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Supporting Information

Precise fluorination of polymeric donors towards efficient non-fullerene organic solar cells with balanced open circuit voltage, short circuit current and fill factor

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1. Experimental section

^1H, ^{19}F and ^{13}C NMR were recorded using a Bruker DMX-400 spectrometers with deuterated chloroform as solvent at 298 K. Chemical shifts were reported as δ values (ppm) with tetramethylsilane (TMS) as the internal reference. Molecular weight and dispersity of the polymer were determined by high temperature gel permeation chromatography(HT-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. Cyclic voltammetry(CV) was done on a CHI600A electrochemical workstation with Pt disk, Pt plate, and standard calomel electrode(SCE) as working electrode, counter electrode, and reference electrode, respectively, in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile solution. The CV curves were recorded versus the potential of SCE, which was calibrated by the ferrocene-ferrocenium (Fc/Fc^+) redox couple (4.4 eV below the vacuum level). The morphologies of the polymers: Y5/Y6 blend films were investigated by atomic force microscopy(AFM, Agilent Technologies, 5500 AFM/SPM System, USA) in contacting mode with a 2 μm scanner. Transmission electron microscope (TEM) measurements were performed in a JEM-2100F.

2. Materials

All materials were obtained from Sigma-Aldrich (St. Louis, MO, USA) and used without further purification unless otherwise indicated. Tetrakis(triphenylphosphine) palladium ($Pd(PPh_3)_4$, 99%) was purchased from J&K Chemical Ltd. (Beijing, China).(4,8-bis(5-(2-ethylhexyl)-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane)(BDT) and (4,8-bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)benzo [1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane)(BDT-2F) were purchased from Derthon Optoelectronic Materials Science & Technology Co., Ltd. (Shenzhen, China).

3. Device Fabrication and Characterization

Organic solar cells were fabricated on glass substrates commercially pre-coated with a layer of indium tin oxide (ITO) with the structure of ITO/PEDOT: PSS/Donor: Acceptor/PDINN/Ag. Prior to fabrication, the substrates were cleaned using detergent, deionized water, acetone and isopropanol consecutively for every 15 min, and then treated in an ultraviolet ozone generator for 15 min. Then PEDOT:PSS was filtered through a 0.45 um 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°C for 15 min in the air. Then the substrates were transferred to a glovebox, the active layer was spin coated from 16 mg/mL chloroform solution (D/A = 1:1, 0.5% CN, 100°C, 10min) at 2800 rpm for 30s. Finally, the whole device was completed by vacuum evaporating Ag metal electrodes (100 nm) to acquire an area of 6.0 mm^2 cell.

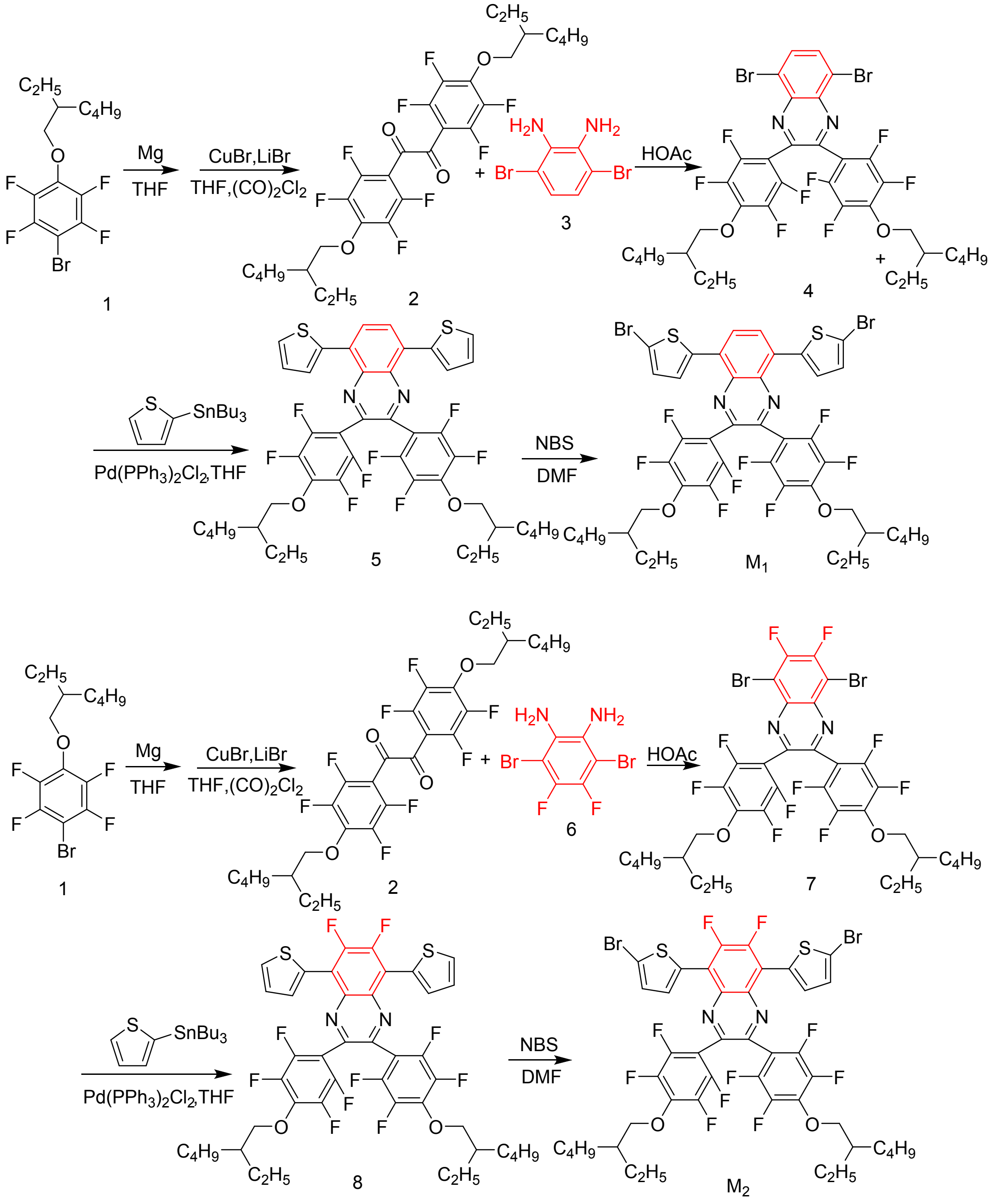
The *J-V* measurement was performed via the solar simulator (SS-F5-3A, Enlitech) along with AM 1.5G spectra whose intensity was calibrated by the certified standard silicon solar cell (SRC-2020, Enlitech) at 100 mV/cm^2. The external quantum efficiency (EQE) data were obtained by using the solar-cell spectral-response measurement system (RE-R, Enlitech).

Charge carrier mobility was measured by SCLC method. The mobility was determined by fitting the dark current to the model of a single carrier SCLC, which is described by:

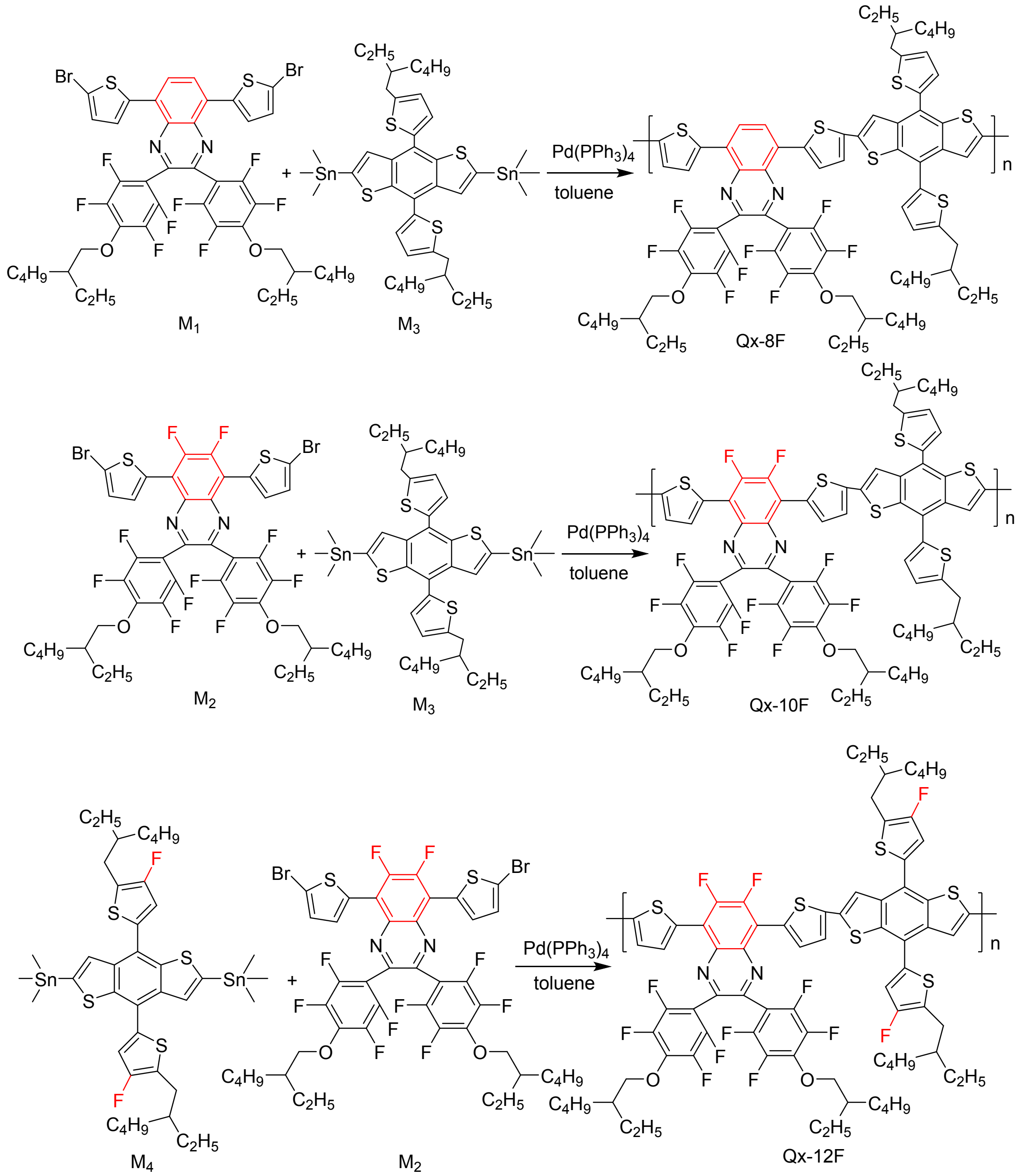
$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu\frac{V^2}{d^3}$$

where J is the current density, μ is the zero-field mobility of holes (μ_h) or electrons (μ_e), ε_0 is the permittivity of the vacuum, ε_r is the relative permittivity of the material, d is the thickness of the blend film, and V is the effective voltage ($V = V_{appl}-V_{bi}$, where V_{appl} is the applied voltage, and V_{bi} is the built-in potential determined by electrode work function difference). Here, V_{bi} = 0.1 V for hole-only devices, V_{bi} = 0 V for electron-only devices.[1] The mobility was calculated from the slope of $J^{1/2}$-V plots.

4. Synthesis

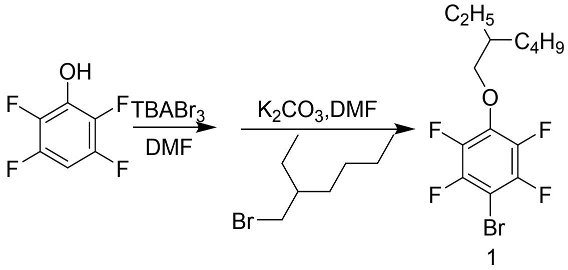


Scheme S1 Synthetic route and chemical structure of monomers



Scheme S2 Synthetic route and chemical structure of polymer

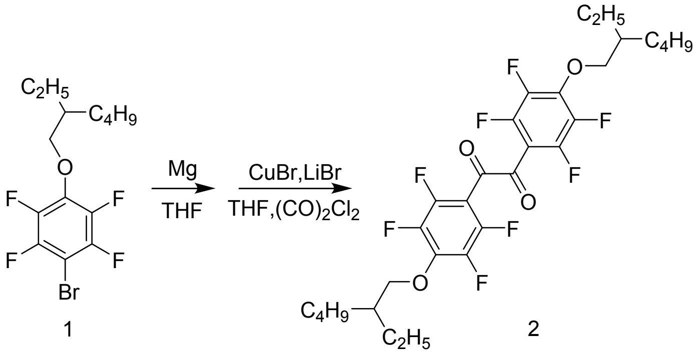
1-bromo-4-(2-ethylhexyloxy)-2,3,5,6-tetrafluorobenzene (1)



2,3,5,6-tetrafluorophenol (16.00g 96.3mmol), $TBABr_3$ (46.44g 96.3mmol) were put into an round bottom flask and add 60 ml DMF. Stir at room temperature for 5 hours, pour into 200 ml of water and then extracted three times with dichloromethane and water. The combined organic phases were dried over magnesium sulfate. Then, the solvents were evaporated under vacuum and the red oil needn't any purify to next step.

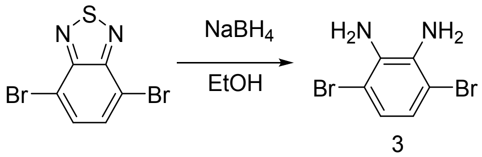
1-bromide-2,3,5,6-tetrafluorophenol(96.3 mmol), K_2CO_3(15.98 g, 115.6 mmol) were put into a three-neck round-bottom flask, and then added 80 mL DMF. Under the argon atmosphere, 1-bromo-2-ethylhexane (18.61 g, 96.3 mmol) was added and the reaction mixture was stirred for12h at 150°C. And then cooled 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 (29.24 g, 85.0% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.29-3.93 (m, 2H), 1.80-1.62 (m, 1H), 1.40-1.17 (m, 4H), 1.09-0.65 (m, 10H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -128.55- -140.41 (m), -150.03- -163.35 (m).

1,2-bis(4-((2-ethylhexyl)oxy)-2,3,5,6-tetrafluorophenyl)ethane-1,2-dione (2)



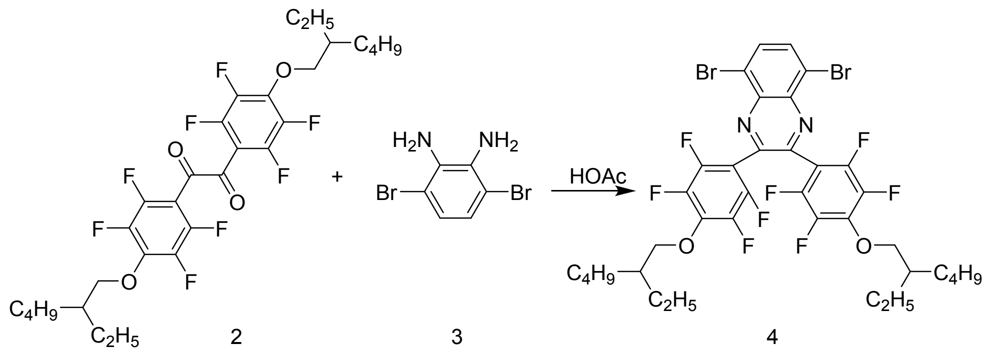
Under vigorous stirring, 1-bromo-4-(2-ethylhexyloxy)-2,3,5,6-tetrafluorobenzene (**1**)(12.00 g, 33.7mmol) was added drop wisely to magnesium turnings (0.49 g, 40.5 mmol) in anhydrous THF(45 mL) which was protected by Ar. During the process, I_2 (12 mg) was added as catalyst in the reaction. The solution was refluxed for 6h 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 (5.86g, 67.4 mmol) and cuprous bromide(4.85 g, 33.7 mmol) dispersed in 60 mL THF under 0°C. Oxalyl chloride (2.01g, 15.8 mmol) was added drop wisely into the above reaction mixture and continued to stir for 30 min. The solution was stirred for another 2 h at room temperature, then 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[2, 3]. The crude product was purified on a silica gel column, eluting with pure hexane. Light yellow viscous liquid was obtained (2.18 g, 21.2% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.22 (d, *J*=5.4 Hz, 4H), 2.05-1.60 (m, 2H), 1.42-1.15 (m, 8H), 1.02-0.63 (m, 20H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -138.18- -149.40 (m), -152.19- -163.70 (m).

3,6-dibromobenzene-1,2-diamine (3)



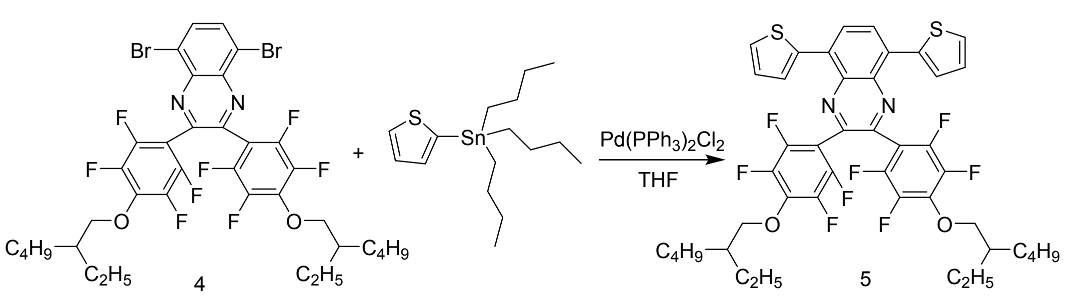
4,7-dibromo[c][1,2,5]thiadiazole (1.70 g, 5.8 mmol) and 60mL C_2H_5OH were put into an round-bottom flask, and then added $NaBH_4$(2.26 g, 58 mmol) in one portion under 0°C. The mixture was stirred at room temperature for 6 h. And the reaction mixture was poured into 200 mL water and then extracted three times with dichloromethane and water. The combined organic phases were dried over magnesium sulfate. Then, the solvents were evaporated under vacuum and the white crude product needn't any purify to next step.

5,8-dibromo-2,3-bis(4-((2-ethylhexyl)oxy)-2,3,5,6-tetrafluorophenyl)-quinoxaline (4)



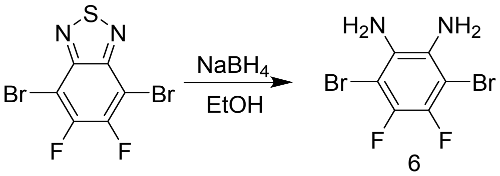
3,6-dibromobenzene-1,2-diamine(**3**) (0.57 g, 2.15 mmol) was suspended in 40mL acetic acid and compound(**2**) (0.84 g, 1.38 mmol) dissolved in 30 mL acetic acid was added. The suspension was heated to 60°C for 1 h and then the temperature was raised to 120°C for 3h. The solution was stirred over night at 90°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. Yellow viscous liquid was obtained (0.92g, 79.1% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 2H), 4.79-3.79 (m, 4H), 1.87-1.61 (m, 2H), 1.43-1.14 (m, 8H), 1.04-0.70 (m, 20H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -143.09 (dd, *J*=21.8, 8.0 Hz), -152.19- -165.58 (m).

2,3-bis(4-((2-ethylhexyl)oxy)-2,3,5,6-tetrafluorophenyl)-5,8-di(thiophen-2-yl)quinoxaline (5)



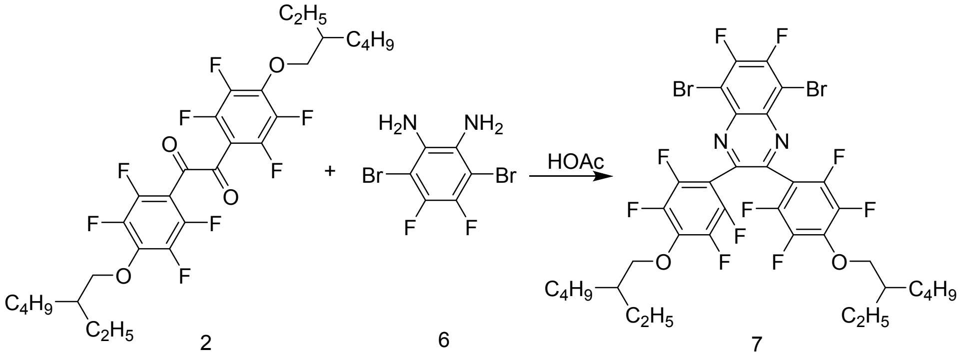
To a solution of compound (**4**) (1.05 g, 1.25 mmol), tributyl(thiophene-2-yl)-stannane(1.40 g,3.76 mmol) and $PdCl_2(PPh_3)_2$(0.035 g, 0.05 mmol) in dry toluene(25 mL) and the reaction mixture was heated to reflux for 48h under an argon atmosphere. The reaction mixture was allowed to cool to room temperature and then concentrated under reduced pressure. The crude product was chromatographically purified on a silica gel column eluting with dichloromethane/hexane (1:9, v/v) to afford compound **5** as an orange solid (0.96 g, 91.0% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J*=7.3 Hz, 2H), 7.91-7.62 (m, 2H), 7.48 (d, *J*=5.1 Hz, 2H), 7.16 (dd, *J*=5.0, 3.8 Hz, 2H), 4.21 (d, *J*=5.4 Hz, 4H), 1.93-1.61 (m, 2H), 1.41-1.15 (m, 8H), 1.11-0.75 (m, 20H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -130.88 – -143.29 (m), -153.60 – -158.61 (m).

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



6 was synthesized according to the synthetic method of **3**. White crude product was obtained.

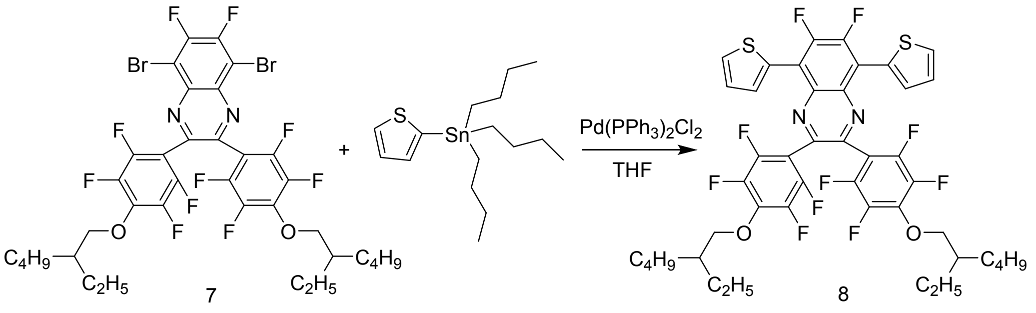
5,8-dibromo-2,3-bis(4-((2-ethylhexyl)oxy)-2,3,5,6-tetrafluorophenyl)-6,7-difluoroquinoxaline(7)



7 was synthesized according to the synthetic method of **4**. Light yellow viscous liquid was obtained(0.95 g, 79.1% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.21 (d, *J*=5.3 Hz, 4H), 1.87-1.61 (m,2H), 1.40-1.09 (m, 8H), 1.03-0.61 (m, 20H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -125.48 (s), -143.28 (dd, *J* = 23.4, 9.6 Hz), -156.12 (dd, *J* = 21.0, 7.1 Hz).

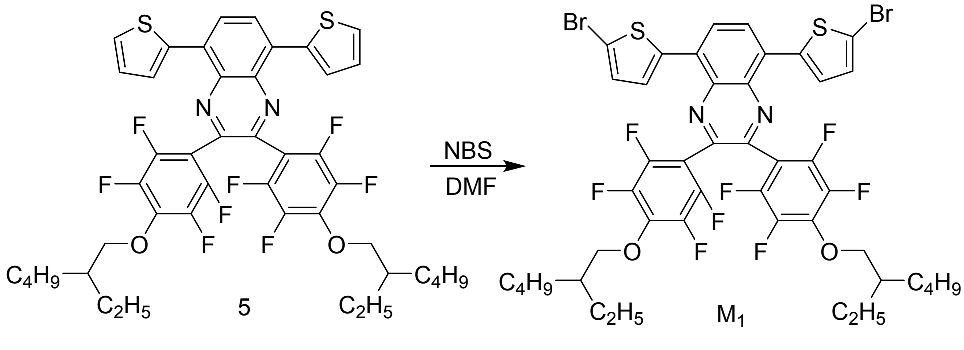
2,3-bis(4-((2-ethylhexyl)oxy)-2,3,5,6-tetrafluorophenyl)-6,7-difluoro-5,8-

di(thiophen-2-yl)quinoxaline(8)



8 was synthesized according to the synthetic method of **5**. An orange solid was obtained (1.01g, 91.0% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.00 (d, *J*=3.3 Hz, 2H), 7.43-7.09 (m, 2H), 7.48 (d, *J*=5.1 Hz, 2H),4.22 (d, *J*=5.4 Hz, 4H), 1.84-1.61 (m, 2H), 1.45-1.11 (m, 8H), 1.11-0.69 (m, 20H). ^{19}F NMR (376 MHz, CDCl$_3$) δ -121.44- -130.44 (m), -143.27 (dt, *J* = 22.0, 11.1 Hz), -156.12 (dt, *J* = 11.4, 8.5 Hz).

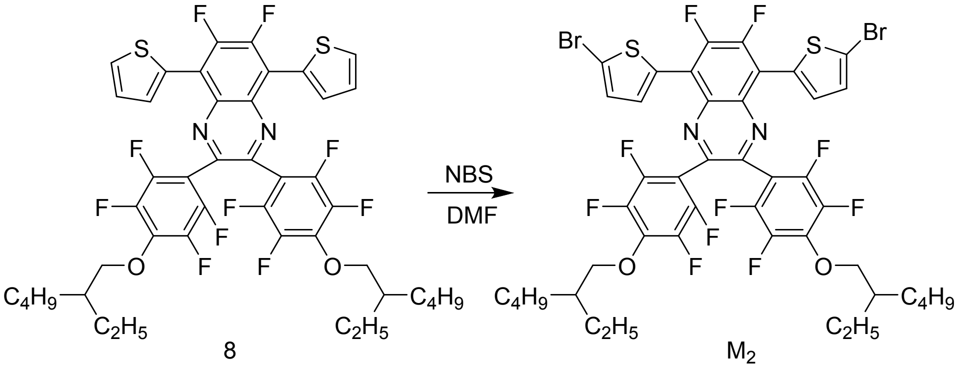
5,8-bis(5-bromothiophen-2-yl)-2,3-bis(4-((2-ethylhexyl)oxy)-2,3,5,6-tetrafluorophenyl)-quinoxaline (M1)



To a solution of compound (**5**) (0.92 g, 1.13 mmol) in dimethyl formamide (20 mL) was added N-bromosuccinimide (NBS) (0.51 g, 2.83 mmol) in portions under 40 mins. 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 dichlor-omethane/hexane (1:8, v/v) to afford **M1** as a red solid (0.92 g, 81.2% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.18 (s, 2H), 7.56 (t, *J*=12.9 Hz, 2H), 7.12 (t, *J*=8.1 Hz, 2H), 4.25 (d, *J*=5.5 Hz, 4H), 1.89-1.64 (m, 2H), 1.40-1.15 (m, 8H), 1.05-0.69 (m, 20H). ^{19}F NMR (376 MHz, CDCl$_3$) δ -121.44- -130.44 (m), -143.15 (dt, *J* = 23.3, 9.7 Hz), -157.22 (dt, *J* = 11.4, 8.0 Hz). ^{13}C NMR

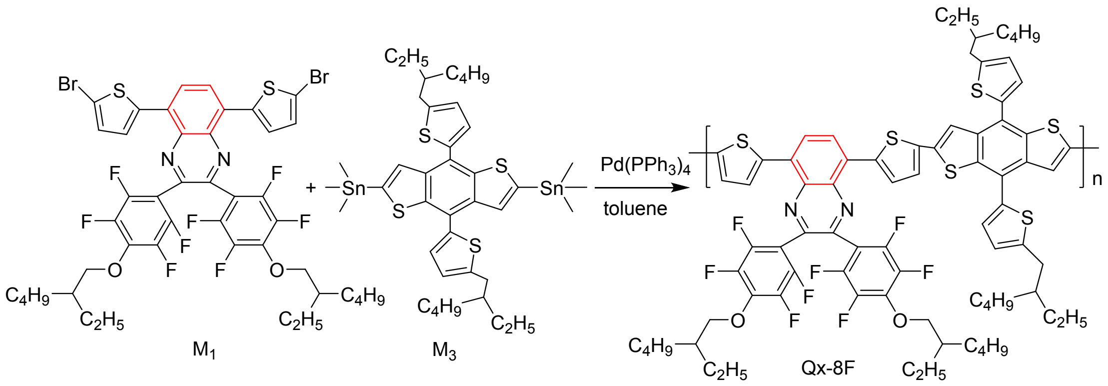
(101 MHz, $CDCl_3$) δ154.54, 152.55, 150.57, 147.76, 139.06, 133.86, 133.69, 133.66, 132.24, 131.42, 131.04, 130.98, 129.76, 127.89, 123.12, 118.83, 117.26, 116.70, 115.95, 115.80, 99.99, 77.26, 77.01, 76.75, 69.62, 31.59, 29.70, 29.36, 29.26, 29.23, 26.08, 14.09, 11.01. MS: m/z calc. for $C_{44}H_{40}Br_2F_8N_2O_2S_2$ 1004.7312; found 1004.7337.

5,8-bis(5-bromothiophen-2-yl)-2,3-bis(4-((2-ethylhexyl)oxy)-2,3,5,6-tetrafluorophenyl)-6,7-Difluoroquinoxaline (M2)



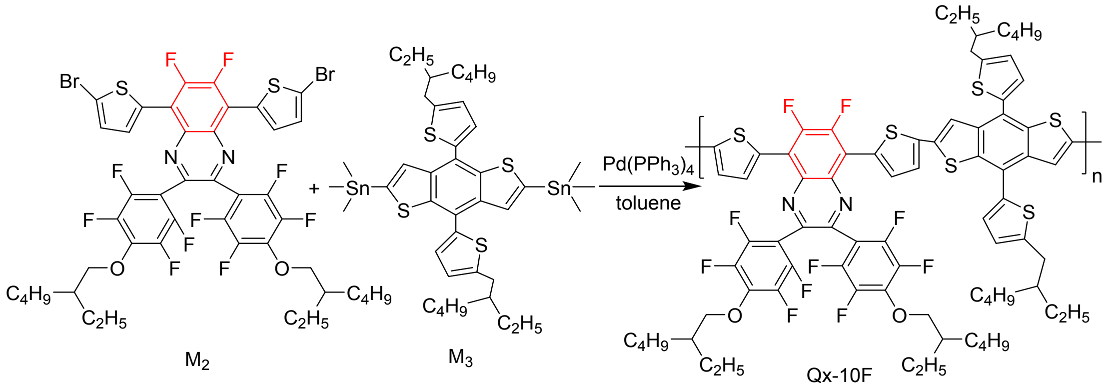
M2 was synthesized according to the synthetic method of **M1**. A red solid was obtained (0.94g, 79.8% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J*=4.1 Hz, 2H), 7.19 (d, *J*=4.2 Hz, 2H), 4.19 (t, *J*=37.3 Hz, 4H), 1.72 (tt, *J*=22.8, 11.3 Hz, 2H), 1.41-1.23 (m, 8H), 0.92 (ddd, *J*=20.8, 12.4, 7.1 Hz, 20H). ^{19}F NMR (376 MHz, $CDCl_3$) -108.47 – -120.27 (m), -143.27 (dt, *J*=22.2, 11.2 Hz), -156.12 (dt, *J*=11.2, 8.3 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.52, 151.16, 150.97, 148.57, 148.38, 144.53, 144.32, 143.74, 142.15, 141.83, 141.62, 141.18, 140.98, 133.96, 131.86, 131.32, 131.24, 131.16, 129.45, 125.69, 125.56, 118.99, 116.99, 114.71, 114.61, 40.53, 32.52, 30.07, 28.87, 25.77, 22.94, 14.10, 10.91. MS: m/z calc. for $C_{44}H_{38}Br_2F_{10}N_2O_2S_2$ 1040.7120; found 1040.7140.

Polymer Qx-8F



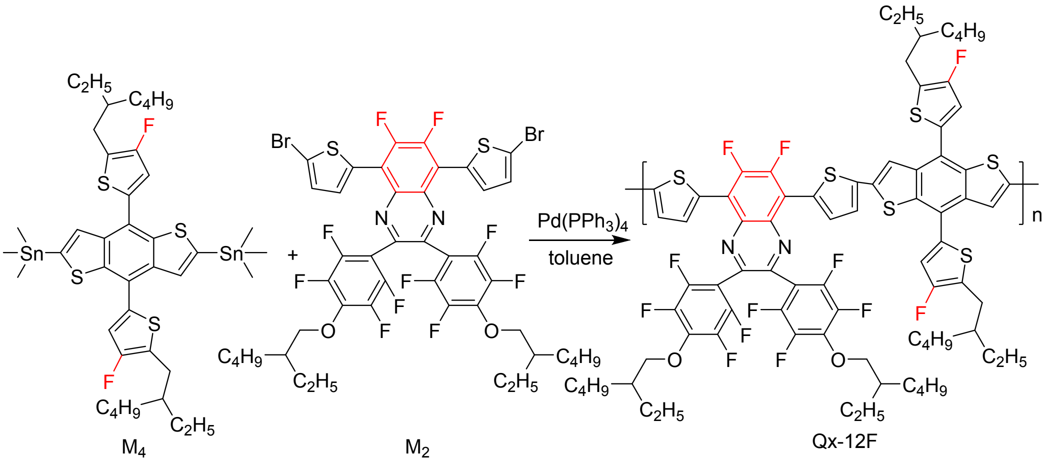
In a 50 mL two-necked flask, **M1** (0.1453 g, 0.15 mmol) and **M3** (0.1360 g, 0.15 mmol) were dissolved in 15 mL anhydrous toluene. The reaction system was purged with Ar for 10 min to remove the oxygen. $Pd(PPh_3)_4$ (10 mg) as the catalyst was added quickly into the flask, then purged with Ar for 5 min again. The reaction was allowed to warm to 110°C and stirred for 24 h. Cooled the mixture to ambient temperature, the reaction mixture was poured into 200 mL of methanol and stirred for 30 min to precipitate out the crude polymer. Filtered and collected the filter residue. Finally, the residue was 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 as deep green solid (151mg, 53.4% yield). **Qx-8F** has a number average molecular weight (Mn) of 25.69 kDa, with a dispersity of 2.47.

Polymer Qx-10F



Qx-10F was synthesized according to the synthetic method of **Qx-8F**. The chloroform fraction was collected and evaporated under vacuum to afford the target polymer as deep green solid (178mg, 62.2% yield).**Qx-10F** has a M_n of 30.25 kDa, with a dispersity of 2.36.

Polymer Qx-12F



Qx-12F was synthesized according to the synthetic method of **Qx-8F**. The chloroform fraction was collected and evaporated under vacuum to afford the target polymer as deep blue solid (162mg, 57.8% yield).**Qx-12F** has a M_n of 27.13 kDa, with a dispersity of 2.24.

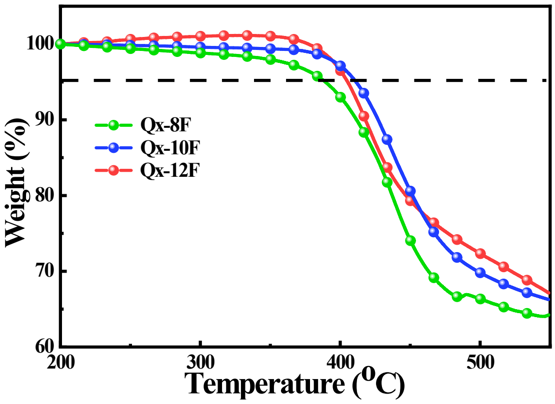


Figure S1. TGA curves of Qx-8F, Qx-10F and Qx-12F

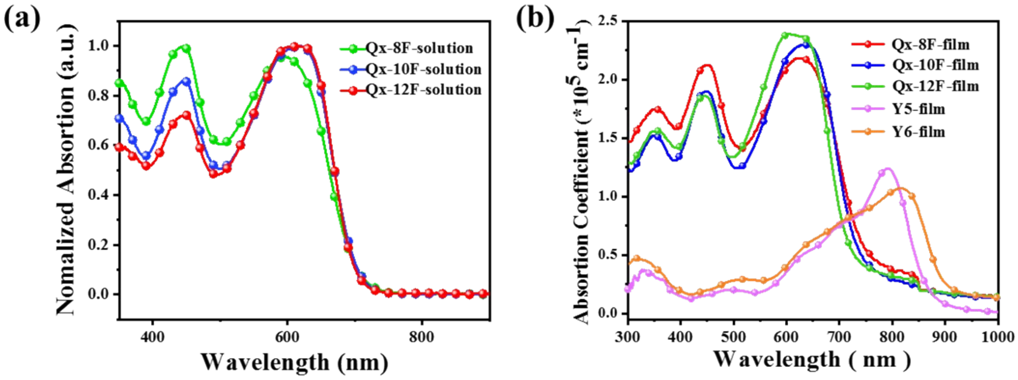


Figure S2. (a)The normalized absorption spectra of three polymer donors in the solution and (b) the absorption coefficients of donors and acceptors in the film.

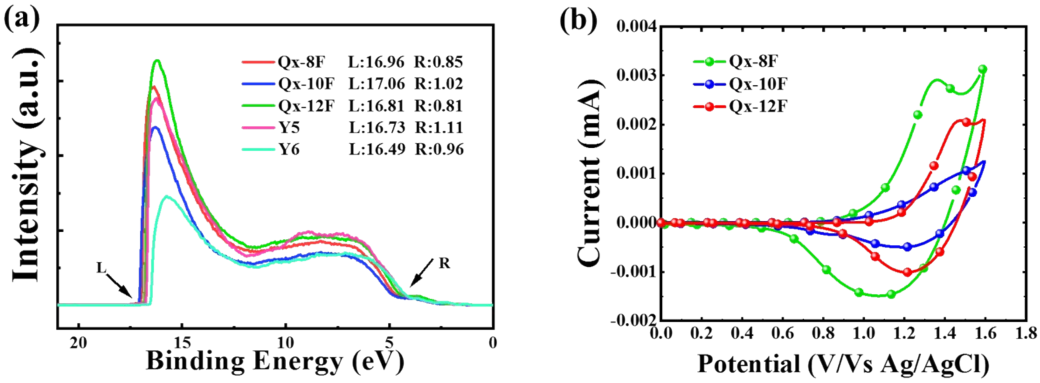


Figure S3.(a) UPS (He I; hv= 21.22 eV) data of neat Qx-8F, Qx-10F, Qx-12F, Y5 and Y6 films.(b)Cyclic voltammograms of Qx-8F, Qx-10F and Qx-12F in the positive direction.

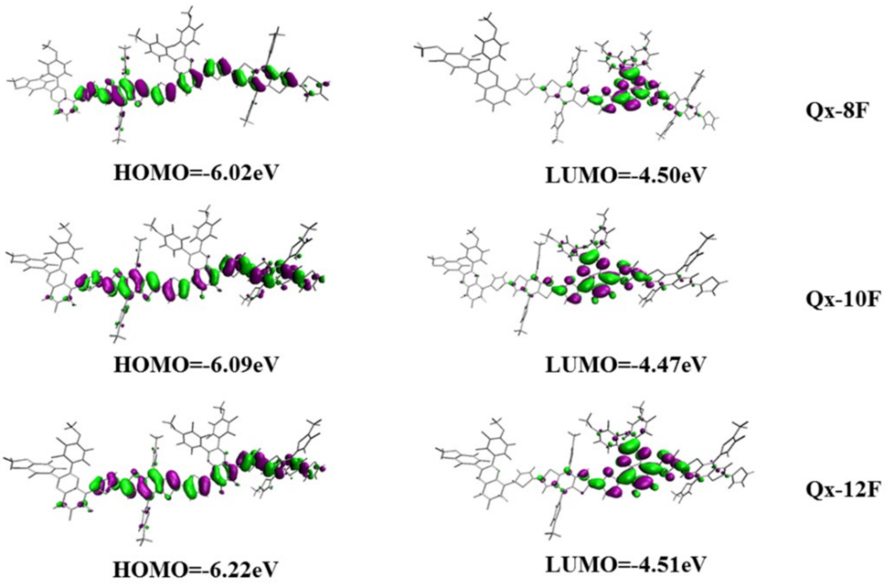


Figure S4.LUMO and HOMO for polymers. Calculations were simulated at the level of DFT/B3LYP/6-31G (d, p).

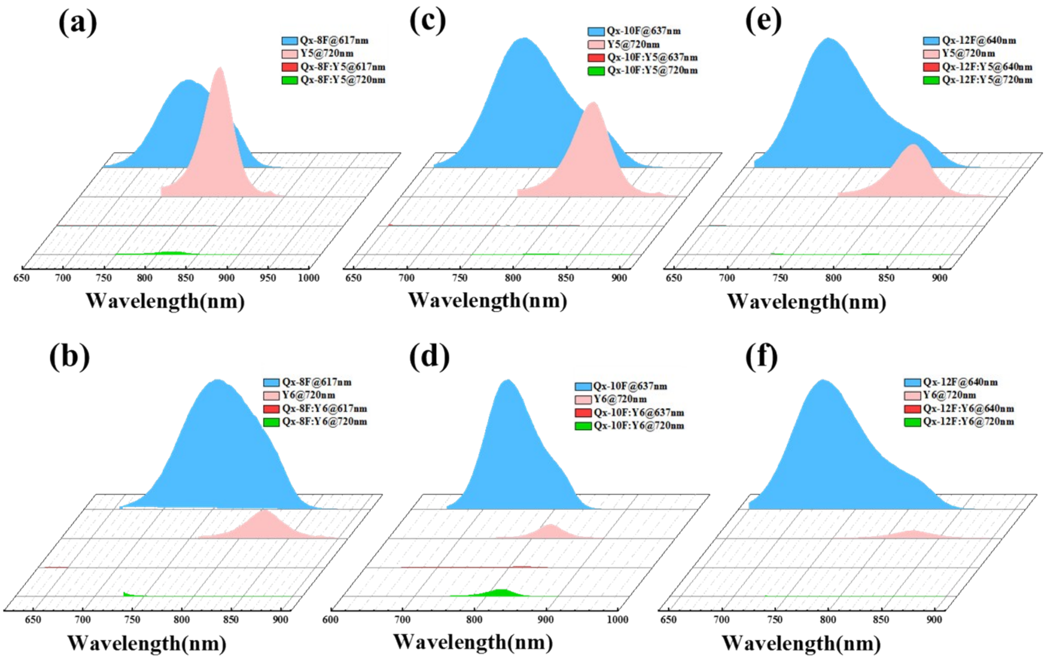


Figure S5. (a) PL spectra of Qx-8F film, Y5 film and Qx-8F:Y5 blended film excited at 617 and 720 nm. (b) PL spectra of Qx-10F film, Y5 film and Qx-10F:Y5 blended film excited at 637 and 720 nm. (c) PL spectra of Qx-12F film, Y5 film and Qx-12F:Y5 blended film excited at 640 and 720 nm. (d) PL spectra of Qx-8F film, Y6 film and Qx-8F:Y6 blended film excited at 617 and 720 nm. (e) PL spectra of Qx-10F film, Y6 film and Qx-10F:Y6 blended film excited at 637 and 720 nm. (f) PL spectra of Qx-12F film, Y6 film and Qx-12F:Y6 blended film excited at 640 and 720 nm.

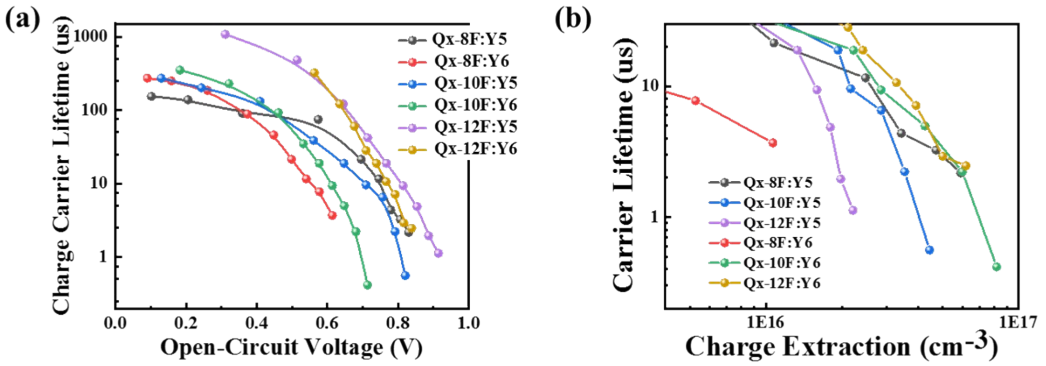


Figure S6. (a) Charge carrier lifetime τdetermined from the TPV measured under open-circuit condition and plotted as a function of open-circuit voltage, and (b) Charge carrier lifetimeτvs. charge density; carrier densities determined from charge-extraction (CE) measurements.

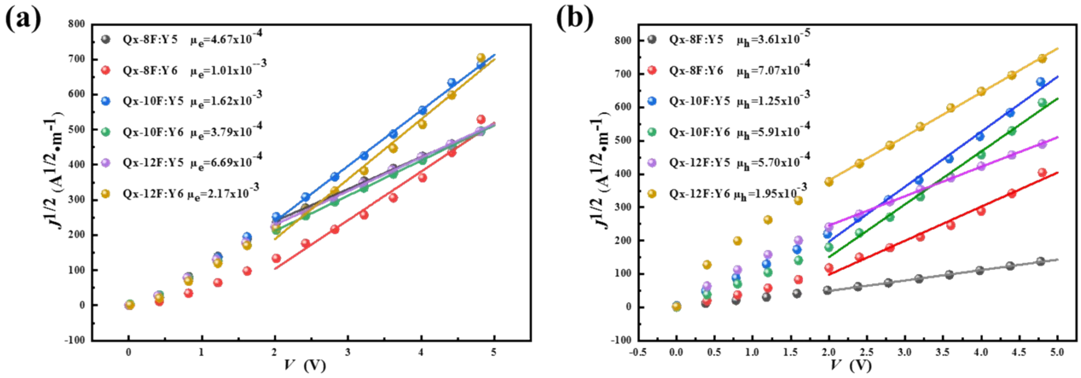


Figure S7. The electron (a) and hole mobilities (b) of blended films with donor and acceptor Y5/Y6.

Table S1. Hole and electron mobilities of devices

Devices	μ_e[cm^2 V^{-1}s^{-1}]	μ_h[cm^2 V^{-1}s^{-1}]	μ_e/μ_h
Qx-8F:Y5	4.67×10^{-4}	3.61×10^{-5}	12.93
Qx-10F:Y5	1.01×10^{-3}	7.07×10^{-4}	1.43
Qx-12F:Y5	1.62×10^{-3}	1.25×10^{-3}	1.30
Qx-8F:Y6	3.79×10^{-4}	5.91×10^{-4}	0.64
Qx-10F:Y6	6.69×10^{-4}	5.70×10^{-4}	1.18
Qx-12F:Y6	2.17×10^{-3}	1.95×10^{-3}	1.12

Table S2. Photovoltaic performance parameters of the OSCs based on polymers:Y5

Devices	V_{oc} [V]	J_{sc} [mA cm^{-2}]	J_{calc} [b] [mA cm^{-2}]	FF [%]	PCE$_{max}$ [%]
Qx-8F:Y5[a]	0.81	20.53	20.13	61.35	10.23
Qx-10F:Y5[a]	0.87	18.77	18.40	64.27	10.54
Qx-12F:Y5[a]	0.92	9.76	8.31	59.92	5.39

[a] In CF, with CN (0.5% volume) (1 : 1, w/w). [b] Calculated by EQE measurement.

Table S3. Photovoltaic parameter of Qx-12F:Acceptor=1:1.2 based devices with 90°C,10min

Acceptor	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
Y6	0.84	24.82	69.05	14.38
N3	0.81	23.07	72.85	13.58
ITIC	0.90	17.97	65.38	10.52
IT-4F	0.83	18.03	74.21	11.09

Table S4 Photovoltaic parameter of Qx-12F:Y6 with different D:A

Qx-12F:Y6	Annealing	Additive (%)	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
1:1.5	90°C,10min	0.5CN	0.84	23.06	66.68	12.23
1:1.2	90°C,10min	0.5CN	0.84	20.72	71.83	12.43
1:1.1	90°C,10min	0.5CN	0.85	22.09	70.41	13.84
1:1	90°C,10min	0.5CN	0.84	24.24	71.43	14.55
1:0.9	90°C,10min	0.5CN	0.85	22.89	71.42	14.29

Table S5. Photovoltaic parameter of Qx-12F:Y6

Qx-12F:Y6	Annealing	Additive (%)	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
1:1	90°C,10min	0.5CN	0.84	22.99	73.85	14.28
1:1	90°C,10min	/	0.85	23.24	69.33	13.63
1:1	/	0.5CN	0.86	21.57	73.51	13.66
1:1	/	/	0.86	22.18	68.87	13.11

Table S6. Photovoltaic parameter of Qx-12F:Y6=1:1 based devices with 90°C,10min

Additive (%)	Voc [V]	Jsc [mA cm^{-2}]	FF [%]	PCE [%]
0.2CN	0.84	23.31	67.40	14.16
0.3CN	0.84	22.55	72.10	14.44
0.4CN	0.85	22.03	71.82	14.31
0.5CN	0.85	23.78	72.41	14.63
0.6CN	0.84	24.24	69.05	14.38
0.9CN	0.85	19.09	66.66	11.44

Table S7. Photovoltaic parameter of Qx-12F:Y6=1:1 based devices with 0.5CN

Annealing	Voc [V]	Jsc [mA cm^{-2}]	FF [%]	PCE [%]
90°C,10min	0.847	21.82	68.37	14.07
100°C,5min	0.845	21.71	68.78	14.14
100°C,8min	0.845	22.99	67.53	13.55
100°C,10min	0.847	24.55	72.88	15.21
110°C,10min	0.838	22.33	67.40	13.52
150°C,5min	0.819	22.35	65.67	12.96

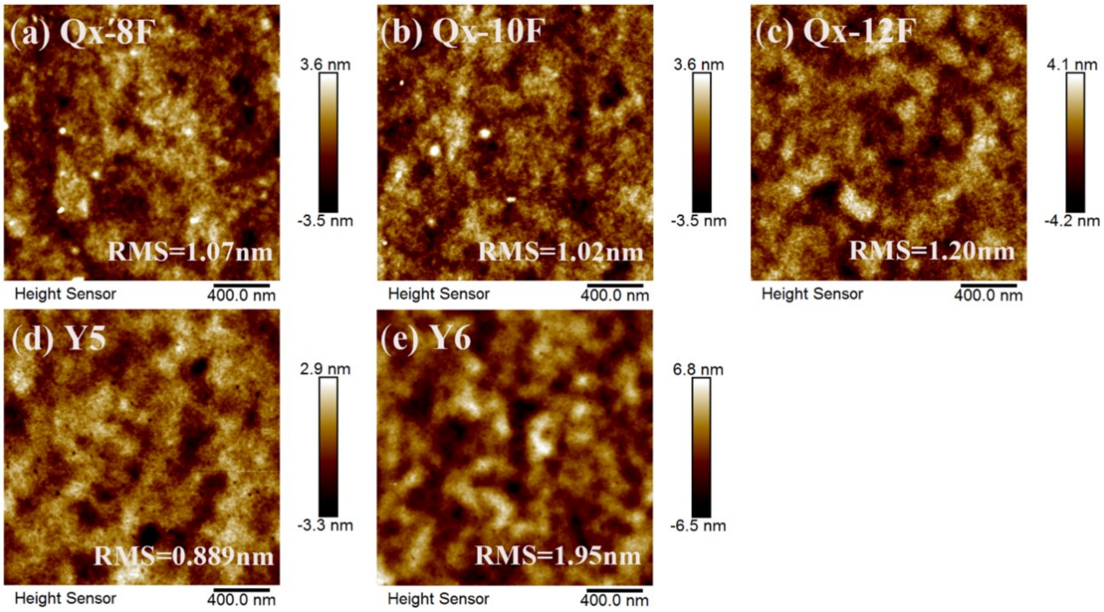


Figure S8. AFM height (a, b, c, d, e) images of neat Qx-8F, Qx-10F, Qx-12F, Y5 and Y6 films.

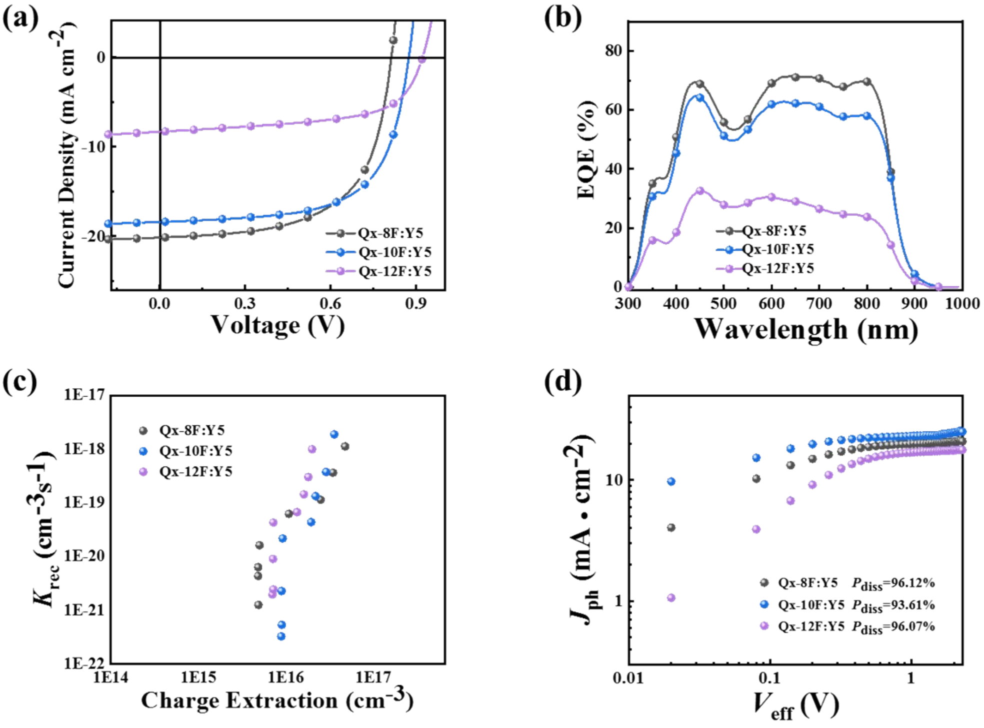


Figure S9. (a) $J-V$ curves. (b) The corresponding EQE spectra of the OSCs.(c) Nongeminate recombination rate constant k_{rec}, extracted from τ and n, as a function of n.(d) The plots of photocurrent (J_{ph}) vs. effective internal field (V_{eff}).

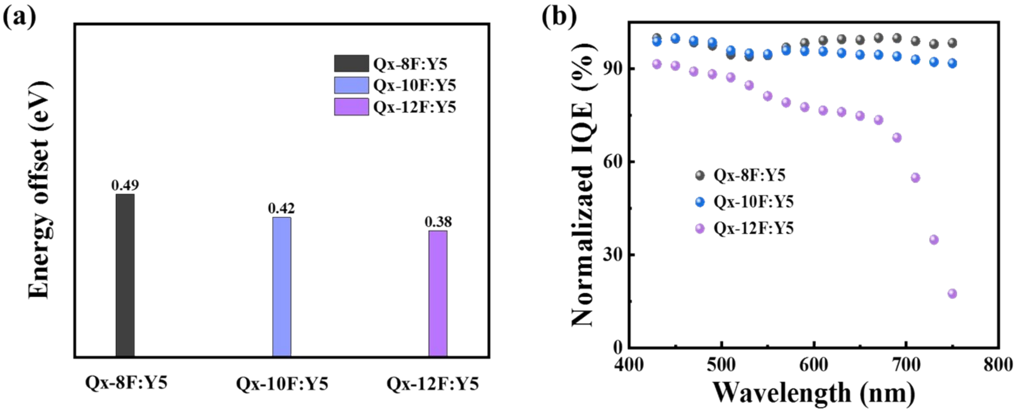
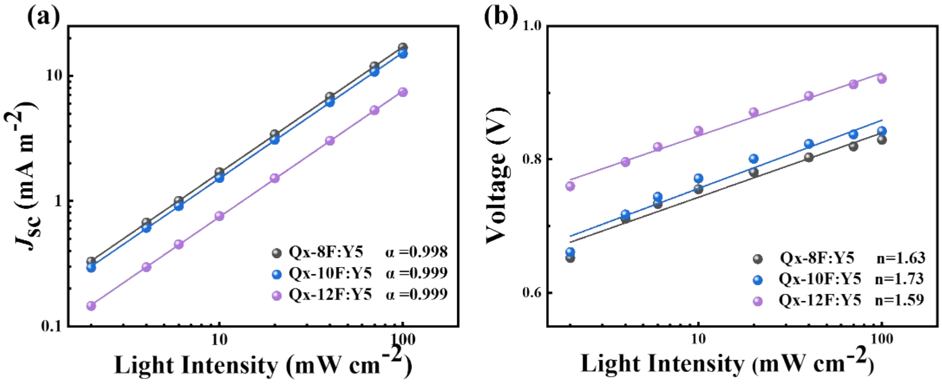


Figure S10. (a) HOMO offset in there devices. (b) The IQE of the HOMO offset driven PHT process, normalized to that of PET.



FigureS11. (a) J_{SC} and (b) V_{OC} of OSCs based on acceptor Y5 on light intensity.

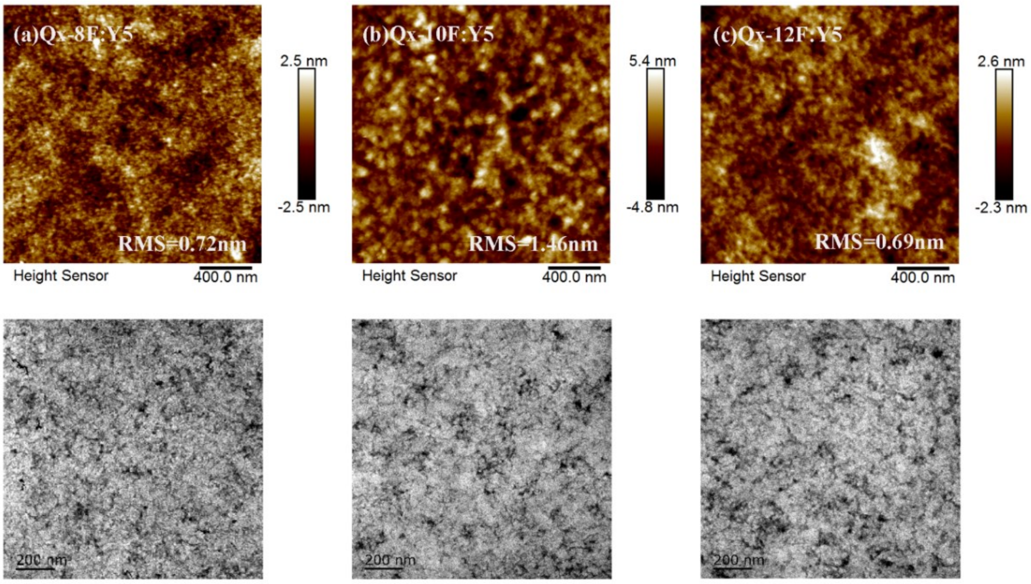


Figure S12. AFM heightimages and TEM images of Qx-8F:Y5, Qx-10F:Y5, and Qx-12F:Y5 blends.

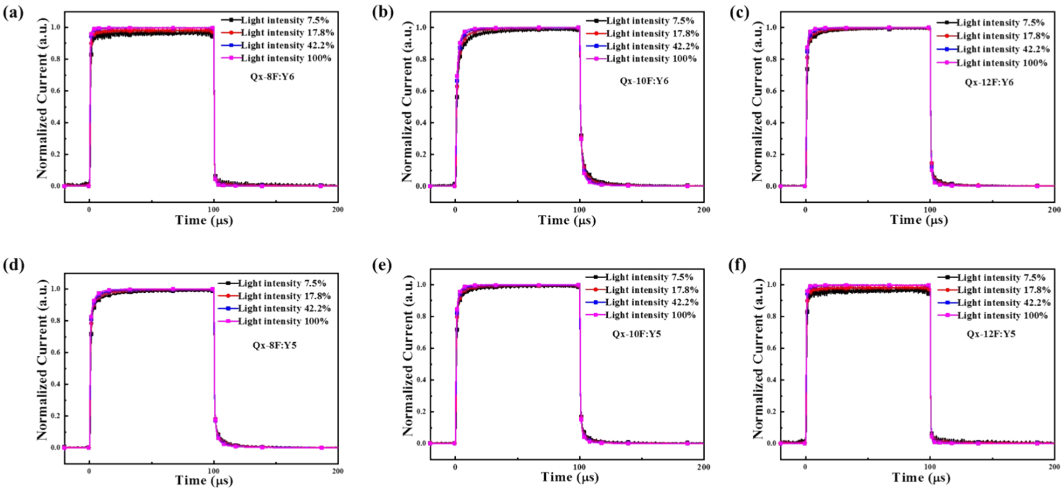


Figure S13. Short-circuit charge extraction transients normalized by the total charge density extracted for different light intensities in the range 0.07–1.0 Suns. As the light intensity is increased, the extraction time decreases.

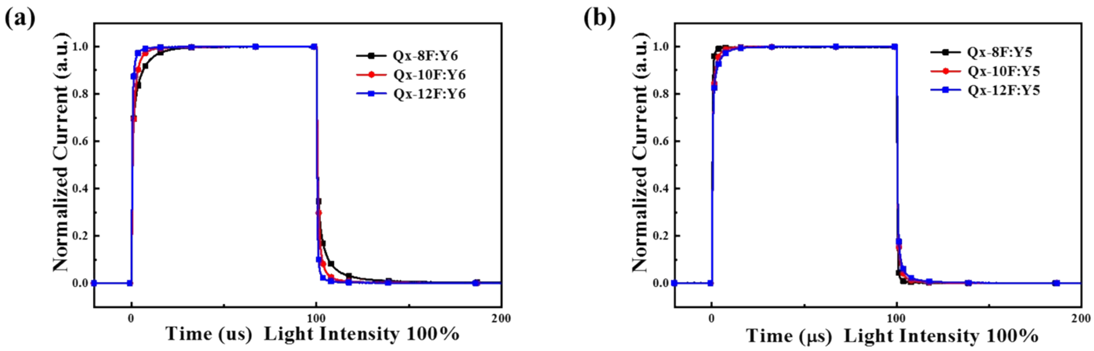


Figure S14. (a) The normalized transient photocurrent responses of polymer:Y6 (light intensity 100%), (b) the normalized transient photocurrent responses of polymer:Y5 (light intensity 100%), the rise/fall time of the polymer:Y5 devices are both ~ 2 μ s.

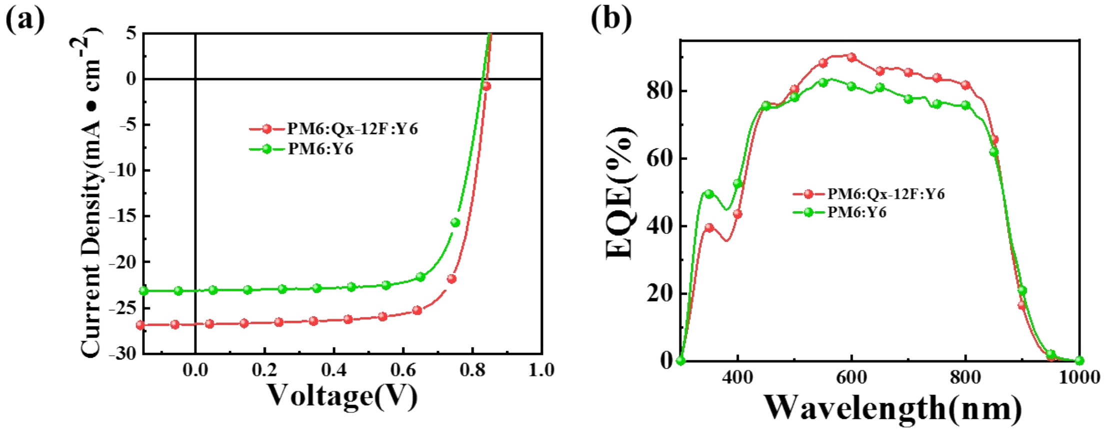


Figure S15. (a) $J-V$ curves under the illumination of AM 1.5 G, 100 mW cm^{-2}. (b) The corresponding EQE spectra of the OSCs.

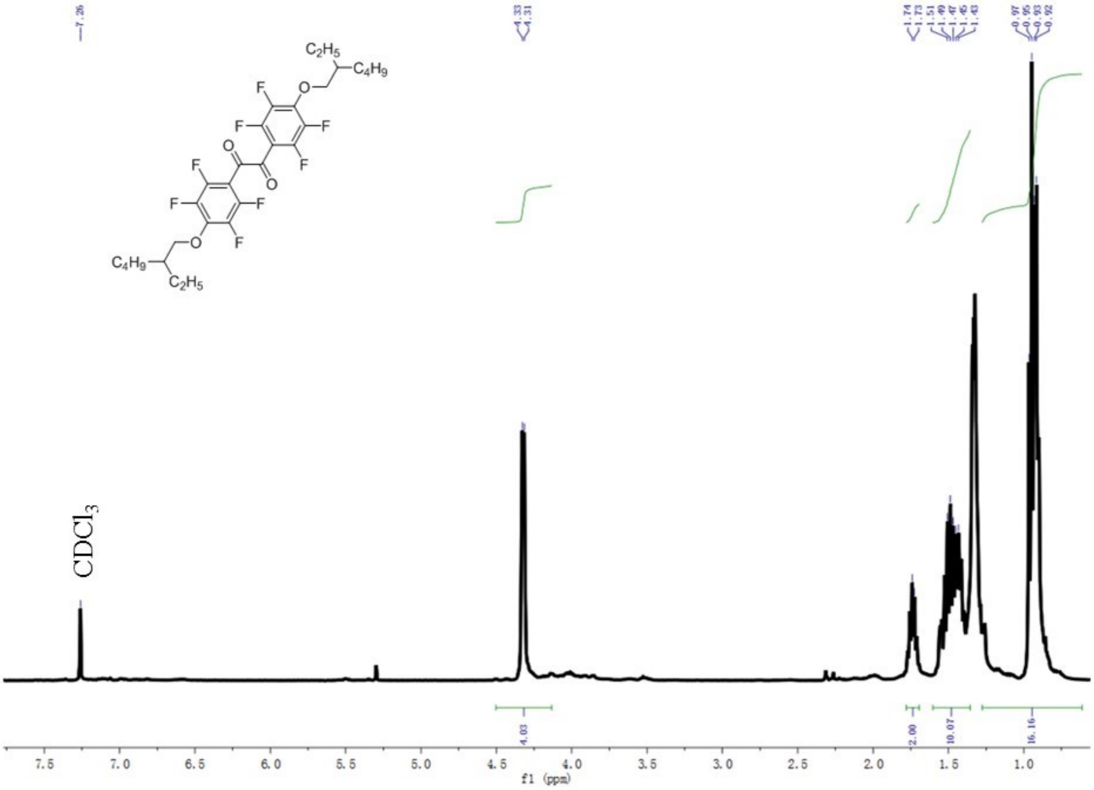


Figure S16.^{1}H NMR spectrum of 1,2-bis(4-((2-ethylhexyl)oxy)-2,3,5,6-tetrafluorophenyl)ethane-1,2-dione(**2**)

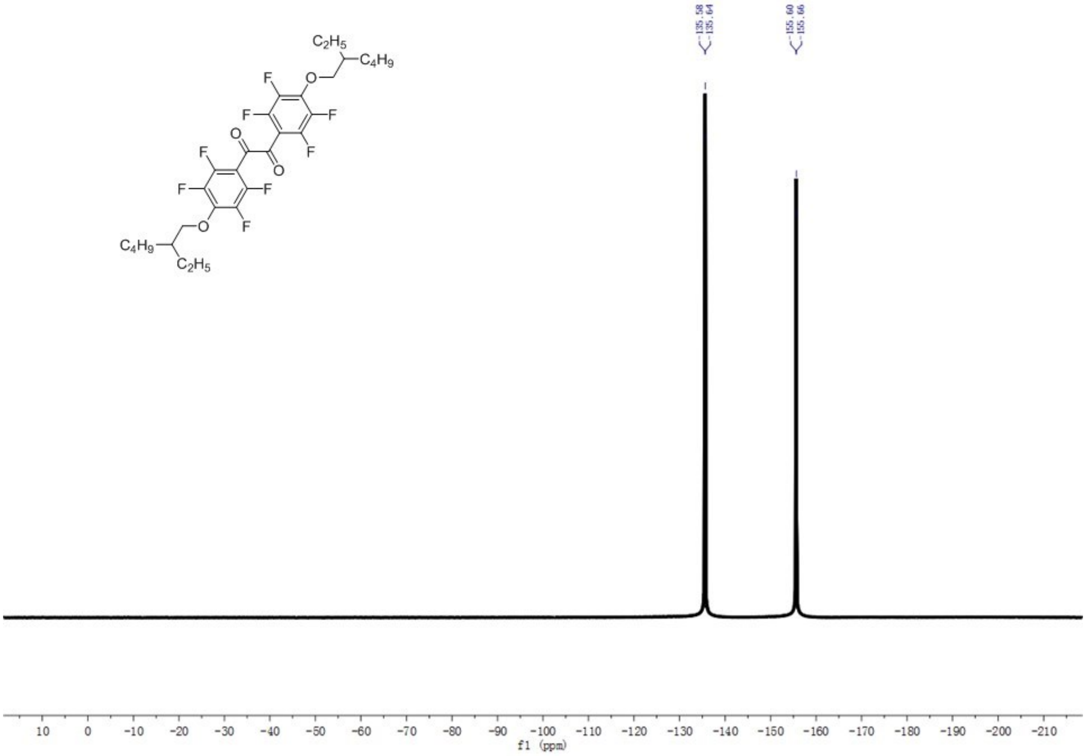


Figure S17.^{19}F NMR spectrum of 1,2-bis(4-((2-ethylhexyl)oxy)-2,3,5,6-tetrafluorophenyl)ethane-1,2-dione(**2**)

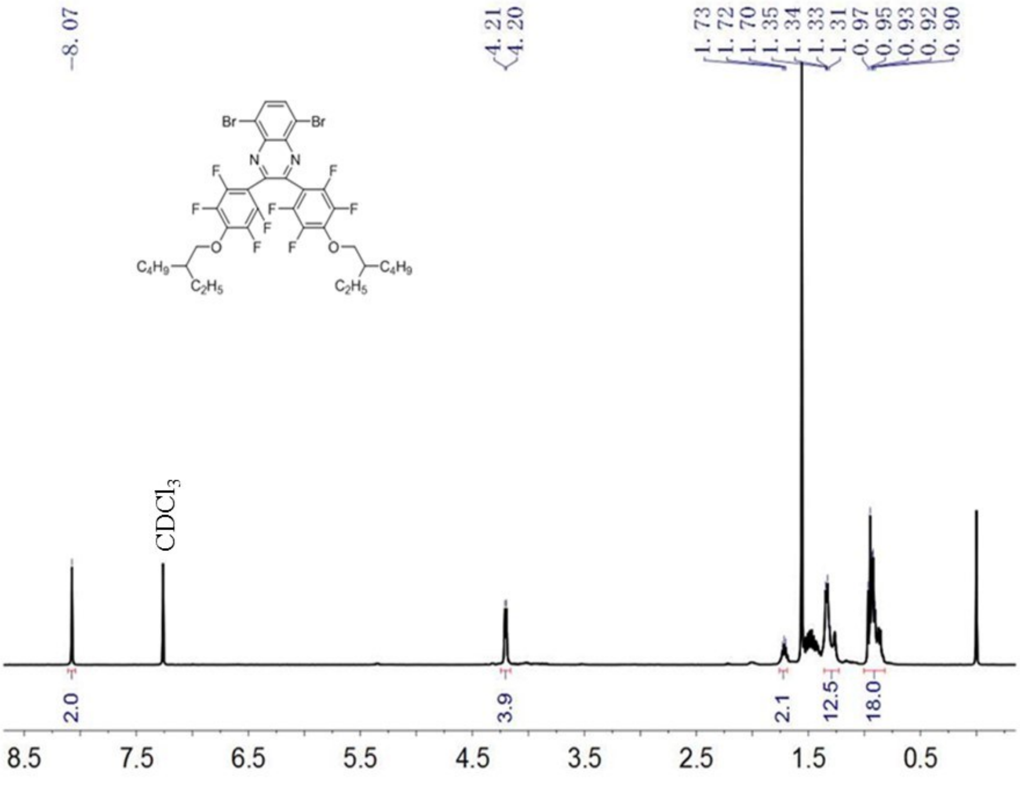


Figure S18.^{1}H NMR spectrum of 5,8-dibromo-2,3-bis(4-((2-ethylhexyl)oxy)-2,3,5,6-tetrafluorophenyl)-quinoxaline(**4**)

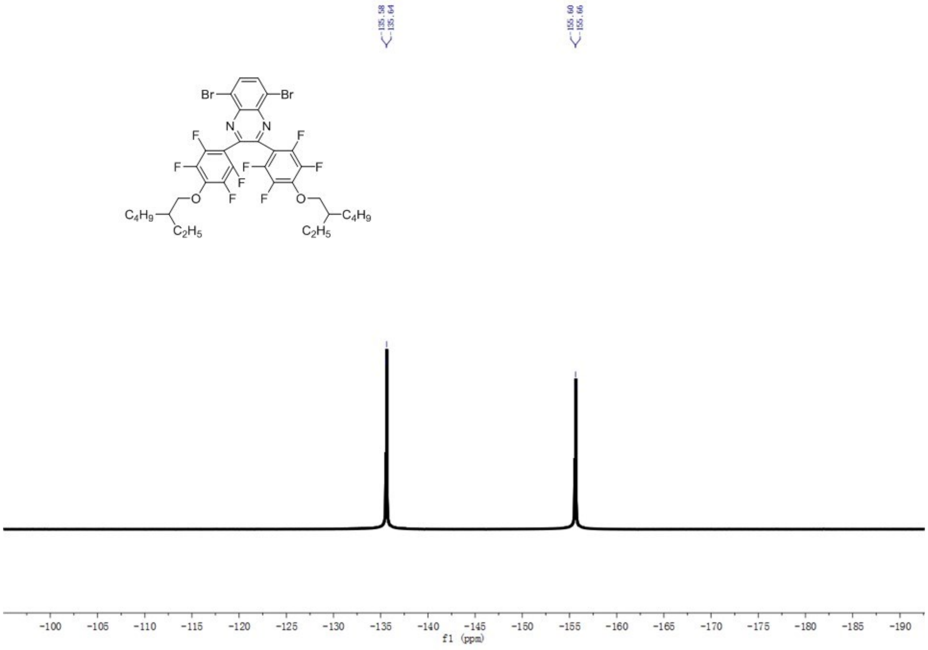


Figure S19. ^{19}F NMR spectrum of 5,8-dibromo-2,3-bis(4-((2-ethylhexyl)oxy)-2,3,5,6-tetrafluorophenyl)-quinoxaline(**4**)

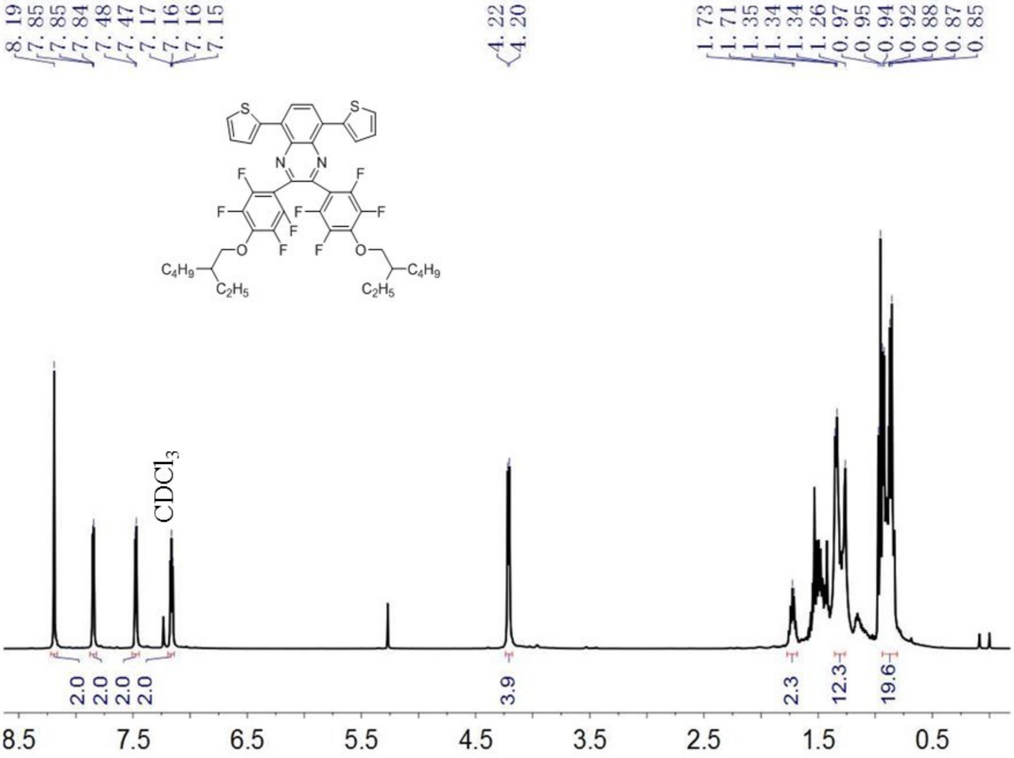


Figure S20. ^{1}H NMR spectrum of 2,3-bis (4-((2-ethylhexyl)oxy)-2,3,5,6-tetrafluorophenyl)-5,8-di(thiophen-2-yl)quinoxaline(**5**)

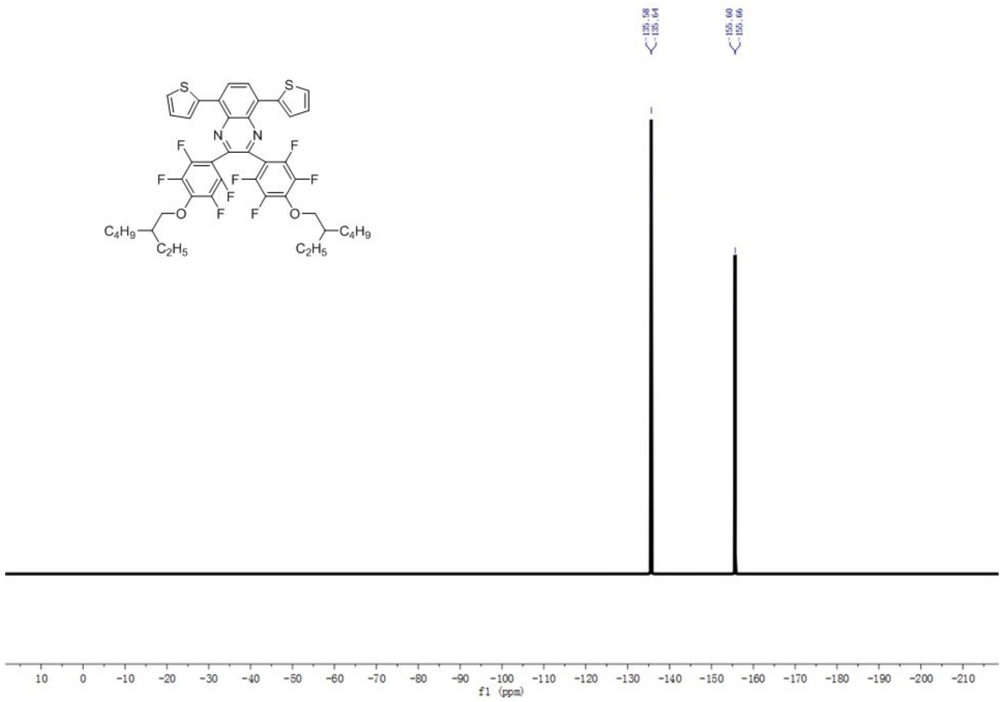
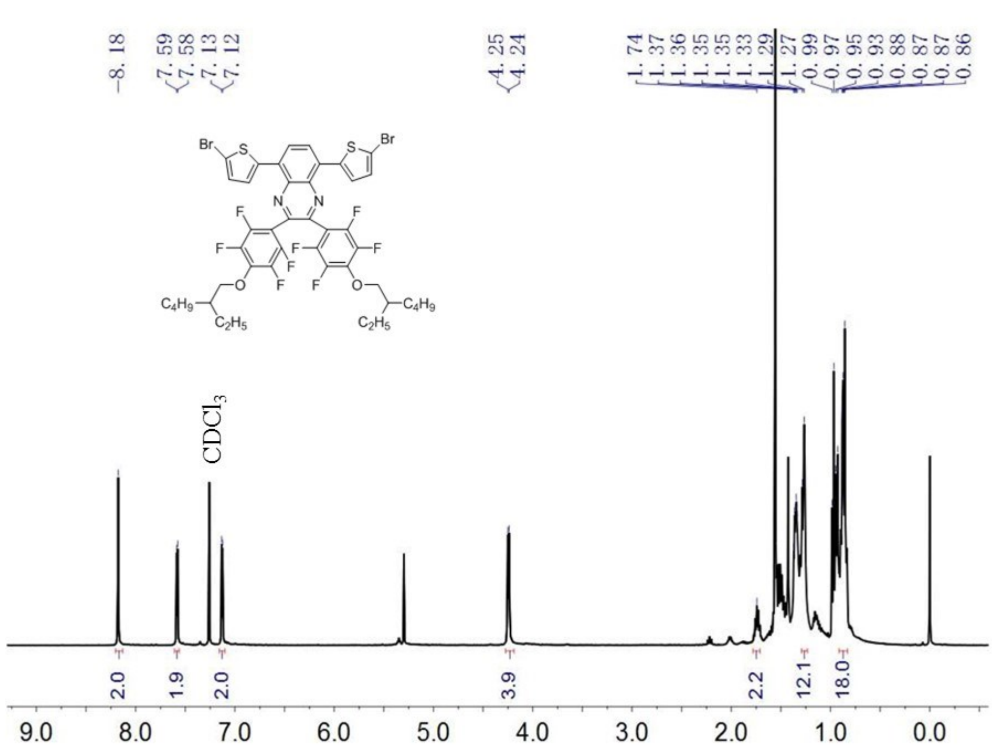


Figure S21.^{19}F NMR spectrum of 2,3-bis (4-((2-ethylhexyl)oxy)-2,3,5,6-tetrafluorophenyl)-5,8-di(thiophen-2-yl)quinoxaline(**5**) **Figure S22.**^{1}H NMR spectrum



of 5,8-bis(5-bromothiophen-2-yl) -2,3-bis(4-((2-ethylhexyl)oxy)-2,3,5,6-tetrafluorophenyl)-quinoxaline(**M1**)

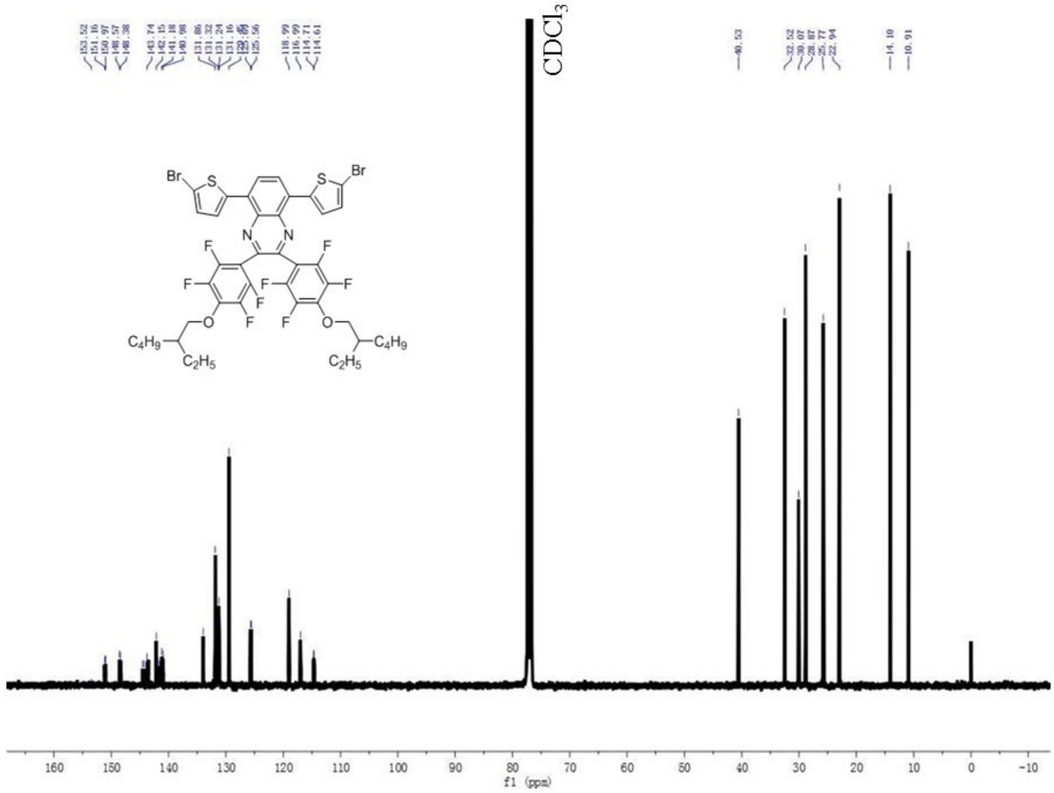


Figure S23.^{13}C NMR spectrum of 5,8-bis(5-bromothiophen-2-yl) -2,3-bis(4-((2-ethylhexyl)oxy)-2,3,5,6-tetrafluorophenyl)-quinoxaline(**M1**)

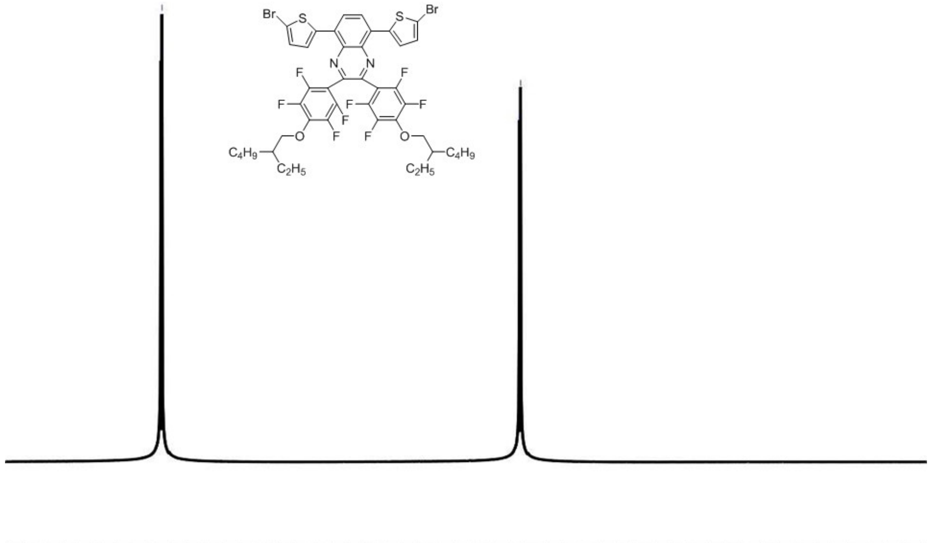


Figure S24.^{19}F NMR spectrum of 5,8-bis(5-bromothiophen-2-yl) -2,3-bis(4-((2-ethylhexyl)oxy)-2,3,5,6-tetrafluorophenyl)-quinoxaline(**M1**)

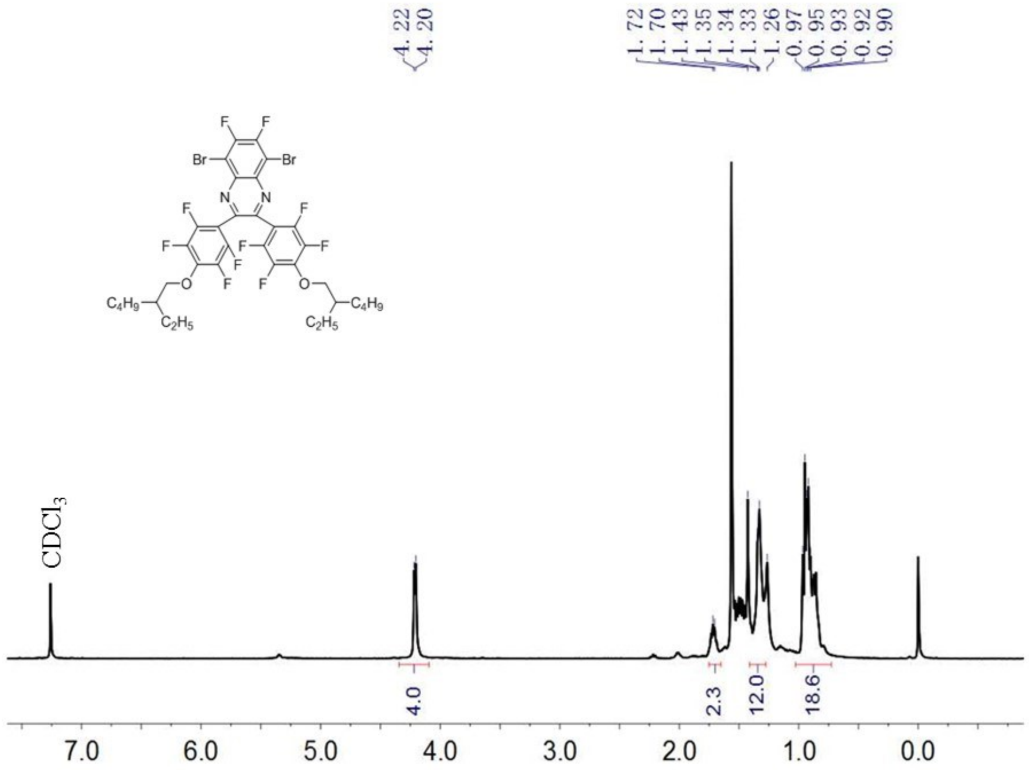


Figure S25. ^{1}H NMR spectrum of 5,8-dibromo-2,3-bis(4-((2-ethylhexyl)oxy) - 2,3,5,6-tetrafluorophenyl)-6,7-difluoroquinoxaline(**7**)

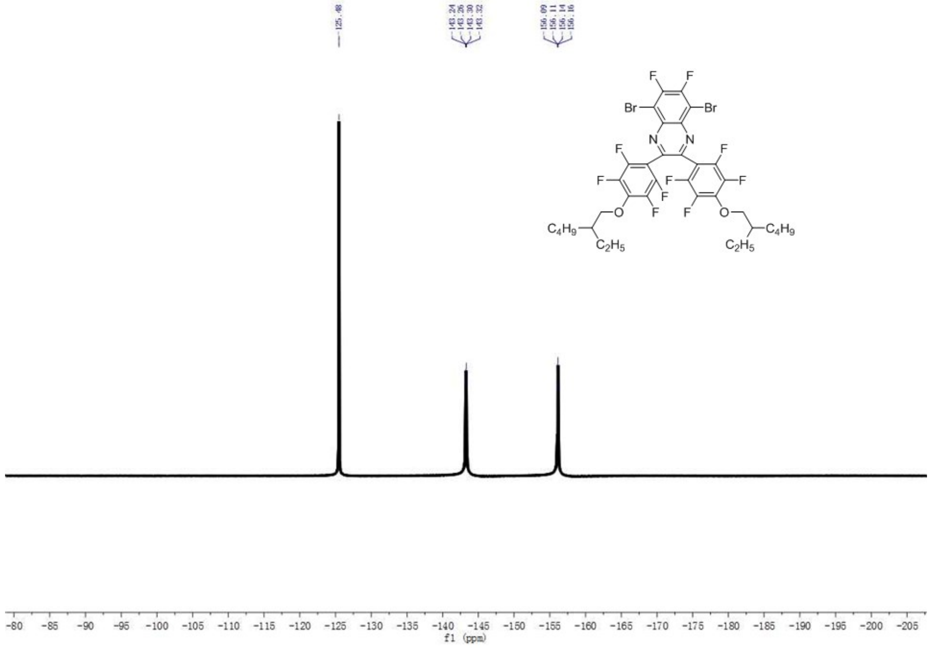


Figure S26. ^{19}F NMR spectrum of 5,8-dibromo-2,3-bis(4-((2-ethylhexyl)oxy) - 2,3,5,6-tetrafluorophenyl)-6,7-difluoroquinoxaline(**7**)

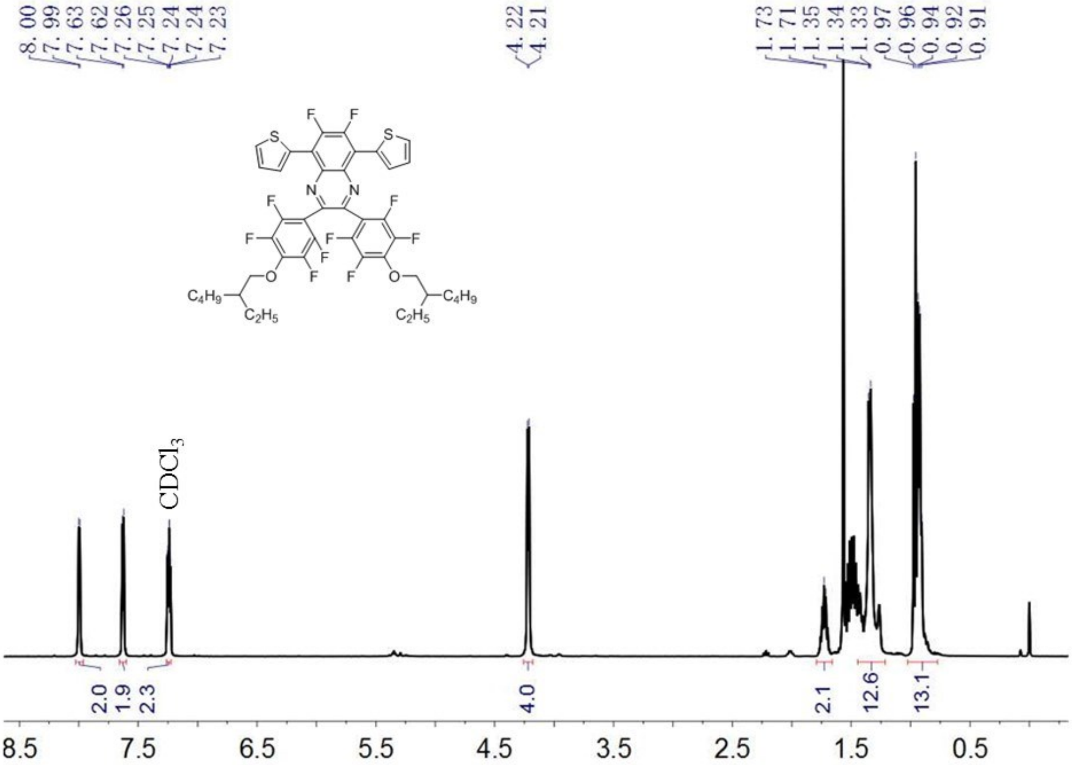


Figure S27.^{1}H NMR spectrum of 2,3-bis(4-((2-ethylhexyl)oxy)-2,3,5,6-tetrafluorophenyl)-6,7-difluoro-5,8-di(thiophen-2-yl)quinoxaline(**8**)

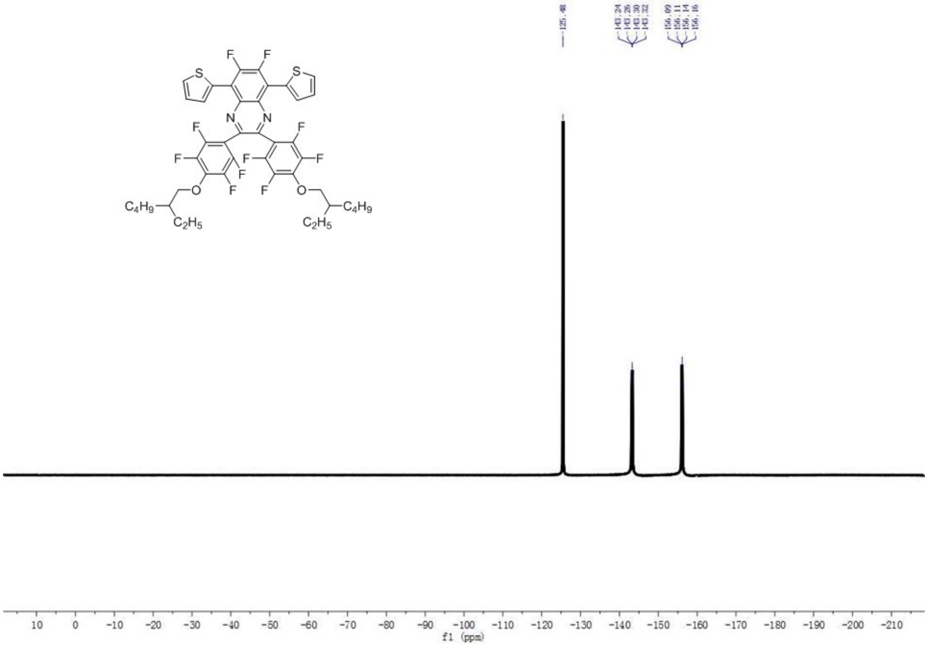


Figure S28.^{19}F NMR spectrum of 2,3-bis(4-((2-ethylhexyl)oxy)-2,3,5,6-tetrafluorophenyl)-6,7-difluoro-5,8-di(thiophen-2-yl)quinoxaline(**8**)

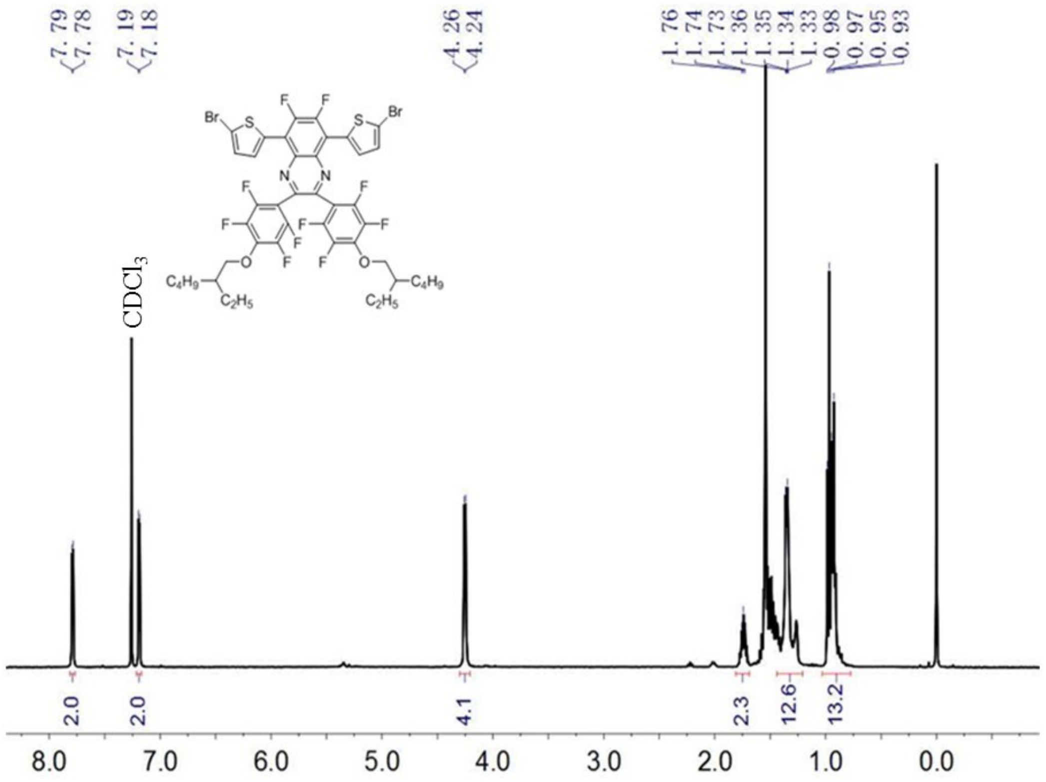


Figure S29. ^{1}H NMR spectrum of 5,8-bis(5-bromothiophen-2-yl)-2,3-bis(4- ((2-ethylhexyl)oxy)-2,3,5,6-tetrafluorophenyl)-6,7-Difluoroquinoxaline(**M2**)

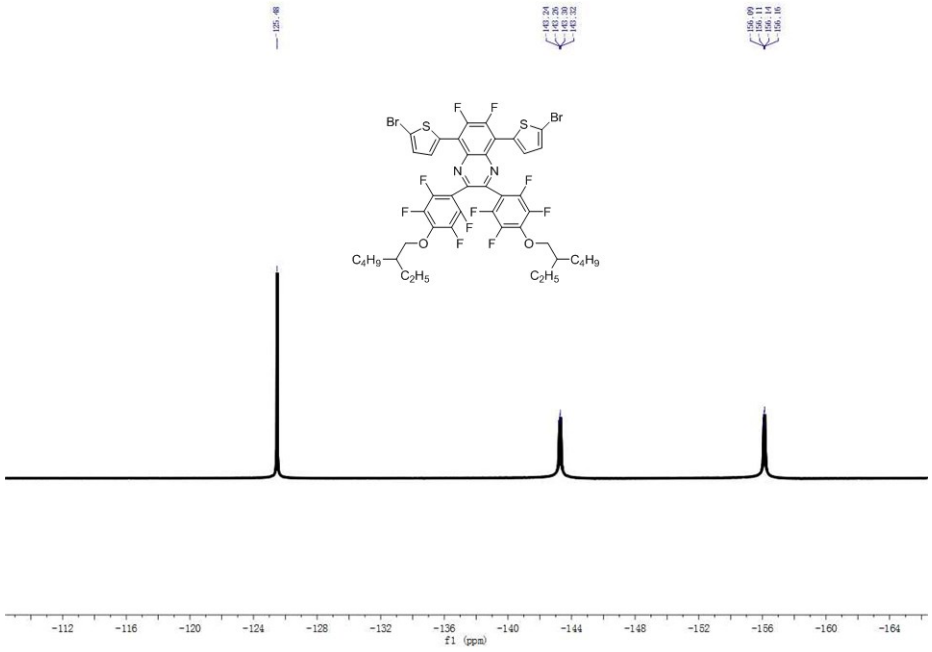


Figure S30. ^{19}F NMR spectrum of 5,8-bis(5-bromothiophen-2-yl)-2,3-bis(4- ((2-ethylhexyl)oxy)-2,3,5,6-tetrafluorophenyl)-6,7-Difluoroquinoxaline(**M2**)

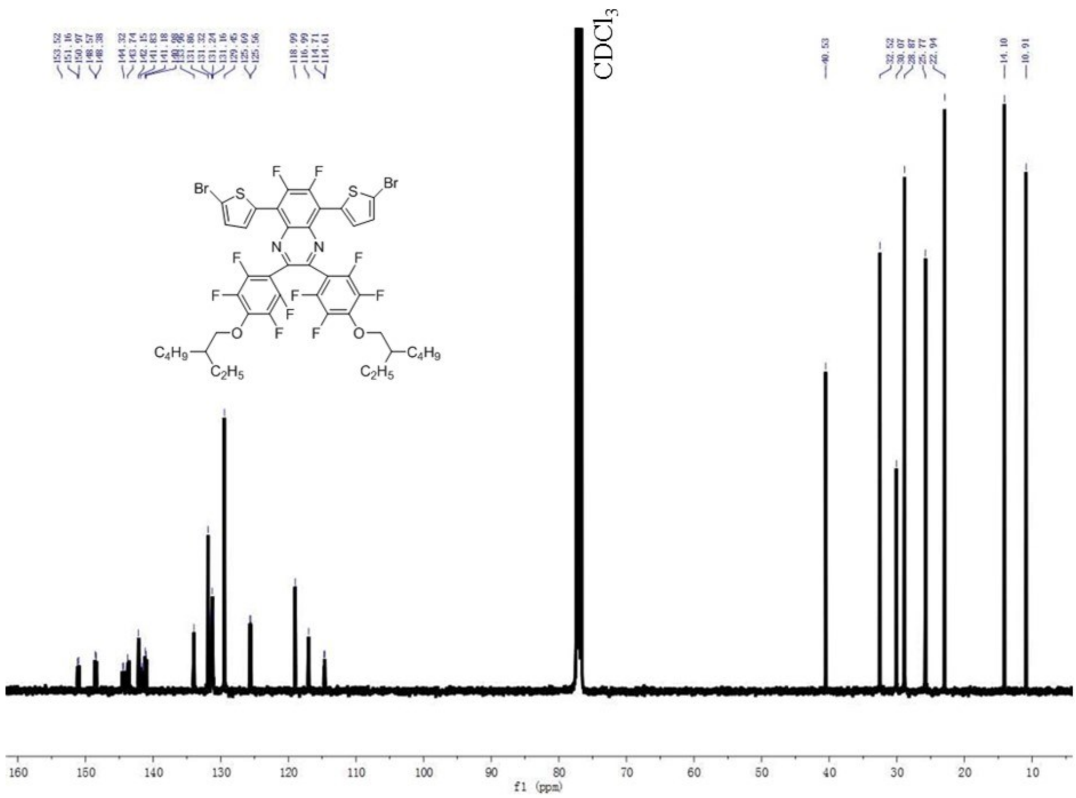


Figure S31. ^{13}C NMR spectrum of 5,8-bis(5-bromothiophen-2-yl)-2,3-bis(4- ((2-ethylhexyl)oxy)-2,3,5,6-tetrafluorophenyl)-6,7-Difluoroquinoxaline(**M2**)

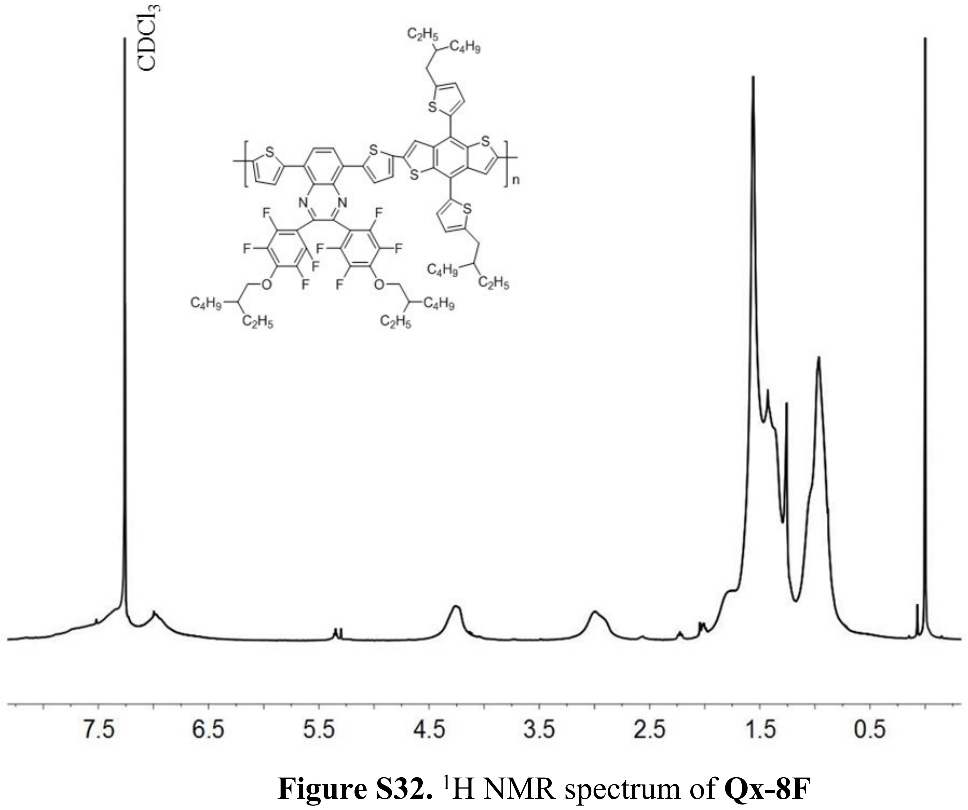


Figure S32. ^{1}H NMR spectrum of **Qx-8F**

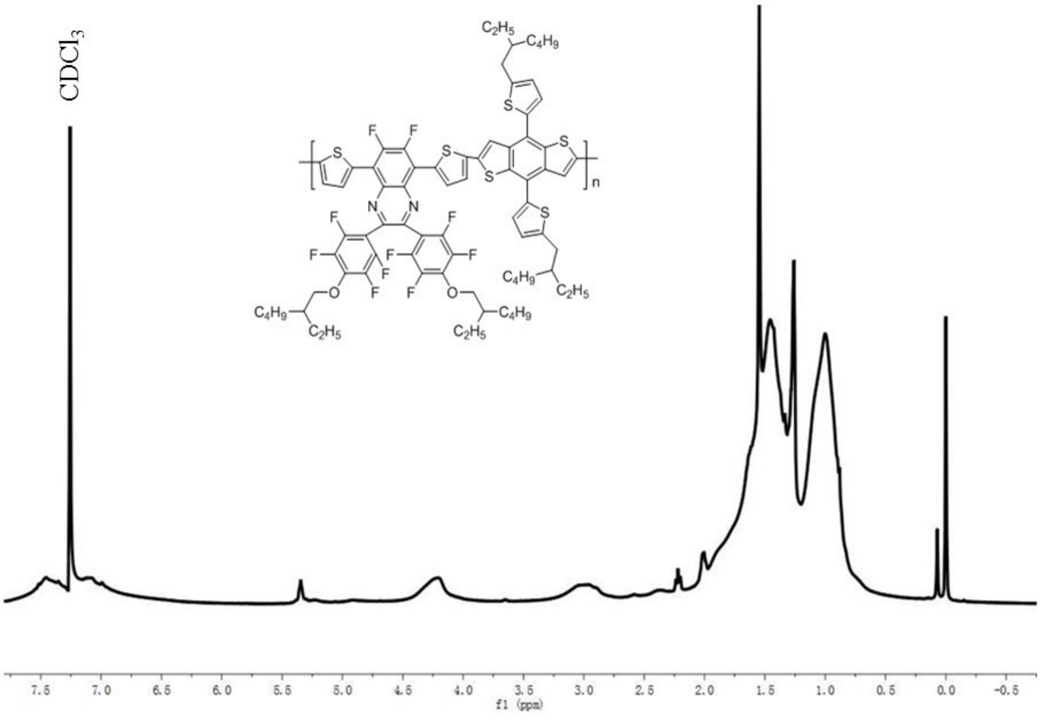


Figure S33. ^{1}H NMR spectrum of **Qx-10F**

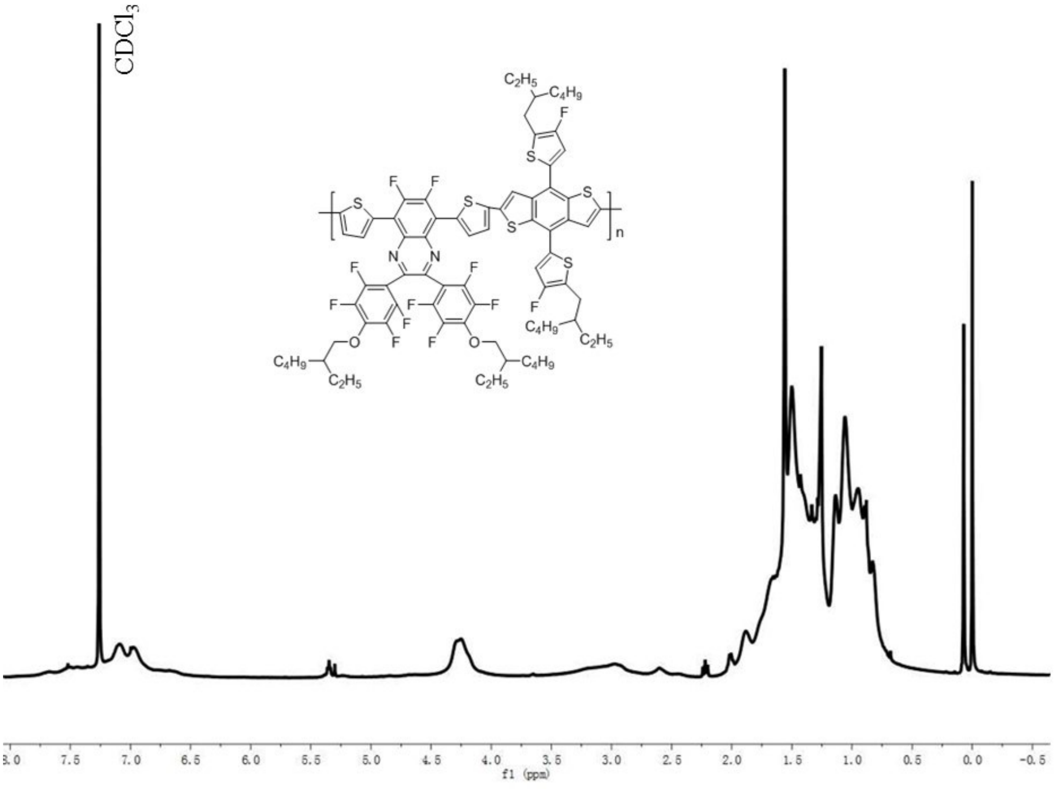


Figure S34. ^{1}H NMR spectrum of **Qx-12F**

MW Averages

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Mn: 25694
Mv: 56923
Mw: 63702
Mz: 122137
Mz+1: 195616
PD: 2.4793

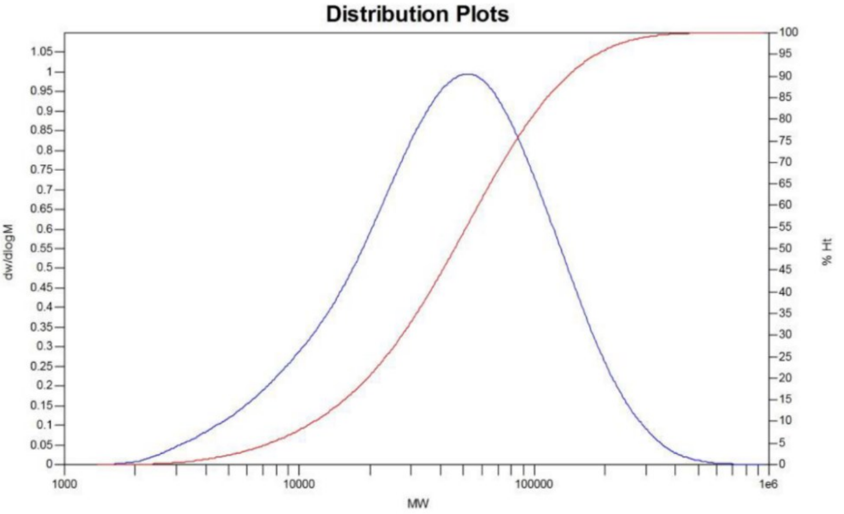


Figure S35. GPC data of polymer **Qx-8F**

MW Averages

Mp: 61016
Mn: 30252
Mv: 64517
Mw: 71504
Mz: 129045
Mz+1: 196657
PD: 2.3636

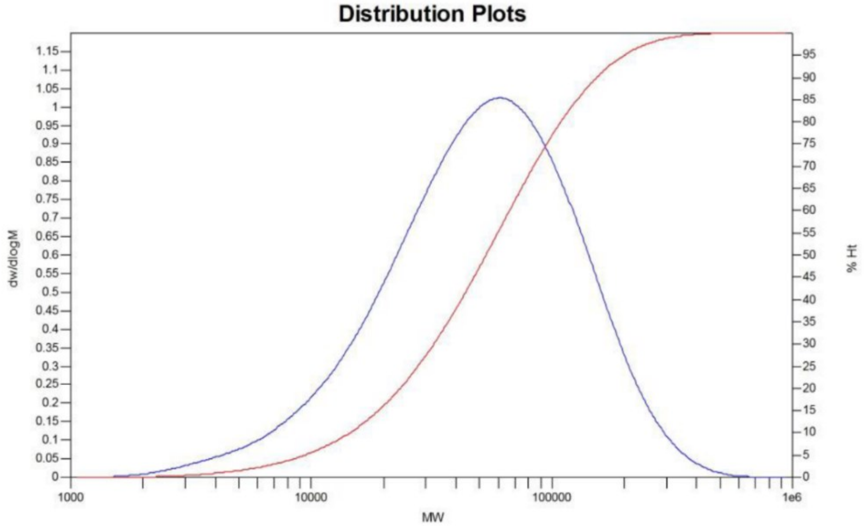
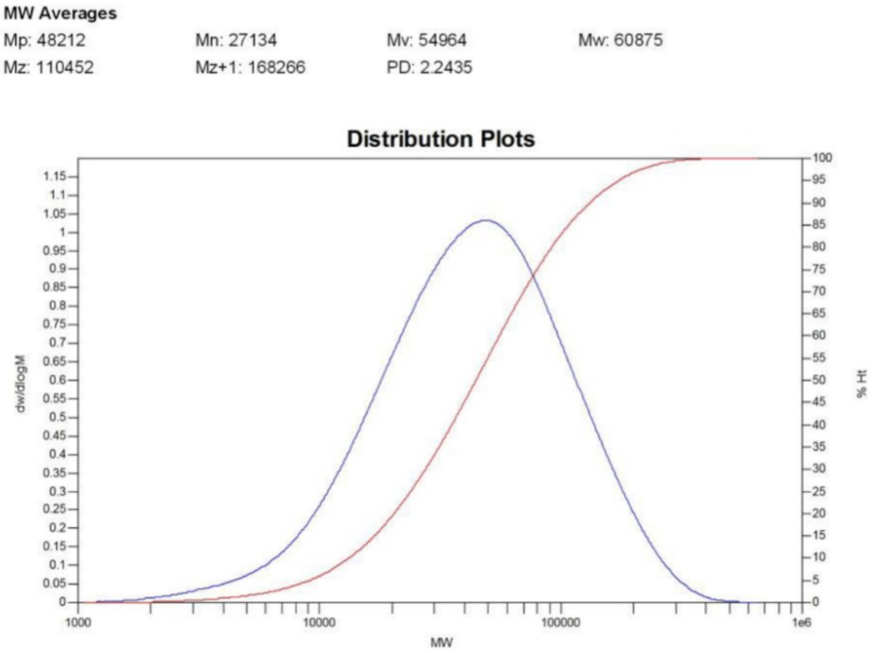


Figure S36. GPC data of polymer **Qx-10F**



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MW Averages
Mp: 48212          Mn: 27134          Mv: 54964          Mw: 60875
Mz: 110452         Mz+1: 168266       PD: 2.2435
```

Figure S37. GPC data of polymer **Qx-12F**

Supplementary references

1. J. Yuan, Y. Zhang, L. Zhou, G. Zhang, H.-L. Yip, T.-K. Lau, X. Lu, C. Zhu, H. Peng, P. A. Johnson, M. Leclerc, Y. Cao, J. Ulanski, Y. Li and Y. Zou, *Joule*, 2019, **3**, 1140-1151.
2. S. Xu, L. Feng, J. Yuan, Z. G. Zhang, Y. Li, H. Peng and Y. Zou, *ACS Appl Mater Interfaces*, 2017, **9**, 18816-18825.
3. S. Xu, X. Wang, L. Feng, Z. He, H. Peng, V. Cimrová, J. Yuan, Z.-G. Zhang, Y. Li and Y. Zou, *Journal of Materials Chemistry A*, 2018, **6**, 3074-3083.