(100 nm). The ITO substrates were first scrubbed by detergent and then solicited with deionized water, acetone and isopropanol subsequently, and dried overnight in an oven. The glass substrates were treated by UV-Ozone for 30 min before used. PEDOT:PSS (Heraeus Clevios P VP AI 4083) was spin-cast onto the ITO substrates at 4000 rpm for 30 s, and then dried at 150 °C for 15 min in air. The donor:acceptor blends (1.0:1.0 weight ratio) were dissolved in chloroform (the total concentration of blend solutions was 16 mg mL^{-1} and the $PC_{71}BM$ was used as Second receptor with various ratio (0%, 5%, 10%, 20%, 30%), for all blends and stirred overnight in room temperature in a nitrogen-filled glove box. The blend solution was spin-cast at 2500 rpm for 30 s. Active layers were annealed at 95 °C hotplate for 5 min after being coated. A thin PDIN layer was coated on the active layer, followed by the deposition of Ag (100 nm) (evaporated under 5×10^{-5} Pa through a shadow mask). The optimal active layer thickness measured by a Bruker Dektak XT stylus profilometer was about 105 nm. The current density-voltage (J-V) curves of all encapsulated devices were measured using a Keithley 2400 Source Meter in air under AM 1.5G (100 mW cm^{-2}) using a Newport solar simulator. The light intensity was calibrated using a standard Si diode (with KG5 filter, purchased from PV Measurement to bring spectral mismatch to unity). Optical microscope (Olympus BX51) was used to define the device area (6.0 mm^2). EQEs were measured using an Enlitech QE-S EQE system equipped with a standard Si diode. Monochromatic light was generated from a Newport 300W lamp source.

3. Chemical Synthesis

The novel medium bandgap donor polymers, namely, PBDTTS-2FClQx, had been synthesized and characterized. The detailed synthesis procedures of PBDTTS-2FClQx are depicted in Scheme S1. All compounds were synthesized through Williamson reaction, Sonogashira coupling, Still coupling, condensation reaction and so on. Finally, then through typical Stille coupling reaction, the PBDTTS-2FClQx was obtained by BDTTS and monomer M9, with high yield of over 85%. The afforded copolymer was purified by Soxhlet extraction with methanol, acetone, dichloromethane (DCM) and chloroform (CF), respectively, followed by a fast silica gel column chromatography with chloroform as solvent to remove the oligomers and other impurities. Both polymers show good solubility in common organic solvents, such as chloroform (CF), chlorobenzene (CB) and dichlorobenzene (o-DCB) at room temperature.



Scheme S1. Synthetic routes of PBDTTS-2FClQx.

3.1. Synthesis of 5-bromo-1-((2-ethylhexyl)oxy)-2,3-difluorobenzene (**M1**)

5-Bromo-2,3-difluorophenol (**R1**, 2.09 g, 10.0 mmol), potassium carbonate (1.36 g, 11.0 mmol), bromoisooctane (1.94 g, 10 mmol) were sequentially dissolved in DMF (30 mL) The reaction was carried out at 150 °C for 8 h under the protection of N2. The mixture was cooled to room temperature, then poured into water (100 mL) and extracted with DCM (50 mL x 3). The organic layers were combined, washed with water (200 mL×3), dried, and spun under reduced pressure to remove the solvent. The residue was separated by column chromatography with PE as the eluent to obtain 2.92 g of a colorless transparent liquid with a yield of 91.0%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 – 6.90 (m, 1H), 6.87 (d, J = 6.4 Hz, 1H), 3.88 (d, J = 5.8 Hz, 2H), 1.76 (dt, J = 12.3, 6.1 Hz, 1H), 1.53 – 1.29 (m, 8H), 0.93 (t, J = 7.8 Hz, 6H).

3.2. Synthesis of 4-bromo-1-chloro-2-((2-ethylhexyl)oxy)benzene (**M2**)

5-bromo-2-chlorophenol (R2, 2.09 g, 10.0 mmol), potassium carbonate (1.36 g, 11.0 mmol), bromoisooctane (1.94 g, 10 mmol) were sequentially dissolved in DMF

(30 mL) The reaction was carried out at 150 °C for 8 h under the protection of N_2. The mixture was cooled to room temperature, then poured into water (100 mL) and extracted with DCM (50 mL x 3). The organic layers were combined, washed with water (200 mL×3), dried, and spun under reduced pressure to remove the solvent. The residue was separated by column chromatography with PE as the eluent to obtain 2.92 g of a colorless transparent liquid with a yield of 91.0%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, J = 2.4 Hz, 1H), 7.29 (dd, J = 8.8, 2.4 Hz, 1H), 6.78 (d, J = 8.8 Hz, 1H), 3.87 (d, J = 9.1 Hz, 2H), 1.77 (dt, J = 12.3, 6.1 Hz, 1H), 1.59 - 1.37 (m, 4H), 1.37-1.26 (m, 4H), 0.92 (dt, J = 14.0, 7.2 Hz, 6H)

1.3. Synthesis of ((4-chloro-3-((2-ethylhexyl)oxy)phenyl)ethynyl)trimethylsilane (**M3**)

M2 (1.00 g, 3.3 mmol), trimethylethynylsilicon (162.1 mg, 1.65 mmol), $PdCl_2(PPh_3)_2$ (115.8 mg, 0.165 mmol) and CuI (62.85 mg, 0.33 mmol) were added sequentially to Et_3N (30 mL) and reacted at 65 °C for 24 h under the protection of N_2. The mixture was cooled to room temperature, then poured into water (100 mL) and extracted with DCM (70 mL x 3). The organic layers were combined, washed with water (200 mL×3), dried, and the solvent was removed under reduced pressure. The residue was separated by column chromatography with PE as the eluent to obtain 890.0 mg of colorless transparent liquid with a yield of 80.0%. The obtained product was directly used in the next reaction.

1.4. Synthesis of 1-chloro-2-((2-ethylhexyl)oxy)-4-ethynylbenzene (**M4**)

M3 (890.0 mg, 2.64 mmol), K2CO3 (396.0 mg, 3.96 mmol) were added to THF/CH3OH (1:1, 20 mL) and stirred at room temperature for 24 h. The mixture was poured into water (100 mL) and extracted with DCM (70 mL x 3). The organic layers were combined, washed with water (200 mL×3), dried, and spun off under reduced pressure to remove the solvent. The residue was separated by column chromatography with PE as the eluent to obtain 630.0 mg of colorless transparent liquid with a yield of 90.0%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 7.8 Hz, 1H), 7.02 (s, 1H), 6.99 (d, J = 1.4 Hz, 1H), 3.89 (d, J = 5.7 Hz, 2H)), 3.09 (s, 1H), 1.78 (dt, J = 12.2, 6.1 Hz, 1H), 1.55 – 1.30 (m, 8H), 0.94 (t, J = 7.5 Hz, 6H) [109]. ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.56, 130.09, 124.81, 124.24, 121.36, 116.40, 82.98, 77.59, 71.55, 39.30, 30.48, 29.05, 23.89, 23.04, 14.11, 11.16。

1.5. Synthesis of 5-((4-chloro-3-((2-ethylhexyl)oxy)phenyl)ethynyl)-1-((2-ethylhexyl) oxy)-2,3-difluorobenzene (**M5**)

M1 (764.2 mg, 2.38 mmol), M4 (630.0 mg, 2.38 mmol), $PdCl_2(PPh_3)_2$ (84.0 mg, 0.119 mmol) and CuI (23.8 mg, 0.238 mmol) were sequentially added to Et_3N/Toluene (1:1, 30 mL) under the protection of N_2 at 65 °C for 24 h. The mixture was cooled to room temperature, then poured into water (100 mL) and extracted with DCM (70 mL x 3). The organic layers were combined, washed with water (200 mL×3), dried, and the solvent was removed under reduced pressure. The residue was separated by column chromatography with PE as the eluent to obtain 1.01 g of a colorless transparent liquid with a yield of 84.0%.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 7.9 Hz, 1H), 7.03 (d, J = 7.9 Hz, 2H), 6.92 (dd, J = 16.9, 6.9 Hz, 2H), 3.92 (d, J = 4.8 Hz, 4H), 1.79 (dq, J = 12.7, 6.3 Hz, 2H)。

1.6. Synthesis of 1-(4-chloro-3-((2-ethylhexyl)oxy)phenyl)-2-(3-((2-ethylhexyl)oxy)-

4,5-difluorophenyl)ethane-1,2-dione (**M6**)

Compound M5 (1.01 g, 2.0 mmol) and I2 (305 mg, 1.2 mmol) were dissolved in DMSO (40 mL), protected with N2, and placed in the dark at 155 °C for 5 h. The mixture was cooled to room temperature, then poured into water (100 mL) and extracted with DCM (70 mL x 3). The organic layers were combined, washed with water (200 mL×3), dried, and evaporated under reduced pressure to remove the solvent. The residue was separated by column chromatography with PE:DCM (V:V=10:1) as the eluent to obtain 913.0 mg of pale yellow liquid with a yield of 85.1%.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.45 (dd, J = 13.9, 7.5 Hz, 2H), 7.33 (t, J = 9.0 Hz, 2H), 5.30 (s, 3H), 3.98 (t, J = 5.2 Hz, 4H), 1.79 (tq, J = 12.1, 6.0 Hz, 2H), 1.57 – 1.38 (m, 9H)。

1.7. Synthesis of 5,8-dibromo-2-(4-chloro-3-((2-ethylhexyl)oxy)phenyl)-3-(3-((2-ethy-lhexyl)oxy)-4,5-difluorophenyl)-6,7-difluoroquinoxaline (**M7**)

1,4-Dibromo-2,3-difluoro-5,6-dinitrobenzene (447.0 mg, 1.23 mmol), iron powder (821.0 mg, 14.8 mmol) were dissolved in acetic acid (30 mL), N_2 Under the protection, the reaction was carried out at 80 °C for 5 h, then the iron powder was removed, compound M6 (660.0 mg, 1.23 mmol) was added, and the reaction was carried out at 80 °C for 8 h under the protection of N2. The mixture was cooled to room temperature, then poured into water (100 mL) and extracted with DCM (70 mL x 3). The organic layers were combined, washed with water (200 mL × 3), dried, and spun under reduced pressure to remove the solvent. The residue was separated by column chromatography with PE:DCM (V:V=5:1) as eluent to obtain 760.5 mg of yellow viscous liquid with a yield of 77.0%。^{1}H NMR (400 MHz, CDCl$_3$) δ 7.40 (d, J = 8.1 Hz, 1H), 7.22 (d, J = 8.5 Hz, 1H), 7.17 (dd, J = 9.3, 5.0 Hz, 2H), 6.90 (d, J = 6.8 Hz, 1H), 3.78 (d, J = 5.6 Hz, 2H), 3.67 (d, J = 5.9 Hz, 2H), 1.74 (dt, J = 12.3, 6.1 Hz, 1H), 1.66 (dd, J = 12.3, 6.1 Hz, 1H), 1.51–1.27 (m, 16H), 0.96–0.88 (m, 12H)。

1.8. Synthesis of 2-(4-chloro-3-((2-ethylhexyl)oxy)phenyl)-3-(3-((2-ethylhexyl)oxy) -4,5-difluorophenyl)-6,7-difluoro-5,8-di(thiophen-2-yl)quinoxaline (**M8**)

Compound M7 (418.0 mg, 0.52 mmol), 2-tributyltinylthiophene (583.0 mg, 1.56 mmol), Pd(PPh3)4 (30.0 mg, 0.026 mmol) were dissolved in toluene (20 mL), under N2 protection, The reaction was carried out at 110 °C for 24 h. The mixture was cooled to room temperature, then poured into water (100 mL) and extracted with DCM (70 mL x 3). The organic layers were combined, washed with water (200 mL×3), dried, and spun under reduced pressure to remove the solvent. The residue was separated by column chromatography with PE:DCM (V:V=5:1) as eluent to obtain 307.0 mg of golden yellow solid in 73.0% yield.^{1}H NMR (400 MHz, CDCl$_3$) δ 8.03 (s, 2H), 7.63 (d, J = 4.9 Hz, 1H), 7.60 (d, J = 5.0 Hz, 1H), 7.46 (s, 1H), 7.37 (d, J = 8.2 Hz, 1H), 7.27 (s, 1H), 7.21 (dd, J = 15.5, 8.9 Hz, 2H), 7.14 (t, J = 7.3 Hz, 2H), 3.88 (d, J = 5.6 Hz, 2H), 3.77 (d, J = 5.6 Hz, 2H), 1.73 (dd, J = 15.2, 9.1 Hz, 2H), 1.36 (dd, J=31.3, 12.1 Hz, 16H), 0.9–0.90 (m, 12H)。MALDI-MS (m/z) of C44H45ClF4N2O2S2 for [M+]: calcd.809.42; found. 810.17。

1.9. Synthesis of 5,8-bis(5-bromothiophen-2-yl)-2-(4-chloro-3-((2-ethylhexyl)oxy) phenyl)-3-(3-((2-ethylhexyl)oxy)-4,5-difluorophenyl)-6,7-difluoroquinoxaline (**M9**)

M8 (275.2 mg, 0.34 mmol) was dissolved in chloroform (20 mL), NBS (133.0 mg, 0.75 mmol) was added in portions under dark conditions, and the reaction was carried out at room temperature for 12 h. The reaction was poured into water (100 mL) and extracted with DCM (70 mL x 3). The organic layers were combined, washed with water (200 mL×3), dried, and the solvent was removed under reduced pressure. The residue was separated by column chromatography with PE:DCM (V:V=5:1) as the eluent to obtain an orange-yellow solid 256.5 mg with a yield of 78.0%.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (t, J = 3.5 Hz, 2H), 7.56 (s, 1H), 7.34 (d, J = 8.2 Hz, 1H), 7.30 (d, J = 6.9 Hz, 1H), 7.19 (d, J = 1.8 Hz, 1H), 7.18 (d, J = 1.8 Hz, 1H), 6.97 (s, 1H), 6.95 (s, 1H), 4.02 (d, J = 5.2 Hz, 2H), 3.93 (d, J = 5.4 Hz, 2H), 1.86–1.73 (m, 2H), 1.53–1.27 (m, 16H), 0.98–0.90 (m, 12H)。MALDI-MS (m/z) of $C_{44}H_{43}ClBr_2F_4N_2O_2S_2$ for [M+]: calcd.967.21; found. 967.95.

1.10. Synthesis of copolymer **PBDTTS-2FClQx**

In a 10 mL single-neck flask, M9 (193.4 mg, 0.2 mmol), BDTTS-Sn2 (193.7 mg, 0.2 mmol), Pd(PPh3)4 (8.0 mg), 10 mL of HPLC-grade toluene, and under N2 protection were added successively. The reaction was placed in a thermostatic pot at 110 °C, and the reaction changes were observed at all times. After the reaction stopped, sedimentation in methanol, suction filtration, Soxhlet extraction to wash the crude product (methanol-acetone-n-hexane-dichloromethane-trichloromethane), after concentration, purification by flash column chromatography, concentration, methanol sedimentation, extraction Filtration and vacuum drying gave 203.0 mg of black solid product. Molecular weight: M_n = 107.3 kDa, PDI = 3.34. Calc. for C78H83N2ClF4S8O2,%: C, 64.68; H, 5.78; Cl, 2.45; F, 5.25; N, 1.93; O, 2.21; S, 17.71, Found: C, 64.78; H, 5.73; Cl, 2.52; F, 5.21; N, 1.87; O, 2.29; S, 17.61

4.^{1}H NMR, ^{13}C NMR and mass spectra of compounds.

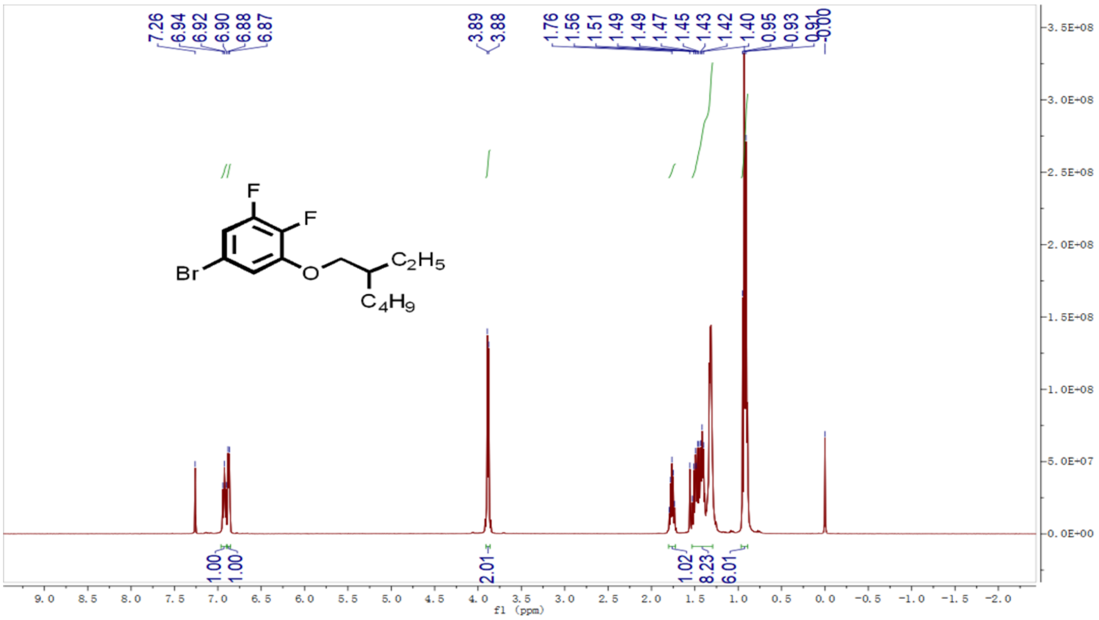


Fig.S1. ^{1}H NMR spectrum of compound M1 ($CDCl_3$).

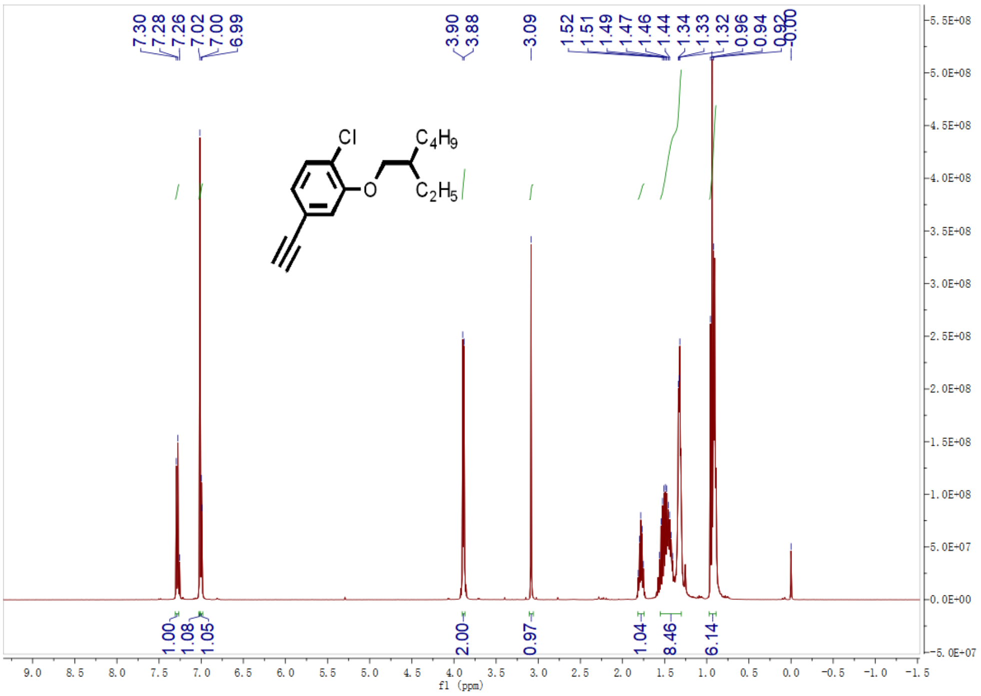


Fig.S2. ^{1}H NMR spectrum of compound M4 ($CDCl_3$).

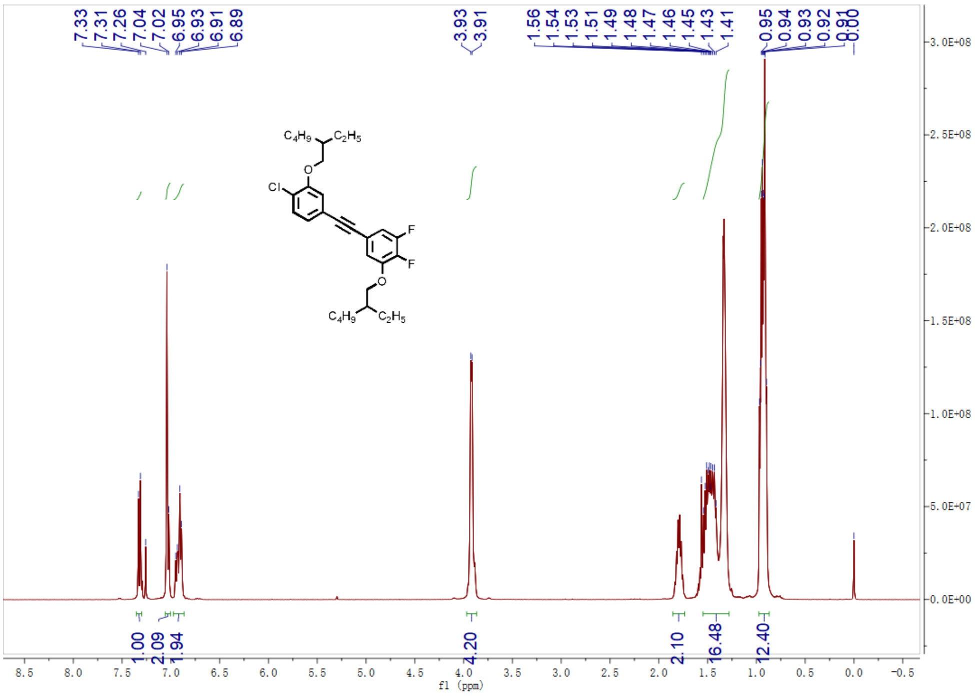


Fig.S3. ^{1}H NMR spectrum of compound M5 ($CDCl_3$).

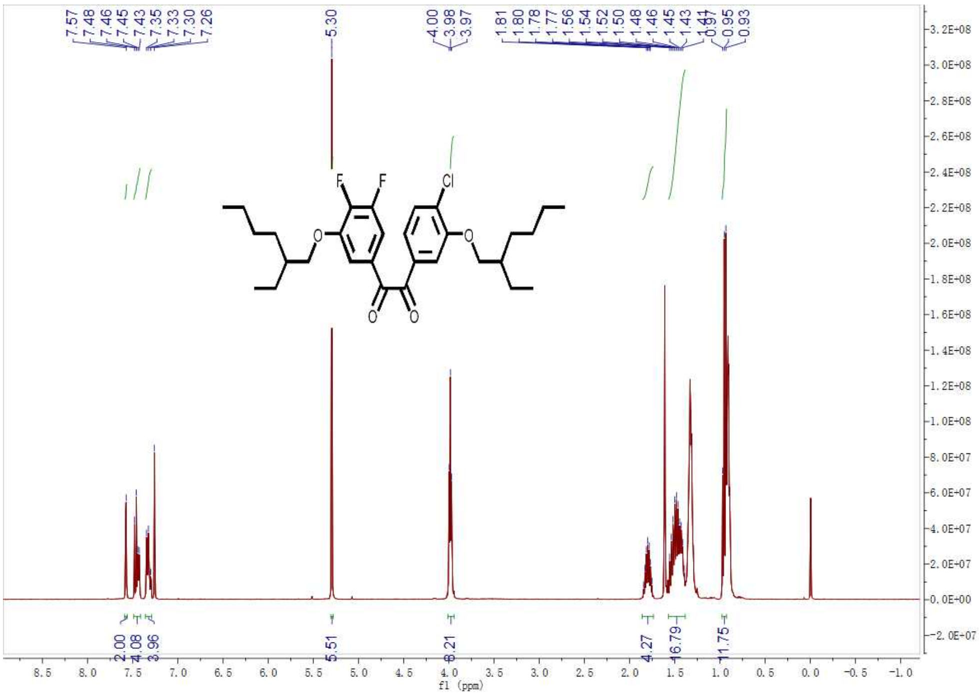


Fig.S4. ^{1}H NMR spectrum of compound M6 ($CDCl_3$).

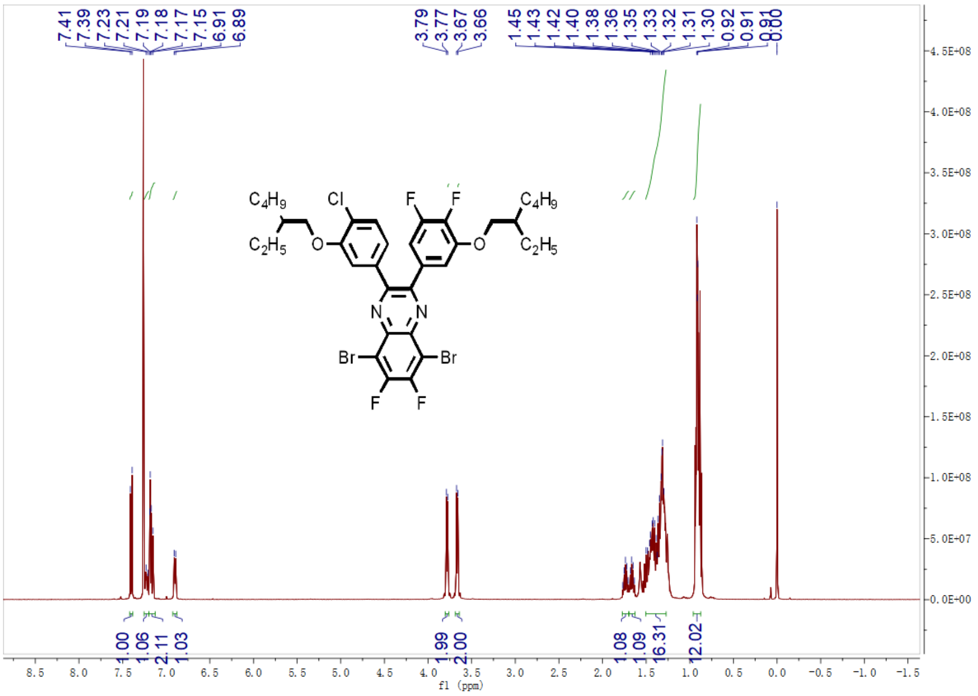


Fig.S5. ^{1}H NMR spectrum of compound M7 ($CDCl_3$).

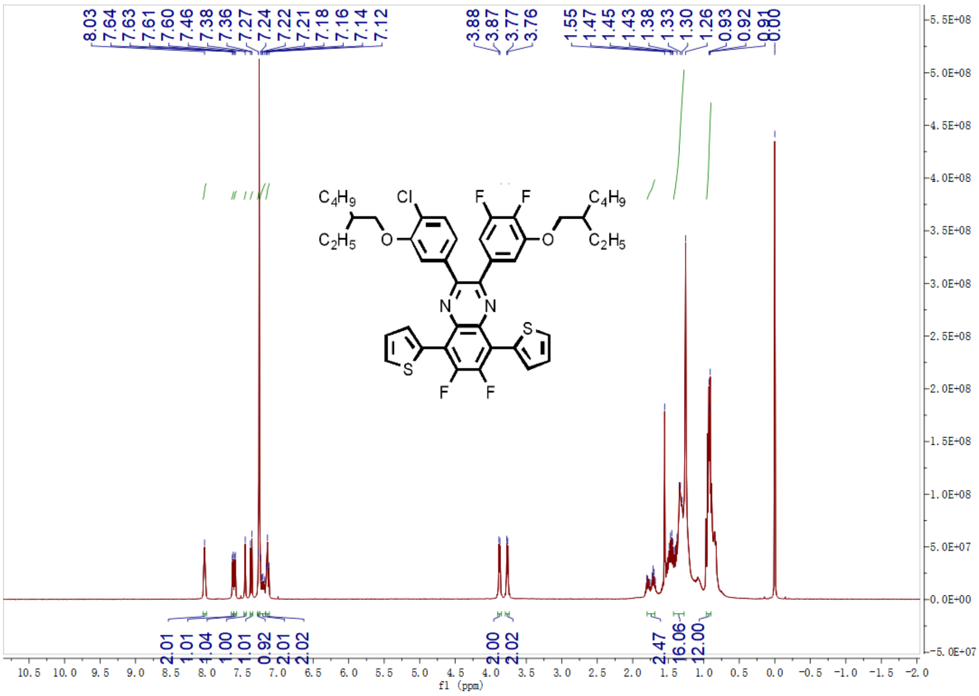


Fig.S6. ^{1}H NMR spectrum of compound M8 ($CDCl_3$).

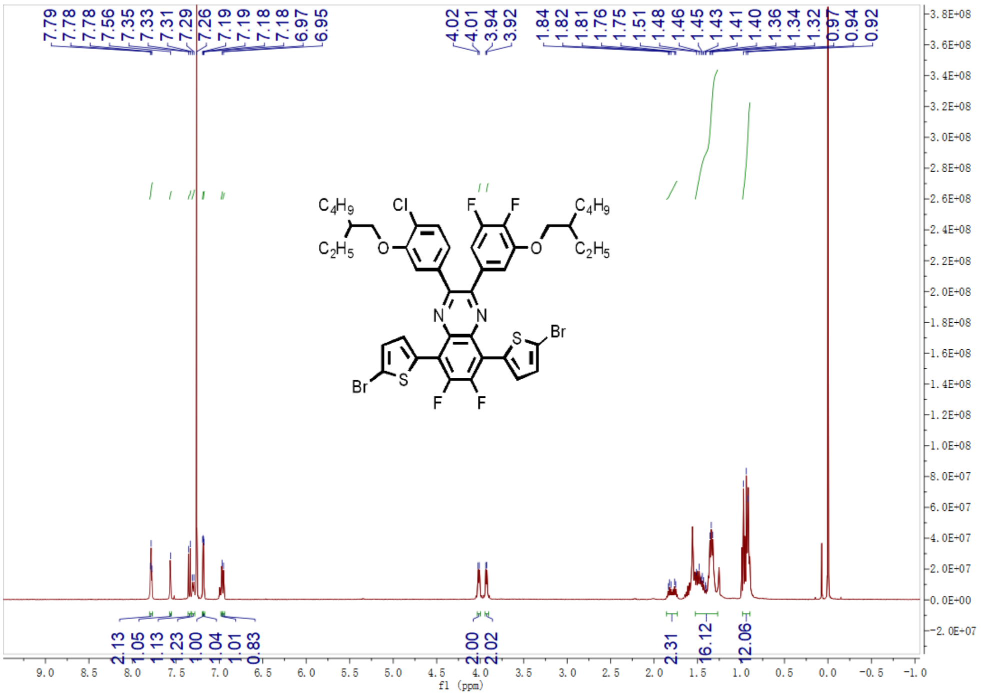


Fig.S7. ^{1}H NMR spectrum of compound M9 ($CDCl_3$).

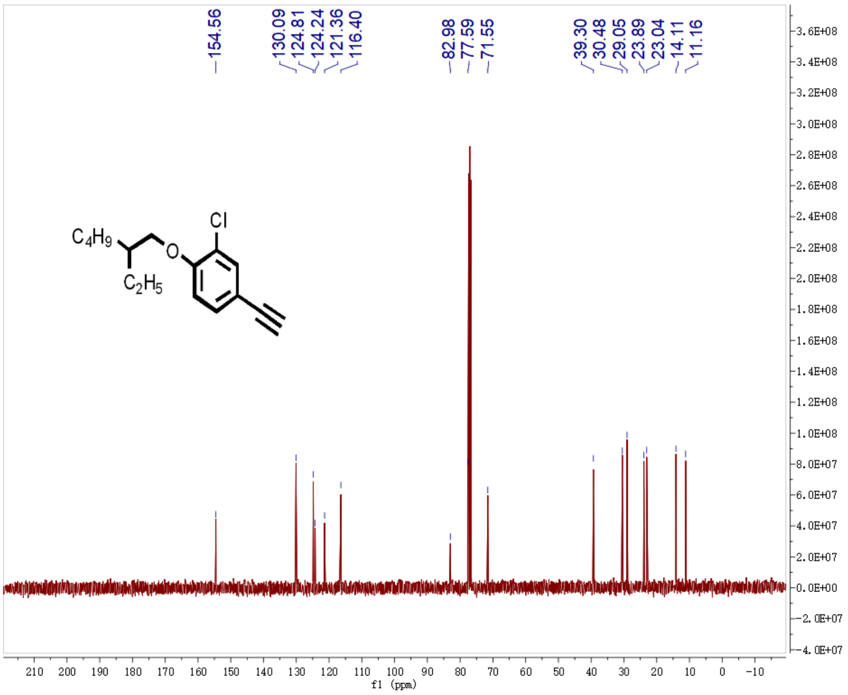


Fig.S8. ^{13}C NMR spectrum of compound M4 ($CDCl_3$).

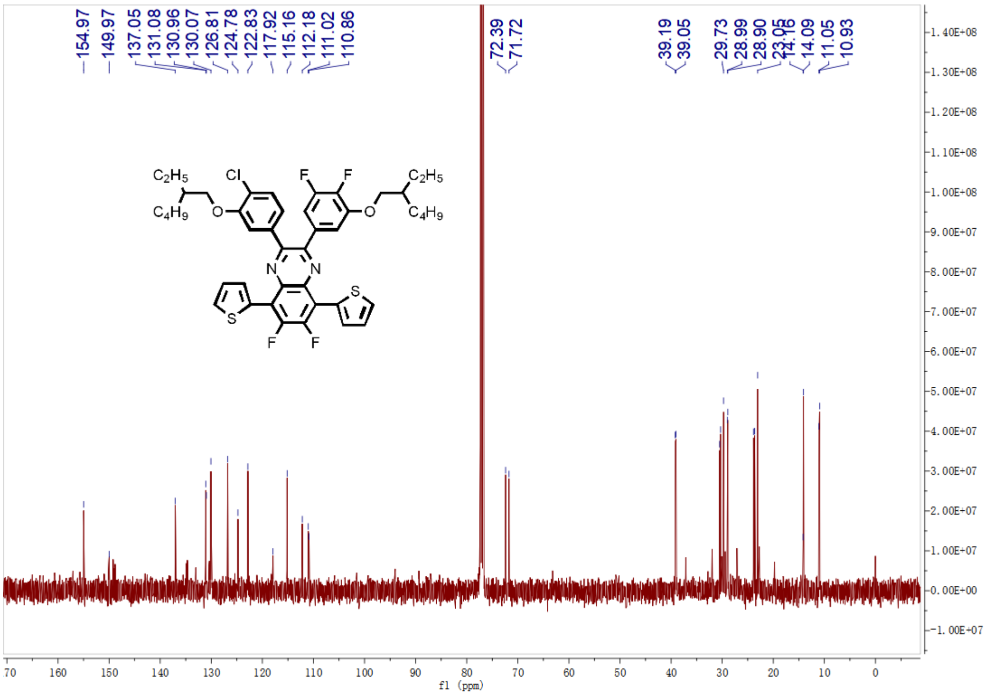


Fig.S9. ^{13}C NMR spectrum of compound M8 ($CDCl_3$).

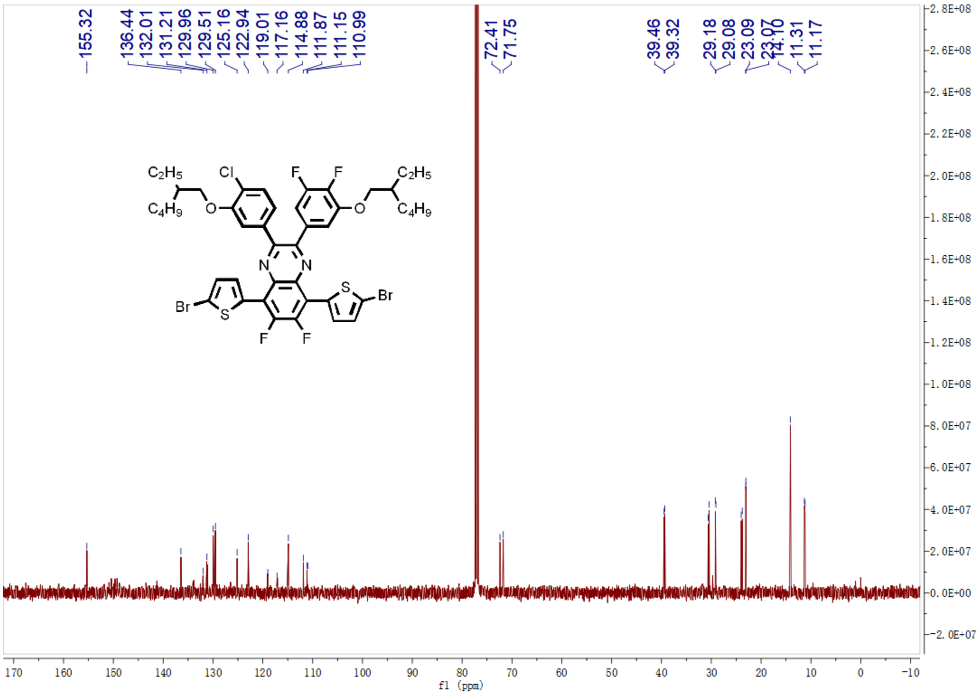


Fig.S10. ^{13}C NMR spectrum of compound M9 ($CDCl_3$).

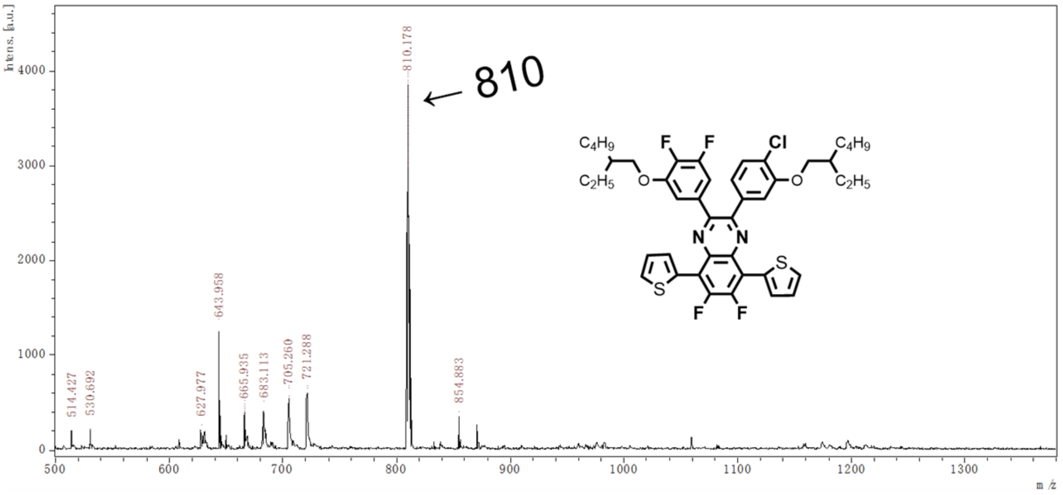


Fig.S11. MALDI-TOF MS spectrum of compound M8 ($CDCl_3$).

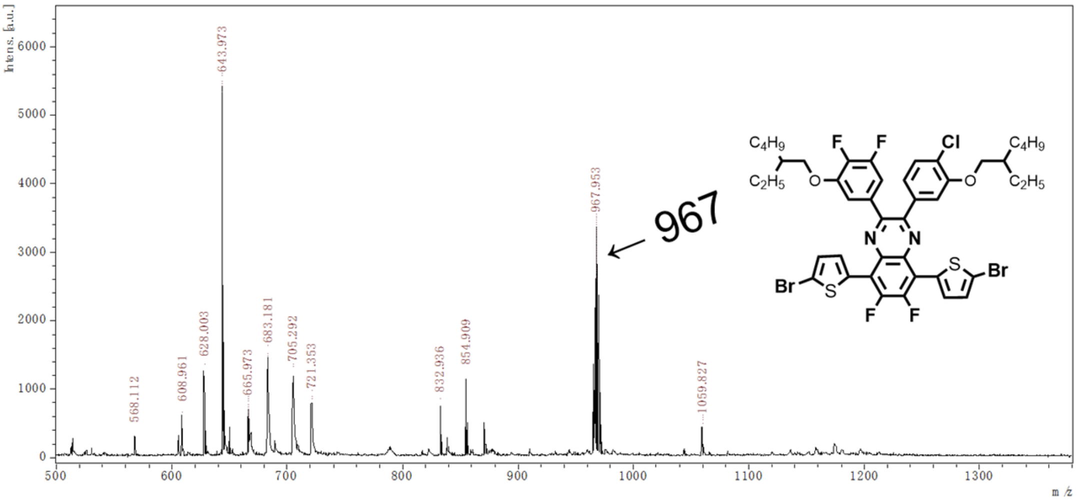


Fig.S12. MALDI-TOF MS spectrum of compound M9 ($CDCl_3$).

5. TGA, DSC, optical, CV, electron and Hole Mobilities data

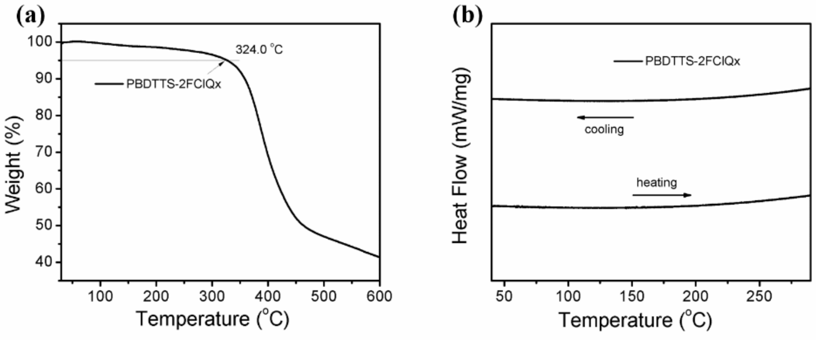


Fig.S13. (a) TG and (b) DSC analysis (10 ºC min^{-1}) of PBDTTS-2FClQx, respectively.

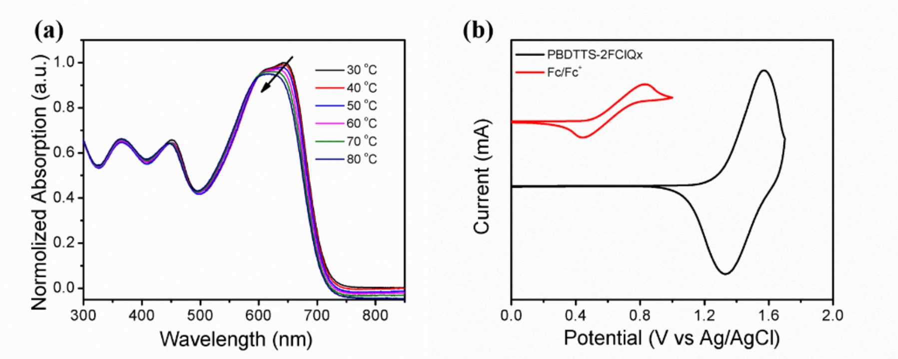


Fig.S14. (a) Temperature-dependent absorption spectra of PBDTTS-2FClQx at temperature interval of 10 °C and (b) CV curve of PBDTTS-2FClQx, respectively.

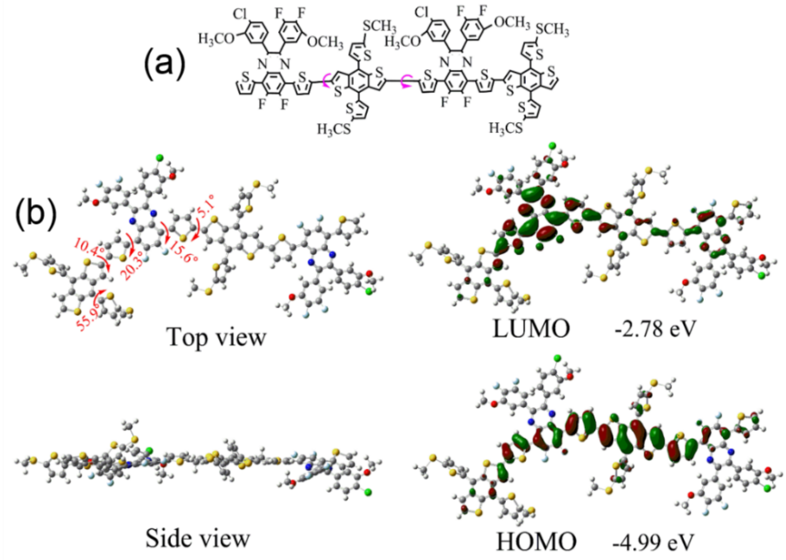


Fig.S15. (a) Molecular structure of the PBDTTS-2FClQx dimer; (b) Optimized molecular geometries, molecular frontier orbitals of HOMOs and LUMOs for the copolymer obtained by Gaussian 09 at the B3LYP/def2-SVP level.

6. Photovoltaic properties of the PBDTTS-2FClQx:Y6:PC$_{71}$BM-based OSCs.

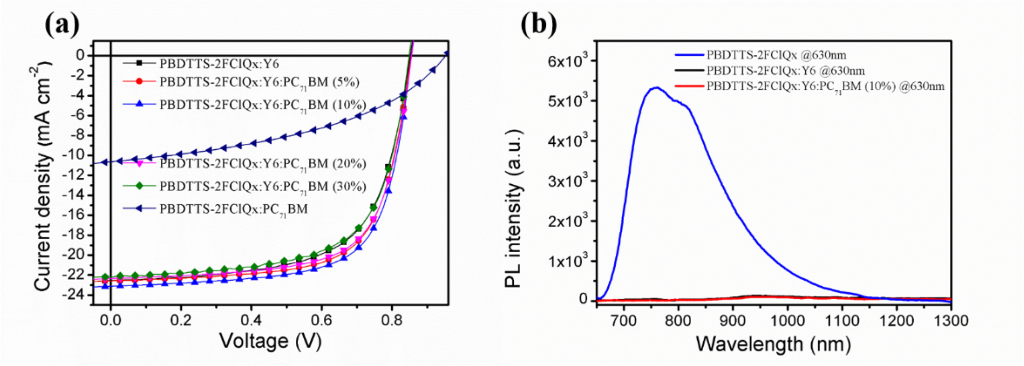


Fig.S16. (a) *J*-*V* curves of OSCs in different PC$_{71}$BM ratio (AM 1.5, 100 mW cm^{-2}); (b) (f) PL spectra of the copolymer PBDTTS-2FClQx and blend films excited at 630 nm.

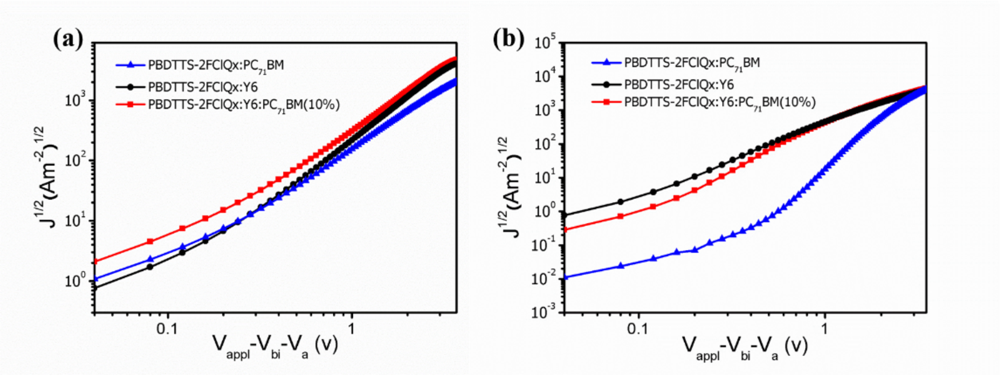


Fig.S17. SCLC fittings of electron- and hole-only devices based on the PBDTTS-2FClQx blend films.

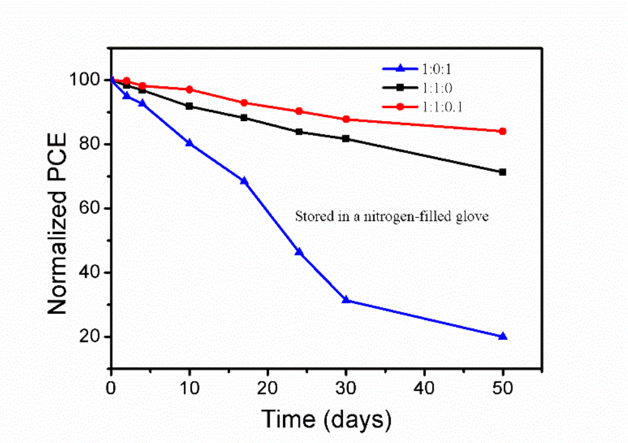


Fig.S18. Stability curves of binary and optimal ternary OSCs under standard sunlight irradiation based on the PBDTTS-2FClQx blend films..

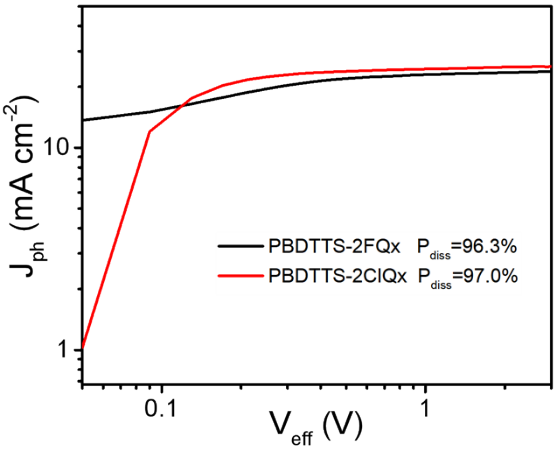


Fig.S19. The dependence of photocurrent density (J_{ph}) and effective voltage (V_{eff}) curve based on PBDTTS-2FQx and PBDTTS-2ClQx devices

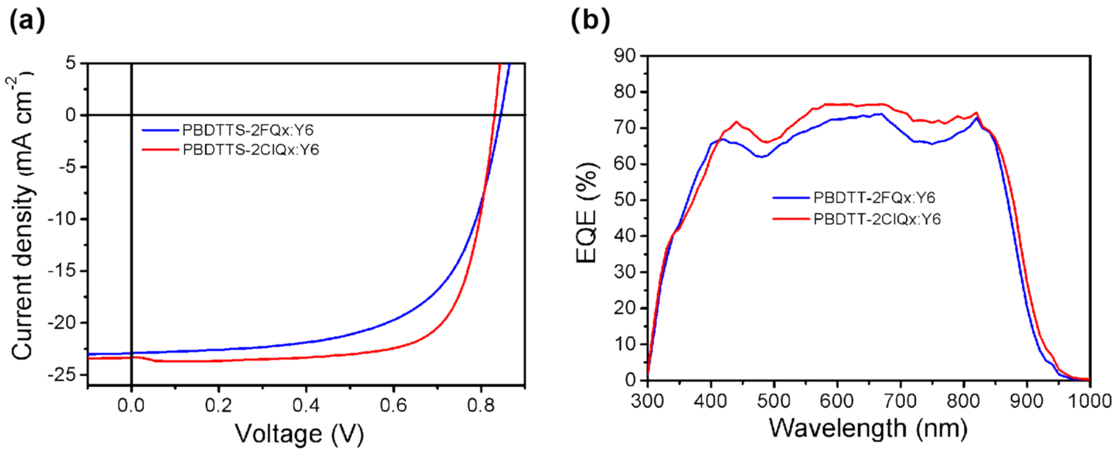


Fig.S20. (a) *J-V* curves (AM 1.5G, 100 mW cm^{-2}); (b) EQE curves curve based on PBDTTS-2FQx and PBDTTS-2ClQx devices

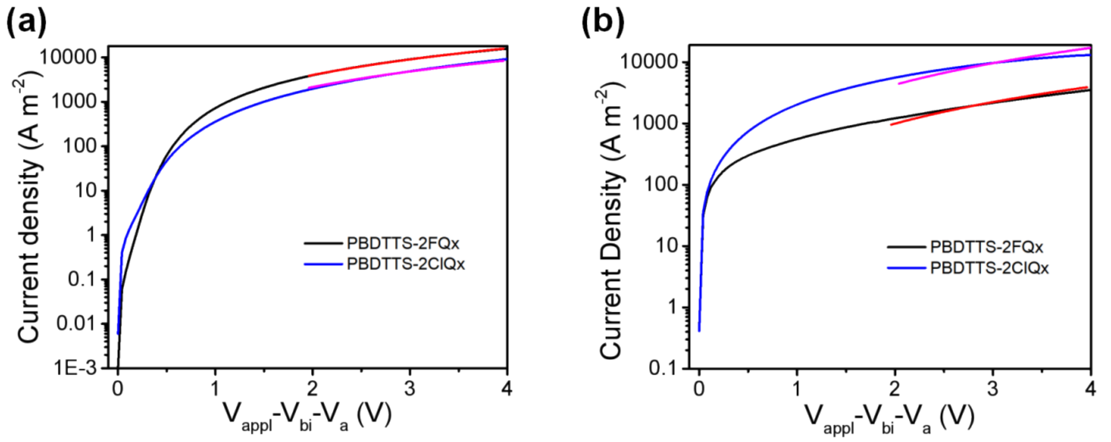


Fig.S21. SCLC fittings of electron- and hole-only devices based on PBDTTS-2FQx and PBDTTS-2ClQx:Y6 blend films

Table S1. Photovoltaic parameters of OSCs in different $PC_{71}BM$ ratio under simulated AM 1.5 G illumination at 100 mW cm^{-2}.

$PC_{71}BM$(ratio)	V_{OC} (V)	J_{SC} (mA cm^{-2})	*FF* (%)	PCE_{max}(%)
0%	0.851	22.54	64.68	12.41
5%	0.854	22.56	68.31	13.16
10%	0.855	23.09	68.86	13.59
20%	0.856	22.33	68.01	12.99
30%	0.858	22.14	65.51	12.30

100％	0.951	10.61	43.33	4.37

Table S2. Summary of surface free energy of neat PBDTTS-2FClQx, Y6 and $PC_{71}BM$ films calculated from contact angles measurements.

Active layer materials	θ_{Water} (^{o})	$\theta_{Diiodomethane}$ (^{o})	γ (mN m^{-1})
PBDTTS-2FClQx	90.5	48	36.21
Y6	84.3	41	39.25
$PC_{71}BM$	91.8	23.2	45.36