

## Supporting Information

### Contents

1. Materials and measurements
2. Synthesis
3. TGA and CV
4. DFT calculations
5. Solar cells performance
6. NMR and HR-MALDI of the compounds

## 1. Materials and measurements

The synthetic procedures were performed under argon atmosphere. Commercial chemicals (from sigma-Aldrich, JK Chemical and TCI) were used as received.  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra of intermedia products and monomers were recorded at 400 MHz and 600MHz on a Bruker AVANCE spectrometer with TMS as the internal standard. Cyclic voltammetry was performed under an inert atmosphere at a scan rate of  $0.1 \text{ V s}^{-1}$  and 1 M tetrabutylammonium hexafluorophosphate in acetonitrile as the electrolyte, a glassy-carbon working electrode coated with samples, a platinum-wire auxiliary electrode, and an Ag/AgCl as a reference electrode. Thermogravimetric analysis data were obtained from a TGA8000 Thermogravimetric Analyzer (PerkinElmer).

OSCs use conventional device configuration as ITO/PEDOT: PSS/active layer/PFN-Br/Ag. Photovoltaic devices were made by spin-coating the PEDOT: PSS aqueous solution through a 0.45mm filter, at 6000 rpm for 40 s onto pre-cleaned, patterned ITO substrates and then heat the ITO substrate in air at  $150 \text{ }^\circ\text{C}$  annealing for 0.5 h. The polymer donor:NT-acceptor (D:A=1:1, 16  $\text{mg mL}^{-1}$  in total) was dissolved in chloroform (CF) with 1-chloronaphthalene (CN) (0.5%, v/v) additive. The blended solution was spin-coated on the PEDOT: PSS layer at 3000 rpm for 40s. It was then annealed at  $90 \text{ }^\circ\text{C}$  for 5 minutes. Then PFN-Br methanol solution with a concentration of  $1.0 \text{ mg mL}^{-1}$  was deposited on the active layer at a speed of 3500 rpm for 30 seconds to provide a PFN-Br cathode modification layer. The thin films were then transferred into the  $\text{N}_2$ -filled glove box. 80 nm of Ag layer were then deposited onto the active layer by shadow masks. The thickness of the active layer is about 100 nm.

The active area of the cells was  $0.04 \text{ cm}^2$ . The  $J$ - $V$  characteristics were measured by a Keithley 2400 source meter unit under AM1.5G spectrum from a solar simulator (Enlitech model SS-F5-3A). Solar simulator illumination intensity was determined at  $100 \text{ mW cm}^{-2}$  using a monocrystal silicon reference cell with KG5 filter. Short circuit currents under AM1.5G conditions were estimated from the spectral response and convolution with the solar spectrum. The external quantum efficiency was measured by a Solar Cell Spectral Response Measurement System QE-R3011 (Enli Technology Co., Ltd.). The thickness of the active layers in the photovoltaic devices was measured on a Veeco Dektak XT profilometer.

Space-charge-limited-current (SCLC) measurements were carried out using a Keithley 2400 source/measure. Electron-only devices were constructed using the ITO/ PEDOT:PSS /active

layer/MoO<sub>3</sub>/Ag architecture, while hole-only devices were constructed using the ITO/ZnO/active layer/PFN-Br/Ag architecture. Current-voltage sweeps were carried out in the region of -6 V to 6 V in steps of 0.03 V at a slow rate. The carrier mobilities were measured using the space-charge-limited-current (SCLC) model, which is described by:  $J = 9_{\epsilon_0\epsilon_r\mu} V^2 / 8L^3$ , where J is the current density, L is the film thickness of active layer,  $\epsilon_0$  is the permittivity of free space ( $8.85 \times 10^{-12}$  F m<sup>-1</sup>),  $\epsilon_r$  is the relative dielectric constant of the transport medium,  $\mu$  is the hole or electron mobility, V is the internal voltage in the device and  $V = V_{appl} - V_r - V_{bi}$ , where  $V_{appl}$  is the applied voltage to the device,  $V_r$  is the voltage drop due to contact resistance and series resistance across the electrodes, and  $V_{bi}$  is the built-in voltage due to the relative work function difference of the two electrodes. The thickness of the BHJ blend for SCLC measurement was about 100 nm. The electron mobility can be calculated from the slope of the J<sup>1/2</sup>-V curves.

GIWAXS measurements were conducted on a Xenocs-SAXS/WAXS system with X-ray wavelength of 1.5418 Å. The film samples were irradiated at a fixed angle of 0.2°. All film samples were prepared by spin-coating CF/1-CN solutions on Si substrates.

Atomic force microscopy (AFM) images were recorded using a Digital Instruments Nano scope IIIa multimode atomic force microscope in tapping mode under ambient conditions.

## 2. Synthesis

**Synthesis of Compound M2.** 1,2,5,6-tetrahydronaphthalene-1,2,5,6-tetraamine (2 g, 10.40 mmol) dissolve in 100 ml water, heat to complete dissolution, dissolve sodium nitrite (3.59 g, 52 mmol) in 10 ml water, drop it into the above solution, stir for one hour. The remained solid in the filter was collected and dried (2.08 g, 95.0%). The product is directly used for the next reaction.

**Synthesis of Compound M3.** **M2** (1 g, 4.76 mmol), 3- (bromomethyl)heptane (3.73 g, 19.04 mmol) and anhydrous potassium carbonate (3.91 g, 28.56 mmol) were dissolved into N, N-dimethylformamide (50 mL). The reaction mixture was stirred at 80 °C for 12 h, and the solvent was removed by vacuum evaporation. The resulting solid was purified by silica gel chromatography (dichloromethane as eluent) to afford **M3** as a brownish yellow solid (1.70 g, 20.5%). <sup>1</sup>HNMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  (ppm) 8.505-8.528 (d,  $J=9.2$ Hz, 2H), 8.013-8.036 (d,  $J=9.2$ Hz, 2H), 4.718-4.736 (d,  $J=7.2$ Hz, 4H), 2.284-2.347 (t,  $J=25.2$ Hz, 2H), 1.279-1.475 (m,  $J=78.4$ Hz, 32H), 0.960-0.997 (t,  $J=14.8$ Hz, 8H), 0.883-0.918 (t,  $J=14$ Hz, 12H).

**Synthesis of Compound M4.** **M3** (1 g, 2.3 mmol) 3 dissolve in hydrobromic acid, heat until completely dissolved, add liquid bromine (1.1 g, 6.9 mmol) drop by drop, stir overnight at room

temperature. The mixture was poured into saturated sodium bisulfate aqueous solution with dichloromethane. The organic layer was dried over NaSO<sub>4</sub>, concentrated in vacuo, and purified by column chromatography using petroleum ether as the eluent. (1.2 g, 87.70%). <sup>1</sup>HNMR (CDCl<sub>3</sub>, 400 MHz): δ (ppm) 8.650 (s, 2H), 4.716-4.734 (d, *J*=7.2Hz, 4H), 2.313-2.344 (t, *J*=12.4Hz, 2H), 1.254-1.427 (m, *J*=69.2Hz, 43H), 0.936-0.973 (t, *J*=14.8Hz, 8H), 0.854-0.900 (t, *J*=18.4Hz, 12H).

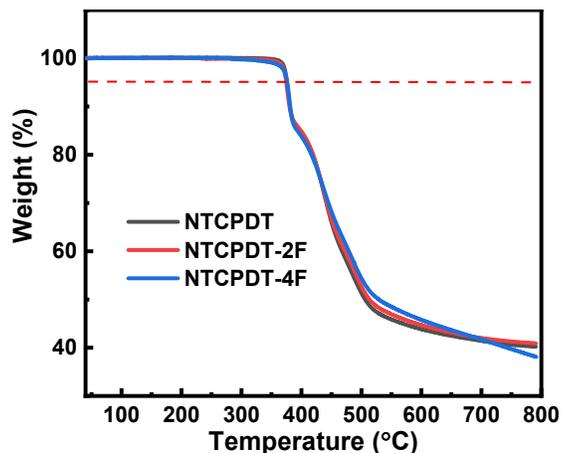
Synthesis of Compound **M6**. A mixture of **M4** (500 mg, 0.84 mmol), **M5** (1.3 g, 1.85 mmol), was dissolved into toluene (15 mL) under nitrogen protection. After Pd(PPh<sub>3</sub>)<sub>4</sub> (48.5 mg, 0.04 mmol), was added into the mixture, the mixture was deoxygenated with nitrogen purging for 20 min. The reaction mixture was stirred at 110 °C for 14 hours. After cooling down, the reaction mixture was extracted with dichloromethane. The organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered. After removing the solvent from filtrate, the crude product was purified by column chromatography on silica gel using dichloromethane as eluent yielding orange solid (2.1 g, 88.59%). <sup>1</sup>HNMR (CDCl<sub>3</sub>, 400 MHz): δ (ppm) 9.866 (s, 2H), 8.727 (s, 2H), 8.212 (s, 2H), 7.604-7.620 (t, *J*=6.4Hz, 2H), 4.810-4.827 (d, *J*=6.8Hz, 4H), 2.353 (s, 3H), 1.939-2.108 (m, 12H), 1.255-1.438 (m, 32H), 0.917-1.048 (m, 67H), 0.735-0.768 (t, *J*=13.2Hz, 16H), 0.613-0.668 (m, 26H).

Synthesis of **NTCPDT**: A mixture of **M6** (100 mg, 0.08 mmol), (E)-2-isocyano-2-(3-oxo-2,3-dihydro-1H-inden-1-ylidene) acetonitrile (46.6 mg, 0.24 mmol), pyridine (0.1 mL) and chloroform (10 mL) was stirred at reflux for 10 hours. After cooling down to room temperature, methanol (10 mL) was added and filtered. The residue was purified by column chromatography on silica gel using chloroform as eluent yielding a deep blue solid (94.2 mg, 71.6%). <sup>1</sup>HNMR (CDCl<sub>3</sub>, 400 MHz): δ (ppm) 8.948(s, 2H), 8.765 (s, 2H), 8.673-8.693 (m, 2H), 8.287 (s, 2H), 7.914-7.935 (m, 2H), 7.706-7.767 (m, 6H), 4.844-4.861 (d, *J*=6.8Hz 4H), 2.382 (s, 2H), 2.012-2.145 (m, 8H), 1.378-1.466 (t, *J*=35.2Hz, 20H), 0.940-1.079 (m, 45H), 0.731-0.812 (m, 8H), 0.651-0.688 (t, *J*=14.8Hz 19H). <sup>13</sup>CNMR (600 MHz, CDCl<sub>3</sub>) δ (ppm) 188.516, 165.937, 147.934, 142.445, 140.502, 139.975, 139.322, 137.911, 136.886, 134.735, 134.059, 125.086, 124.293, 123.401, 123.144, 122.543, 120.169, 118.060, 115.164, 673.148, 59.931, 54.091, 43.330, 40.602, 35.481, 34.325, 34.041, 30.625, 28.589, 28.462, 27.548, 27.337, 24.012, 22.989, 22.841, 22.793, 14.106, 13.993, 10.647. (HR-MALDI-TOF): *m/z*: 1642.36. (calcd for C<sub>102</sub>H<sub>118</sub>N<sub>10</sub>O<sub>2</sub>S<sub>4</sub>: 1643.84).

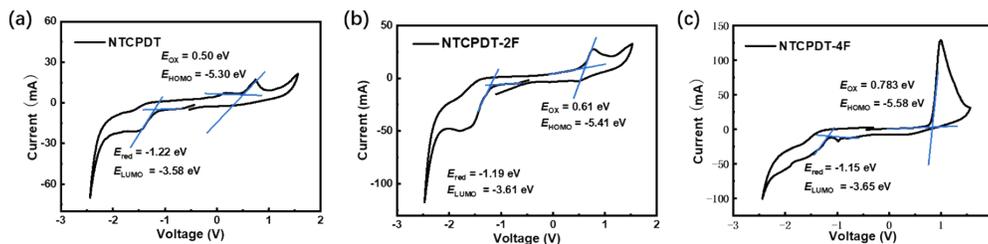
Synthesis of **NTCPDT-2F**: A mixture of **M6** (100 mg, 0.08 mmol), ((E)-2-(6-fluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)-2-isocyanoacetonitrile (50.9 mg, 0.24 mmol), pyridine (0.1 mL) and chloroform (10 mL) was stirred at reflux for 10 hours. After cooling down to room temperature, methanol (10 mL) was added and filtered. The residue was purified by column chromatography on silica gel using chloroform as eluent yielding a deep blue solid (101.1 mg, 75.2%). <sup>1</sup>HNMR (CDCl<sub>3</sub>, 400 MHz): δ (ppm) 8.937(s, 2H), 8.779 (s, 2H), 8.357-8.385 (m, 2H), 8.289 (s, 2H), 7.900-7.933 (m, 2H), 7.697 (s, 2H), 7.374-7.420 (m, 2H), 4.845-4.862 (d, J=6.8Hz, 4H), 2.381 (s, 3H), 2.011-2.144 (m, 8H), 1.376-1.464 (t, J=35.2Hz, 16H), 0.938-1.078(m, 42H), 0.730-0.803(m, 10H), 0.646-0.684(t, J=15.2Hz, 16H). <sup>13</sup>CNMR (600 MHz, CDCl<sub>3</sub>) δ (ppm)187.107, 166.263, 165.523, 158.787, 148.297, 142.458, 140.502, 139.266, 138.138, 133.037, 125.459, 124.312, 123.152, 122.608, 121.291, 121.105, 118.166, 114.741, 112.553, 67.934, 59.955, 54.118, 43.327, 40.609, 35.547, 35.469, 34.310, 34.043, 30.623, 28.582, 28.460, 27.544, 27.327, 24.013, 22.987, 22.834, 22.785, 14.137, 13.987, 10.639. (HR-MALDI-TOF): m/z: 1678.32. (calcd for C<sub>102</sub>H<sub>116</sub>F<sub>2</sub>N<sub>10</sub>O<sub>2</sub>S<sub>4</sub>: 1679.82).

Synthesis of **NTCPDT-4F**: A mixture of **M6** (100 mg, 0.08 mmol), (E)-2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)-2-isocyanoacetonitrile (55.2 mg, 0.24 mmol), pyridine (0.1 mL) and chloroform (10 mL) was stirred at reflux for 10 hours. After cooling down to room temperature, methanol (10 mL) was added and filtered. The residue was purified by column chromatography on silica gel using chloroform as eluent yielding a deep blue solid (94.0 mg, 68.5%).<sup>1</sup>HNMR (CDCl<sub>3</sub>, 400 MHz): δ (ppm) 8.918(s, 2H), 8.778 (s, 2H), 8.494-8.535 (m, 2H), 8.292 (s, 2H), 7.654-7.691 (t, J=14.8Hz, 4H), 4.848-4.865 (d, J=6.8Hz 4H), 2.381 (s, 3H), 1.377-1.465 (t, J=35.2Hz, 20H), 0.939-1.060 (m, 53H), 0.649-0.806 (m, 34H). <sup>13</sup>CNMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 186.00, 166.57, 159.93, 159.20, 158.35, 148.59, 142.42, 140.47, 139.25, 137.99, 136.37, 134.40, 124.32, 123.16, 122.60, 119.21, 118.18, 114.72, 112.12, 77.34, 77.02, 76.70, 67.64, 59.99, 54.14, 43.27, 40.60, 35.55, 35.49, 34.31, 34.06, 30.62, 28.57, 28.46, 27.53, 27.33, 24.01, 22.98, 22.85, 22.80, 14.10. (HR-MALDI-TOF): m/z: 1715.65. (calcd for C<sub>102</sub>H<sub>114</sub>F<sub>4</sub>N<sub>10</sub>O<sub>2</sub>S<sub>4</sub>: 1715.80).

### 3. TGA and CV

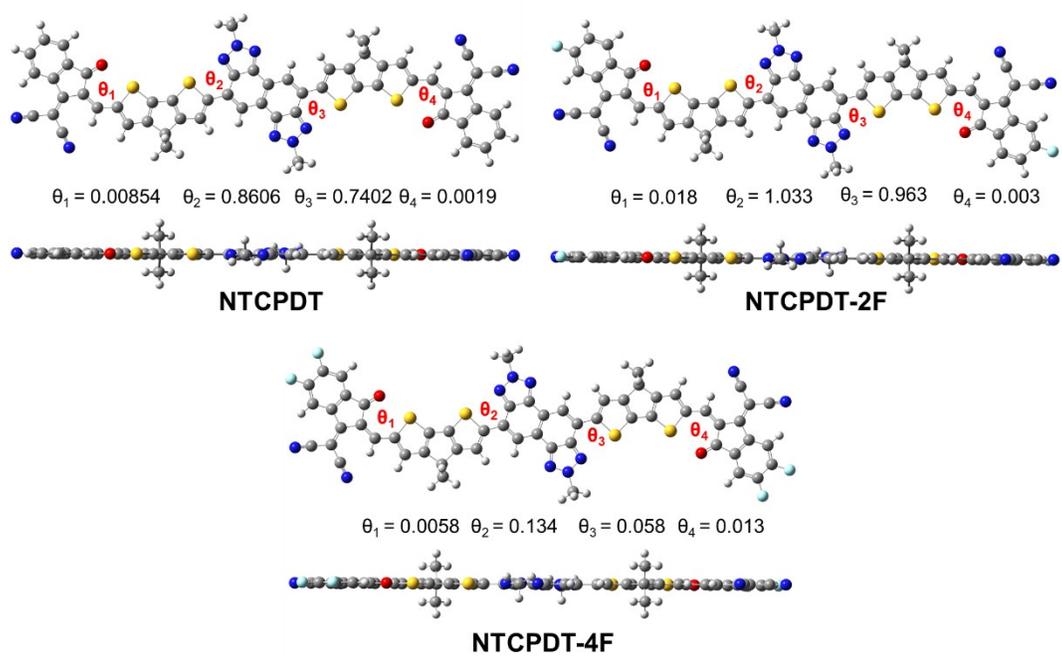


**Figure S1.** TGA plot with a heating rate of 10 °C/min under N<sub>2</sub> atmosphere. Temperature for 5% weight loss of NTCPDT, NTCPDT-2F and NTCPDT-4F are 375.84 °C ,374.54 °C and 376.26 °C respectively.



**Figure S2.** Cyclic voltammogram measured in thin films of (a) NTCPDT, (b) NTCPDT and (c) NTCPDT-4F thin film. Potential vs. Fc/Fc<sup>+</sup>.  $E_{HOMO} = -(E_{onset} + 4.8)$  eV;  $E_{LUMO} = -(E_{onset} + 4.8)$  eV.

### 4. DFT calculations



**Figure S3.** The geometric structures of NTCPDT, NTCPDT-2F and NTCPDT-4F calculated via the DFT method using B3LYP/6-31G\*.

## 5. Solar cells performance

**Table S1.** The solar cells optimization based on the photoactive layers spin-coated from different solvent. The thickness of the active layers is  $\sim 100$  nm.

	Solvent	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (V)	FF	PCE (%)
PBDB-T:NTCPDT	CB	8.51	0.95	0.39	3.19
	CF	9.44	0.96	0.43	3.90
	CF/0.2%CN	10.85	0.93	0.40	4.01
	CF/0.5%CN	12.32	0.96	0.52	6.19
	CF/0.75%CN	10.82	0.96	0.52	5.36
	CF/1%CN	10.74	0.96	0.51	5.24
PBDB-T:NTCPDT-2F	CB	16.32	0.85	0.41	5.76
	CF	16.50	0.86	0.44	6.17
	CF/0.2%CN	16.90	0.89	0.50	7.63
	CF/0.5%CN	17.71	0.89	0.51	8.08
	CF/0.75%CN	17.68	0.89	0.50	7.93
	CF/1%CN	16.24	0.88	0.50	7.11
PBDB-T:NTCPDT-4F	CB	10.91	0.88	0.45	4.33
	CF	18.12	0.85	0.48	7.42
	CF/0.2%CN	19.27	0.86	0.53	8.80
	CF/0.5%CN	20.01	0.86	0.63	10.79
	CF/0.75%CN	18.70	0.85	0.52	8.32
	CF/1%CN	18.47	0.84	0.50	7.62

**Table S2.** The solar cells optimization based on the photoactive layers with different annealing temperatures and thicknesses.

	Annealing TA (°C)	Thickness (nm)	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (V)	FF	PCE (%)
PBDB-T:NTCPDT	25	120	8.84	0.95	0.40	3.35
	80	110	12.32	0.96	0.52	6.19
	150	105	10.00	0.94	0.43	4.10
PBDB-T:NTCPDT-2F	25	118	15.83	0.86	0.43	5.84
	80	106	17.71	0.89	0.51	8.08
	150	95	16.43	0.89	0.51	7.40
PBDB-T:NTCPDT-4F	25	125	17.94	0.84	0.49	7.43
	80	108	20.01	0.86	0.63	10.79
	150	113	17.51	0.84	0.60	8.91

**Table S3.** Photovoltaic parameters of 6 devices based on PBDB-T:NTCPDT fabricated from CF/0.5% CN at 80 °C.

No.	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (V)	FF	PCE (%)
1	12.32	0.96	0.52	6.19
2	10.82	0.96	0.52	5.36
3	10.74	0.96	0.61	5.24
4	11.25	0.96	0.51	5.51
5	10.65	0.95	0.55	5.56
6	11.70	0.95	0.52	5.78
average	11.25±0.65	0.96±0.005	0.54±0.04	5.61±0.34

**Table S4.** Photovoltaic parameters of 6 devices based on PBDB-T:NTCPDT-2F fabricated from CF/0.5% CN at 80 °C.

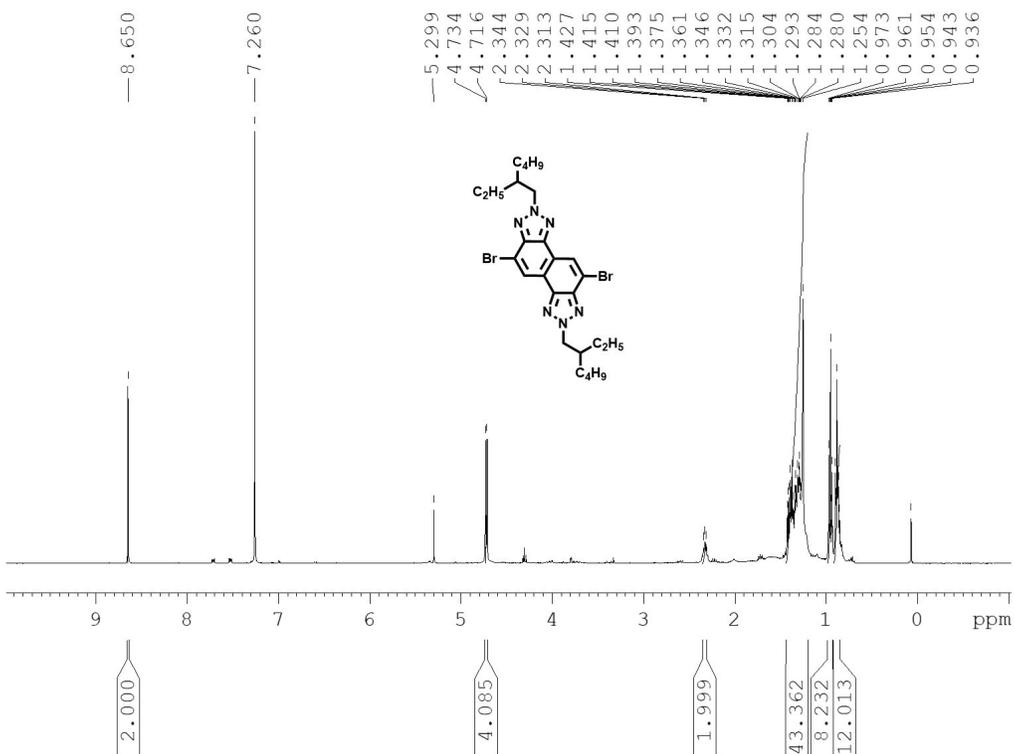
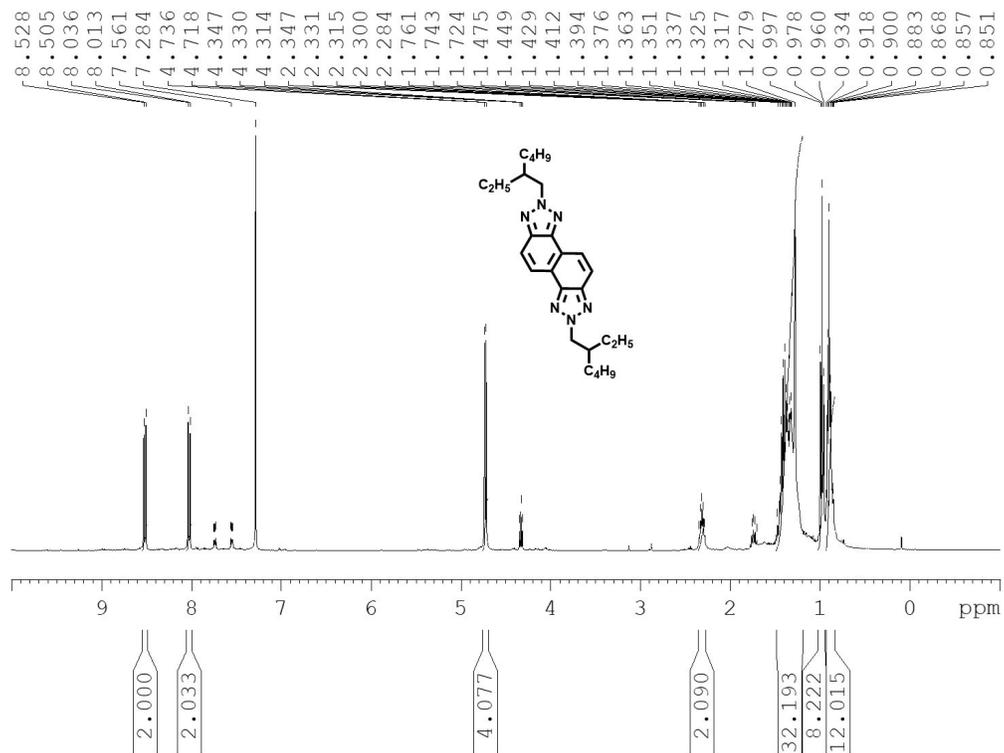
No.	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (V)	FF	PCE (%)
1	17.71	0.89	0.51	8.08
2	17.07	0.89	0.53	7.99
3	17.22	0.88	0.50	7.59
4	17.27	0.90	0.51	7.95
5	16.24	0.89	0.52	7.51
6	16.79	0.89	0.54	8.06
average	17.05±0.50	0.89±0.006	0.52±0.01	7.86±0.25

**Table S5.** Photovoltaic parameters of 6 devices based on PBDB-T:NTCPDT-4F fabricated from CF/0.5% CN at 80 °C.

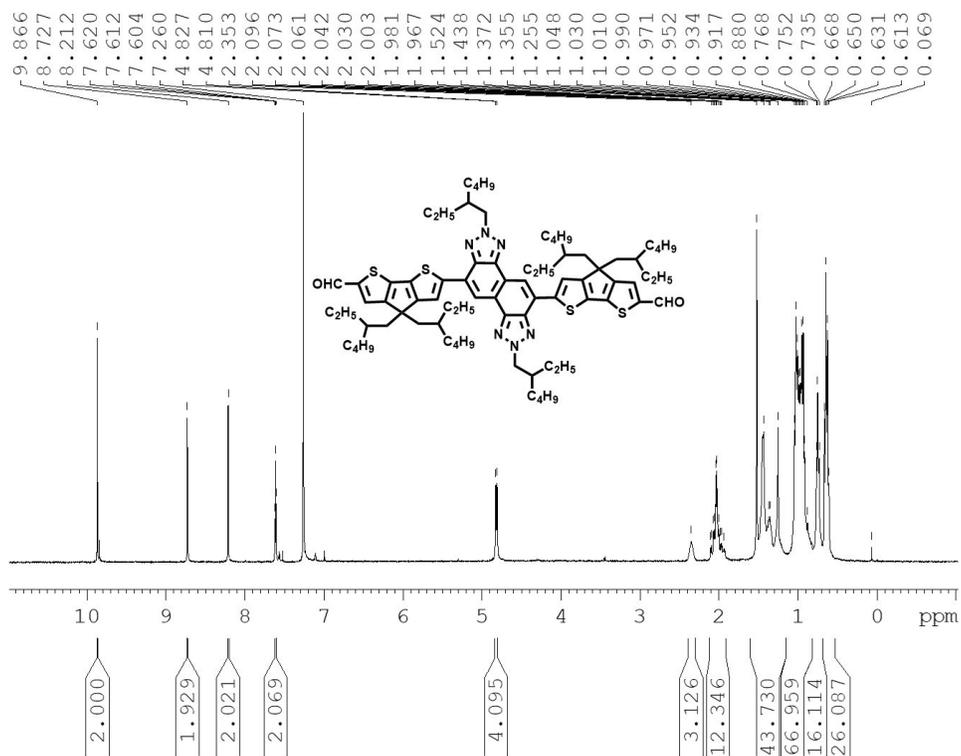
No.	$J_{sc}$ (mA/ cm <sup>2</sup> )	$V_{oc}$ (V)	FF	PCE (%)
1	20.01	0.86	0.63	10.79
2	19.03	0.86	0.58	9.47
3	17.71	0.86	0.62	9.42
4	20.00	0.86	0.54	9.51
5	19.25	0.85	0.56	9.61
6	18.65	0.85	0.60	9.51
average	19.11±0.87	0.86±0.005	0.59±0.03	9.72±0.53



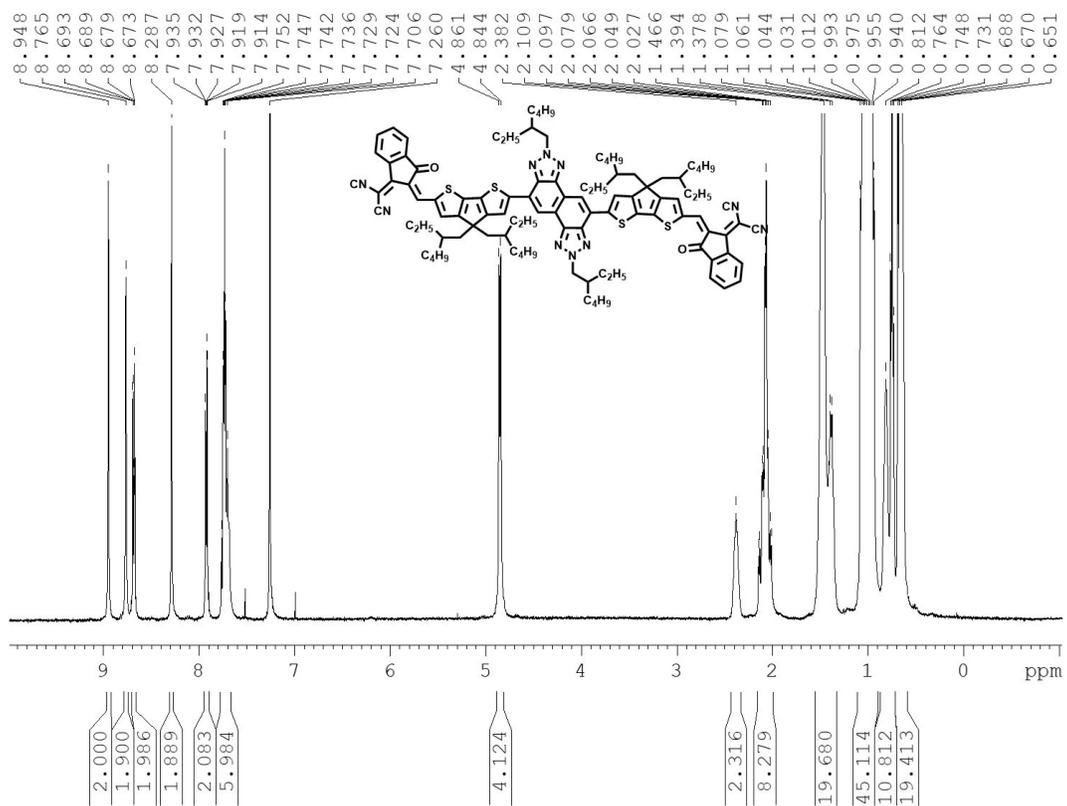
## 6. NMR and HR-MALDI of the compounds



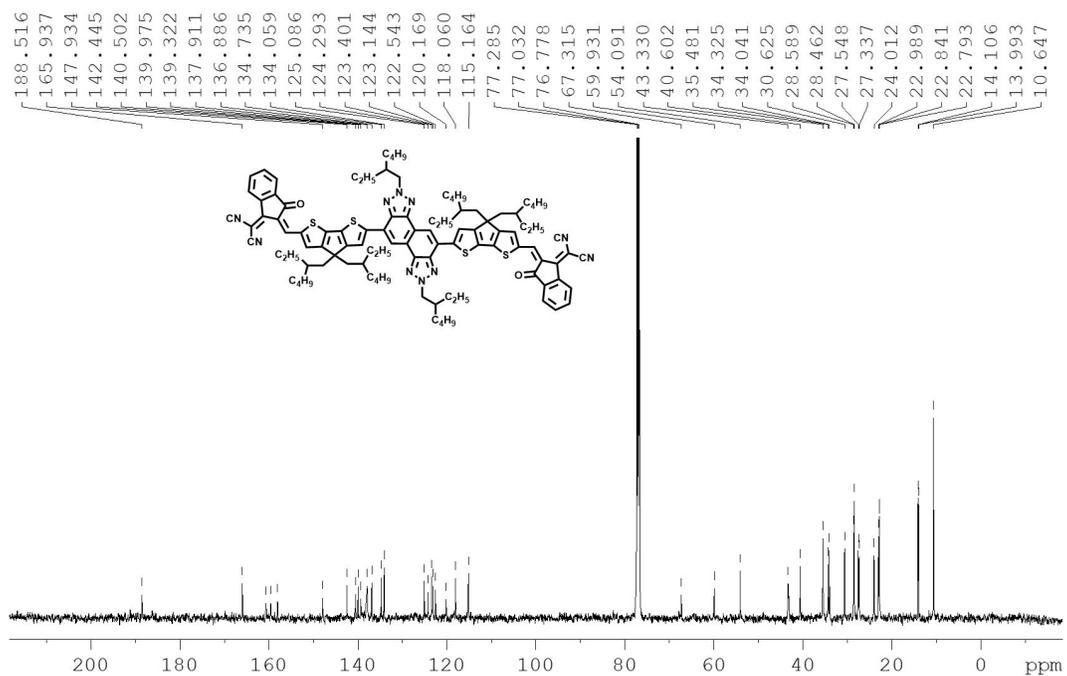
**Figure S5.**  $^1\text{H-NMR}$  of the compound **M4** recorded in  $\text{CDCl}_3$ .



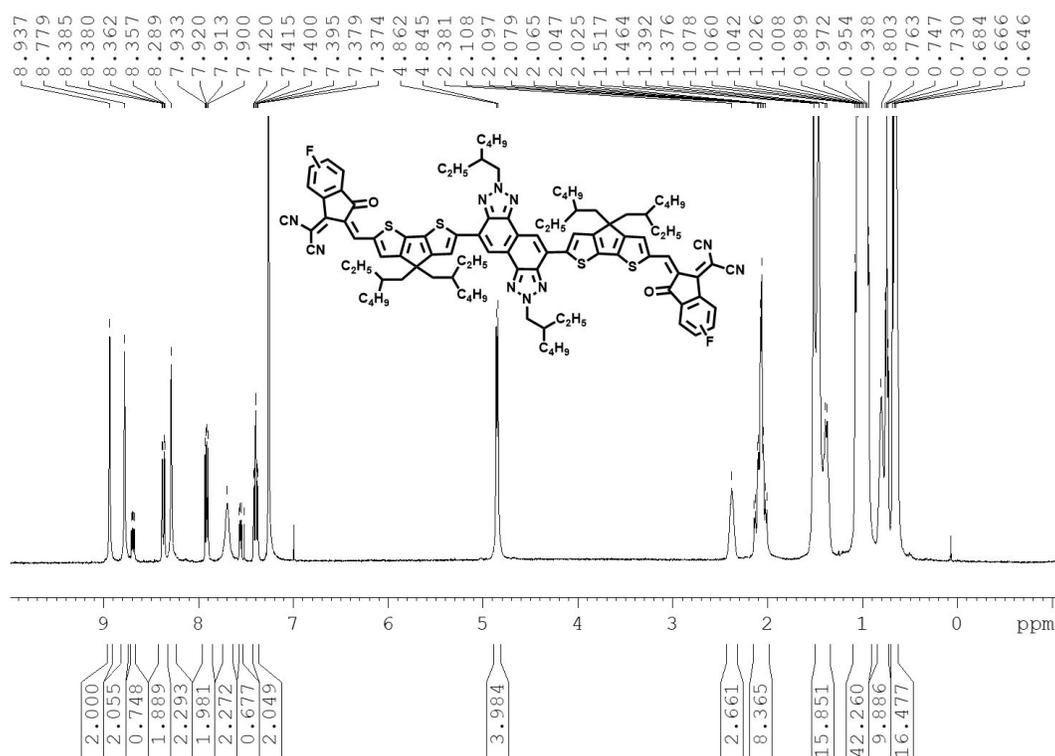
**Figure S6.**  $^1\text{H-NMR}$  of the compound **M6** recorded in  $\text{CDCl}_3$ .



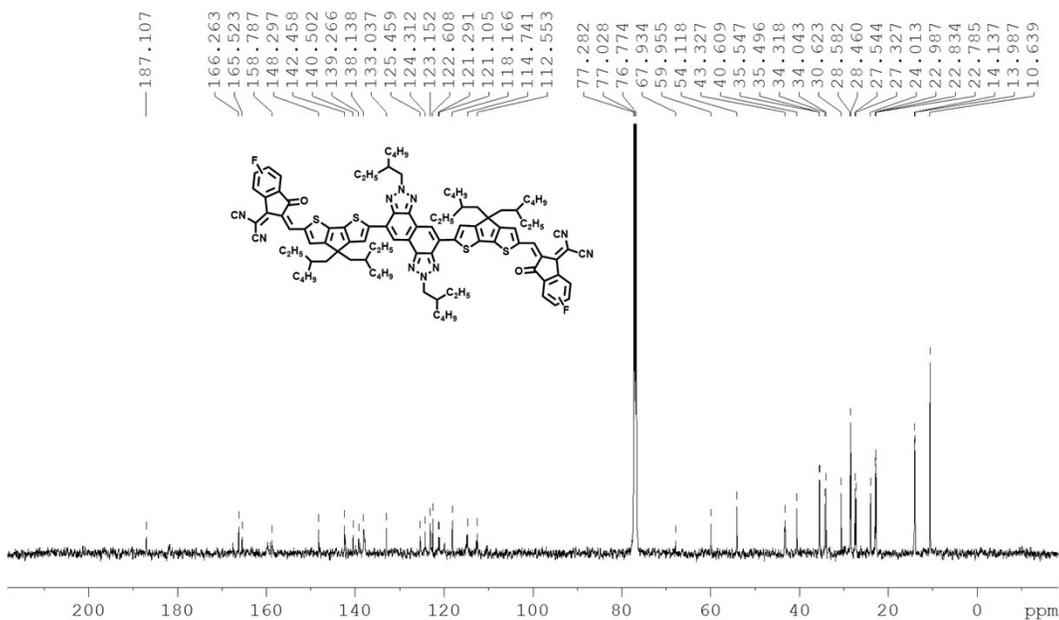
**Figure S7.** <sup>1</sup>H-NMR of the NTCPDT recorded in CDCl<sub>3</sub>.



**Figure S8.** <sup>13</sup>C-NMR of the compound NTCPDT recorded in CDCl<sub>3</sub>.



**Figure S9.** <sup>1</sup>H-NMR of the compound NTCPDT-2F recorded in CDCl<sub>3</sub>.



**Figure S10.** <sup>13</sup>C-NMR of the compound NTCPDT-2F recorded in CDCl<sub>3</sub>.

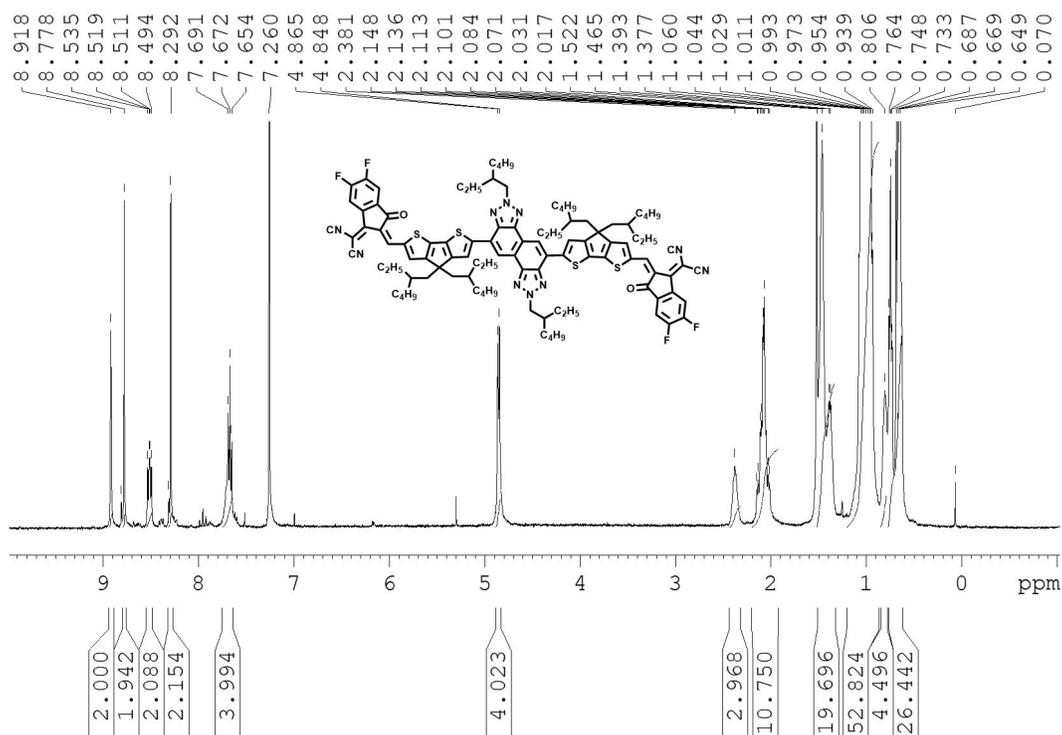


Figure S11. <sup>1</sup>H-NMR of the compound NTCPDT-4F recorded in CDCl<sub>3</sub>.

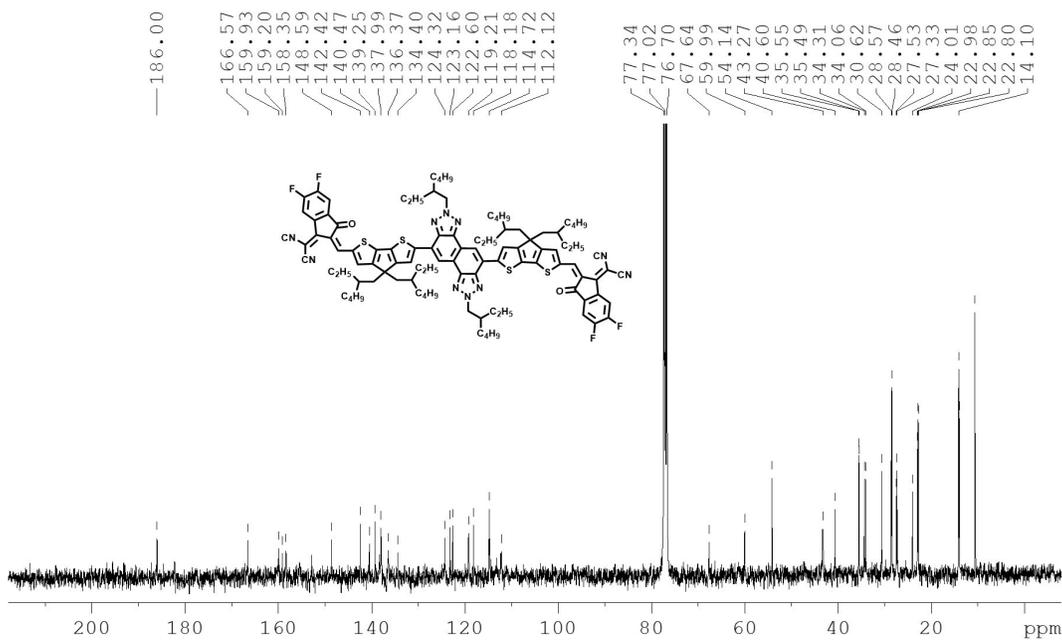
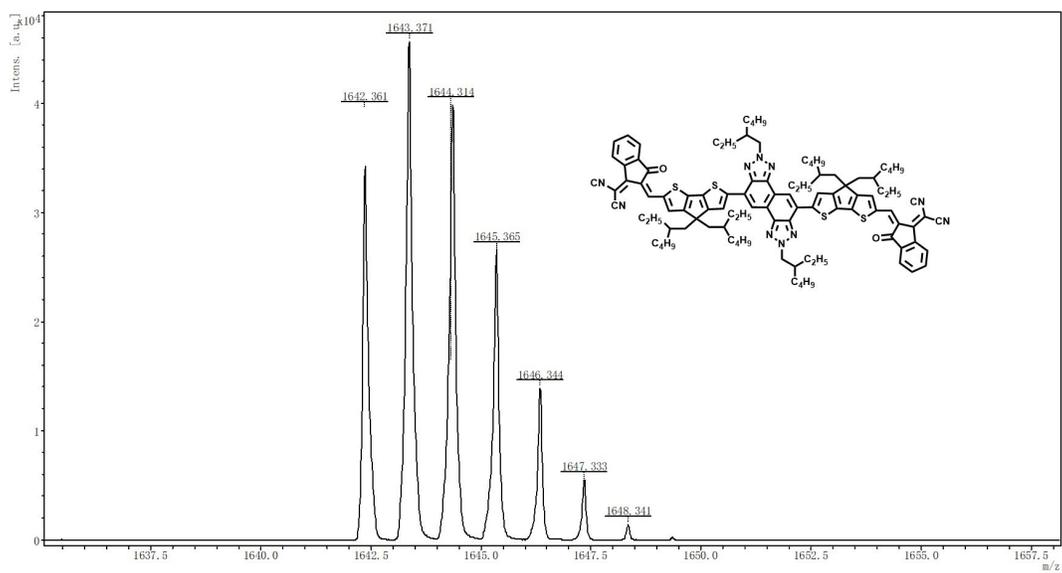
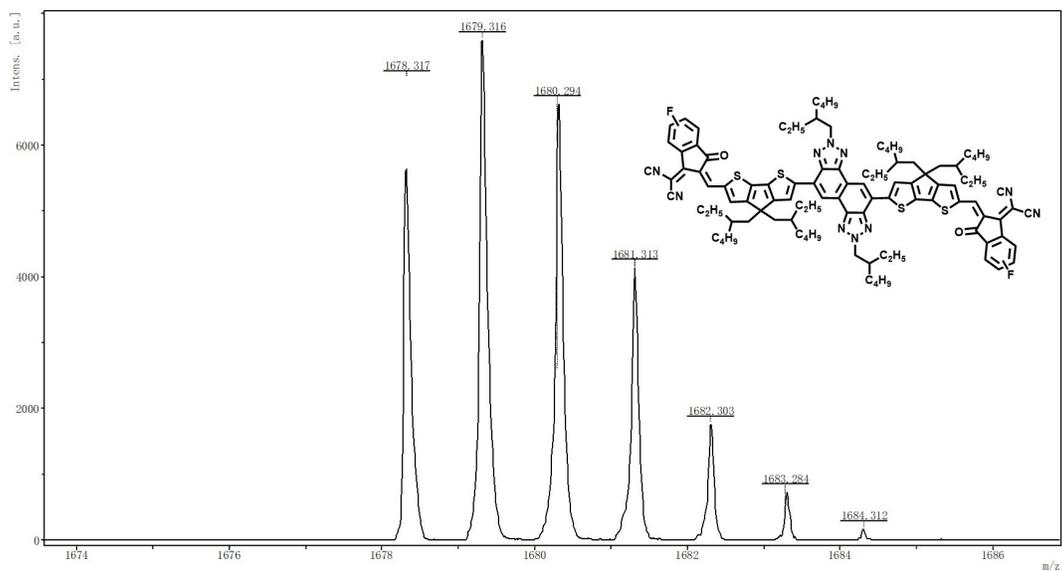


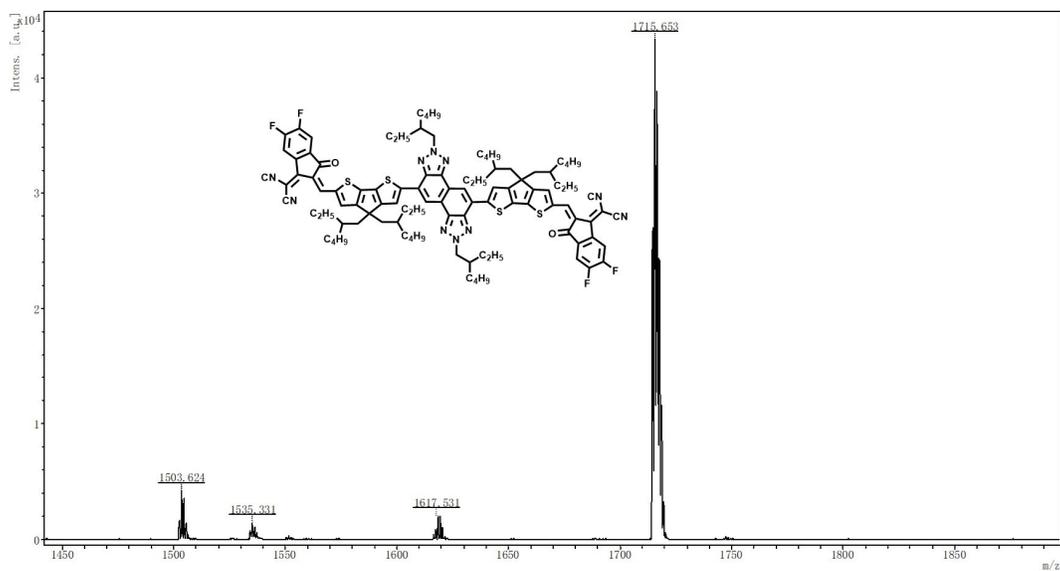
Figure S12. <sup>13</sup>C-NMR of the compound NTCPDT-4F recorded in CDCl<sub>3</sub>.



**Figure S13.** HR-MALDI of the compound NTCPDT recorded in  $\text{CDCl}_3$ .



**Figure S14.** HR-MALDI of the compound NTCPDT-2F recorded in  $\text{CDCl}_3$ .



**Figure S15.** HR-MALDI of the compound NTC PDT-4F recorded in CDCl<sub>3</sub>