

# **Study of photovoltaic performances for symmetrical and asymmetrical chlorinated thiophene-bridges-based conjugated polymers.**

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## **Contents**

1. Instruments.
2. Measurements.
3. Synthetic detail.
4. Figure S1-S12.
5. Table S1-S7.

## 1. Instruments.

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded in deuterated solvents on a Bruker AVANCE 300 or 400 MHz NMR spectrometer at room temperature. Thermo gravimetric analysis (TGA) were carried out using TGA-2050 Thermogravimetry Analyze. Elemental analysis of polymers was performed on a FLASH EA1112 elemental analyzer. Molecular weight and polydispersity ( $\mathcal{D}$ ) of both polymers were estimated by gel permeation chromatography (GPC) method with monodispersed polystyrene as standard and *o*-dichlorobenzene as eluent at 145 °C. The current density-voltage ( $J$ - $V$ ) measurements were 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 mW/cm<sup>2</sup>. The EQE spectrum was measured through the Solar Cell Spectral Response Measurement System QE-R3011 (Enli Technology Co., Ltd., Taiwan). Silicon diode was used as reference cell in both  $J$ - $V$  and EQE.

## 2. Measurements

**Optical characterizations:** UV-vis absorption spectra of polymers in diluted chlorobenzene solution and in films were measured on a Hitachi U-3100 UV-vis spectrophotometer. The film samples were prepared by spin-coating onto quartz plates (1×1 cm<sup>2</sup>) using 10 mg mL<sup>-1</sup> chlorobenzene solution.

**Cyclic Voltammetry (CV):** The cyclic voltammetry was measured on a CH1650D electrochemical workstation with a three-electrode cell in anhydrous acetonitrile solvents. The Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M) was dissolved into above solution. The scan rate was fixed at 50 mV/s at room temperature under argon. A Ag/Ag<sup>+</sup> wire, A platinum wire, and a glassy carbon electrode were employed as the reference electrode counter electrode, and working electrode, respectively. The potential of Ag/Ag<sup>+</sup> reference electrode was calibrated by using ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) as the redox couple.

**Polymer solar cells fabrication and testing:** All devices were fabricated with the conventional device architecture of ITO/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)/BHJ/PFN-Br/Al. Pre-patterned indium tin oxide (ITO)-coated glass with a sheet

resistance of 10–15 ohm/square was cleaned sequential sonication in deionized water, acetone and isopropanol twice for 15 min. Then it was transferred to oven and dried at 150 °C for 15 min. After ultraviolet-ozone treatment for 20 min, the 10 nm layer of PEDOT:PSS (Heraeus Materials, 4083) was spin-coated on ITO. The substrates were annealed for 15 min at 150 °C, and transferred to the nitrogen-filled glovebox. The active layer materials were prepared according to the description under corresponding Table S1-S6. Finally, PFN-Br was spin-coated (3000rpm, 30s) onto the active layer as the cathode buffer layer, and the whole device was completed by vacuum evaporating Al metal electrodes (100 nm) to acquire an area of 4 mm<sup>2</sup> cell. Device  $J-V$  characteristics were measured under 100 mW cm<sup>-2</sup> of the standard AM 1.5G spectrum. The spectral mismatch factor was calibrated to be unity via a National Institute of Metrology (NIM) certificated silicon reference cell with a KG3 filter. All EQE curves were measured using the solar cell spectral response measurement system QE-R3011 (Enli Technology Ltd., Taiwan), which was calibrated by monocrystalline silicon solar cell in advance.

**Carrier mobility measurement:** The SCLC method was used to measure the charge carrier mobilities of blend films, the hole-only and electron-only device architecture are ITO/PEDOT:PSS/BHJ/Au and ITO/ZnO/BHJ/Al, respectively.

**GIWAXS Characterization:** GIWAXS measurements were performed by using a XEUS SAXS/WAXS system. Samples were prepared on Si substrates using blend solutions identical to those devices used. The wavelength of the X-ray beam is 1.54 Å, and the incident angle was 0.2°. Scattered X-rays were detected by using a Dectris Pilatus 300 K photon counting detector. The crystal coherence length (CCL) was obtained using the Scherrer equation.

**AFM characterizations:** All film samples were prepared using spin-coating onto ITO/PEDOT:PSS substrates. The measurements were carried out by a Nanoscope V (Veeco) IN tapping mode.

**Density functional theory (DFT) calculation:** The molecular modeling calculations were conducted using the Gaussian 09 program based on the density functional theory method using B3LYP/6-31G (d, p) level.

### 3. Synthetic detail

#### **1-bromo-3-(4-chloro-5-(triisopropylsilyl)thiophen-2-yl)-5,7-bis(2-ethylhexyl)-4H,8H-benzo[1,2-c:4,5-c']dithiophene-4,8-dione (3)**

1,3-dibromo-5,7-bis(2-ethylhexyl)-4H,8H-benzo[1,2-c:4,5-c']dithiophene-4,8-dione (1.37g, 2.28mmol) and (3-chloro-5-(trimethylstannyl)thiophen-2-yl)triisopropylsilane (1.0g, 2.28mmol) was dissolved in 60 mL of toluene. The mixture was protected by blowing a stream of argon for 10 min. The 0.06 mmol of Pd(PPh<sub>3</sub>)<sub>4</sub> was added. The mixture was heated to 110°C and stirred for 20h. The reaction was quenched with water and extracted with dichloromethane (3×20 mL). After removing the organic solvents, the crude product was purified by column chromatography with PE:DCM=2:1 as eluent to afford compound **3** (0.7g, 40%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.71 (s, 1H), 3.39-3.18 (m, 4H), 1.77-1.76 (d, J=4Hz, 2H), 1.61-1.54 (m, 3H), 1.43-1.26 (m, 17H), 1.18-1.16 (d, J = 8 Hz, 18H), 0.95-0.86 (m, 11H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, ppm) δ 176.5, 176.3, 154.6, 154.1, 143.5, 137.7, 135.5, 133.4, 133.0, 132.7, 132.5, 132.0, 131.9, 118.6, 41.27, 40.96, 32.82, 32.73, 28.83, 28.70, 26.08, 26.05, 23.13, 18.85, 14.22, 14.19, 12.42, 10.94, 10.90. HRMS (MALDI) [+H] C<sub>39</sub>H<sub>56</sub>BrClO<sub>2</sub>S<sub>3</sub>Si m/z calc. 794.21, found 794.21.

#### **1-(4-chloro-5-(triisopropylsilyl)thiophen-2-yl)-5,7-bis(2-ethylhexyl)-3-(thiophen-2-yl)-4H,8H-benzo[1,2-c:4,5-c']dithiophene-4,8-dione (4)**

Compound **3** (1.85g, 2.32 mmol) was dissolved in 100 mL of toluene. 2-(tributylstannyl)thiophene(1g, 2.78mmol) was added into the solution. The mixture was protected by blowing a stream of argon for 10 min. The 0.07 mmol of Pd(PPh<sub>3</sub>)<sub>4</sub> was added. The mixture was heated to 110°C and stirred for 1 day. The reaction was quenched with water and extracted with dichloromethane (3×20 mL). After removing the organic solvents, the crude product was purified

by column chromatography with PE:DCM=8:1 as eluent to afford compound **4** (1.5g, 80%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.79 (s, 1H), 7.75-7.74 (d, J=4Hz, 1H), 7.51-7.50 (d, J=4Hz, 1H), 7.13-7.11 (t, J=8Hz, 1H), 3.35-3.19 (m, 4H), 1.78-1.75 (m, 2H), 1.62-1.55 (m, 3H), 1.42-1.26 (m, 17H), 1.19-1.17 (m, 18H), 0.95-0.83 (m, 11H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, ppm) δ 177.75, 177.66, 153.74, 153.47, 142.89, 140.84, 138.35, 133.41, 133.23, 133.18, 133.00, 132.87, 132.81, 132.47, 132.00, 130.84, 129.65, 127.37, 41.39, 41.06, 33.81, 33.76, 32.89, 32.85, 28.95, 28.74, 26.16, 26.09, 23.17, 23.15, 18.90, 14.28, 14.29, 12.46, 11.04, 10.94. HRMS (MALDI) [+H] C<sub>43</sub>H<sub>59</sub>ClO<sub>2</sub>S<sub>4</sub>Si m/z calc. 798.29, found 798.29.

**1-(4-chlorothiophen-2-yl)-5,7-bis(2-ethylhexyl)-3-(thiophen-2-yl)-4H,8H-benzo[1,2-c:4,5-c']dithiophene-4,8-dione (5)**

Compound **4** (1.0g, 1.29 mmol) was dissolved in 50 mL of anhydrous THF under argon. TBAF(1.43ml, 1.43mmol) was dropwise added into the solution at 0 °C and stirred for 1h. The reaction was quenched with water and extracted with dichloromethane. The combined organic layers were dried over anhydrous MgSO<sub>4</sub>. After removing the organic solvents, the crude product was purified by column chromatography using PE:DCM=5:1 as eluent to afford compound **5** (0.8g, 89%). <sup>1</sup>H NMR (300 MHz, Acetone, ppm) δ 7.88-7.86 (d, J=6Hz, 1H), 7.75 (s, 2H), 7.64 (s, 1H), 7.21-7.18 (t, J=9Hz, 1H), 3.31-3.29 (d, J=6Hz, 4H), 1.82-1.78 (m, 2H), 1.44-1.29 (m, 16H), 0.95-0.85 (m, 12H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, ppm) δ 177.38, 177.22, 153.63, 153.49, 142.82, 140.63, 133.99, 133.22, 133.11, 132.97, 132.78, 132.27, 130.77, 129.81, 129.68, 127.17, 125.19, 123.84, 41.17, 33.68, 32.86, 28.87, 26.11, 23.11, 14.24, 10.95. (MALDI) [+H] C<sub>34</sub>H<sub>39</sub>ClO<sub>2</sub>S<sub>4</sub> m/z calc. 642.15, found 642.15.

**1-(5-bromo-4-chlorothiophen-2-yl)-3-(5-bromothiophen-2-yl)-5,7-bis(2-ethylhexyl)-4H,8H-**

### **benzo[1,2-c:4,5-c']dithiophene-4,8-dione (6)**

Compound **5** (0.66g, 1.02 mmol) was dissolved in 40 mL of anhydrous THF under argon. LDA (2.05ml, 4.1mmol) was dropwise added into the solution at -78°C and stirred 1.5h. The anhydrous THF dissolving carbon tetrabromide (1.7g, 5.13mmol) was dropwise into the solution and stirred 3.5h at room temperature. The reaction was quenched with water and extracted with dichloromethane. The combined organic layers were dried over anhydrous MgSO<sub>4</sub>. After removing the organic solvents, the crude product was purified by column chromatography with PE:DCM=4:1 as eluent to afford compound **6** (0.38g, 46%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ 7.39-7.38 (m, 2H), 7.03-7.02 (d, J=4Hz, 1H), 3.32-3.19 (m, 4H), 1.75-1.72 (m, 2H), 1.41-1.25 (m, 16H), 0.95-0.90 (m, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm) δ 177.33, 177.17, 154.34, 154.19, 141.77, 140.02, 134.36, 133.31, 132.59, 132.45, 132.28, 131.71, 130.42, 129.71, 128.96, 126.73, 118.63, 114.37, 41.14, 33.64, 32.81, 28.88, 26.02, 23.01, 14.18, 10.84. (MALDI)[-H] C<sub>34</sub>H<sub>39</sub>Br<sub>2</sub>ClO<sub>2</sub>S<sub>4</sub> m/z calc. 799.97, found 799.97.

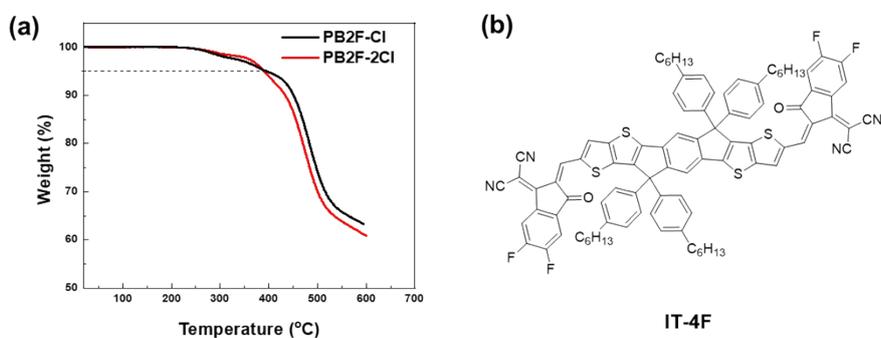
### **Synthesis of PB2F-Cl.**

Compound **8** (0.2 mmol) and monomer **6** (0.2 mmol) were dissolved in anhydrous chlorobenzene (7 mL) in a microwave vial and deoxygenated with Argon for 10 min. Pd(PPh<sub>3</sub>)<sub>4</sub> (23 mg, 0.02 mmol) was then added under Argon. The resulting mixture was heated under microwave irradiation at 135 °C for 5 h, after which it was allowed to cool to room temperature. Then the polymer was precipitated from methanol. The precipitated was further purified by column chromatography using chloroform as the eluent to obtain dark solid (200 mg, 78%). Molecular weight by GPC (145 °C): M<sub>n</sub> = 14.8 kg mol<sup>-1</sup>, D = 3.0. Elemental analysis: Calcd. for C<sub>68</sub>H<sub>75</sub>ClF<sub>2</sub>O<sub>2</sub>S<sub>8</sub>: C 65.12, H 6.03; found: C 65.61, H 6.08.

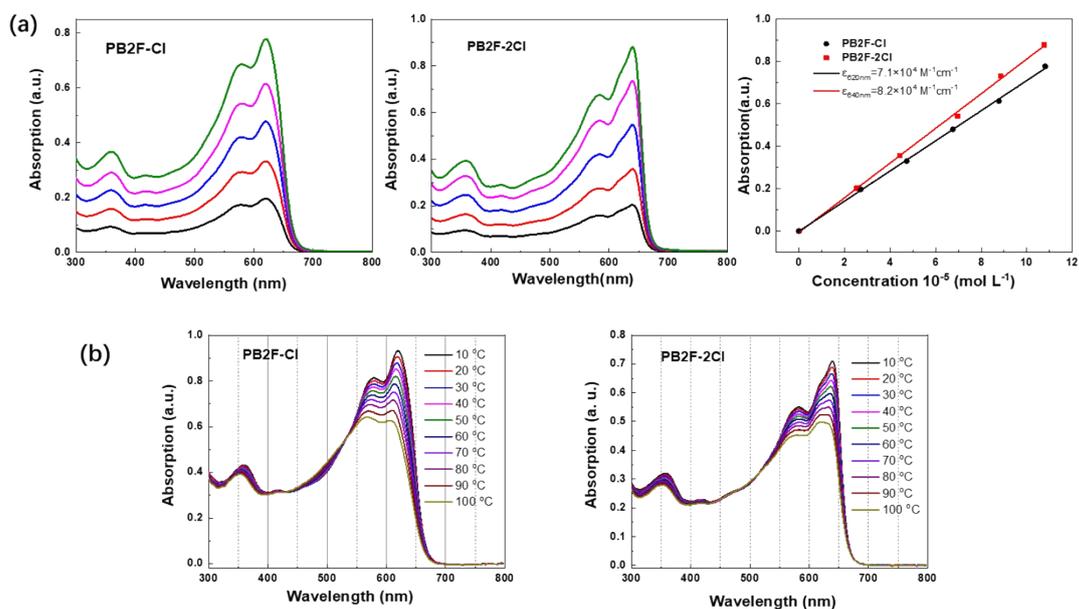
### **Synthesis of PB2F-2Cl.**

Compound **8** (0.2 mmol) and monomer **7** (0.2 mmol) were dissolved in anhydrous chlorobenzene (7 mL) in a microwave vial and deoxygenated with Argon for 10 min. Pd(PPh<sub>3</sub>)<sub>4</sub> (23

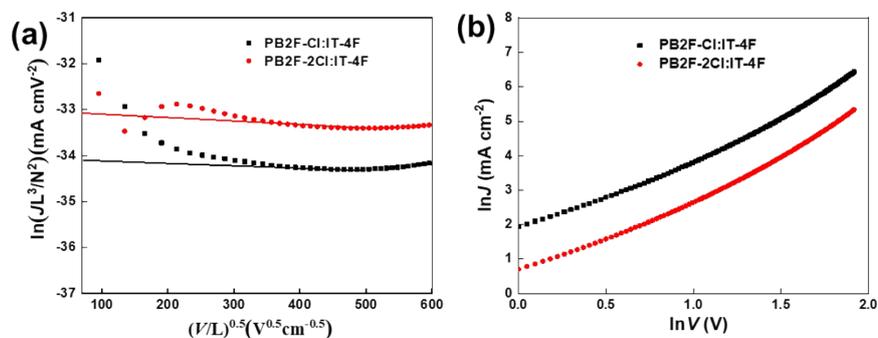
mg, 0.02 mmol) was then added under Argon. The resulting mixture was heated under microwave irradiation at 135 °C for 5 h, after which it was allowed to cool to room temperature. Then the polymer was precipitated from methanol. The precipitated was further purified by column chromatography using chloroform as the eluent to obtain dark solid (188 mg, 75%). Molecular weight by GPC (145 °C):  $M_n = 15.8 \text{ kg mol}^{-1}$ ,  $D = 3.5$ . Elemental analysis: Calcd. for  $C_{68}H_{75}Cl_2F_2O_2S_8$ : C 65.12, H 6.03; found: C 65.04, H 6.01.



**Figure S1.** (a) TGA curves of polymers **PB2F-Cl** and **PB2F-2Cl** at a heating rate of  $10 \text{ °C min}^{-1}$  under nitrogen, (b) The chemical structure of IT-4F.

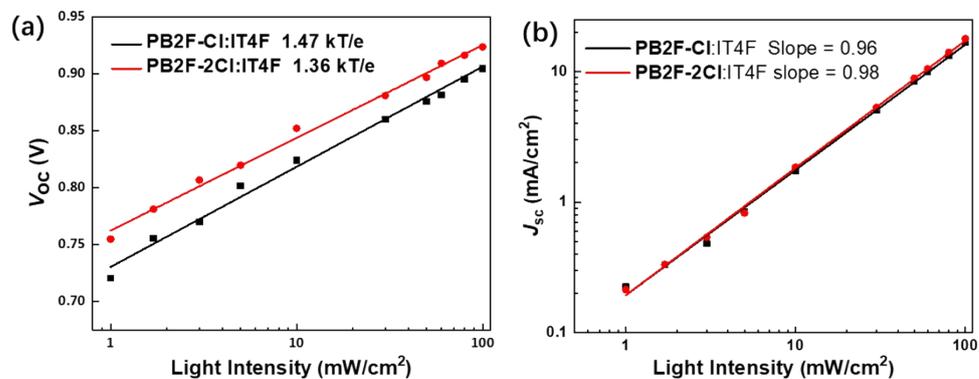


**Figure S2.** (a) The calculations of molar extinction coefficients of **PB2F-Cl** and **PB2F-2Cl** in chlorobenzene at 20 °C. (b) Temperature-dependent absorption spectra of **PB2F-Cl** and **PB2F-2Cl** in chlorobenzene as the temperature decreased from 100 to 0 °C.

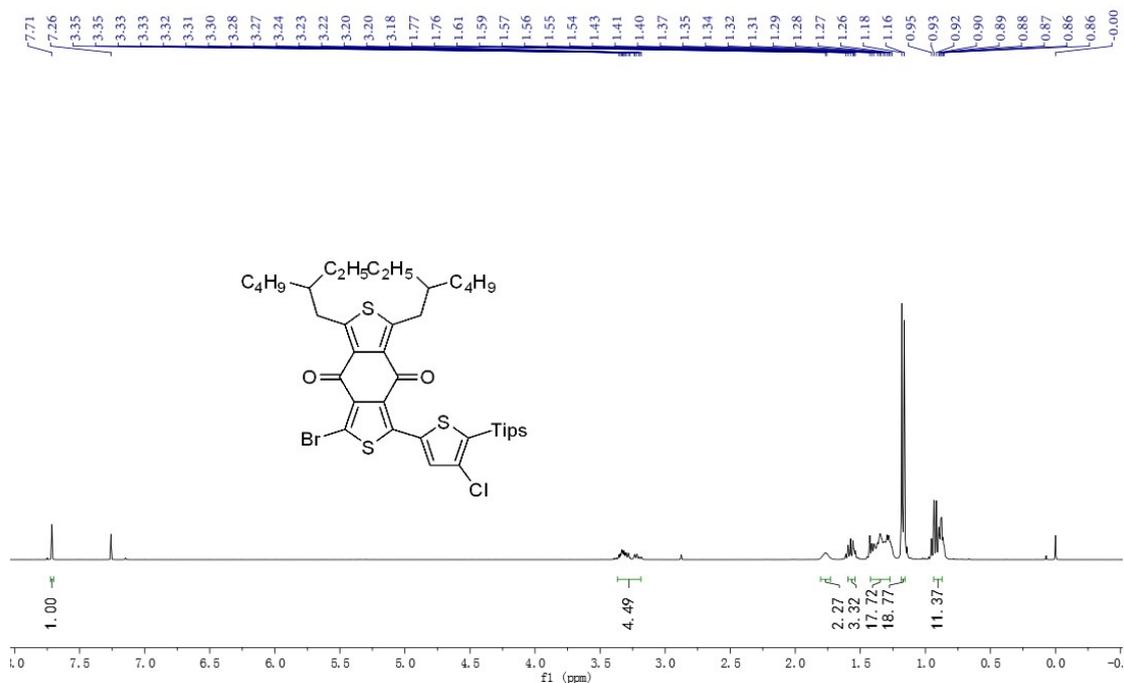


**Figure S3.** Plots for the calculation of hole and electron mobilities of **PB2F-Cl:IT-4F** and **PB2F-**

2Cl:IT-4F obtained from the (a) hole-only and (b) electron-only devices.



**Figure S4.** The light intensity versus (b)  $V_{oc}$  and (c)  $J_{sc}$  for **PB2F-Cl:IT-4F** and **PB2F-2Cl:IT-4F**-based PSC devices.



**Figure S5.**  $^1\text{H}$  NMR spectrum of compound **3** in  $\text{CDCl}_3$ .

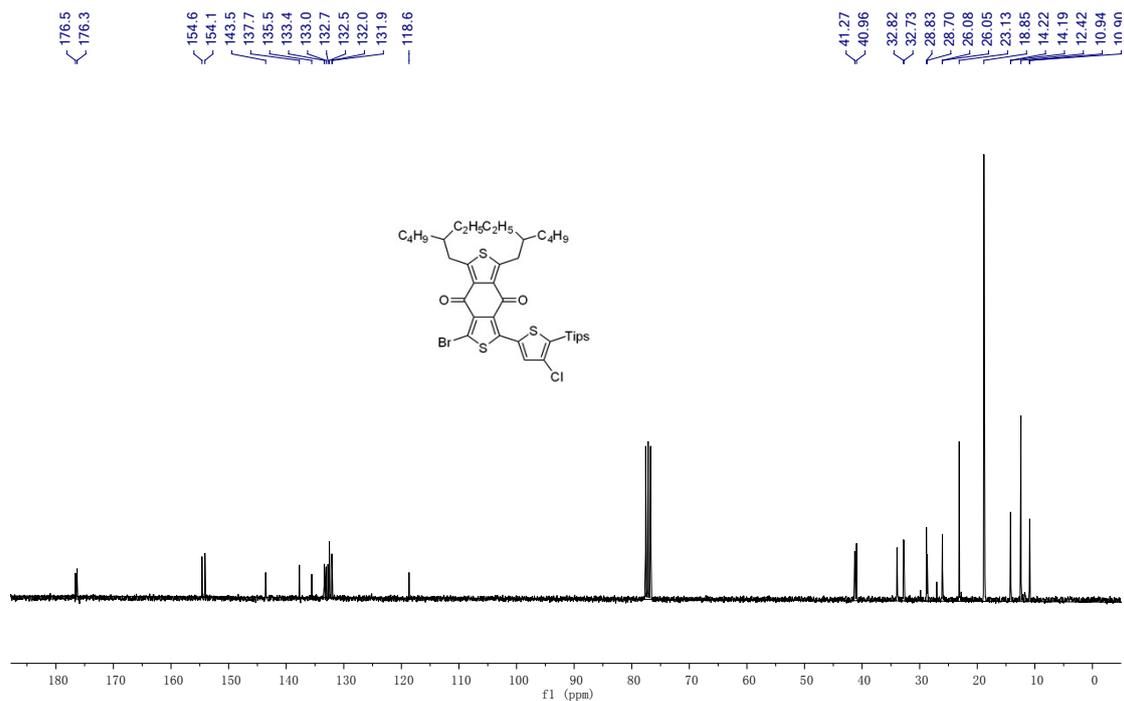


Figure S6. <sup>13</sup>C NMR spectrum of compound 3 in CDCl<sub>3</sub>.

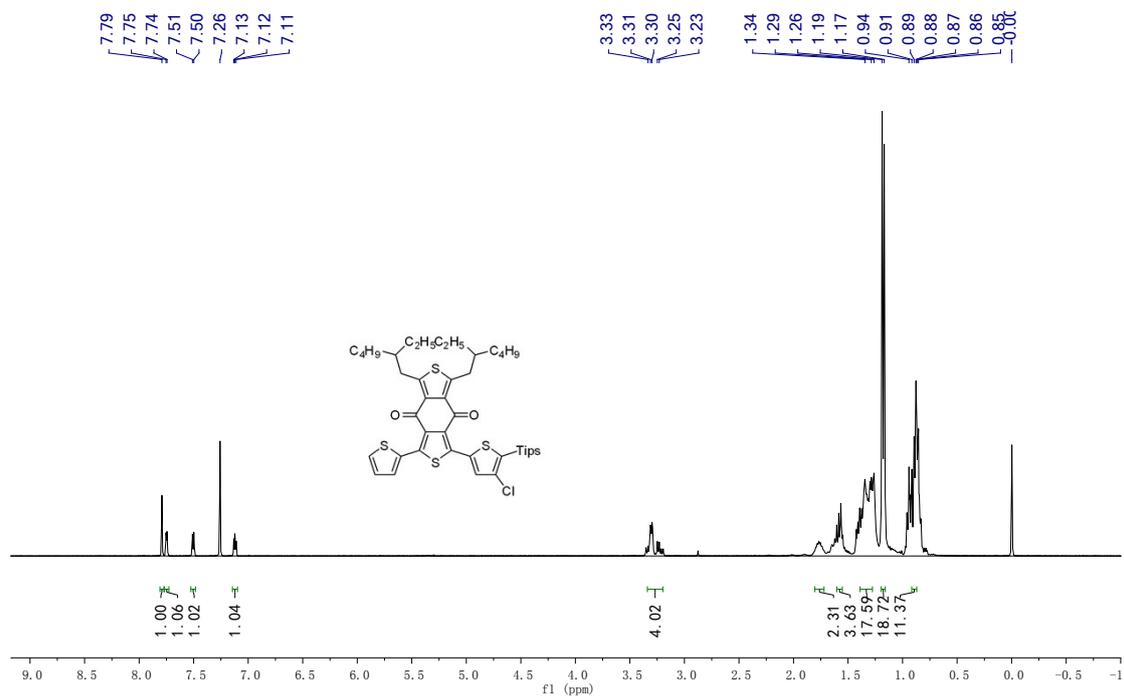


Figure S7. <sup>1</sup>H NMR spectrum of compound 4 in CDCl<sub>3</sub>.

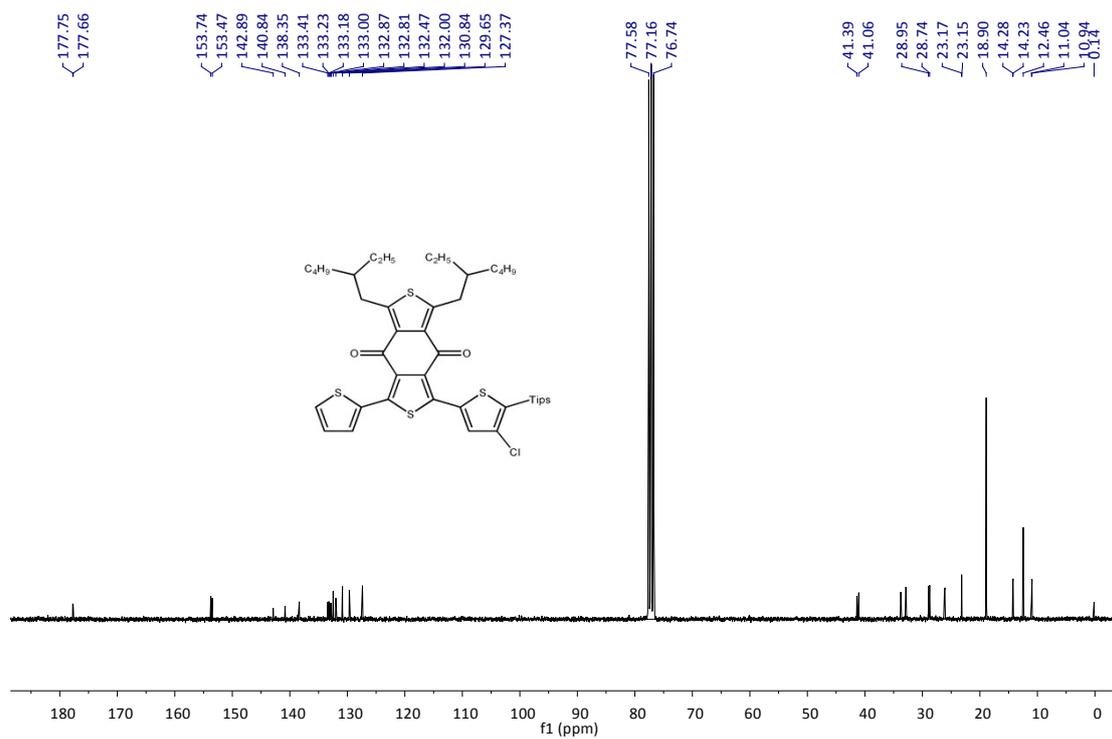


Figure S8. <sup>13</sup>C NMR spectrum of compound 4 in CDCl<sub>3</sub>.

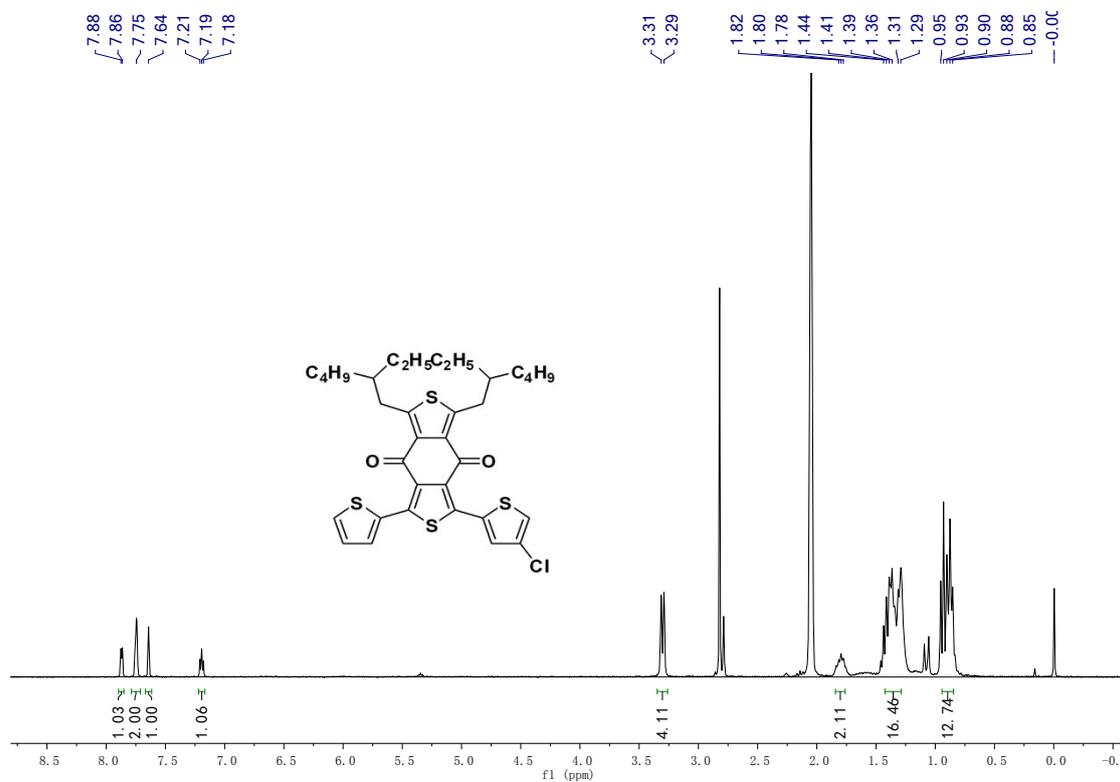
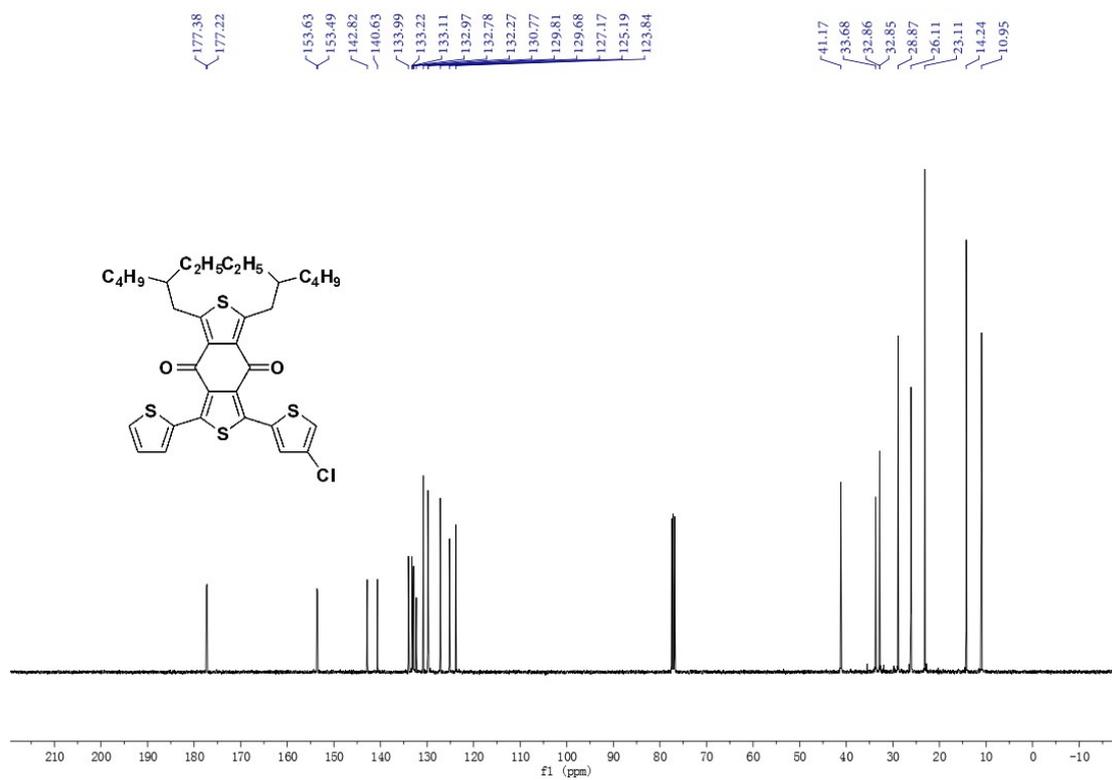
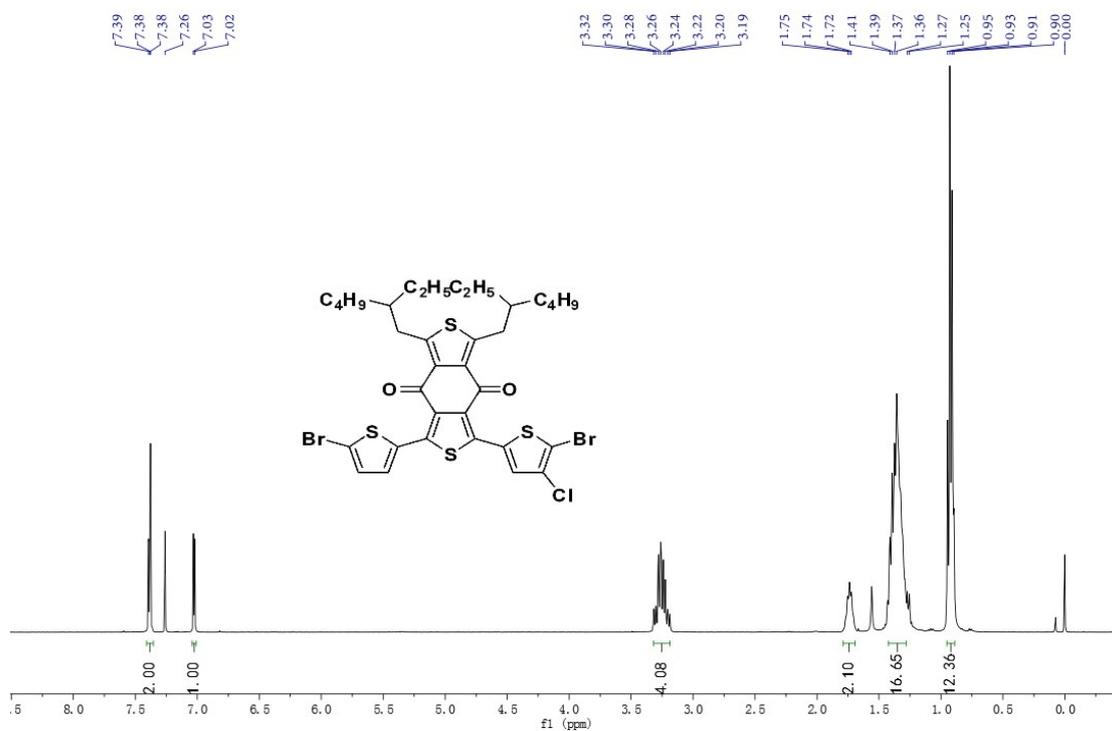


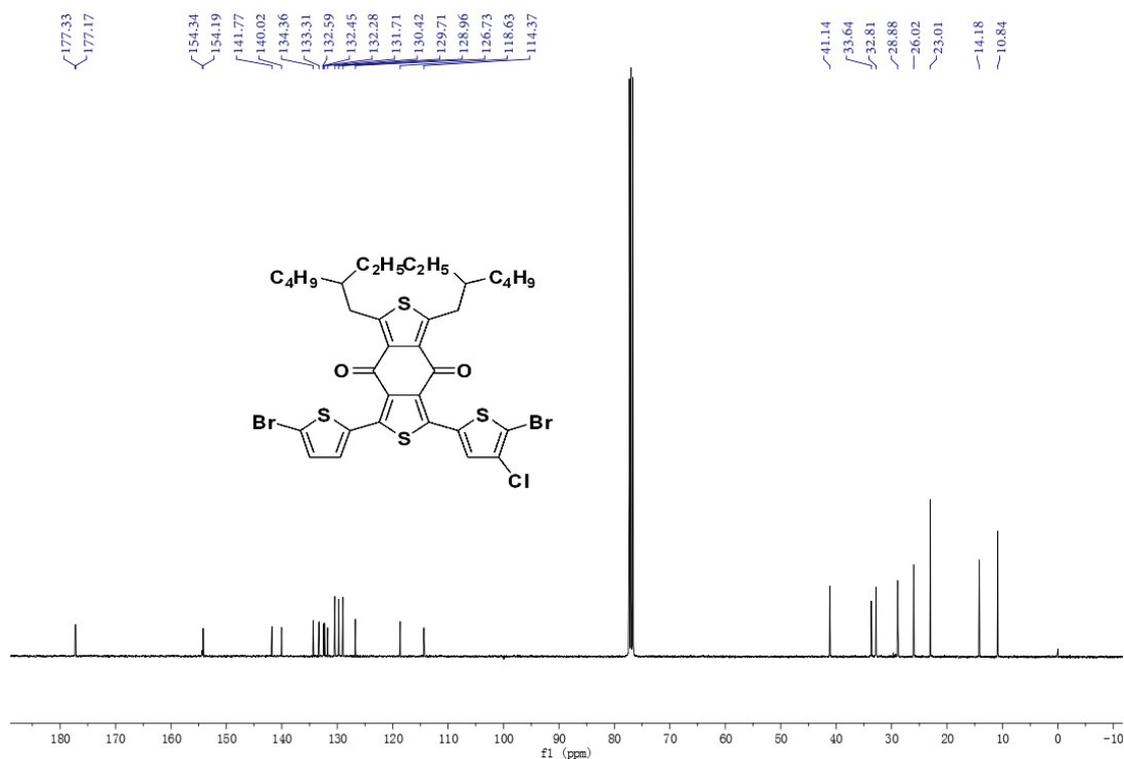
Figure S9. <sup>1</sup>H NMR spectrum of compound 5 in CD<sub>3</sub>COCD<sub>3</sub>.



**Figure S10.**  $^{13}\text{C}$  NMR spectrum of compound **5** in  $\text{CDCl}_3$ .



**Figure S11.**  $^1\text{H}$  NMR spectrum of compound **6** in  $\text{CDCl}_3$ .



**Figure S12.** <sup>13</sup>C NMR spectrum of compound **6** in CDCl<sub>3</sub>.

**Table S1.** Summary of photovoltaic parameters for the best PCE of the **PB2F-CI:IT-4F**-based PSCs with different D:A weight ratios (w/w) under simulated AM 1.5 G (100 mW cm<sup>-2</sup>) illumination.

D:A ratio	$V_{OC}$ (V)	$J_{SC}$ (mA cm <sup>-2</sup> )	$FF$ (%)	$PCE$ (%)
1.5:1	0.942	12.3	59.07	6.85
1:1	0.935	15.11	60.11	8.49
1:1.5	0.930	14.13	57.39	7.54

**PB2F-CI:IT-4F** were dissolved in chlorobenzene solution with a concentration of 10 mg mL<sup>-1</sup>. The solution was heated to 60 °C until total dissolution. The resulting solution was spin-coated onto PEDOT:PSS modified ITO in succession. The thickness (around 95 nm) of film was controlled the spin-coating speed at 1000-1500 r.m.p. Subsequently, the active layer was annealed at 100 °C for 10 min.

**Table S2.** Summary of photovoltaic parameters for the best PCE of the **PB2F-Cl:IT-4F**-based PSCs with different DIO ratio (v/v) under simulated AM 1.5 G (100 mW cm<sup>-2</sup>) illumination.

DIO ratio	$V_{OC}$ (V)	$J_{SC}$ (mA cm <sup>-2</sup> )	$FF$ (%)	$PCE$ (%)
0	0.935	15.11	60.11	8.49
0.5%	0.904	18.98	62.98	10.81
1%	0.884	15.52	63.05	8.65
2%	0.888	15.04	62.62	8.36

**PB2F-Cl:IT-4F** (1:1 w/w) were dissolved in chlorobenzene solution with a concentration of 10 mg mL<sup>-1</sup>. The solution was heated to 60 °C until total dissolution. The DIO was added into above solution. After 30 min, the resulting solution was spin-coated onto PEDOT:PSS modified ITO in succession. The thickness (around 90 nm) of film was controlled the spin-coating speed at 1000 r.m.p. Subsequently, the active layer was annealed at 100 °C for 10 min.

**Table S3.** Summary of photovoltaic parameters for the best PCE of the **PB2F-Cl:IT-4F**-based PSCs with different annealing temperature under simulated AM 1.5 G (100 mW cm<sup>-2</sup>) illumination.

Annealing temperature (°C)	$V_{OC}$ (V)	$J_{SC}$ (mA cm <sup>-2</sup> )	$FF$ (%)	$PCE$ (%)
80	0.901	17.55	57.57	9.10
100	0.904	18.98	62.98	10.81
120	0.884	18.06	56.52	9.02
140	0.875	18.69	51.84	8.48
160	0.839	16.37	47.99	6.59

**PB2F-Cl:IT-4** (1:1 w/w) were dissolved in chlorobenzene solution with a concentration of 10 mg mL<sup>-1</sup>. The solution was heated to 60 °C until total dissolution. The 0.5% DIO was added into above solution. After 30 min, the resulting solution was spin-coated onto PEDOT:PSS modified ITO in succession. The thickness (around 90 nm) of film was controlled the spin-coating speed at 1000 r.m.p. Subsequently, the active layer was annealed at 80-160 °C for 10 min.

**Table S4.** Summary of photovoltaic parameters for the best PCE of the **PB2F-2Cl:IT-4F**-based PSCs with different D:A weight ratios (w/w) and 0.5% DIO under simulated AM 1.5 G (100 mW cm<sup>-2</sup>) illumination.

D:A ratio	$V_{OC}$ (V)	$J_{SC}$ (mA cm <sup>-2</sup> )	$FF$ (%)	$PCE$ (%)
1.5:1	0.929	19.64	63.81	11.64
1:1	0.926	20.89	66.12	12.79
1:1.5	0.911	20.7	53.42	10.09

**PB2F-2Cl:IT-4F** were dissolved in chlorobenzene solution with a concentration of 11 mg mL<sup>-1</sup>. The solution was heated to 60 °C until total dissolution. The resulting solution was spin-coated onto PEDOT:PSS modified ITO in succession. The thickness (around 90 nm) of film was controlled the spin-coating speed at 1000-1500 r.m.p. Subsequently, the active layer was annealed at 100 °C for 10 min.

**Table S5.** Summary of photovoltaic parameters for the best PCE of the **PB2F-2Cl:IT-4F**-based PSCs with different DIO ratio (v/v) under simulated AM 1.5 G (100 mW cm<sup>-2</sup>) illumination.

DIO ratio	$V_{OC}$ (V)	$J_{SC}$ (mA cm <sup>-2</sup> )	$FF$ (%)	$PCE$ (%)
0	0.954	18.77	59.34	10.63
0.5%	0.926	20.89	66.12	12.79
1%	0.912	10.32	37.37	3.52
2%	0.929	6.85	35.63	2.27

**PB2F-2Cl:IT-4F** (1:1 w/w) were dissolved in chlorobenzene solution with a concentration of 11 mg mL<sup>-1</sup>. The solution was heated to 60 °C until total dissolution. The DIO was added into above solution. After 30 min, the resulting solution was spin-coated onto PEDOT:PSS modified ITO in succession. The thickness (around 90 nm) of film was controlled the spin-coating speed at 1000-1400 r.m.p. Subsequently, the active layer was annealed at 100 °C for 10 min.

**Table S6.** Summary of photovoltaic parameters for the best PCE of the **PB2F-2Cl:IT-4F**-based PSCs with different annealing temperature under simulated AM 1.5 G (100 mW cm<sup>-2</sup>) illumination.

Annealing temperature (°C)	$V_{OC}$ (V)	$J_{SC}$ (mA cm <sup>-2</sup> )	$FF$ (%)	$PCE$ (%)
80	0.930	20.65	58.67	11.27
100	0.926	20.89	66.12	12.79
120	0.920	20.73	61.49	11.73
140	0.914	20.55	56.27	10.57
160	0.894	20.64	53.82	9.93

**PB2F-2Cl :IT-4F** (1:1 w/w) were dissolved in chlorobenzene solution with a concentration of 11 mg mL<sup>-1</sup>. The solution was heated to 60 °C until total dissolution. The 0.5% DIO was added into above solution. After 30 min, the resulting solution was spin-coated onto PEDOT:PSS modified ITO in succession. The thickness (around 90 nm) of film was controlled the spin-coating speed at 1100 r.m.p. Subsequently, the active layer was annealed at 80-160 °C for 10 min.

**Table S7.** Hole and electron mobilities for blended films.

Materials	Hole mobilities (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	Electron mobilities (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	Hole/Electron
<b>PB2F-Cl:IT-4F</b>	5.35×10 <sup>-6</sup>	3.07×10 <sup>-5</sup>	5.73
<b>PB2F-2Cl:IT-4F</b>	1.45×10 <sup>-5</sup>	1.19×10 <sup>-5</sup>	0.80

