

# Supporting Information

## Non-fused ring electron acceptors employing diphenylamine substituted 2,2'-bithiazole cores for organic solar cell applications

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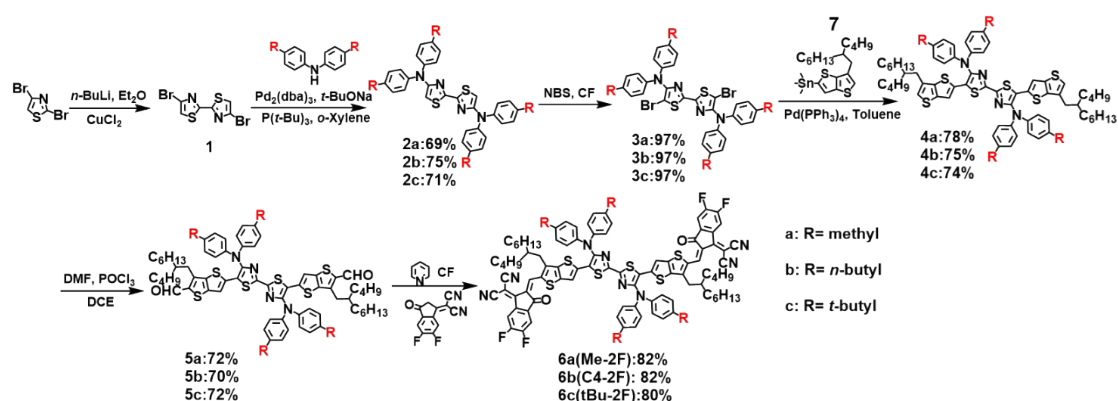
## 1. General methods

UV-Vis-NIR absorption spectra were recorded on a Perkin Elmer Lambda 950 spectrophotometer. Nuclear magnetic resonance (NMR) spectra were obtained on a Bruker 400 MHz spectrometer. High Resolution Mass Spectroscopy (HR-MS) measurements were performed on an Agilent1290/Bruker maXis impact. Geometry and orbital calculations of polymers were carried out based on the density functional theory (DFT) CAM-B3LYP together with 6-31G(d,p) basis set by using the Gaussian 16 package on Swordfish-Cluster at the Shanghai Supercomputer Center. Thermogravimetric analysis (TGA) were performed on a TA instrument (TA Discovery TGA550) with about 5 mg acceptor samples at a rate of 10 °C / min. Differential scanning calorimetry (DSC) measurements were carried out on a Discovery DSC250 instrument with about 5 mg acceptor samples at a rate of 5 °C / min in the temperature range of 30 to 330 °C. The  $J$ - $V$  curves of the OSC devices were measured under a solar simulator (Newport Oriel VeraSol<sup>2</sup>™ Class AAA) with light intensity set at 100 mW·cm<sup>-2</sup>. The intensity and spectrum of the lamp was calibrated by a standard silicon solar cell and a set of optical calibration filters. EQE measurements were carried out by using a halogen lamp (150W, LSP-T75, Newport), a monochromator (CS260-RG-3-MC-A, Newport), an optical chopper (Newport), a pre-current amplifier (Model SR570, Stanford) and a phase-locked amplifier (SR830 DSP Lock-In Amplifier, Stanford). EL spectra were recorded by a fluorescence spectrometer (KYMERA-328I-B2, Andor technology LTD) with cooled silicon array (DU970P-BVF) and InGaAs detector (DU491A-1.7), and the injection current was 1 mA. PL measurements were conducted using the same setup, and a laser was used to excite the samples. Highly sensitive EQE (sEQE) measurements were conducted by using a measurement system containing a halogen lamp light source (LSH-75, Newport), a monochromator (CS260-RG-3-MC-A, Newport), a current amplifier, a chopper and a phase-locked amplifier (SR830, Newport). The overtone wavelengths from the monochromator were removed by a set of long-pass optical filters (Newport). The EQE<sub>EL</sub> measurements were done in a dark measurement box. A Keithley 2400 Source Meter was used to inject electric current into the solar cell. Light emitted by the solar cell was detected by a Si photodiode collected to a Keithley 6482 PicoAmmeter. GIWAXS samples were prepared on Si substrates using identical blend solutions like those used in devices. The 10 keV X-ray beam was incident at a grazing angle of 0.11°-0.15°, which maximized the scattering

intensity from the samples. In-plane and out-of-plane sector averages were calculated using the Nika software package. The uncertainty for the peak fitting of the GIWAXS data is 0.3 Å. Tapping-mode atomic force microscopy (AFM) images were recorded by a Bruker Dimension Icon.

## 2. Materials and Synthesis

Polymer donor PM6 (Poly[(2,6-(4,8-bis(5-(2-ethylhexyl-3-fluoro)thiophen-2-yl)-benzo[1,2-b:4,5-b']dithiophene))-alt-(5,5-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-c']dithiophene-4,8-dione)]) and the interface material PFN-Br were purchased from Solarmer Material (Beijing) Inc. PEDOT:PSS (CLEVIOS P VP AL 4083) was purchased from Heraeus. Compound **1** was synthesized following the procedure from the literature.<sup>1</sup> Except otherwise stated, all the other reagents and chemicals were purchased from commercial suppliers and were used directly without further purification.



**Scheme S1.** Synthetic steps for NFREAs

### Synthesis of compound **2**

**2a**: Compound **1** (432 mg, 1.33 mmol), di-*p*-tolylamine (653.5 mg, 3.31 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (61 mg · 0.067 mmol), tri-*tert*-butylphosphine (10% in Toluene, 0.27 mL, 0.27 mmol), NaOt-Bu (509 mg, 5.3 mmol), and dry *o*-xylene (20 mL) were added to a flame-dried schlenk flask at nitrogen atmosphere. The solution was stirred at 140 °C for 14h. After cooling, the reaction mixture was filtered by a short silica gel column and the filtrate was evaporated to dryness under reduced pressure. Purification by column chromatography (eluent: dichloromethane/petroleum ether 1:2 v/v) gave **2a** as a yellow solid (513 mg, 0.92 mmol, 69% yield). <sup>1</sup>H NMR (chloroform-*d*, 298 K, 400 MHz, δ/ppm): 7.09(d, J = 8 Hz, 8H), 7.04(d, J = 8 Hz, 8H), 6.27(s, 2H), 2.32(s, 12H).

**2b**: Bis(4-butylphenyl)amine was synthesized according to a reported literature. 2b was synthesized by the same procedure of 2a and obtained as an orange thick oil. <sup>1</sup>H NMR (chloroform-d, 298 K, 400 MHz, δ/ppm): 7.08 (q, J = 8 Hz, 16H), 6.29(s, 2H), 2.59(t, J = 8Hz, 8H), 1.65-1.57(m, 8H), 1.38(q, J = 8 Hz, 8H), 0.95(t, J = 8Hz, 12H).

**2c** was synthesized by the same procedure of 2a and obtained as an orange thick oil. <sup>1</sup>H NMR (chloroform-d, 298 K, 400 MHz, δ/ppm): 7.29 (d, J = 8 Hz, 8H), 7.07(d, J= 8 Hz, 8H), 6.34(s, 2H), 1.34(s, 36H).

#### *Synthesis of compound 3*

**3a**: Compound 2a (300 mg, 0.54 mmol) was dissolved in dry CF (20 mL) and cooled to 0 °C under nitrogen. NBS (220 mg, 1.24 mmol) was added to the solution in portions with the absence of light. After stirring for 1h, the solvent was directly evaporated under reduced pressure. The crude product was purified by flush column chromatography with dichloromethane/petroleum ether (1:2 v/v) to afford a yellow solid (374 mg, 0.52 mmol, 97% yield). <sup>1</sup>H NMR (chloroform-d, 298 K, 400 MHz, δ/ppm):7.09(d, J = 8 Hz, 8H), 6.91(d, J = 8 Hz, 8H), 2.31(s, 12H).

**3b** was synthesized by the same procedure of 3a and obtained as a yellow solid. <sup>1</sup>H NMR (chloroform-d, 298 K, 400 MHz, δ/ppm): 7.07 (d, J = 8 Hz, 8H), 6.93(d, J= 8 Hz, 8H), 2.57(t, J= 8 Hz, 8H), 1.4-1.26(m, 16H), 1.31(t, J= 8 Hz, 12H).

**3c** was synthesized by the same procedure of 3a and obtained as a yellow solid. HNMR: <sup>1</sup>H NMR (chloroform-d, 298 K, 400 MHz, δ/ppm): 7.27 (d, J = 8 Hz, 8H), 6.96(d, J= 8 Hz, 8H), 1.31(s, 36H).

#### *Synthesis of compound 4*

**Compound 7**: 3-(2-butylloctyl)thieno[3,2-b]thiophene (1.05g, 3.4 mmol) was added to a flame-dried bottom flask with two necks, followed by 3 consecutive cycles of vacuum nitrogen filling. Then 10 mL dry THF was added by syringe and the mixture was cooled to -78 °C (liquid nitrogen/acetone) under a dry nitrogen atmosphere. A solution of n-BuLi (2.34 mL, 3.74 mmol) in hexane (1.6 M) was added dropwise to the solution in 10 minutes, and was stirred at that temperature for 1h. After that, trimethyltin chloride (1.01g, 5.07 mmol) in dry THF (5 mL) was added dropwise through syringe within 10 minutes. The resulting mixture was directly warmed to room temperature and reacted for further 3h before quenched with enough water. The mixture was extracted with

dichloromethane for three times, washed with enough saturated sodium chloride aqueous solution. The combined organic phases were dried over anhydrous MgSO<sub>4</sub>, filtered and concentrated under reduced pressure to afford a light pink oil (1.39g). The crude product was used directly for the next step without further purification.

**4a:** Compound 3a (300 mg, 0.42mmol), compound 7 (495 mg, 1.05 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (48.4 mg, 0.042 mmol) and dry toluene (30 mL) were added to a flame-dried schlenk flask at nitrogen atmosphere. The solution was stirred at 110 °C for 16h. After cooling, the solvent was directly evaporated under reduced pressure and the crude product was purified by column chromatography with dichloromethane/petroleum ether (1:5 v/v) to afford an orange solid (387mg, 0.33mmol, 78% yield). <sup>1</sup>H NMR (chloroform-d, 298 K, 400 MHz, δ/ppm): 7.33 (s, 2H), 7.03(q, J= 8 Hz, 16H), 6.90(s, 2H), 2.54(d, J = 8 Hz, 4H), 2.28(s, 12H), 1.72(m, 2H), 1.26-1.21(m, 32H), 0.88-0.83 (m, 12H).

**4b** was synthesized by the same procedure of 4a and obtained as an orange solid. <sup>1</sup>H NMR (chloroform-d, 298 K, 400 MHz, δ/ppm): 7.31 (s, 2H), 7.03(s, 16H), 6.90(s, 2H), 2.55-2.51(m, 12H), 1.72(m, 2H), 1.36-1.21(m, 48H), 0.93-0.82(m, 24H).

**4c** was synthesized by the same procedure of 4a and obtained as an orange solid. <sup>1</sup>H NMR (chloroform-d, 298 K, 400 MHz, δ/ppm): 7.32 (s, 2H), 7.24(d, J= 8 Hz, 8H), 7.06(d, J= 8 Hz, 8H), 6.90(s, 2H), 2.54(d, J = 8 Hz, 4H), 2.01(m, 2H), 1.28-1.22(m, 68H), 0.85-0.83(m,12H).

#### *Synthesis of compound 5*

**5a:** Compound 4a (350 mg, 0.30 mmol) and DMF (1.40 g, 19.2 mmol) were dissolved in DCE (30 mL) under nitrogen and cooled to 0 °C under nitrogen. POCl<sub>3</sub> (0.45 mL, 4.8 mmol) was added to the solution dropwise and stirred at that temperature for further 30 minutes. Then the solution was heated to 85°C for 12 hours. After cooling, saturated sodium bicarbonate solution was added and stirred for 1 hour. The mixture was extracted with chloroform for three times, the combined organic phases were dried over anhydrous MgSO<sub>4</sub>, filtered and concentrated under reduced pressure. The residue was purified by column chromatography with dichloromethane/petroleum ether (1:1 v/v) to afford an orange-red sticky solid (270 mg, 0.22 mmol, 72% yield).

<sup>1</sup>H NMR (chloroform-d, 298 K, 400 MHz, δ/ppm): 10.00(s, 2H), 7.32(s, 2H), 7.06(d, J = 8 Hz, 8H), 6.99(d, J = 8 Hz, 8H), 2.90(d, J = 8 Hz, 4H), 2.29(s, 12H), 1.78(m, 2H), 1.25-1.20(m, 32H), 0.86-

0.81(m, 12H).

**5b** was synthesized by the same procedure of 5a and obtained as an orange-red sticky solid. <sup>1</sup>H NMR (chloroform-d, 298 K, 400 MHz, δ/ppm): 10.00(s, 2H), 7.30(s, 2H), 7.04(q, J = 8 Hz, 16H), 2.89(d, J = 8 Hz, 4H), 2.54(t, J = 8 Hz, 8H), 1.78(m, 2H), 1.36-1.23(m, 48H), 0.93-0.84(m, 24H).

**5c** was synthesized by the same procedure of 5a and obtained as an orange-red sticky solid. <sup>1</sup>H NMR (chloroform-d, 298 K, 400 MHz, δ/ppm): 10.00(s, 2H), 7.30(s, 2H), 7.26(d, J = 8 Hz, 8H), 7.04(d, J = 8 Hz, 8H), 2.90(d, J = 8 Hz, 4H), 1.77(m, 2H), 1.28-1.20(m, 68H), 0.87-0.80(m, 12H).

#### *Synthesis of three NFREAs*

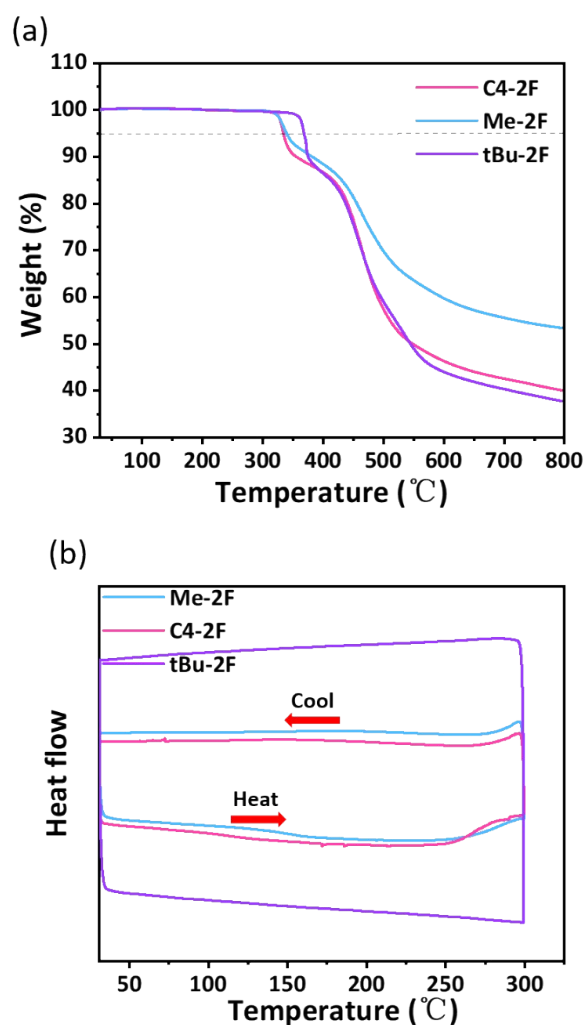
**Me-2F**: Compound 5a (80 mg, 0.065 mmol), 5,6-difluoro-3-(dicyanomethylidene)indan-1-one (60 mg, 0.26 mmol) and dry chloroform (10 mL) were added to a flame-dried schlenk flask at nitrogen atmosphere. Then dry pyridine (0.1 mL) was added to the mixture. The mixture was stirred at 70°C for 16 hours and the solvent was removed under reduced pressure. The crude product was purified by column chromatography with dichloromethane/petroleum ether (1:1 v/v) to afford a black solid (88 mg, 0.053 mmol, 82% yield). <sup>1</sup>H NMR (chloroform-d, 298 K, 400 MHz, δ/ppm): 8.90(s, 2H), 8.50(dd, J<sub>1</sub> = 8 Hz, J<sub>2</sub> = 4 Hz, 2H), 7.65(t, J = 8 Hz, 2H), 7.10-7.02(m, 18H), 2.93(d, J = 8 Hz, 4H), 2.30(s, 12H), 1.80(m, 2H), 1.32-1.14(m, 32H), 0.83-0.79(m, 12H). <sup>13</sup>C NMR (chloroform-d, 298K, 101 MHz, δ/ppm): 185.75, 158.97, 156.81, 155.85, 153.37, 153.23, 153.08, 152.07, 150.93, 143.34, 142.64, 142.08, 136.43, 136.05, 135.88, 134.64, 133.36, 130.07, 127.41, 122.33, 120.88, 118.49, 115.10, 114.90, 114.41, 112.88, 112.69, 69.27, 53.57, 39.41, 34.97, 33.58, 33.33, 31.94, 29.85, 29.66, 29.01, 26.77, 23.03, 22.76, 20.98, 14.26, 14.19. MS (MALDI-TOF): m/z calcd for C<sub>96</sub>H<sub>86</sub>F<sub>4</sub>N<sub>8</sub>O<sub>2</sub>S<sub>6</sub>: 1651.52 [M]<sup>+</sup>, Found: 1651.82.

**C4-2F** was synthesized by the same procedure of Me-2F and obtained as a black solid. <sup>1</sup>H NMR (chloroform-d, 298 K, 400 MHz, δ/ppm): 8.92(s, 2H), 8.50(dd, J<sub>1</sub> = 8 Hz, J<sub>2</sub> = 4 Hz, 2H), 7.65(t, J = 8 Hz, 2H), 7.13-7.03(m, 18H), 2.92(d, J = 8 Hz, 4H), 2.55(t, J = 8 Hz, 8H), 1.77(m, 2H), 1.60-1.53(m, 8H), 1.37-1.15(m, 40H), 0.91(t, J = 8 Hz, 12H), 0.83-0.79(m, 12H). <sup>13</sup>C NMR (chloroform-d, 298K, 101 MHz, δ/ppm): 185.79, 159.10, 156.86, 153.36, 153.22, 153.02, 152.03, 150.97, 143.40, 142.57, 142.15, 138.42, 135.97, 135.89, 129.35, 127.18, 122.21, 120.94, 118.63, 114.94, 114.46, 112.85, 69.31, 53.57, 39.45, 35.18, 34.93, 33.77, 33.58, 33.32, 31.93, 29.66, 29.01, 26.77, 23.02, 22.76, 22.56, 14.25, 14.18, 14.13. MS (MALDI-TOF): m/z calcd for C<sub>108</sub>H<sub>110</sub>F<sub>4</sub>N<sub>8</sub>O<sub>2</sub>S<sub>6</sub>: 1819.70 [M]<sup>+</sup>, Found

1819.94.

**tBu-2F** was synthesized by the same procedure of Me-2F and obtained as a black solid.  $^1\text{H}$  NMR (chloroform-d, 298 K, 400 MHz,  $\delta/\text{ppm}$ ): 8.90(s, 2H), 8.53(dd,  $J_1 = 8$  Hz,  $J_2 = 4$  Hz, 2H), 7.65(t,  $J = 8$  Hz, 2H), 7.31(d,  $J = 8$  Hz, 8H), 7.09(d,  $J = 8$  Hz, 10H), 2.90(d,  $J = 8$  Hz, 4H), 1.74(m, 2H), 1.29-1.13(m, 68H), 0.82-0.77(m, 12H).  $^{13}\text{C}$  NMR (chloroform-d, 298K, 101 MHz,  $\delta/\text{ppm}$ ): 185.81, 159.10, 156.78, 153.37, 153.23, 152.80, 152.02, 150.91, 146.62, 143.03, 142.60, 142.10, 136.01, 135.80, 134.71, 126.33, 121.00, 118.70, 115.17, 114.96, 114.45, 112.85, 112.66, 69.33, 39.44, 34.91, 34.48, 33.56, 33.31, 31.89, 31.56, 31.08, 29.86, 29.64, 29.02, 26.76, 23.01, 22.74, 14.24, 14.17. MS (MALDI-TOF):  $m/z$  calcd for  $\text{C}_{108}\text{H}_{110}\text{F}_4\text{N}_8\text{O}_2\text{S}_6$ : 1819.70  $[\text{M}]^+$ , Found 1819.94.

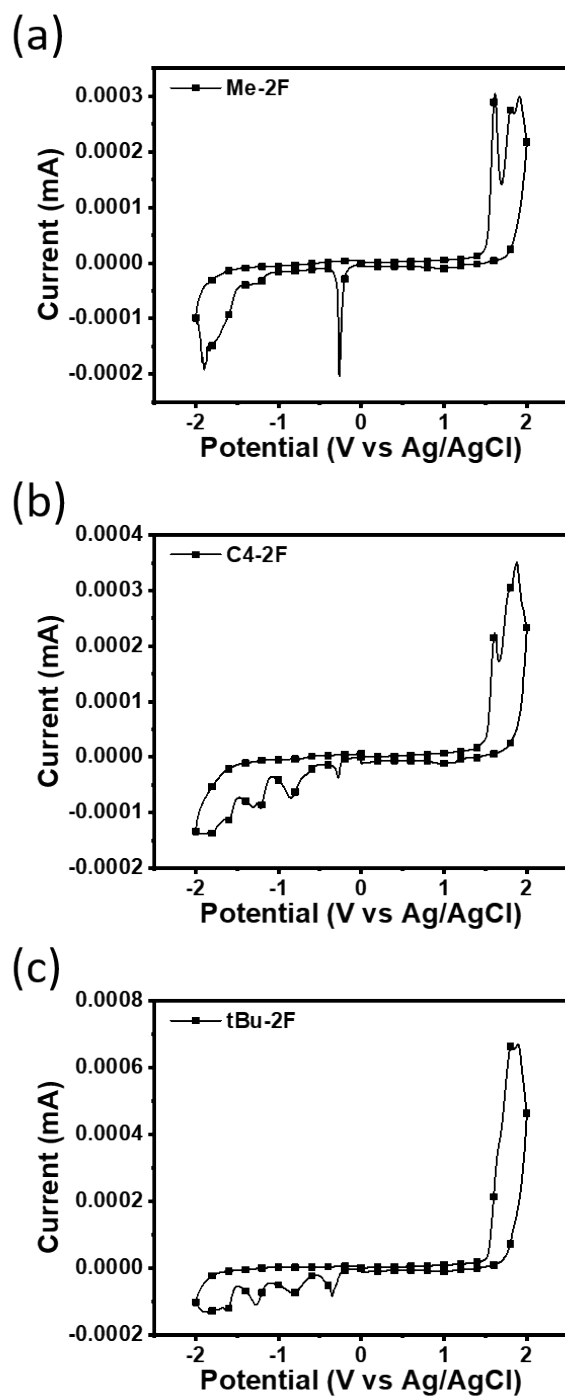
### 3. Thermal analysis



**Figure S1.** (a) TGA and (b) DCS spectrum of Me-2F, C4-2F and tBu-2F.

#### 4. Cyclic voltammetry measurements

Cyclic voltammetry (CV) measurements were tested on a CHI-730 electrochemistry workstation, thin films were drop-cast from acceptor solutions at the concentration of 10 mg/mL in chloroform.  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  were calculated from the equations of " $E_{\text{HOMO}} = (E_{\text{ox}} + 4.8) \text{ eV}$ " and " $E_{\text{LUMO}} = (E_{\text{red}} + 4.8) \text{ eV}$ ", where  $E_{\text{ox}}$  and  $E_{\text{red}}$  were the oxidation and reduction onsets, respectively.



**Figure S2.** Cyclic voltammogram (CV) curves of Me-2F, C4-2F and tBu-2F.



## 5. Photoluminescence quenching

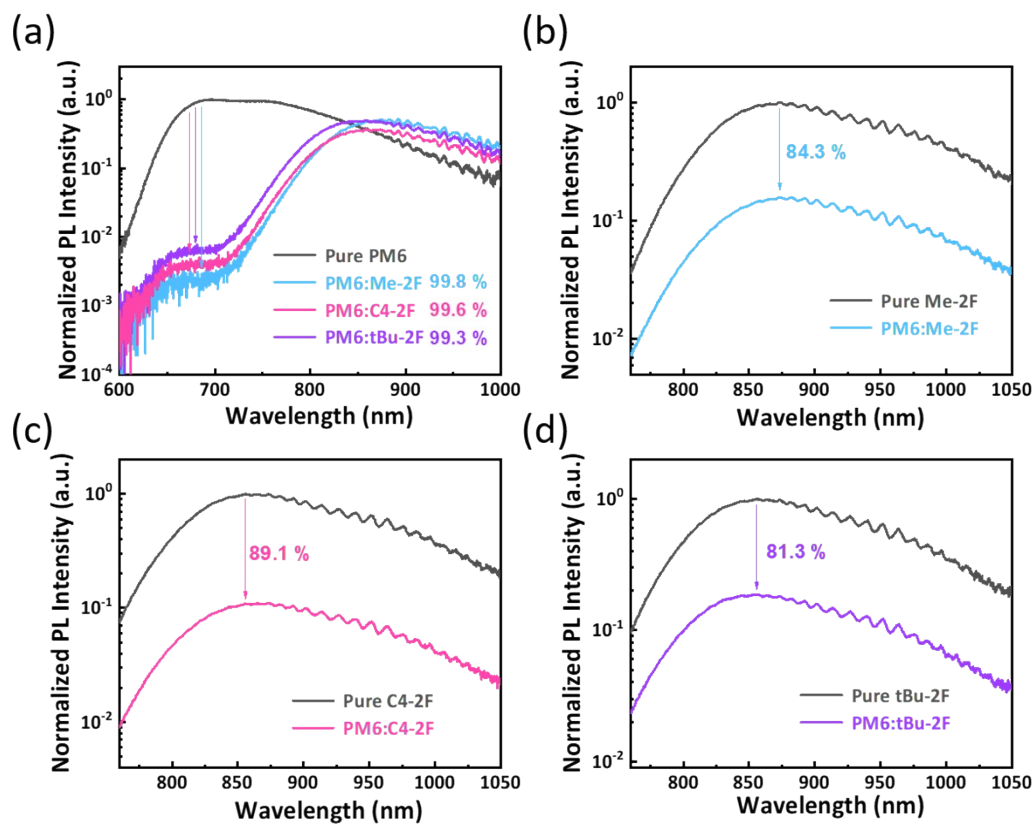


Figure S3. PL spectra of the neat films and the blend films.

## 6. $V_{OC}$ - $P_{light}$ dependence analysis

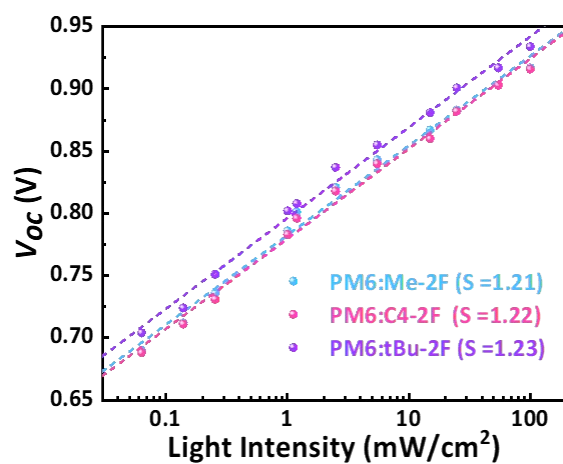
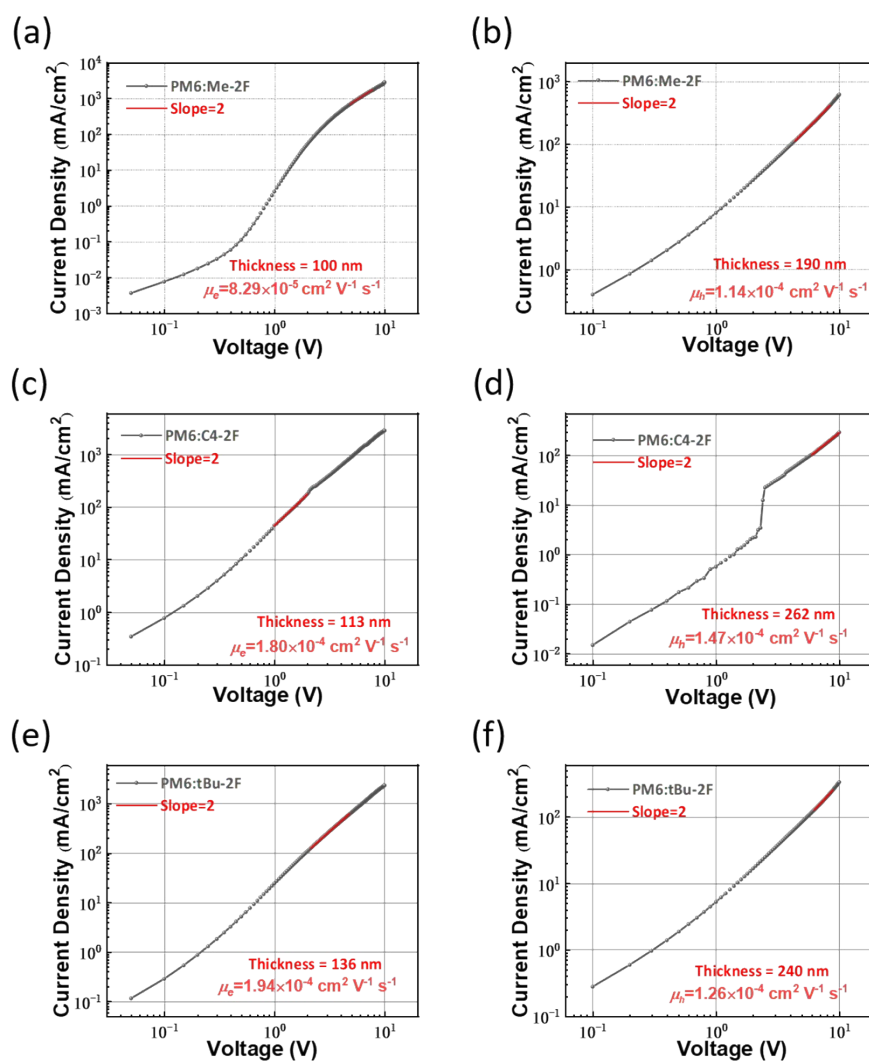


Figure S4.  $V_{OC}$ - $P_{light}$  spectra of optimized devices for Me-2F, C4-2F and tBu-2F.

## 7. SCLC mobility measurements

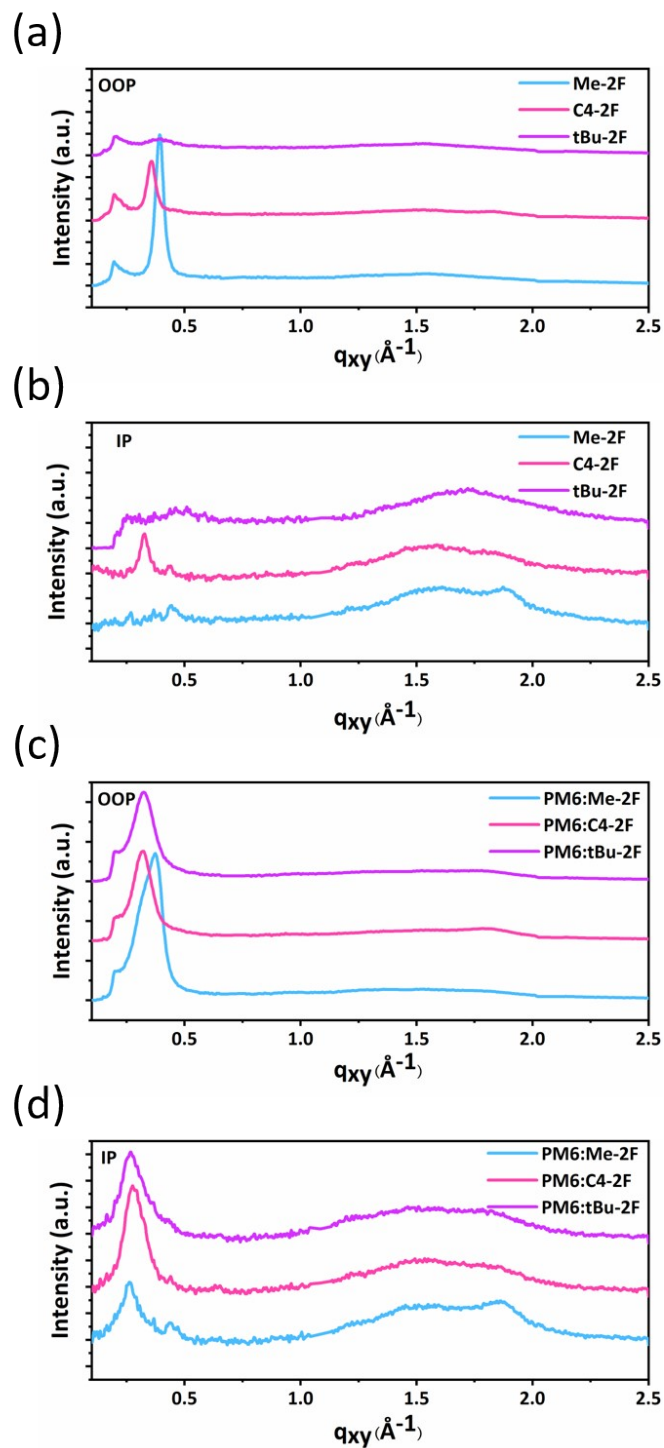
The hole-only device structure was ITO/PEDOT:PSS(4083)/active layer/MoO<sub>3</sub>/Ag and the electron-only device structure was ITO/ZnO/active layer/PFN-Br/Ag. The mobility was determined by fitting the dark current to the model of a single carrier

SCLC, which is described by equation:  $J = \frac{9}{8} \epsilon_0 \epsilon_r \mu \frac{V^2}{d^3}$ , where  $J$  is the current,  $\epsilon_0$  is the permittivity of free space,  $\epsilon_r$  is the relative permittivity of the material,  $\mu$  is the zero-field mobility,  $d$  is the thickness of the polymer layer,  $V$  is the applied voltage. Then hole mobilities were calculated from the slope of the  $J^{1/2}$ - $V$  curves below.



**Figure S5.** SCLC characterization of the blend films in their (a) (c) (e) electron-only devices and (b) (d) (f) hole-only devices

## 8. GIWAXS line-cut profiles



**Figure S6.** Line-cut profiles of the GIWAXS diffraction patterns. (a) (b) for pure films. (c) (d) for blend films

## 9. Photoluminescence spectra

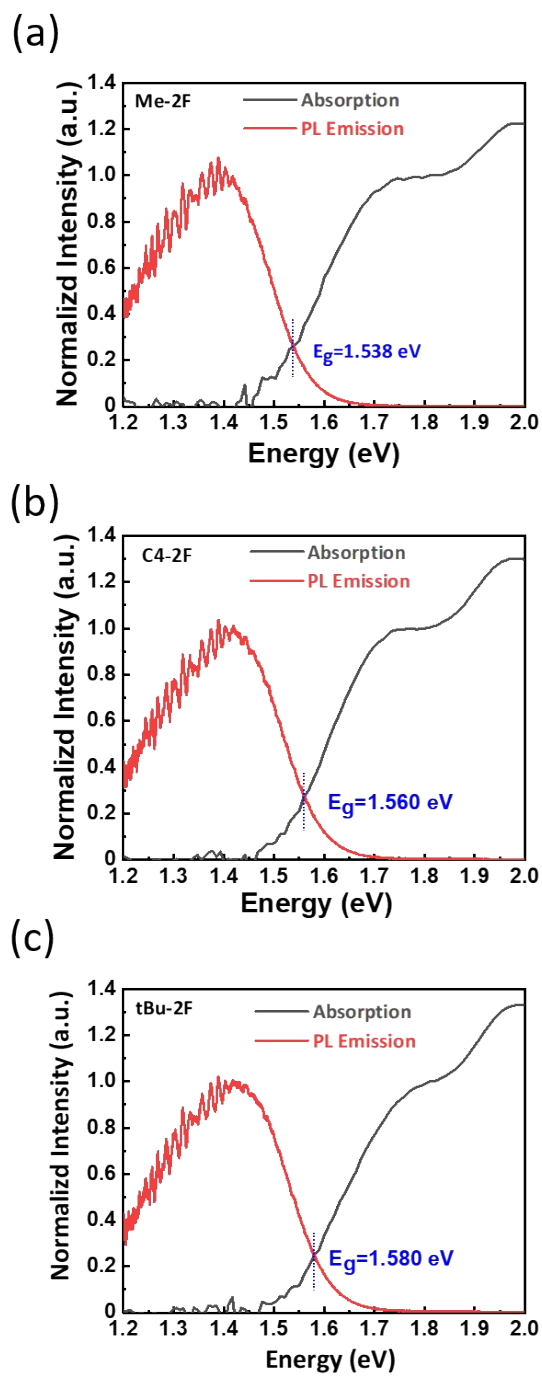
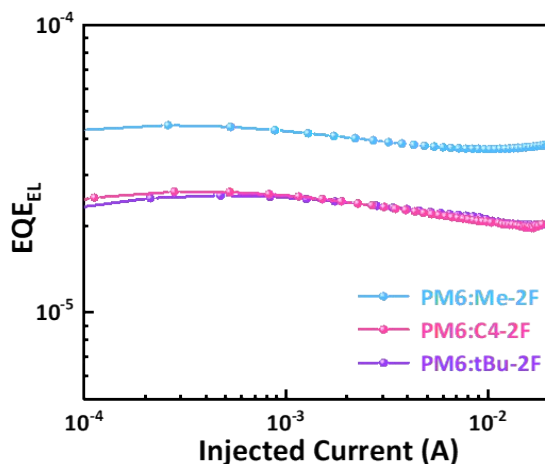


Figure S7. The absorption and photoluminescence spectra of Me-2F, C4-2F and tBu-2F.

## 10. EQE<sub>EL</sub> spectra



**Figure S8.** EQE<sub>EL</sub> curves for PM6:Me-2F, PM6:C4-2F, and PM6:tBu-2F based devices.

## 11. Solar cell fabrication and characterizations

The devices were fabricated with a conventional structure of ITO/PEDOT:PSS(4083)/Active layer/PFN-Br/Ag. The ITO-coated glass was washed with deionized water/detergent, deionized water, acetone and isopropyl in sequence for 15 minutes. Later, the ITO-coated glass was treated under ultraviolet-ozone condition for 20 min. After that, PEDOT:PSS was spin coated onto the glass at 3000 rpm for 40 s and processed by thermal annealing at 150 °C for 15 min. To make PM6 fully dissolved, the blends of PM6:NFREAs was dissolved in chloroform with a total concentration of 16 mg mL<sup>-1</sup> and stirred for at least 2 hours at 40 °C. Afterwards, the blend solution was spin-coated onto the PEDOT: PSS layer and thermal annealed at 90 °C for 10 min. The optimal film thickness of active layer was 100 nm. Subsequently, PFN-Br was spin-coated on the active layer at 3000 rpm with a film thickness of 5 nm. Finally, a 100 nm Ag layer was thermally evaporated onto the active layer in a vacuum chamber (< 10<sup>-6</sup> mbar). The active area of the solar cells was 0.04 cm<sup>2</sup>.

**Table S1.** PM6:Me-2F based devices with different annealing temperatures.

D/A ratio	Annealing	$V_{oc}$ (v)	$J_{sc}$ (mA cm <sup>-2</sup> )	$FF$	PCE (%)
1:1.2	90°C, 5min	0.892	15.66	0.538	7.52
1:1.2	90°C, 10min	0.878	16.42	0.553	7.98
1:1.2	90°C, 15min	0.881	15.49	0.554	7.57

**Table S2.** PM6:Me-2F based devices with different D/A ratios.

D/A ratio	Annealing	$V_{oc}$ (v)	$J_{sc}$ (mA cm <sup>-2</sup> )	$FF$	PCE (%)
1:1.2	90°C, 10min	0.92	17.03	0.62	9.71
1:1.3	90°C, 10min	0.915	17.53	0.649	10.41
1:1.4	90°C, 10min	0.918	16.41	0.676	10.42

**Table S3.** PM6:Me-2F based devices with different additives.

D/A ratio	Annealing	Additive	$V_{oc}$ (v)	$J_{sc}$ (mA cm <sup>-2</sup> )	$FF$	PCE (%)
1:1.4	90°C, 10min	0.5%CN	0.865	15.64	0.513	6.93
1:1.4	90°C, 10min	0.5%DIO	0.78	16.69	0.517	6.73

**Table S4.** PM6:C4-2F based devices with different annealing temperatures.

D/A ratio	Annealing	$V_{oc}$ (v)	$J_{sc}$ (mA cm <sup>-2</sup> )	$FF$	PCE (%)
1:1.2	90°C, 5min	0.901	16.29	0.589	8.65
1:1.2	90°C, 10min	0.885	17.39	0.60	9.24
1:1.2	90°C, 15min	0.893	16.24	0.610	8.85

**Table S5.** PM6:C4-2F based devices with different D/A ratios.

D/A ratio	Annealing	$V_{oc}$ (v)	$J_{sc}$ (mA cm <sup>-2</sup> )	$FF$	PCE (%)
1:1.2	90°C, 10min	0.885	17.39	0.60	9.24
1:1.3	90°C, 10min	0.899	17.19	0.657	10.16
1:1.4	90°C, 10min	0.889	16.40	0.633	9.24

**Table S6.** PM6:C4-2F based devices with different additives.

D/A ratio	Annealing	Additive	$V_{oc}$ (v)	$J_{sc}$ (mA cm <sup>-2</sup> )	$FF$	PCE (%)
1:1.3	90°C, 10min	0.5%CN	0.83	14.65	0.48	5.84
1:1.3	90°C, 10min	0.5%DIO	0.822	16.41	0.574	7.73

**Table S7.** PM6:tBu-2F based devices with different annealing temperatures.

D/A ratio	Annealing	$V_{oc}$ (v)	$J_{sc}$ (mA cm <sup>-2</sup> )	$FF$	PCE (%)
1:1.3	90°C, 5min	0.92	15.07	0.594	8.24
1:1.3	90°C, 10min	0.914	15.84	0.58	8.40
1:1.3	90°C, 15min	0.912	15.25	0.569	7.91

**Table S8.** PM6:tBu-2F based devices with different D/A ratios.

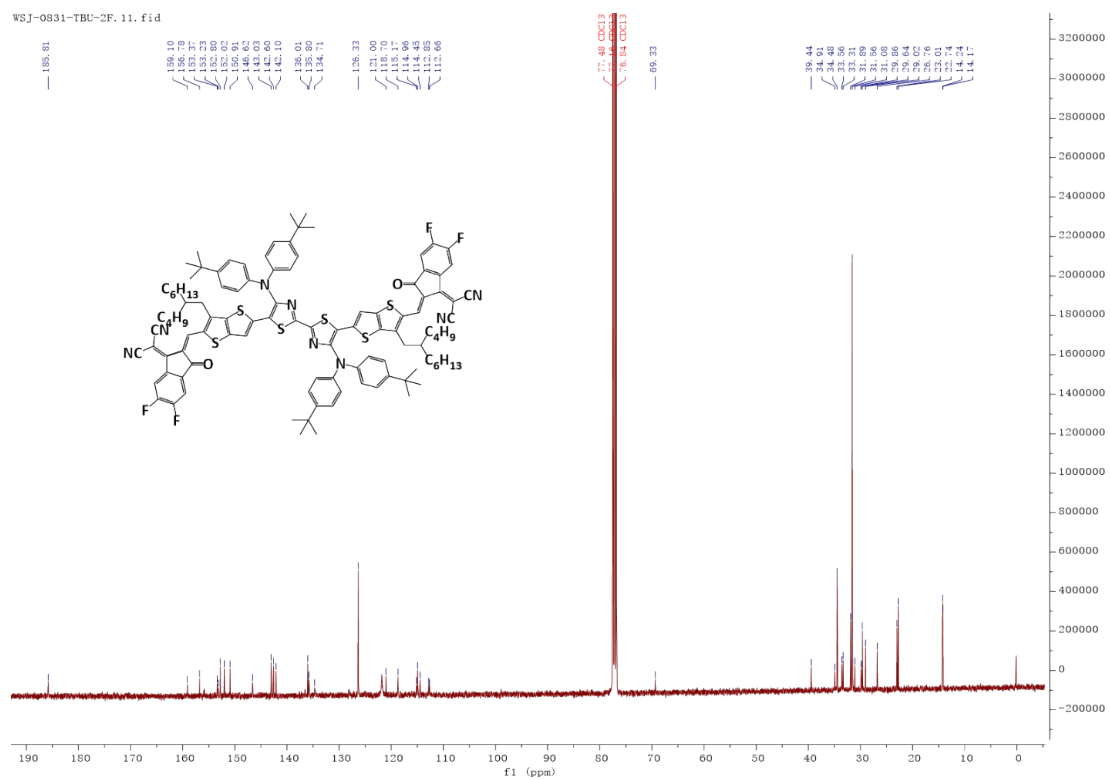
D/A ratio	Annealing	$V_{oc}$ (v)	$J_{sc}$ (mA cm <sup>-2</sup> )	$FF$	PCE (%)
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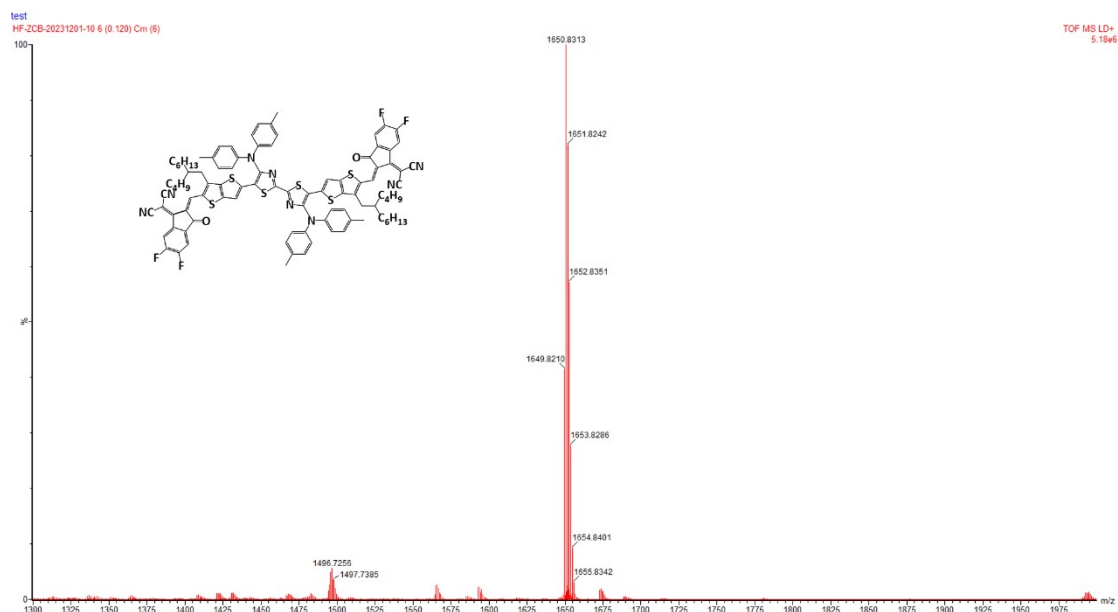




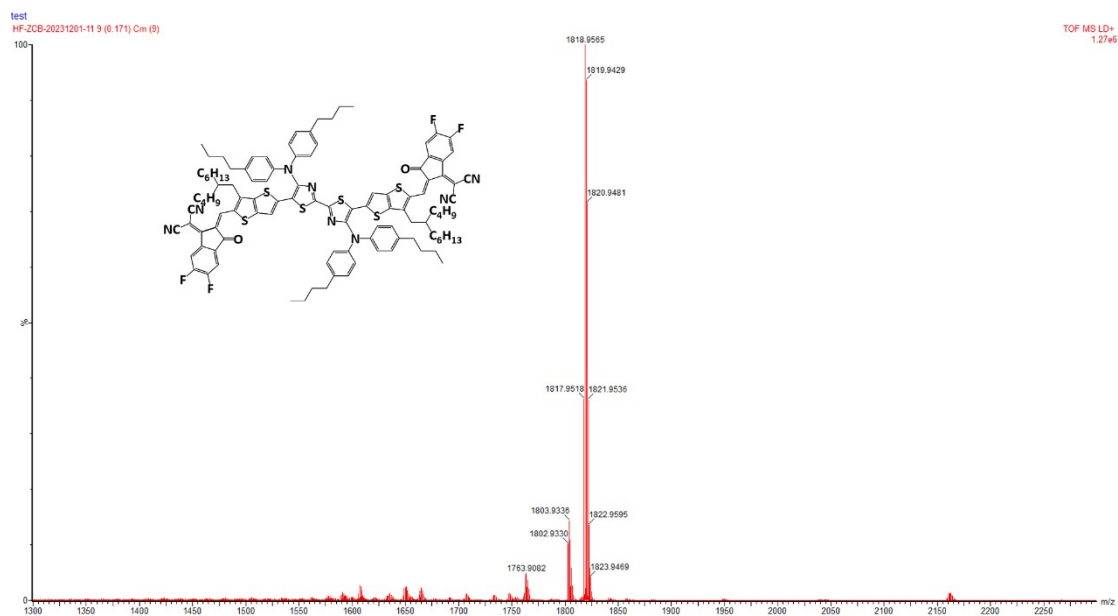




**Figure S14.**  $^{13}\text{C}$ -NMR spectrum of compound tBu-2F,



**Figure S15.** The MALDI-TOF MS plot of Me-2F.



**Figure S16.** The MALDI-TOF MS plot of C4-2F.

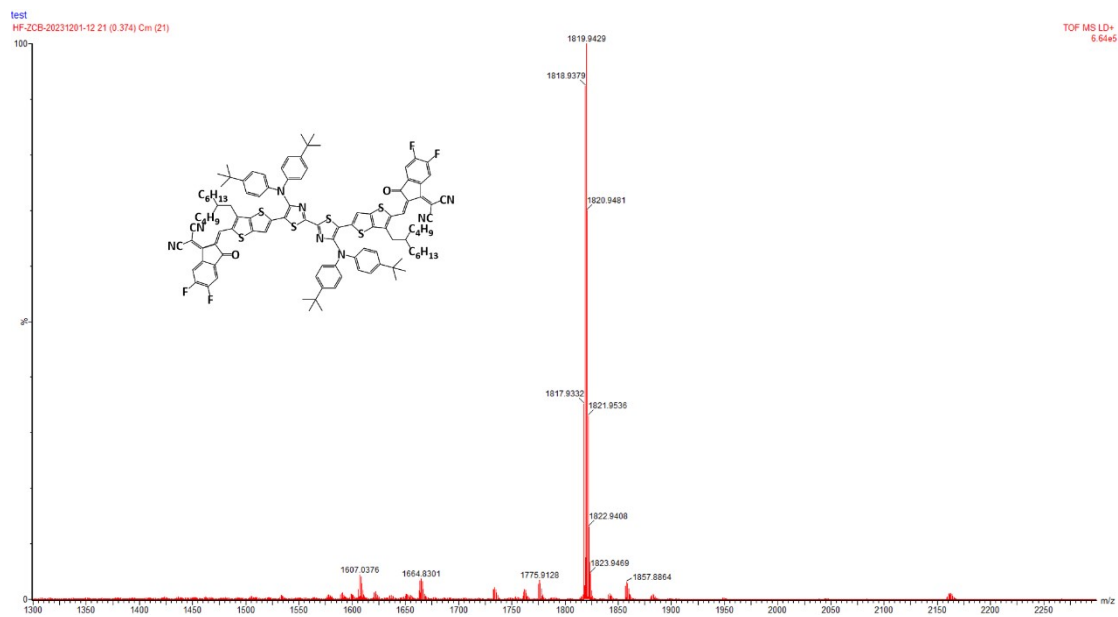


Figure S17. The MALDI-TOF MS plot of tBu-2F.

1. Neidlein. Richard, and Nussbaumer. Thomas, *Heterocycles*, 2000, 52, 10.3987/COM-99-S30.