

## Supporting Information (SI)

# **Synergy of Backbone and Endgroup engineering for Efficient Non-Fused-Ring Asymmetric Electron Acceptors based Organic Solar Cells**

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### 3. References

#### 1. Experimental Section

##### Measurement and characterization

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were taken on a Bruker AV 400 Spectrometer. Mass spectra were measured on a Bruker Daltonics BIFLEX III matrix assisted laser desorption /ionization time-of-flight (MALDI-TOF) analyzer. Thermogravimetric

analyses (TGA) were carried out on a Perkin-Elmer Diamond TG thermal analyzer at a scan rate of 10 °C/min under nitrogen atmosphere. UV-vis absorption spectra were obtained with a JASCO V-570 spectrophotometer. Cyclic voltammetry (CV) experiments were performed with a LK98B II microcomputer based electrochemical analyzer in dichloromethane solutions. All CV measurements were carried out at room temperature with a conventional three-electrode configuration employing a Pt disk, a Pt plate and an Ag/AgCl electrode as working electrode, counter electrode and reference electrode, respectively. Dichloromethane was distilled from calcium hydride under dry argon immediately prior to use. Tetrabutylammonium phosphorus hexafluoride ( $\text{Bu}_4\text{NPF}_6$ , 0.1 M) in dichloromethane was used as the supporting electrolyte, and the scan rate was 100  $\text{mVs}^{-1}$ . For calibration, the redox potential of ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) was measured under the same conditions. Atomic force microscopy (AFM) was performed using multimode 8 atomic force microscope in tapping mode.

## **Device fabrication**

The OSCs were fabricated with the following structure: ITO/PEDOT:PSS/ active layer/PDIN/Ag. ITO substrates were cleaned with isopropyl alcohol, detergent water, deionized water, acetone and c in an ultrasonic bath sequentially for 15 min, and then dried in an oven at 80 °C for 12 h. The PEDOT:PSS was spin-coated at 4800 rpm onto the ITO surface and thermal annealed (150 °C) for 15 min in air, and the thickness of PEDOT:PSS films are all about 25 nm. Then the PEDOT:PSS-coated substrates were transferred into a nitrogen-filled glove box. The weight ratio of PM6:DTS26-IT-4F and PM6:DTS26-IT-4Cl is 1:1 with a total blend concentration of 2  $\text{mg mL}^{-1}$  in chloroform solutions, and the active layer was prepared by spin-coating the blend solution at 2000 rpm and the corresponding film thickness is 90 nm. Then methanol solution of PDIN at a concentration of 2.0  $\text{mg mL}^{-1}$  was deposited atop the active layer at 3000 rpm for 30 s to afford a PDIN cathode buffer layer with thickness of about 5 nm. Then evaporated 100 nm Ag on the devices with a shadow mask under the pressure of ca.  $10^{-4}$  Pa successively. The  $J$ - $V$  characteristics of the devices under

illumination of AM 1.5 G solar simulator (Newport, 100 mW cm<sup>-2</sup>) were measured on a Keithley 2400 Source Measure Unit. The EQE of OSCs were analyzed using a certified newport incident photon conversion efficiency (IPCE) measurement system (Model 66902). The hole mobilities of blend films were investigated by employing the hole-only devices with a structure of ITO/PEDOT:PSS/BHJ/MoO<sub>3</sub>/Ag. The electron mobilities of blend films were performed in the electron-only devices with a structure of ITO/ZnO/BHJ/ PDIN/Ag.

## 1. Synthesis

The synthetic routes to DTS26-IT-4F and DTS26-IT-4Cl were presented in Scheme S1, compound **1** were synthesized by following the literature method.<sup>[1]</sup> The detailed synthetic procedures as follows:

**Synthesis of compound 2:** To a solution of compound **1** (400 mg, 0.85 mmol) in dichloromethane (DCM) (20 mL), BBr<sub>3</sub> (0.64 mL, 1.28 mmol) was dropwise added at 0 °C in a 250 mL round-bottom flask. The mixture was stirred at room temperature for 3 h and the reaction was quenched with ice water. The resulting mixture was extracted by DCM, the combined organic phase was dried over anhydrous MgSO<sub>4</sub>. And compound **2** was obtained as yellow liquid (255 mg) in a yield of 65%. <sup>1</sup>H NMR (400 MHz, chloroform-d) δ 9.89 (s, 1H), 7.62 (s, 1H), 7.40 (s, 1H), 7.25 (s, 1H), 6.14 (s, 1H), 1.87 (d, *J* = 41.0 Hz, 4H), 1.11 (s, 12H), 0.79 (d, *J* = 7.1 Hz, 10H).

**Synthesis of compound 3:** A solution of compound **2** (255 mg, 0.55 mmol), potassium carbonate (152 mg, 1.1 mmol), potassium iodide (91 mg, 0.55 mmol) and 1-bromo-iso-octane (317 mg, 1.65 mmol) in dry N, N-dimethylformamide (DMF) (50 mL) was stirred at 80 °C for 12 h under nitrogen atmosphere in a 250 mL round-bottom flask. The reaction mixture was then cooled to room temperature, the resulting mixture was extracted by CH<sub>2</sub>Cl<sub>2</sub>, the combined organic phase was dried over anhydrous MgSO<sub>4</sub>. Then through a vacuum distillation to remove off the volatile components, the resulting mixture was purified by column chromatography on silica gel using a mixture of petroleum ether (PE) and DCM as an eluent (PE: DCM = 1.5:1, v/v). And compound **3** was obtained as brown oil (234 mg) in a yield of 74%. <sup>1</sup>H

NMR (400 MHz, chloroform-*d*)  $\delta$  9.90 (s, 1H), 7.60 (s, 1H), 7.46 (s, 1H), 7.04 (s, 1H), 3.98 (d,  $J = 5.5$  Hz, 2H), 1.96 – 1.92 (m, 2H), 1.82 (d,  $J = 6.7$  Hz, 3H), 1.54 (d,  $J = 7.2$  Hz, 4H), 1.36 (d,  $J = 3.6$  Hz, 4H), 1.10 (s, 16H), 0.98 (s, 3H), 0.93 (s, 3H), 0.80 (s, 6H).

#### Synthesis of compound 5:

To a solution of dry THF (100 mL) and compound **4** (440 mg, 1.05 mmol), *n*-BuLi (0.79 mL, 1.58 mmol) was added dropwise over the period of 5 min at -78 °C under nitrogen atmosphere. The mixture was stirred at -78 °C for 120 min and DMF (153 mg, 2.1 mmol) was added into the flask in one portion. The reaction was then stirred for 12 h at room temperature, and then was quenched by 50 mL water and was extracted by CH<sub>2</sub>Cl<sub>2</sub>, the combined organic phase was dried over anhydrous MgSO<sub>4</sub>. Then through a vacuum distillation to remove off the volatile components, the resulting mixture was purified by column chromatography on silica gel using a mixture of PE and DCM as an eluent (PE: DCM = 3:1, v/v). And compound **5** was obtained as a yellow oil (234 mg, yield: 52%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  9.87 (s, 1H), 7.70 (s, 1H), 7.40 (d,  $J = 4.7$  Hz, 1H), 7.11 (d,  $J = 4.7$  Hz, 1H), 1.38 (d,  $J = 5.7$  Hz, 2H), 1.25 – 1.13 (m, 17H), 0.98 (dd,  $J = 6.7, 3.6$  Hz, 4H), 0.82 (s, 4H), 0.76 (t,  $J = 7.4$  Hz, 8H).

#### Synthesis of compound 6:

A solution of compound **3** (234 mg, 0.41 mmol), compound **5** (165 mg, 0.37 mmol), Cs<sub>2</sub>CO<sub>3</sub> (362 mg, 1.11 mmol), and trimethylacetic acid (38 mg, 0.37 mmol). Pd<sub>2</sub>(dba)<sub>3</sub> (17 mg, 0.019 mmol) and P(*o*-CH<sub>3</sub>OPh)<sub>3</sub> (13 mg, 0.037 mmol) in dry toluene (50 mL) was stirred at 110 °C for 3 h under nitrogen atmosphere in a 250 mL round-bottom flask. Then through a vacuum distillation to remove off the volatile components, the resulting mixture was purified by column chromatography on silica gel using a mixture of PE and DCM as an eluent (PE: DCM=3:1, v/v). And compound **5** was obtained as yellow oil (300 mg) in a yield of 86.5%. <sup>1</sup>H NMR (400 MHz, chloroform-*d*)  $\delta$  9.89 (d,  $J = 13.2$  Hz, 2H), 7.71 (s, 1H), 7.63 (s, 1H), 7.59 (s, 2H),

7.15 (s, 1H), 4.10 (d,  $J = 5.5$  Hz, 2H), 1.98 (d,  $J = 32.4$  Hz, 6H), 1.39 (s, 5H), 1.21 (dd,  $J = 53.1, 19.2$  Hz, 38H), 1.01 (s, 5H), 0.94 (s, 2H), 0.80 (d,  $J = 6.3$  Hz, 22H).

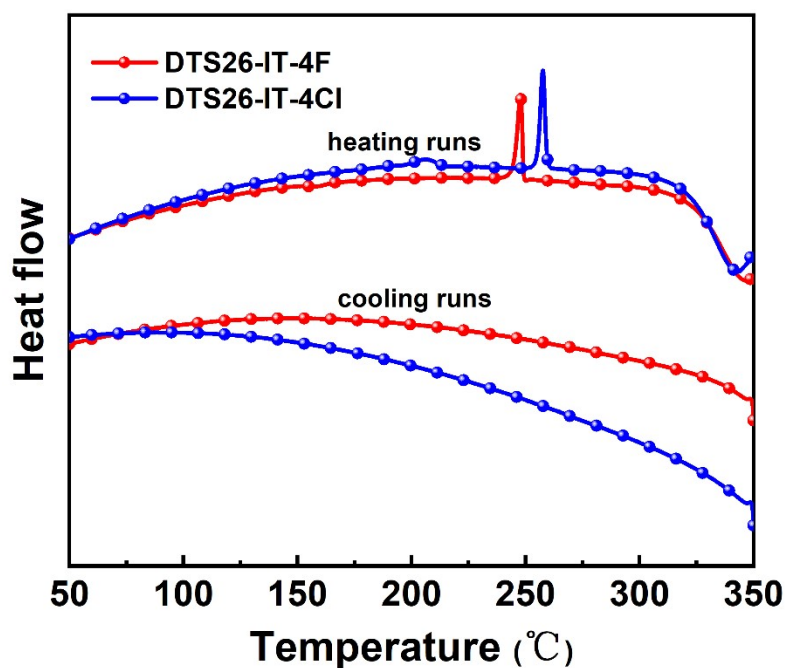
#### Synthesis of compound 7a:

To a solution of compound **6** (150 mg, 0.16 mmol), 2-(5, 6-difluoro-3-oxo-2, 3-dihydro-1H-inden-1-ylidene) malononitrile (147 mg, 0.64 mmol) and dry chloroform (15 mL) was stirred in a two-neck round-bottom flask under the protection of argon. Then, 0.5 mL of pyridine was added slowly. The reaction was stirred for 5 hours at 65°C. The reaction mixture was then cooled to room temperature, the solvent was removed by rotary evaporation. Then, the resulting product was recrystallized from CHCl<sub>3</sub> and Methanol to give DTS26-IT-4F as a blue solid (177 mg) in a yield of 81%. <sup>1</sup>H NMR (400 MHz, chloroform-*d*)  $\delta$  8.98 (s, 1H), 8.93 (s, 1H), 8.55 (d,  $J=6.5$  Hz, 2H), 7.83 (s, 1H), 7.73 – 7.63 (m, 5H), 7.31 (s, 1H), 4.14 (d,  $J=6.0$  Hz, 2H), 2.04 (s, 3H), 1.92 (s, 2H), 1.65 (d,  $J=9.4$  Hz, 2H), 1.43 (s, 6H), 1.35 – 1.29 (m, 2H), 1.28 – 0.94 (m, 38H), 0.81 (dd,  $J=12.5, 5.3$  Hz, 23H).

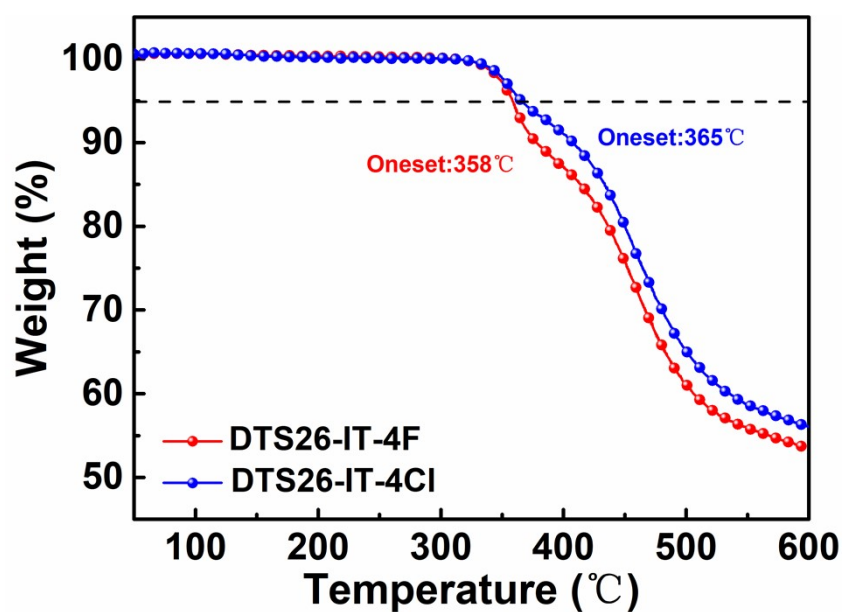
#### Synthesis of compound 7b:

To a solution of compound **6** (150 mg, 0.16 mmol), 2-(5, 6-dichloro-3-oxo-2, 3-dihydro-1H-inden-1-ylidene) malononitrile (168 mg, 0.64 mmol) and dry chloroform (15 mL) was stirred in a two-neck round-bottom flask under the protection of argon. Then, 0.5 mL of pyridine was added slowly. The reaction was stirred for 5 h at 65°C. The reaction mixture was then cooled to room temperature, the solvent was removed by rotary evaporation. Then, the resulting product was recrystallized from CHCl<sub>3</sub> and methanol to give DTS26-IT-4Cl as a blue solid in a yield of 80%(183 mg). <sup>1</sup>H NMR (400 MHz, chloroform-*d*)  $\delta$  9.00 (s, 1H), 8.94 (s, 1H), 8.78 (d,  $J = 11.8$  Hz, 2H), 7.94 (d,  $J = 7.9$  Hz, 2H), 7.84 (s, 1H), 7.72 (s, 2H), 7.64 (s, 1H), 7.32 (s, 1H), 4.14 (d,  $J = 5.9$  Hz, 2H), 2.04 (s, 3H), 1.93 (s, 2H), 1.66 (s, 2H), 1.44 (s, 6H), 1.23 – 0.96 (m, 39H), 0.87 – 0.76 (m, 24H).

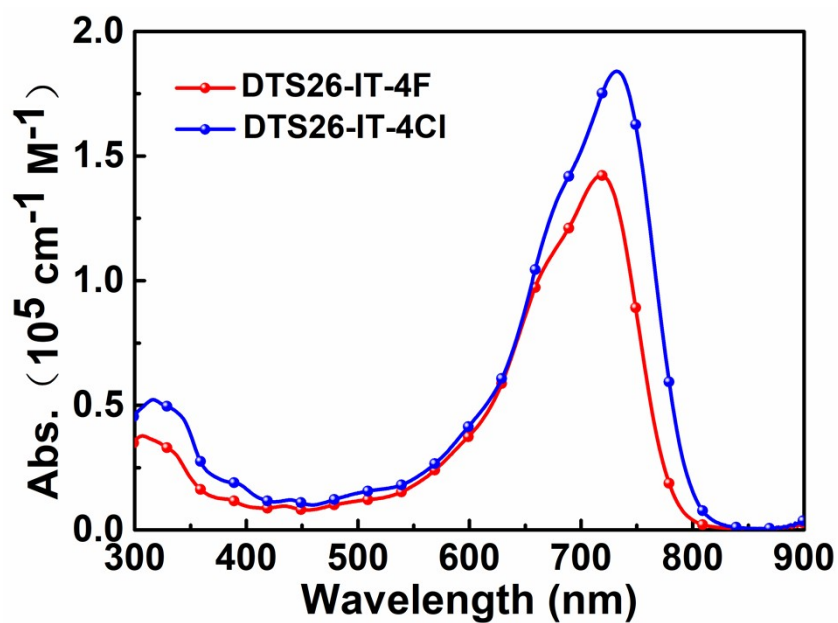
## 2. Supplementary Figures S1-16 and Table S1-S4



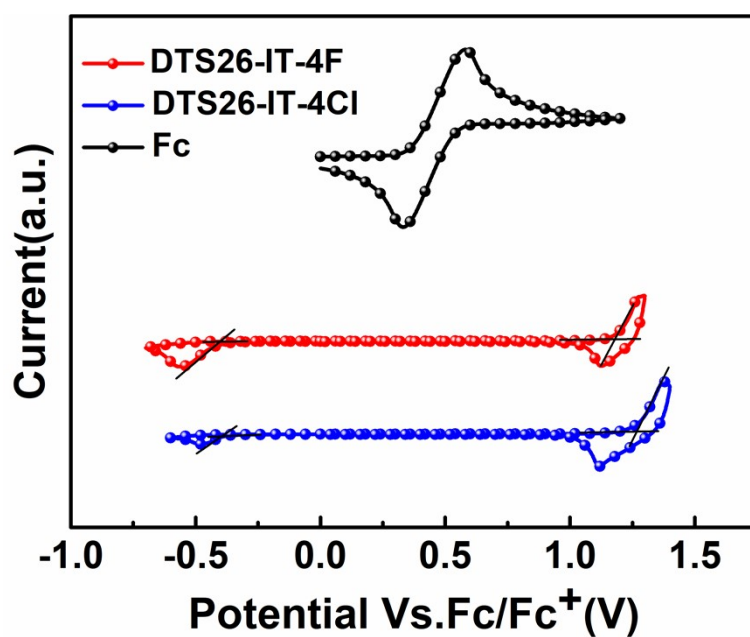
**Figure S1.** The DSC curves of DTS26-IT-4F and DTS26-IT-4Cl at a scan rate of 10 °C min<sup>-1</sup> under nitrogen.



**Figure S2.** The TGA curves of DTS26-IT-4F and DTS26-IT-4Cl at a scan rate of 10 °C min<sup>-1</sup> under nitrogen.

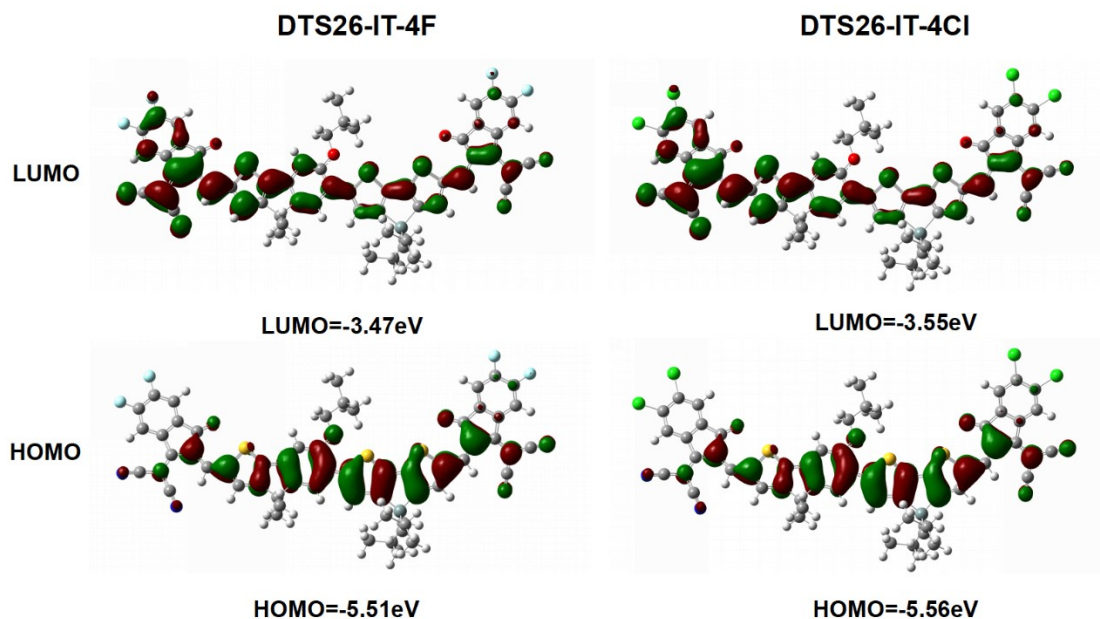


**Figure S3** The absorption spectra with molar absorption coefficients of DTS26-IT-4F and DTS26-IT-4Cl in CF solution.

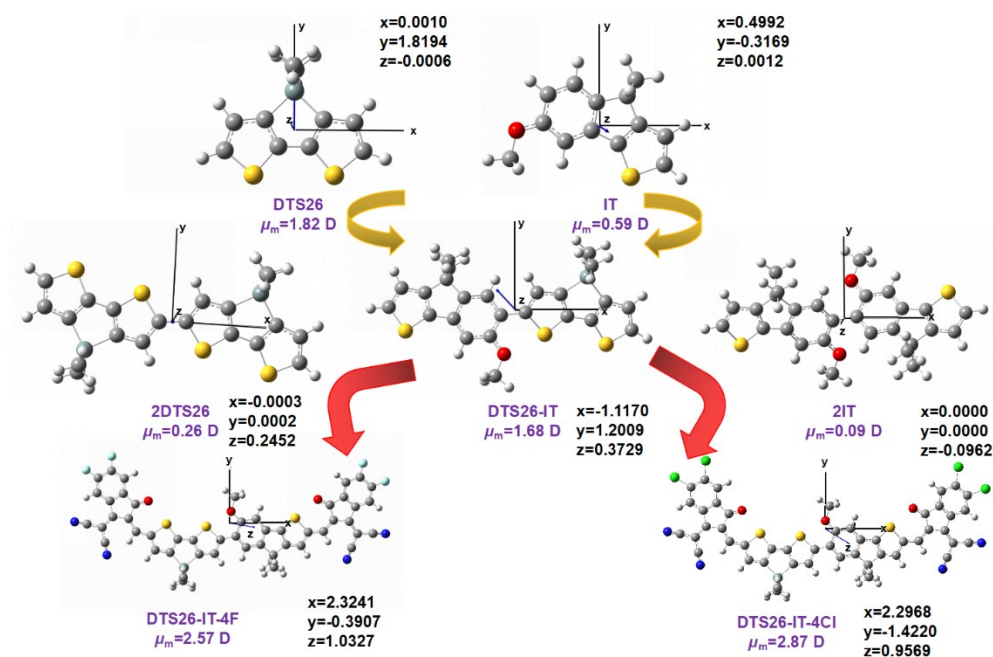


**Figure S4** Cyclic voltammogram curves of DTS26-IT-4F and DTS26-IT-4Cl.

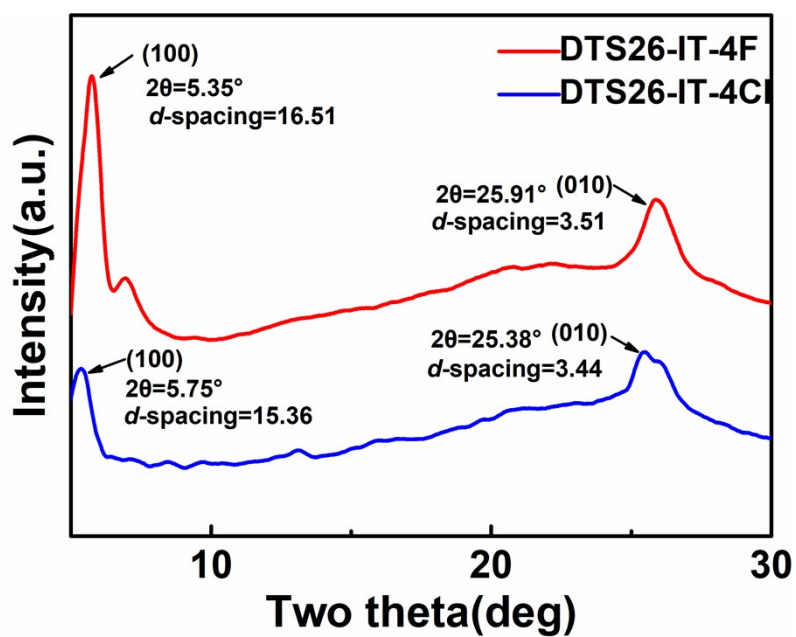




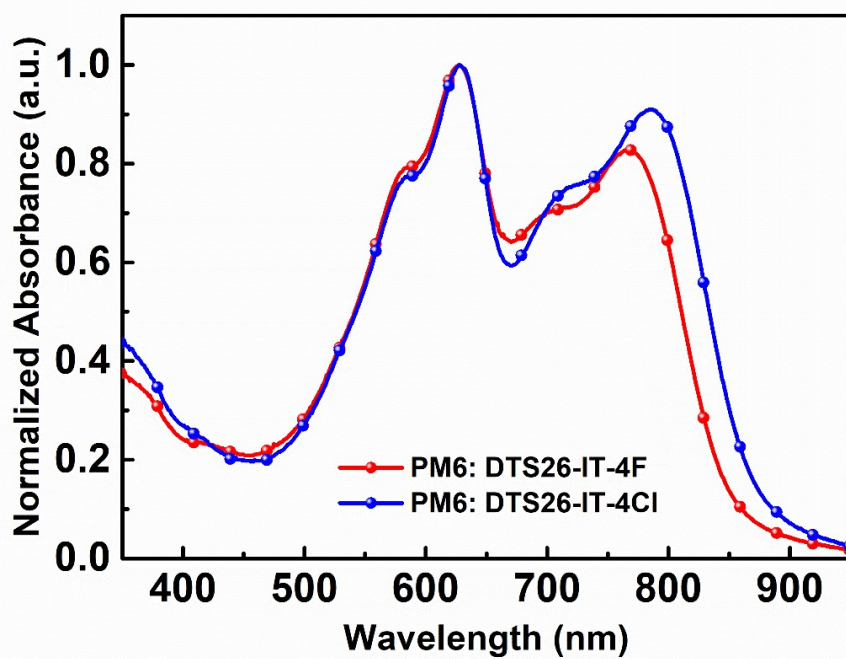
**Figure S5.** HOMO and LUMO electron-distributions and their energy levels of DTS26-IT-4F and DTS26-IT-4Cl calculated by DFT at the B3LYP/6-31G(d, p) level.



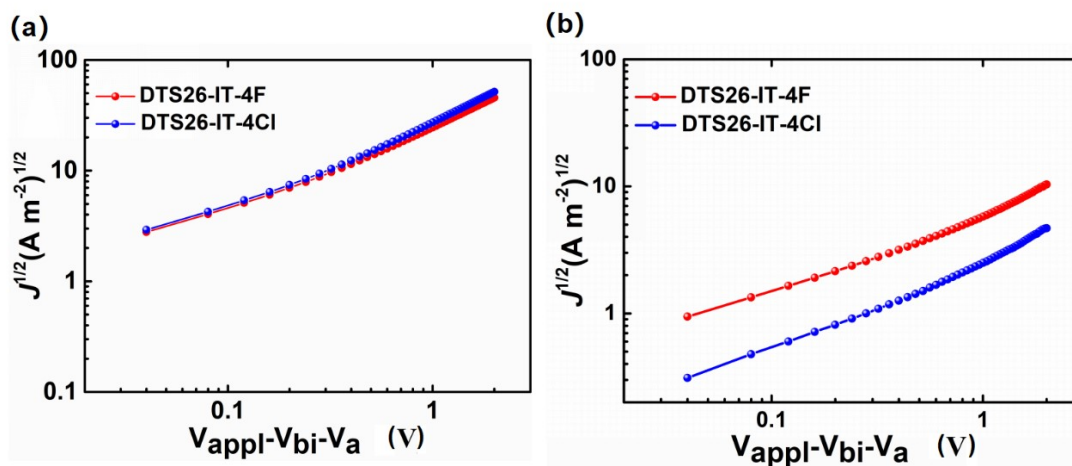
**Figure S6.** The natural dipole moment and of DTS26, IT, 2DTS26, DTS26-IT, 2IT, DTS26-IT-4F and DTS26-IT-4Cl and their vector addition ( $\mu_m$ ) calculated by DFT.



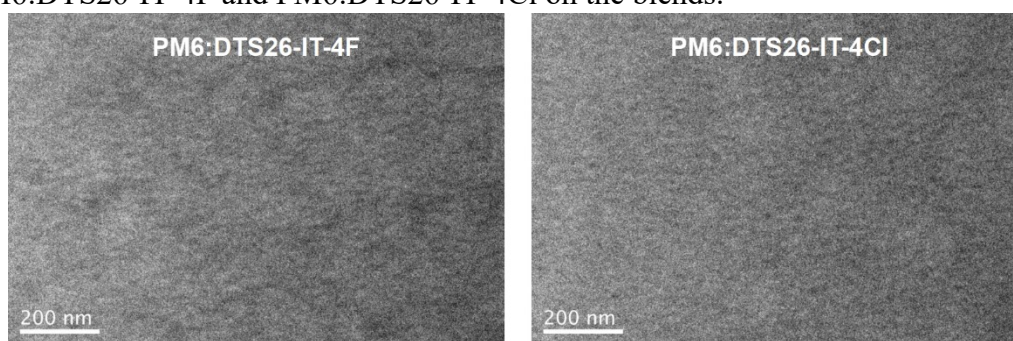
**Figure S7.** The XRD patterns for the DTS26-IT-4F and DTS26-IT-4Cl pure solid powders.



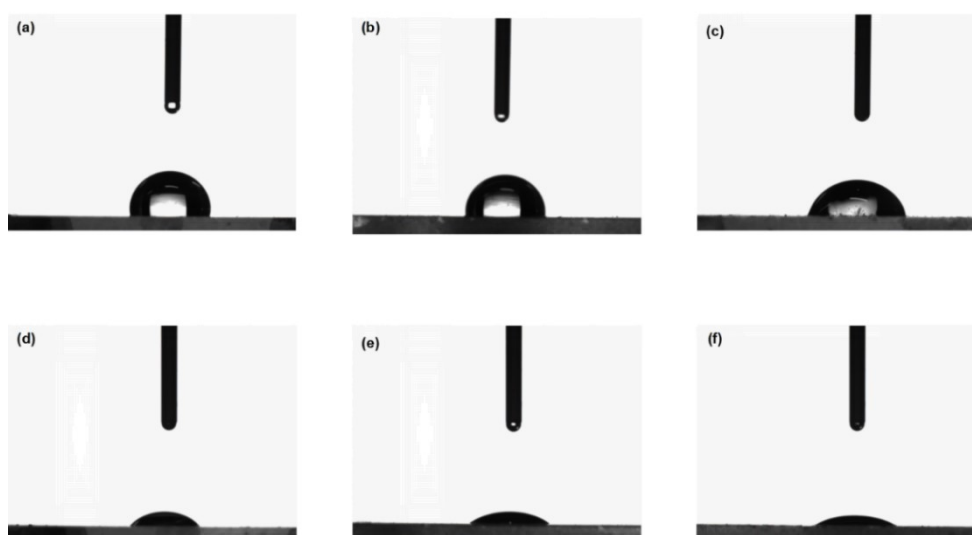
**Figure S8.** The absorption spectra of blend films based on PM6:DTS26-IT-4F and PM6:DTS26-IT-4Cl.



**Figure S9.** (a)  $J^{1/2}$ - $V$  plots of the electron-only devices based on the PM6: DTS26-IT-4F and PM6:DTS26-IT-4Cl. (b)  $J^{1/2}$ - $V$  plots of the hole-only devices based on PM6:DTS26-IT-4F and PM6:DTS26-IT-4Cl on the blends.



**Figure S10.** TEM images of the blend films for PM6:DTS26-IT-4F and PM6:DTS26-IT-4Cl.



**Figure S11.** Views of contact angles of (a) PM6 film, (b) DTS26-IT-4F film, (c) DTS26-IT-4Cl film with deionized water as the wetting liquid; (d) PM6 film, (e) DTS26-IT-4F film and (f) DTS26-IT-4Cl with diiodomethane as the wetting liquid.

**Table S1.** Detailed photovoltaic parameters of the **PM6:DTS26-IT-4F**-based devices processed by varied conditions.

<b>D: A</b>	<b>CN</b>	<b>rate</b>	<b><math>V_{oc}</math> (V)</b>	<b><math>J_{sc}</math> (<math>\text{mA cm}^{-2}</math>)</b>	<b>FF (%)</b>	<b>PCE (%)</b>
1:1	/	1750	0.901	16.23	61.06	8.93
1:1	/	2000	0.905	16.53	61.41	9.18
1:1	/	2250	0.906	15.53	62.94	8.85
1:0.8	/	2000	0.908	16.13	60.15	8.81
1:1	/	2000	0.905	16.53	61.41	9.18
1:1.2	/	2000	0.888	15.84	61.67	8.68
1:1	0.25%CN	2000	0.915	15.36	66.54	9.35
1:1	0.50%CN	2000	0.908	17.99	64.90	10.61
1:1	0.75%CN	2000	0.808	17.23	65.96	10.33

**Table S2.** Detailed photovoltaic parameters of the **PM6:DTS26-IT-4CI**-based devices processed by varied conditions.

<b>D: A</b>	<b>CN</b>	<b>rate</b>	<b><math>V_{oc}</math> (V)</b>	<b><math>J_{sc}</math> (<math>\text{mA cm}^{-2}</math>)</b>	<b>FF (%)</b>	<b>PCE (%)</b>
1:1	/	1750	0.887	17.44	64.20	9.99
1:1	/	2000	0.889	17.82	64.91	10.29
1:1	/	2250	0.889	16.92	64.70	10.20
1:0.8	/	2000	0.884	17.28	65.28	9.97
1:1	/	2000	0.889	17.82	64.91	10.29
1:1.2	/	2000	0.886	17.03	66.56	10.04
1:1	0.25%CN	2000	0.883	17.94	66.84	10.58
1:1	0.50%CN	2000	0.878	19.00	65.95	11.00
1:1	0.75%CN	2000	0.875	18.04	67.53	10.66

**Table S3.** Contact angles and surface energy values of pure films.

Film	Contact angle		Surface energy (mN m <sup>-1</sup> )
	$\Theta_{\text{water}}$ (°)	$\Theta_{\text{oil}}$ (°)	
PM6	99.49	48.5	35.99
DTS26-IT-4F	94.49	34.0	43.5
DTS26-IT-4Cl	82.00	27.5	42.91

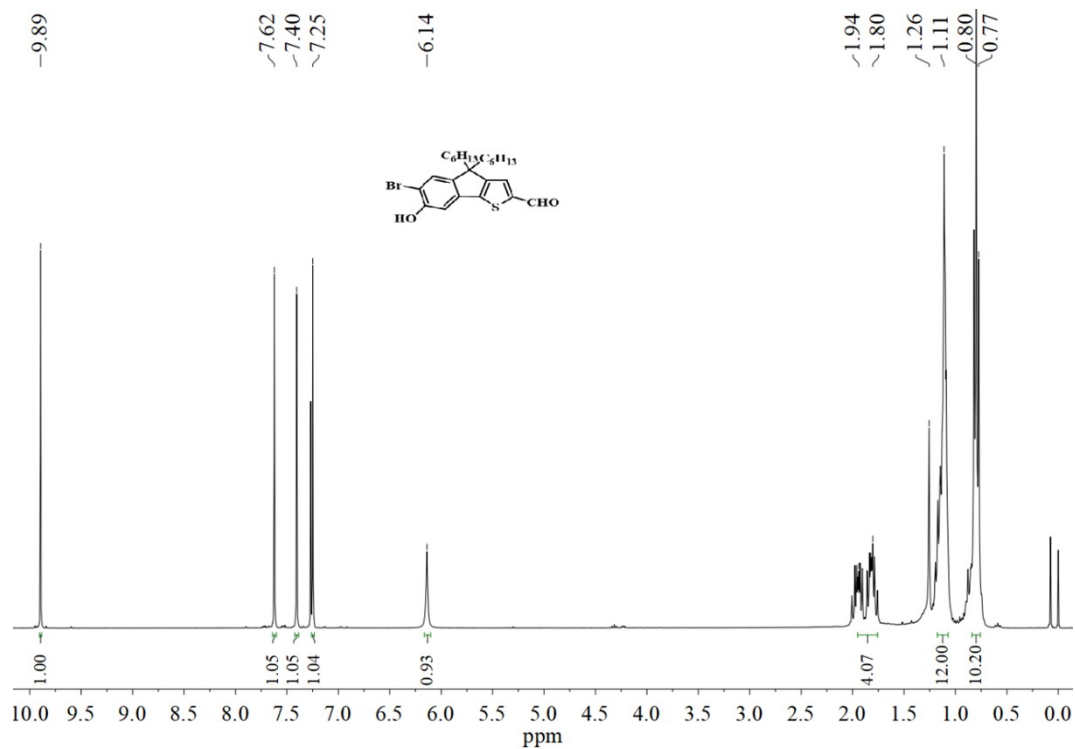


Figure S12. <sup>1</sup>H-NMR spectrum of compound 2.

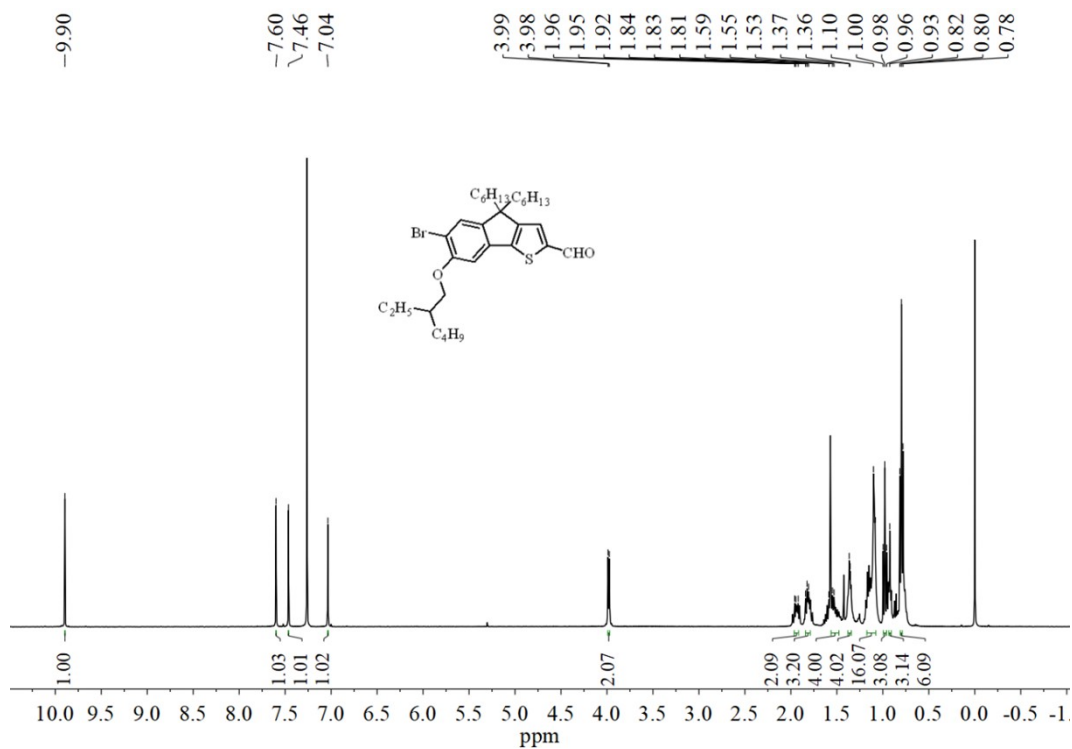


Figure S13. <sup>1</sup>H-NMR spectrum of compound 3.

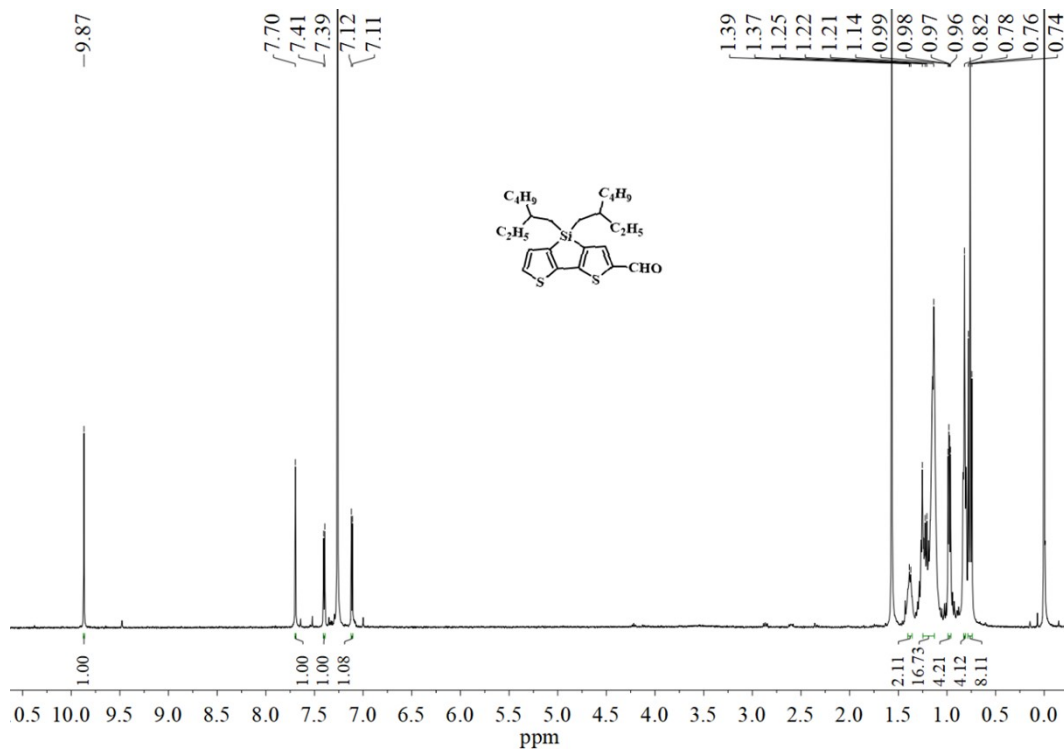


Figure S14.  $^1\text{H}$ -NMR spectrum of compound 5.

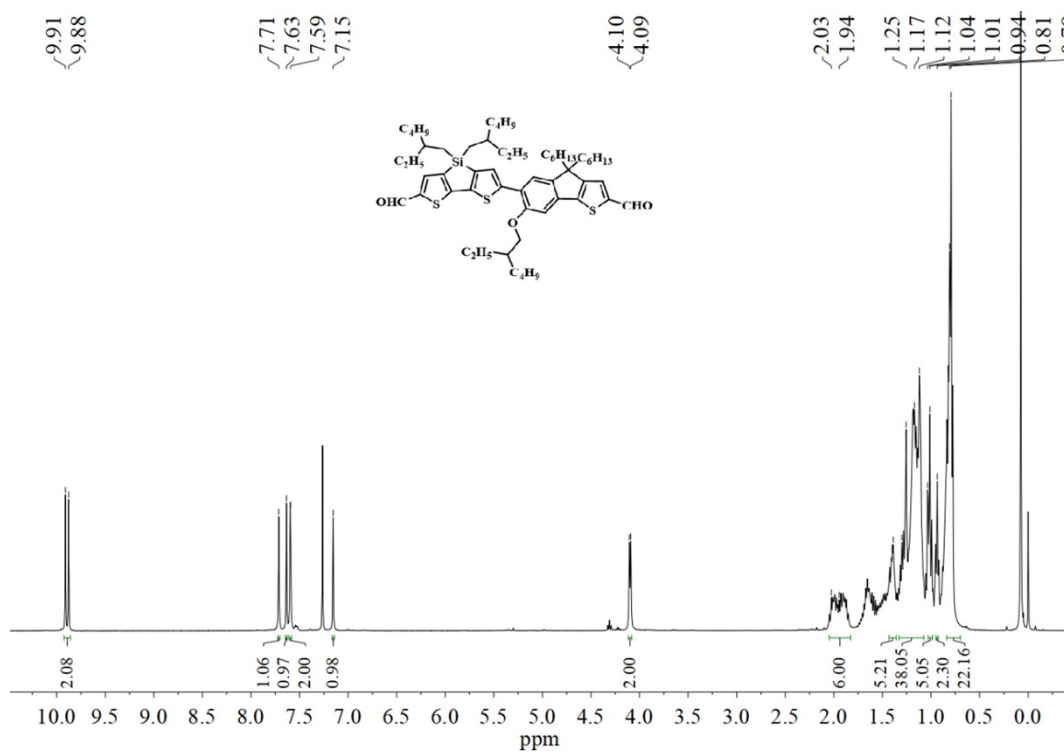


Figure S15.  $^1\text{H}$ -NMR spectrum of compound 6.



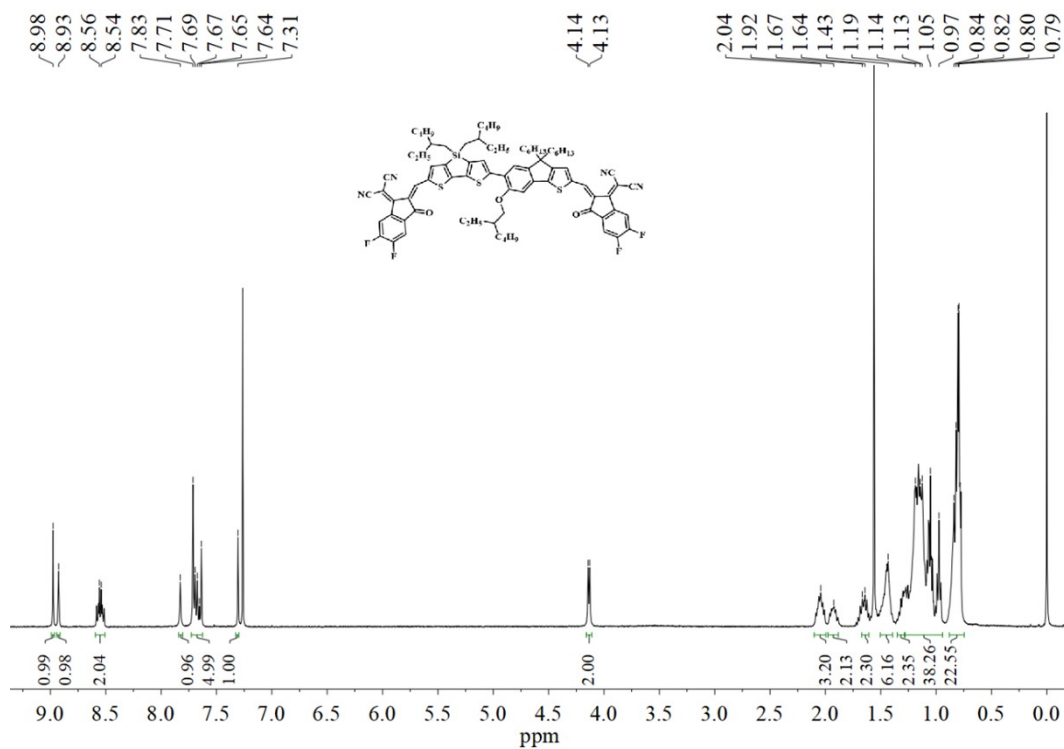


Figure S16. <sup>1</sup>H-NMR spectrum of compound 7a.

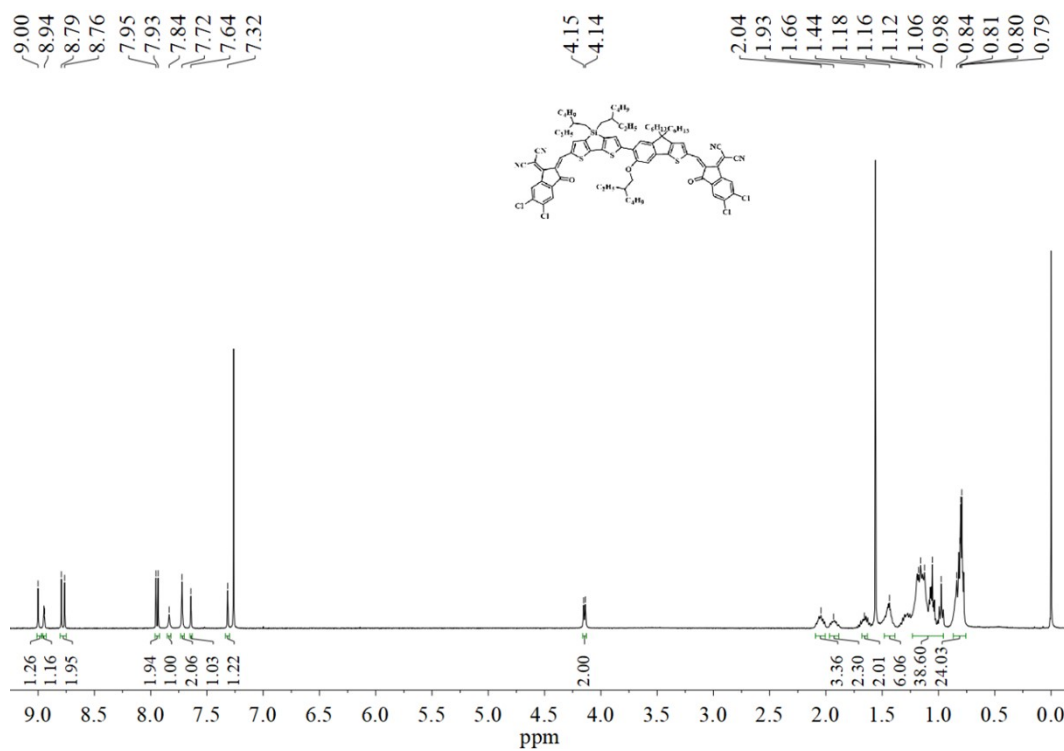
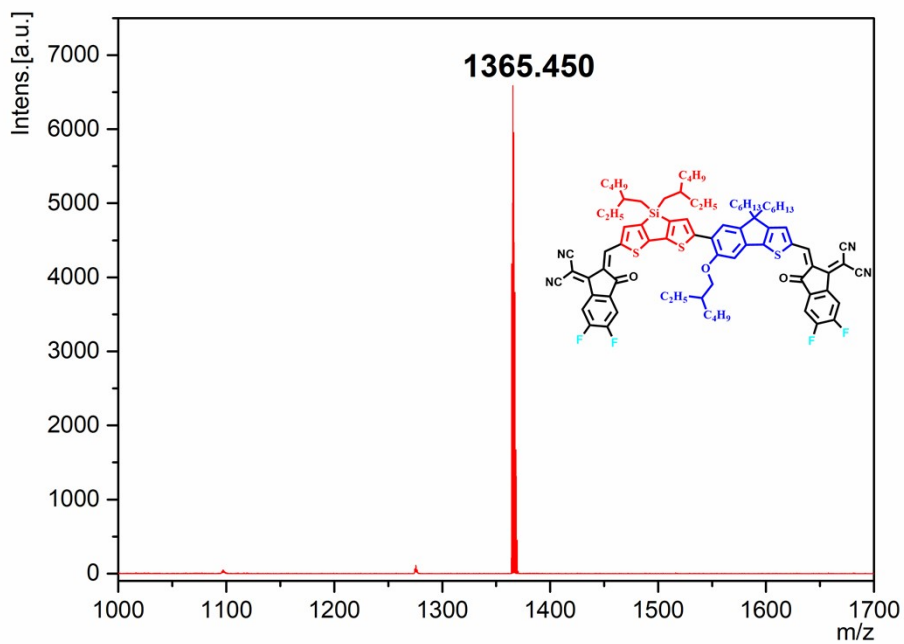
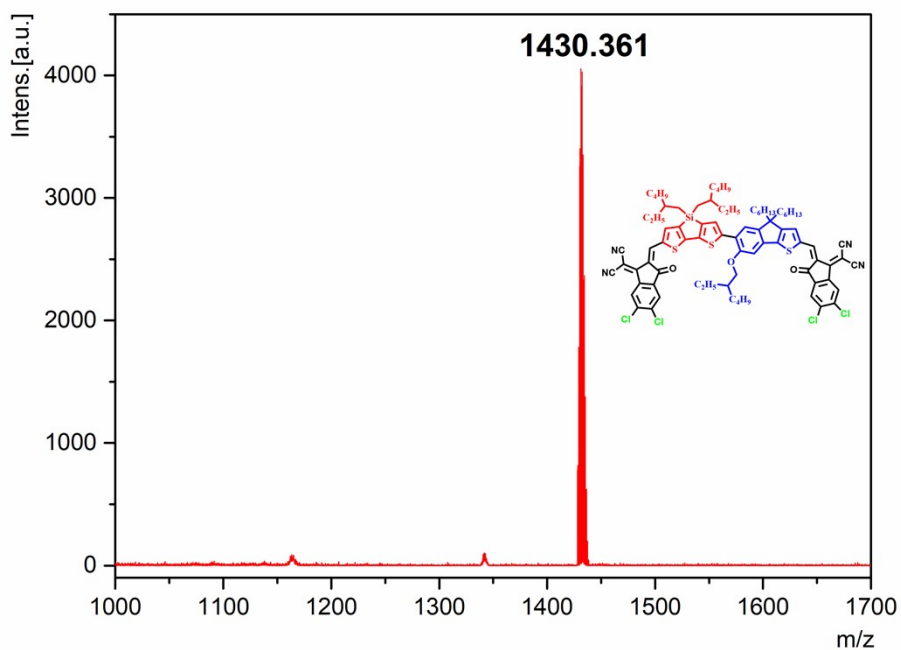


Figure S17. <sup>1</sup>H-NMR spectrum of compound 7b.





**Figure S18.** MS spectrum of DTS26-IT-4F.



**Figure S19.** MS spectrum of DTS26-IT-4Cl.

#### 4. References

- [1]. M. Wang, D. Cai, Z. Yin, S.-C. Chen, C.-F. Du, Q. Zheng, Asymmetric indeno-thiophene based copolymers for bulk heterojunction solar cells with 9.14% efficiency, *Adv. Mater.*, 2016, **28**, 3359-3365.