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Electronic Supplementary Information

Extension of Indacenodithiophene Backbone Conjugation Enables Efficient Asymmetric A-D-A Type Non-Fullerene Acceptors

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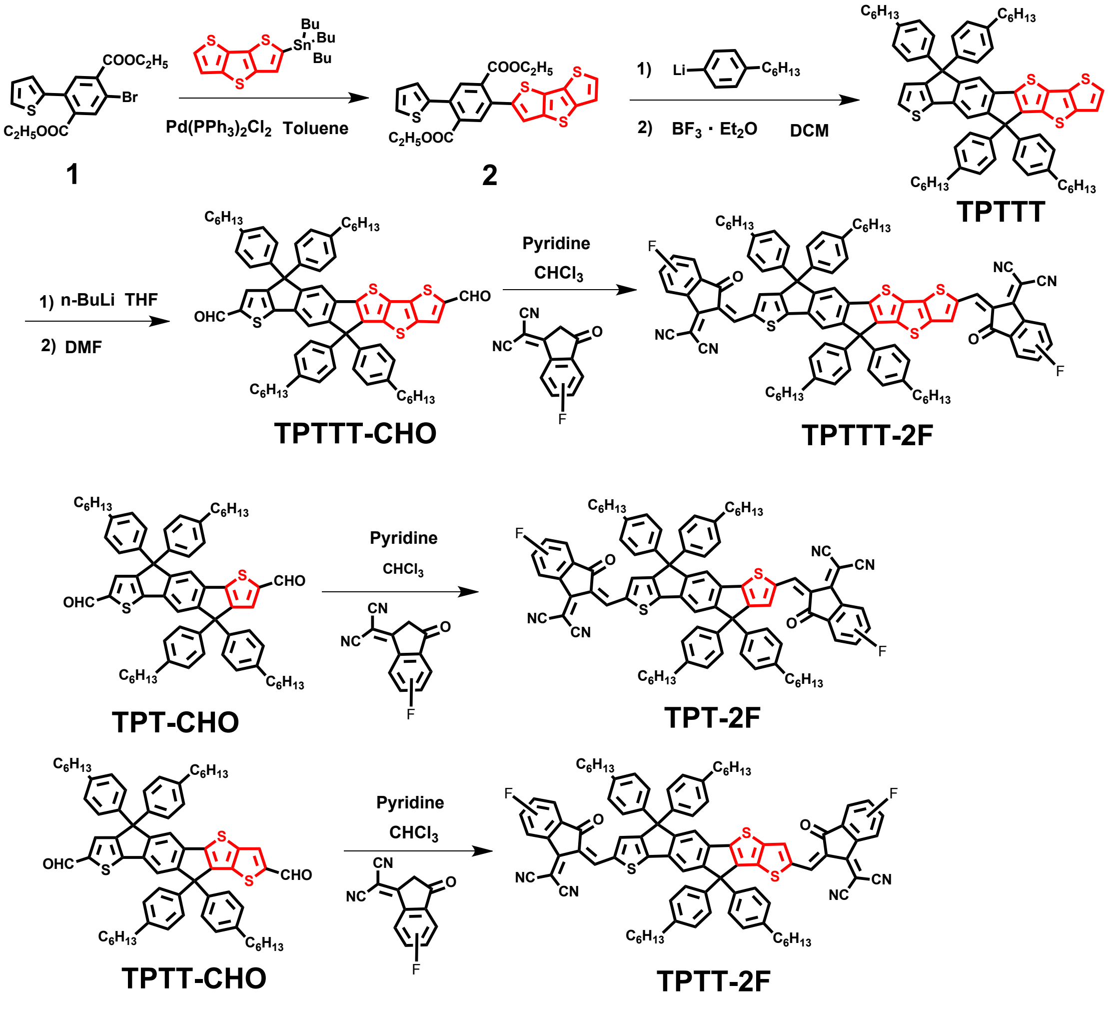
S1.1 Materials synthesis

Unless otherwise stated, all reagents and chemicals were purchased from commercial sources and used without further purification. Anhydrous THF was distilled from sodium/benzophenoneketyl prior to use. Unless otherwise noted, all the the reactions were carried out under nitrogen atmosphere. Diethyl 2-bromo-5-(thiophen-2-yl)terephthalate[1] (compound **1**), **TPT-CHO**,[2] and **TPTT-CHO**[1] were synthesized according to the literature.



Scheme S1. Synthetic routes of TPT-2F, TPTT-2F, and TPTTT-2F.

Synthesis of diethyl 2-(dithieno[3,2-b:2',3'-d]thiophen-2-yl)-5-(thiophen-2-yl)terephthalate (compound ***2****)*

Under the protection of nitrogen, n-BuLi (3.91 mL, 9.78 mmol) was added dropwise to a stirring solution of dithieno[3,2-b:2',3'-d]thiophene (1.92 g, 9.78 mmol) in dry THF

(60 mL) at -78℃. After being kept stirring at -78 ºC for 2 h, tri-n-butyltin chloride (4.77 g, 14.67 mmol) was then injected into the reaction mixture via a syringe, and the reaction mixture was allowed to warm to room temperature and stirred overnight. The resulting mixture was poured into water, followed by extraction with dichloromethane. The combined organic layers were dried with anhydrous $MgSO_4$ and the solvent was removed in vacuo to give crude product, which was used in the next reaction without further purification. To a solution of diethyl 2-bromo-5-(thiophen-2-yl)terephthalate (2.5 g, 6.52 mmol), tributyl(dithieno[3,2-b:2',3'-d]thiophen-2-yl)stannane (4.74 g, 9.78 mmol) and anhydrous toluene (100 mL) was added $Pd(PPh_3)_2Cl_2$ (0.22 g, 0.32 mmol) under nitrogen atmosphere. The reaction mixture was refluxed for overnight and then allowed to cool to room temperature. Water (100 mL) was added and the mixture was extracted with dichloromethane for three times. The combined organic layers were dried over anhydrous $MgSO_4$ and filtered. The filtrate was concentrated under vacuum and purified by column chromatography on silica gel with petroleum ether: ethyl acetate (9:1) as an eluent to give the title compound as a light yellow solid (3.1 g, 95 %). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.88 (s, 1H), 7.86 (s, 1H), 7.41-7.39 (m, 2H), 7.31-7.30 (t, J = 2.6 Hz, 2H), 7.13-7.08 (m, 2H), 4.28-4.21 (m, J = 7.1 Hz, 4H), 1.19-1.13 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 167.58, 167.50, 141.47, 141.42, 140.66, 140.36, 134.22, 133.98, 133.84, 133.20, 132.12, 131.97, 131.51, 130.87, 127.43, 127.12, 126.66, 126.42, 120.78, 120.65, 61.86, 61.77, 13.94, 13.85. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{24}H_{18}O_4S_4$, 498.01; found, 497.5.

Synthesis of ***TPTTT***

To a stirring solution of 1-bromo-4-hexylbenzene (2.9 g, 12.03 mmol) in dry THF (60 mL) at -78℃ was added dropwise n-BuLi (4.8 mL, 12.03 mmol) under nitrogen atmosphere. After being kept stirring at at -78℃ for 1.5 h, a solution of compound 1 (1 g, 2 mmol) in dry THF (10 mL) was added, then the resulting mixture was warmed to room temperature and stirred ovenight. The reaction mixture was poured into water and extracted with dichloromethane for three times. The combined organic phases was dried over with anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was directly dissolved in anhyrous dichloromethane (60 mL). Then BF_3 etherate was added and the reaction mixture was stirred for 12 h at room temperature. After evaporation of solvent, the residue was purified by column chromatography on silica gel with petroleum ether: dichloromethane (9:1) as an eluent to afford a novel asymmetrical fused-7-ring **TPTTT** building block as yellow solid (0.56 g, 27 %). ^1H NMR (300 MHz, $CDCl_3$, δ): 7.51 (s, 1H), 7.45 (s, 1H), 7.29-7.25 (t, 2H), 7.20-7.17 (m, 9H), 7.09-7.07 (d, J = 8.1 Hz, 8H), 7.01-7.00 (d, J = 4.9 Hz, 1H), 2.59-2.53 (q, 8H), 1.59-1.55 (m, 8H), 1.29 (m, 24H), 0.88-0.85 (t, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 156.10, 153.77, 153.22, 147.24, 142.04, 141.85, 141.79, 141.50, 141.46, 141.28, 141.21, 140.17, 136.13, 135.62, 135.57, 132.53, 131.74, 128.49, 128.38, 128.15, 127.97, 127.67, 125.44, 123.21, 120.70, 117.15, 63.13, 62.78, 35.65, 31.79, 31.77, 31.40, 31.34, 29.77, 29.22, 22.66, 14.17; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{68}H_{74}S_4$, 1018.47; found, 1018.8.

Synthesis of ***TPTTT-CHO***

Under the protection of nitrogen, n-BuLi (0.45 mL, 1.14 mmol) was added dropwise to a stirring solution of TPTTT (0.29 g, 0.28 mmol) in dry THF (60 mL) at -78℃. After being kept stirring at -78 ºC for 1 h, the reaction mixture was stirred at room temperature for another 1 h, which was then cooled to -78 ºC again and stirred for 10 mins, then anhydrous *N,N*-Dimethylformamide (DMF) (0.21 g, 2.84 mmol) was injected into the reaction mixture via a syringe, and the reaction mixture was allowed to warm to room temperature and stirred overnight. The resulting mixture was poured into water, followed by extraction with dichloromethane. The combined organic layers were dried with anhydrous $MgSO_4$ and the solvent was removed in vacuo to give crude product, which was futher purified by column chromatography on silica gel with petroleum ether: dichloromethane (1:1.5) as an eluent to afford an orange yellow solid (0.14 g, 46 %). ^1H NMR (300 MHz, $CDCl_3$, δ): 7.91 (s, 1H), 9.82 (s, 1H), 7.85 (s, 1H), 7.65 (d, J = 3.5 Hz, 2H), 7.53 (s, 1H), 7.18-7.15 (m, 8H), 7.11-7.09 (d, J = 8.1 Hz, 8H), 2.60-2.54 (q, 8H), 1.60-1.56 (m, 8H), 1.30-1.29 (m, 24H), 0.87-0.85 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 182.81, 182.63, 156.53, 155.24, 154.19, 150.80, 148.22, 145.91, 145.31, 143.38, 142.37, 142.13, 141.31, 140.75, 140.47, 139.16, 138.58, 137.36, 134.77, 133.08, 132.06, 130.02, 128.69, 128.62, 127.90, 127.71, 118.75, 117.79, 63.21, 62.98, 35.55, 31.70, 31.67, 31.31, 31.24, 29.70, 29.11, 22.58, 22.57, 14.09, 14.07; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{70}H_{74}O_2S_4$, 1074.46; found, 1074.9.

Synthesis of ***TPTTT-2F***

Under nitrogen atmosphere, **TPTTT-CHO** (100 mg, 0.093 mmol), 2-(6-fluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (79 mg, 0.372 mmol) and chloroform (30 mL) was added to 50 mL round bottom flask. After the reaction mixture was stirred at room temperature for 10 mins, pyridine (0.5 mL) was then added. The reaction mixture was allowed to stirr at 65℃ for 12 hours. After removal of solvent of reaction mixture, methanol was added and the precipitate was collected by filtration to get crude product, which was futher purified by column chromatography on silica gel with petroleum ether: dichloromethane (1:1.5) as an eluent to afford a dark solid (110 mg, 81 %). ^1H NMR (300 MHz, $CDCl_3$, δ): 8.92-8.91 (d, J = 5.1 Hz, 1H), 8.89-8.88 (d, J = 3.6 Hz, 1H), 8.72-8.67 (m, 0.5H), 8.38-8.35 (m, 1.5H), 7.98-7.95 (d, 1H), 7.92-7.89 (m, 1.5H), 7.77 (s, 1H), 7.72-7.70 (d, J = 4.5 Hz, 1H), 7.59 (s, 1H), 7.55-7.52 (m, 0.5H), 7.41-7.36 (m, 2H), 7.19-7.12 (m, 16H), 2.61-2.56 (m, 8H), 1.61-1.57 (m, 8H), 1.31-1.26 (m, 24H), 0.89-0.84 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 185.91, 185.87, 166.95, 164.39, 159.24, 159.09, 157.51, 156.72, 155.62, 153.97, 148.05, 147.13, 145.06, 142.02, 141.99, 141.96, 141.93, 141.60, 141.34, 141.29, 141.25, 141.19, 141.15, 139.87, 139.83, 139.33, 138.79, 137.79, 137.65, 137.63, 137.56, 137.19, 137.15, 137.02, 136.32, 134.29, 132.85, 132.04, 131.87, 127.84, 127.75, 126.81, 126.74, 124.87, 121.25, 120.84, 120.65, 118.66, 117.28, 113.47, 113.31, 113.21, 113.06, 111.88, 111.78, 111.62, 111.53, 109.81, 109.57, 69.31, 68.71, 62.25, 61.99, 34.55, 30.69, 30.67, 30.30, 30.24, 28.68, 28.09, 28.08, 21.57, 21.55, 13.08, 13.06; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{94}H_{80}F_2N_4O_2S_4$, 1462.51; found, 1464.2.

Synthesis of ***TPT-2F***

Under nitrogen atmosphere, **TPT-CHO** (80 mg, 0.083 mmol), 2-(6-fluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (71 mg, 0.332 mmol) and chloroform (30 mL) was added to 50 mL round bottom flask. After the reaction mixture was stirred at room temperature for 10 mins, pyridine (0.5 mL) was then added. The reaction mixture was allowed to stirr at 65℃ for 12 hours. After removal of solvent of reaction mixture, methanol was added and the precipitate was collected by filtration to get crude product, which was futher purified by column chromatography on silica gel with petroleum ether: dichloromethane (1:1) as an eluent to afford a dark solid (75 mg, 67 %). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.90-8.89 (d, J = 3.6 Hz, 2H), 8.73-8.69 (q, 0.5H), 8.39-8.36 (m, 1.5H), 7.93-7.90 (m, 1.5H), 7.74-7.72 (t, 4H), 7.75-7.53 (m, 0.5H), 7.44-7.40 (t, 2H), 2.61-2.57 (t, 8H), 1.62-1.56 (m, 8H), 1.31 (m, 24H), 0.89-0.86 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 187.01, 186.92, 168.49, 168.08, 165.07, 164.62, 159.33, 159.31, 158.92, 158.88, 158.18, 158.16, 156.51, 142.46, 142.32, 142.18, 141.49, 141.46, 140.27, 140.04, 139.92, 139.72, 138.70, 138.56, 137.20, 137.15, 135.87, 135.82, 133.14, 133.12, 128.84, 128.71, 128.66, 127.97, 127.85, 127.83, 127.67, 126.08, 125.95, 122.55, 122.36, 122.30, 122.10, 121.79, 120.13, 114.59, 114.40, 114.23, 114.13, 113.03, 112.69, 110.67, 70.29, 69.27, 63.03, 35.59, 31.74, 31.34, 29.74, 29.10, 22.62, 14.14; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{90}H_{80}F_2N_4O_2S_2$, 1350.57; found, 1352.3.

Synthesis of ***TPTT-2F***

Under nitrogen atmosphere, **TPTT-CHO** (100 mg, 0.098 mmol), 2-(6-fluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (83 mg, 0.392 mmol) and chloroform (30 mL) was added to 50 mL round bottom flask. After the reaction mixture was stirred at room temperature for 10 mins, pyridine (0.5 mL) was then added. The reaction mixture was allowed to stirr at 65℃ for 12 hours. After removal of solvent of reaction mixture, methanol was added and the precipitate was collected by filtration to get crude product, which was futher purified by column chromatography on silica gel with petroleum ether: dichloromethane (1:1.5) as an eluent to afford a dark solid (105 mg, 76 %). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.89-8.88 (d, J = 3.3 Hz,1H), 8.86 (s, 1H), 8.72-8.69 (q, 0.5H), 8.38-8.36 (d, J = 8.9 Hz, 1.5H), 8.23-8.21 (d, J = 7.2 Hz, 1H), 7.94-7.89 (m, 1H), 7.78 (s, 1H), 7.71-7.70 (d, J = 4.4 Hz, 1H), 7.59 (s, 1H), 7.57-7.54 (m, 1H), 7.44-7.40 (t, 2H), 7.21-7.11 (m, 16H), 2.60-2.56 (t, 8H), 1.62-1.58 (m, 8H), 1.31-1.29 (m, 24H), 0.87-0.86 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 186.96, 186.65, 168.46, 165.04, 159.86, 159.72, 159.16, 157.92, 156.55, 155.80, 152.88, 148.19, 147.31, 147.14, 146.95, 144.06, 144.04, 142.62, 142.42, 141.14, 141.11, 140.31, 139.79, 138.82, 138.62, 138.61, 138.32, 138.28, 138.25, 137.12, 136.02, 133.10, 128.95, 128.79, 127.94, 127.92, 127.83, 127.74, 126.02, 125.95, 125.91, 125.88, 122.72, 122.01, 121.95, 121.71, 119.82, 118.91, 114.67, 114.48, 114.38, 114.30, 114.21, 114.14, 112.97, 112.66, 99.99, 70.38, 69.97, 63.27, 63.03, 35.62, 35.58, 31.73, 31.34, 31.27, 29.73, 29.17, 29.12, 22.61, 14.12; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{92}H_{80}F_2N_4O_2S_3$, 1406.54; found, 1408.3.

S1.2 Materials Characterization

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 300 spectrometer using deuterated chloroform (CDCl3) as the solvent and trimethylsilane (TMS) as the internal reference at room temperature. UV-visible absorption spectra were measured by a Hitachi (model U-3010) UV–vis spectrophotometer. Mass spectra were recorded on Bruker Daltonics Biflex III MALDI-TOF Analyzer in the MALDI mode. Cyclic voltammetry (CV) measurements were conducted under nitrogen atmosphere at a scan rate of 100 mV s^{-1} using a Zahner IM6e Electrochemical workstation. A platinum plate coated with sample film was used as a working electrode, a platinum wire was used as a counter electrode, a saturated Ag/AgCl electrode was used as a reference electrode, 0.1 M tetra-n-butylammonium hexafluorophosphate

(Bu4NPF6) in anhydrous acetonitrile solution was employed as a supporting electrolyte and Ferrocene/ferrocenium (Fc/Fc+) is used as an internal standard. The onset oxidation potential of ferrocene external standard was determined to be 0.43 eV in our lab. Therefore, the HOMO and LUMO energy level could be calculated from the following equations: HOMO = – (E_{ox}^{onset} + 4.37) eV and LUMO = –(E_{red}^{onset} + 4.37) eV, where E_{ox}^{onset} and E_{red}^{onset} were the onset oxidation potential and onset reduction potential relative to Ag/AgCl, respectively. Atomic force microscopy (AFM) measurements were carried out using a Dimension Icon AFM (Bruker) in the tapping mode. Transmission electron microscopy (TEM) measurements were performed on a JEOL JEM-1400 transmission electron microscope. GIWAXS measurements were accomplished at PLS-II 9A U-SAXS beamline of the Pohang Accelerator Laboratory in Korea.

S1.3 Organic Solar Cells Fabrication and Characterization

Organic solar cells with inverted device architecture of ITO/ZnO/photoactive layer/MoO_3/Ag were fabricated. The ITO-coated glass substrates were firstly cleaned by ultrasonic treatment in detergent deionized water, acetone and isopropyl alcohol for 20 minutes,respectively. After drying for one night, ZnO precursor solution was spin coated at 4000 rpm and the ZnO layer was generated at 200 °C for 15 min in ambient atmosphere. The active layers were spin-coated from a solution of PBT1-C:NFA with weight ratio of 1:1 in chloroform. Solution with 0.25 v% DIO was stirred overnight prior to cast. The active layers were allowed to heat at 100 °C for 10 min in a N_2-filled glovebox. The MoO_3 were deposited by sequential thermal evaporation of 3 nm followed by 90 nm of Ag. The active area of the devices is 4.00 mm^2. Current density-voltage (J-V) characteristics were measured using a Keithley 2400 Source Measure Unit. The currents were measured under 100 mW/cm^2 simulated 1.5 Global (AM 1.5 G) solar simulator (Enli Technology Co., Ltd, SS-F5-3A). The light intensity was calibrated by a standard Si solar cell (SRC-2020, Enli Technology Co., Ltd). EQE spectra were carried out by using a QEX10 Solar Cell IPCE measurement system (PV Measurements, Inc.).

S1.4 Space-Charge Limited Current Measurement

The charge transport properties were evaluated via space charge limited current (SCLC) method. The electron-only devices were fabricated with a structure of ITO/ZnO/photoactive layer/ZrAcac/Al, and the hole-only devices are fabricated with a structure of ITO/PEDOT:PSS/photoactive layer /Ag. The *J*–V curves of devices were fitted by using the Mott–Gurney equation: $J = 9\varepsilon_o\varepsilon_r\mu V^2/8L^3$, where J is the current density, ε_0 is the permittivity of free space, ε_r is the permittivity of the active layer, μ is the hole mobility or electron mobility, V is the internal voltage of the device ($V = V_{appl} - V_{bi}$), where V_{app} is the applied voltage, V_{bi} is the offset voltage (V_{bi} is 0 V here), and L is the film thickness of the active layer. The eletron mobility or hole mobility could be calculated from the slope of the SCLC curve.

S1.5 Figures and Tables

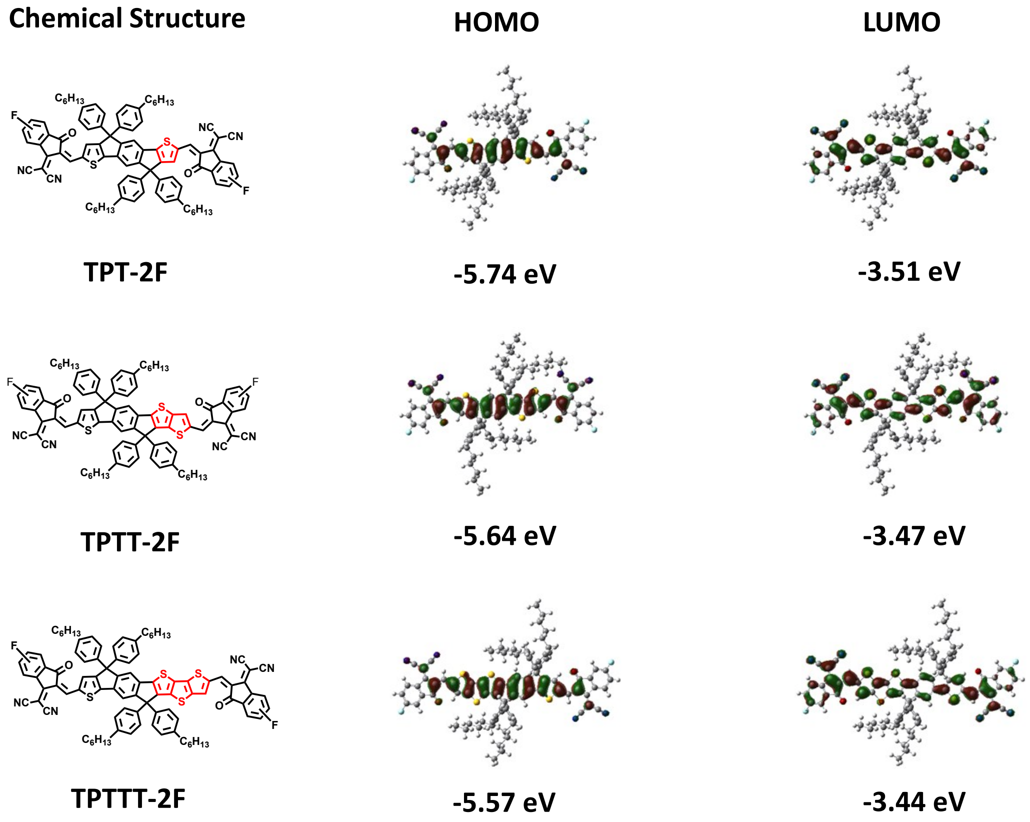


Figure S1. Electron density distributions and frontier molecular orbitals obtained by DFT calculations for TPT-2F, TPTT-2F, and TPTTT-2F.

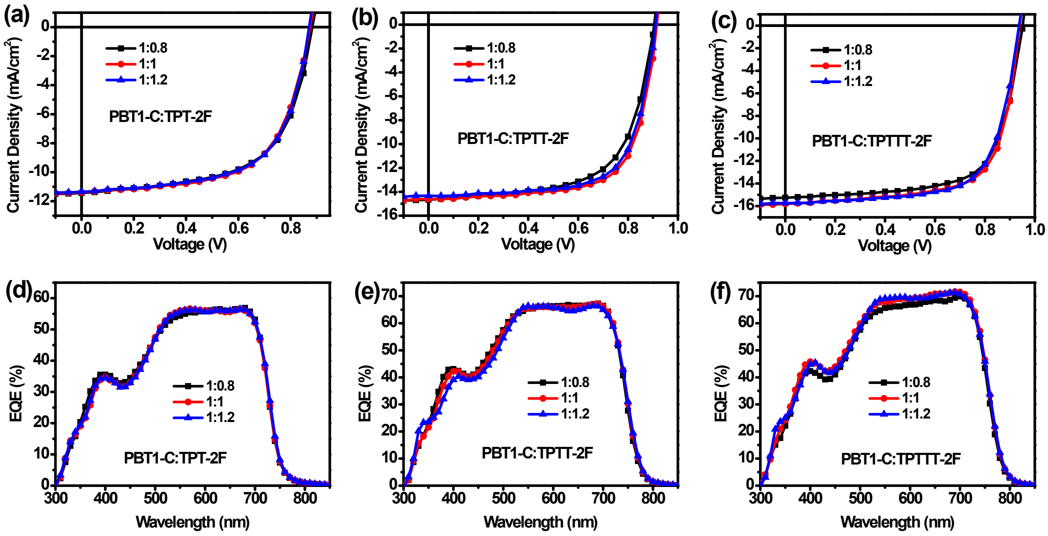


Figure S2. *J*-V curves (a, b, c) and EQE spectra (d, e, f) of OSCs devices based on PBT1-C:NFA blend with different D/A ratio.

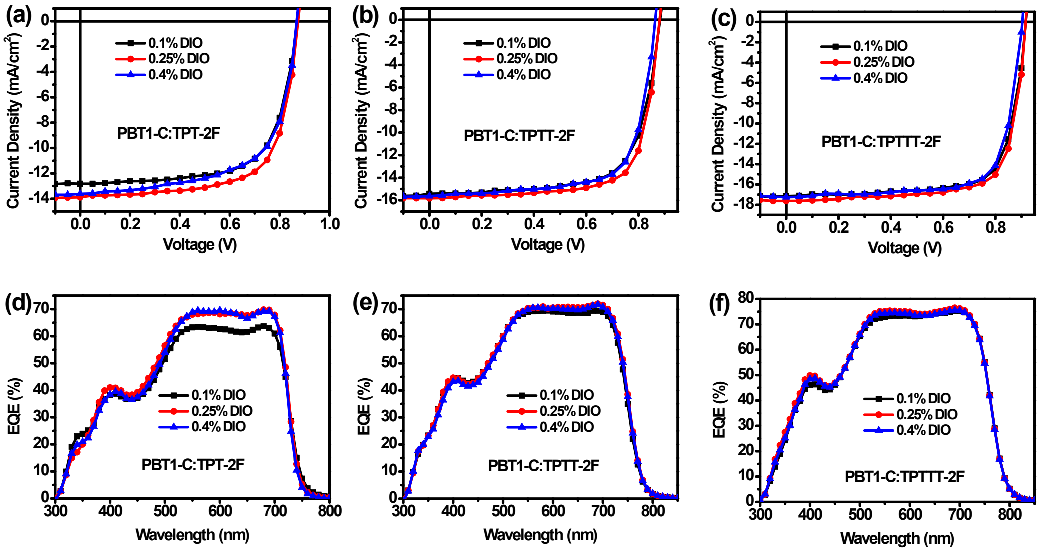


Figure S3. *J*-V curves (a, b, c) and EQE spectra (d, e, f) of OSCs devices based on PBT1-C:NFA blend with different DIO content.

Table S1. OSCs device data of OSCs based on PBT1-C:NFA with different D/A ratio.

NFA	*D/A* (*w/w*)	V_{oc} (V)	J_{sc} (mA/cm^2)	$J_{sc,cal}$ (mA/cm^2)	FF (%)	PCE [a] (%)
	1:1.08	0.883	11.44	11.14	60.7	6.14
		(0.880±0.003)	(11.44±0.15)		(60.30±0.51)	(6.07±0.12)
TPT-2F	1:1	0.874	11.40	11.12	62.0	6.18

		(0.872±0.002)	(11.25±0.11)		(61.94±0.88)	(6.08±0.08)
	1:1.2	0.871	11.35	11.02	62.2	6.15
		(0.868±0.003)	(11.25±0.11)		(61.70±1.07)	(6.02±0.10)
TPTT-2F	1:1.08	0.905	14.67	14.12	63.9	8.48
		(0.907±0.003)	(14.60±0.08)		(62.44±1.10)	(8.27±0.17)
	1:1	0.915	14.60	14.07	69.1	9.23
		(0.911±0.004)	(14.54±0.14)		(67.50±1.11)	(8.93±0.20)
	1:1.2	0.910	14.34	13.88	68.8	8.98
		(0.908±0.002)	(14.04±0.22)		(68.14±0.81)	(68.69±0.20)
TPTTT-2F	1:1.08	0.951	15.26	14.77	68.1	9.88
		(0.950±0.004)	(15.21±0.12)		(67.94±1.16)	(9.80±0.12)
	1:1	0.939	15.81	15.42	69.1	10.26
		(0.942±0.003)	(15.65±0.17)		(69.19±0.68)	(10.19±0.09)
	1:1.2	0.941	15.74	15.32	68.9	10.16
		(0.940±0.004)	(15.46±0.29)		(69.10±1.26)	(10.04±0.12)

a) Average values with standard deviation were obtained from 20 devices.

Table S2. Device data of OSCs based on PBT1-C:NFA (1:1, w/w) with different DIO content.

NFA	**DIO (v/v)**	**Voc (V)**	**Jsc (mA/cm^2)**	**Jsc,cal (mA/cm^2)**	**FF (%)**	**PCE a) (%)**
TPT-2F	0.1%	0.870	12.82	12.44	68.1	7.58
		(0.867±0.004)	(12.73±0.07)		(67.00±1.47)	(7.40±0.20)
	0.25%	0.874	13.89	13.41	68.6	8.33
		(0.871±0.003)	(13.78±0.09)		(66.90±1.52)	(8.02±0.24)
	0.4%	0.868	13.62	13.18	64.10	7.58
		(0.864±0.003)	(13.55±0.07)		(62.54±1.54)	(7.32±0.20)
TPTT-2F	0.1%	0.882	15.42	14.87	68.1	9.52
		(0.885±0.007)	(15.28±0.12)		(69.32±0.59)	(9.38±0.14)
	0.25%	0.881	15.82	15.23	73.0	10.17
		(0.876±0.007)	(15.67±0.15)		(72.72±0.65)	(9.98±0.17)
	0.4%	0.864	15.63	15.04	71.0	9.59
		(0.863±0.002)	(15.58±0.12)		(70.22±1.26)	(9.43±0.16)
TPTTT-2F	0.1%	0.916	17.15	16.58	74.2	11.66
		(0.918±0.004)	(16.94±0.17)		(73.22±1.05)	(11.38±0.24)
	0.25%	0.916	17.63	16.88	74.5	12.03
		(0.916±0.002)	(17.46±0.21)		(73.46±0.91)	(11.78±0.22)
	0.4%	0.903	17.25	16.70	74.5	11.60
		(0.902±0.001)	(17.25±0.16)		(73.76±0.76)	(11.49±0.09)

a) Average values with standard deviation were obtained from 20 devices.

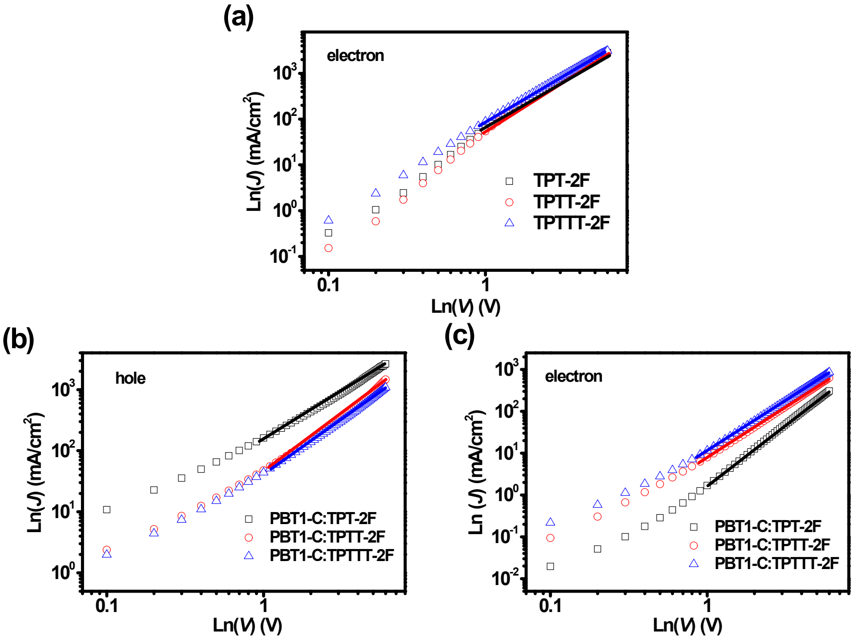


Figure S4. Ln(J)-ln(V) characteristic curves and space-charge-limited current (SCLC) fittings curves of (a) electron-only device based on TPT-2F, TPTT-2F and TPTTT-2F; (b) hole-only device of corresponding blend film, and (c) electron-only device of corresponding blend films.

Table S3. Charge transpot properties of TTPTT-IC, TTPTT-2F, TTPTT-4F and their corresponding blend films

Active layer	Hole mobility (10^{-4} cm^2 V $^{-1}$ s $^{-1}$)	Electron mobility (10^{-4} cm^2 V $^{-1}$ s $^{-1}$)	μ_h/μ_e ratio
TPT-2F	-	4.17±0.06	-
TPTT-2F	-	4.53±0.10	-
TPTTT-2F	-	4.82±0.12	-
PBT1-C: TPT-2F	3.51±0.25	0.71±0.15	4.94
PBT1-C: TPTT-2F	3.05±0.19	1.62±0.19	1.88
PBT1-C: TPTTT-2F	2.30±0.20	2.22±0.16	1.04

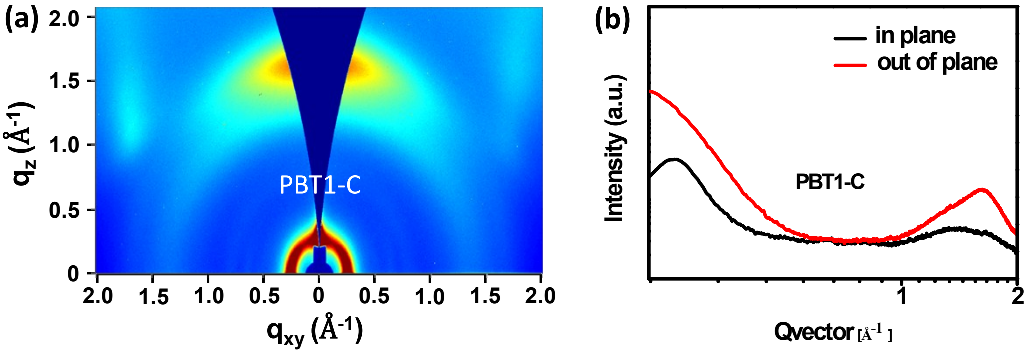


Figure S5. (a) Grazing incidence wide angle X-ray diffraction patterns of PBT1-C. (b) In-plane (black lines) and out-of-plane (red lines) line-cut profiles of GIWAXD results.

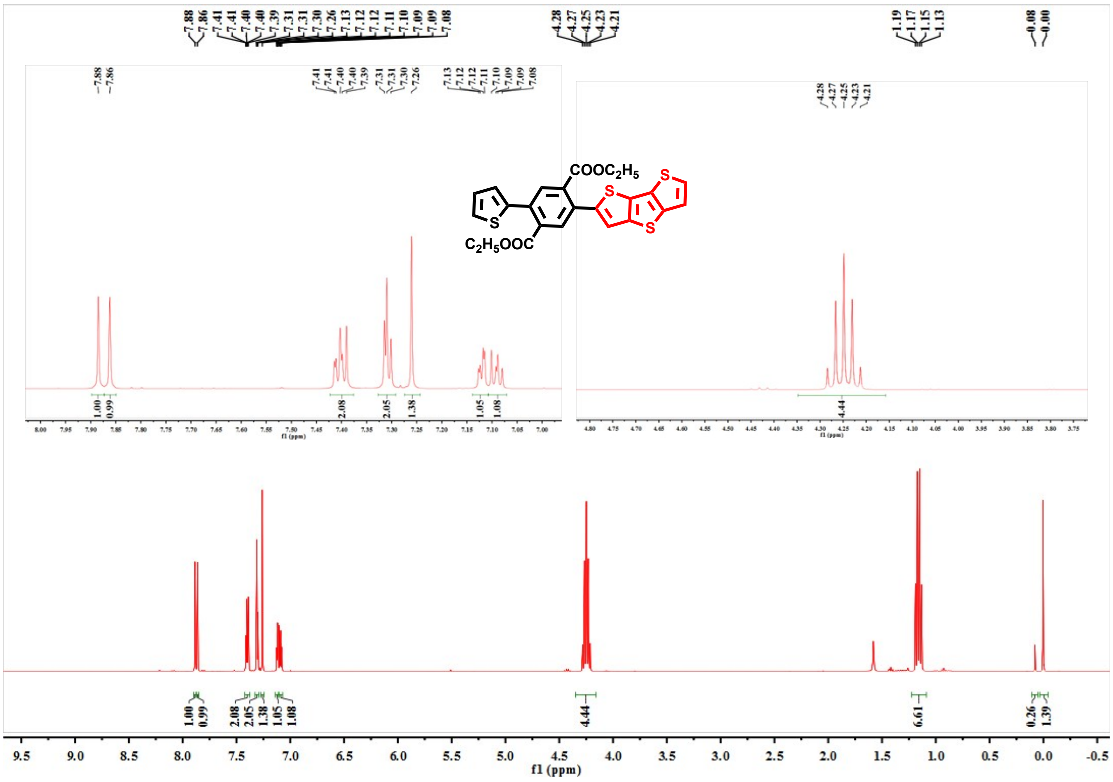


Figure S6. ^{1}H NMR spectrum of compound **2**.

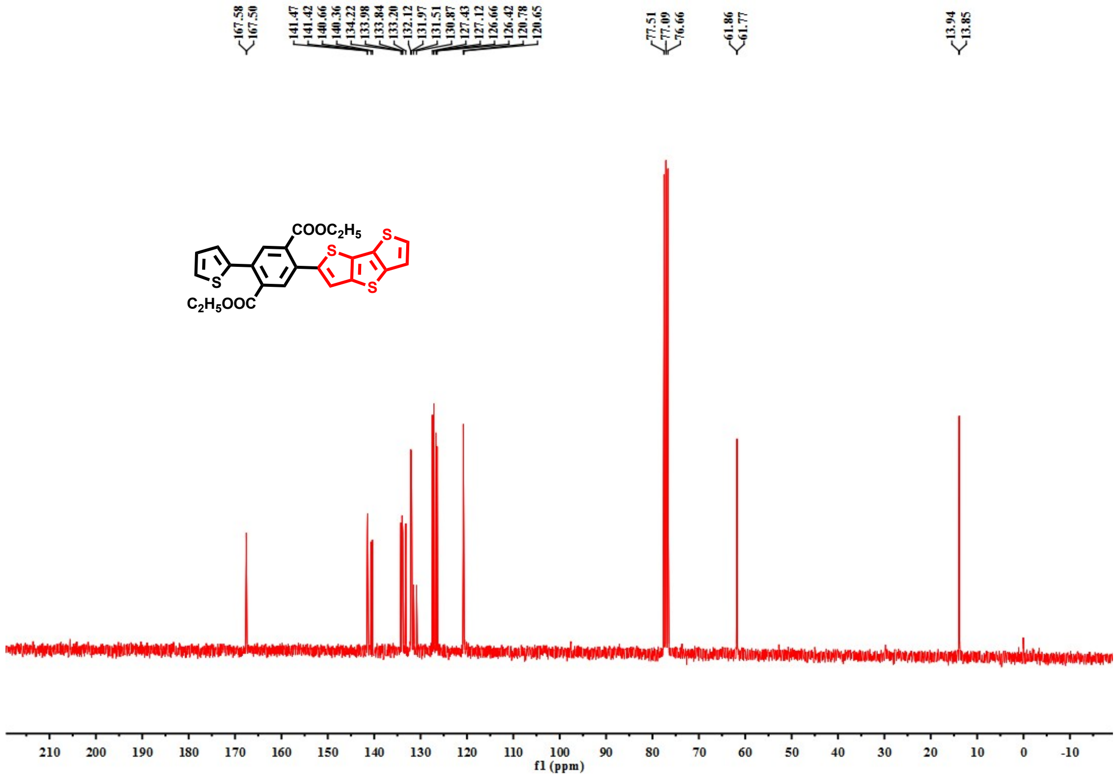
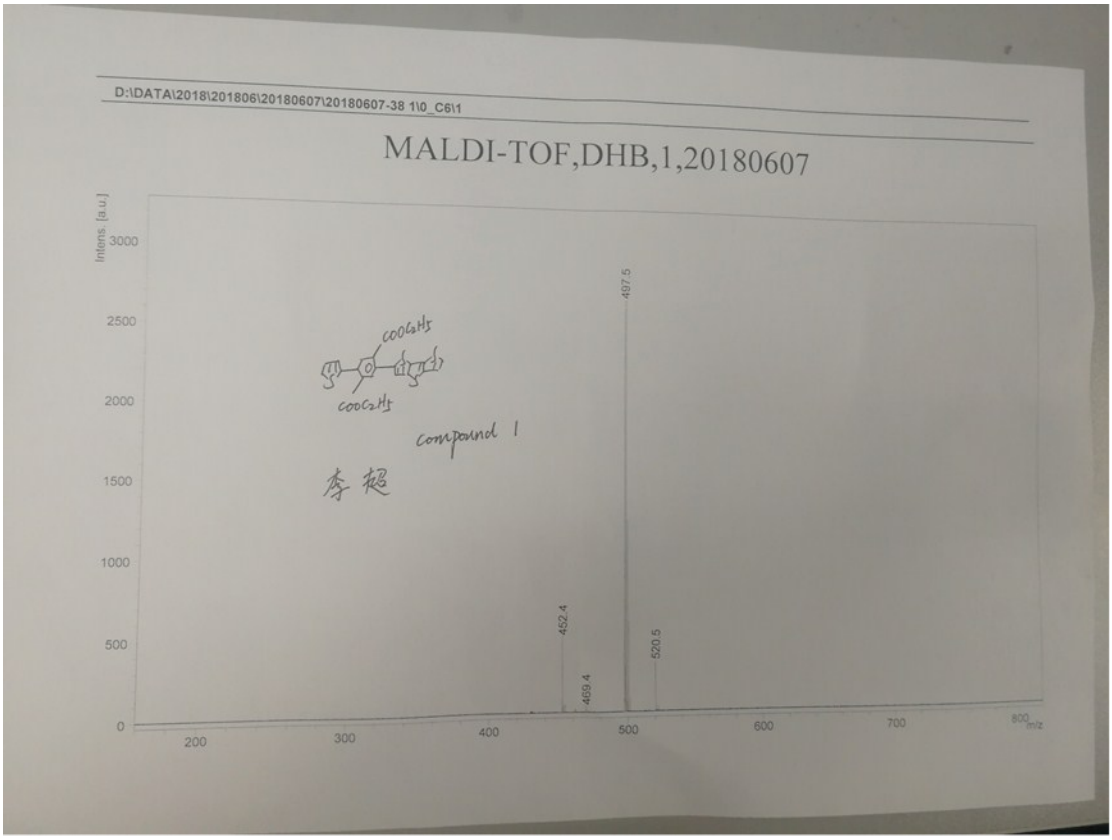


Figure S7. ^{13}C NMR spectrum of compound **2**.



D:\DATA\2018\201806\20180607\20180607-38 1\0_C6\1

MALDI-TOF,DHB,1,20180607

compound 1

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Figure S8. HR-MS spectrum of compound 2.

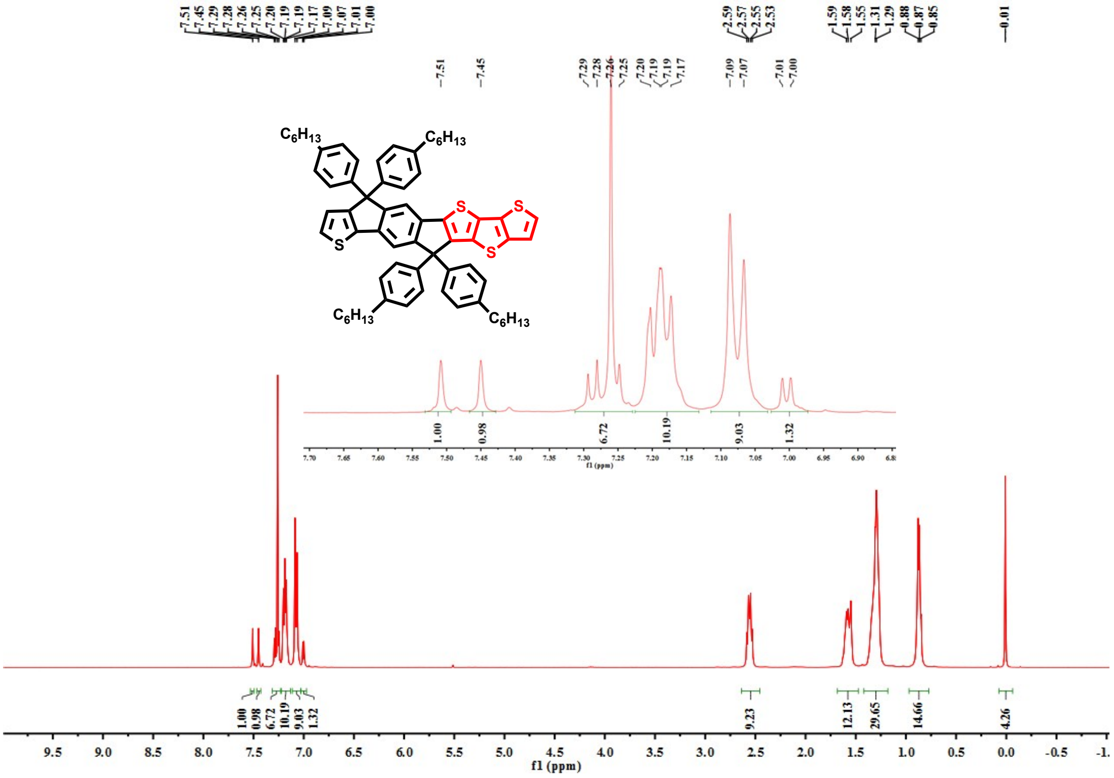


Figure S9. ^{1}H NMR spectrum of **TPTTT**.

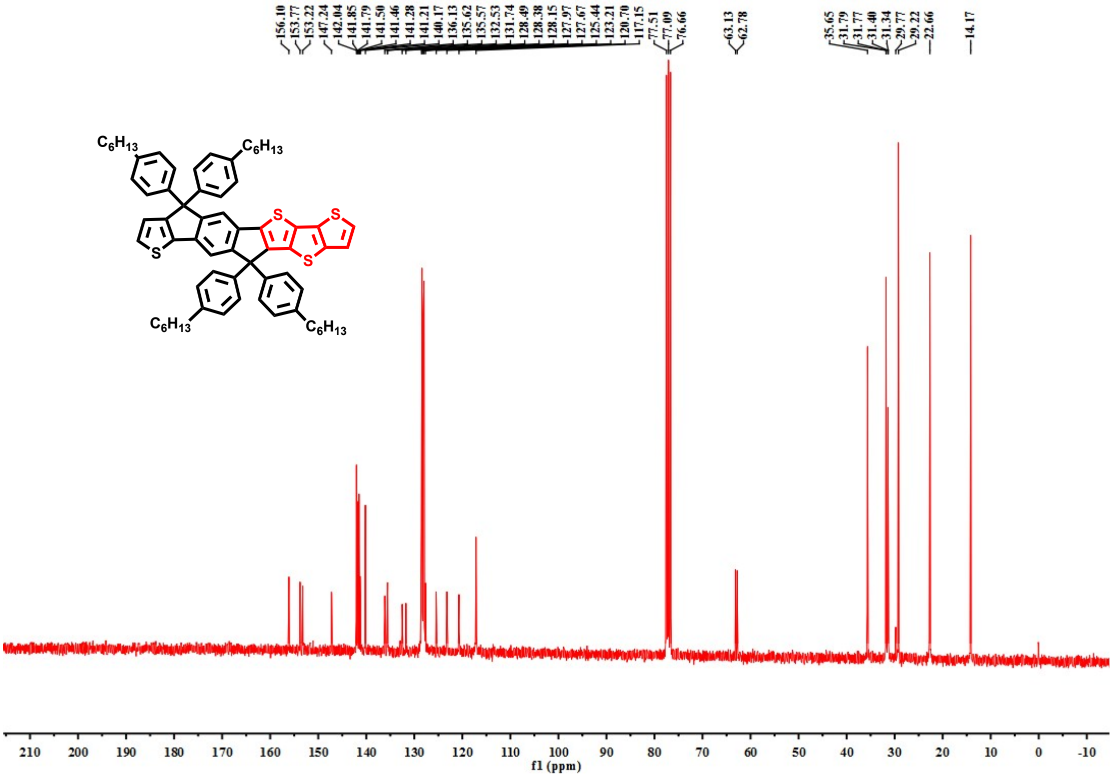


Figure S10. ^{13}C NMR spectrum of **TPTTT**.

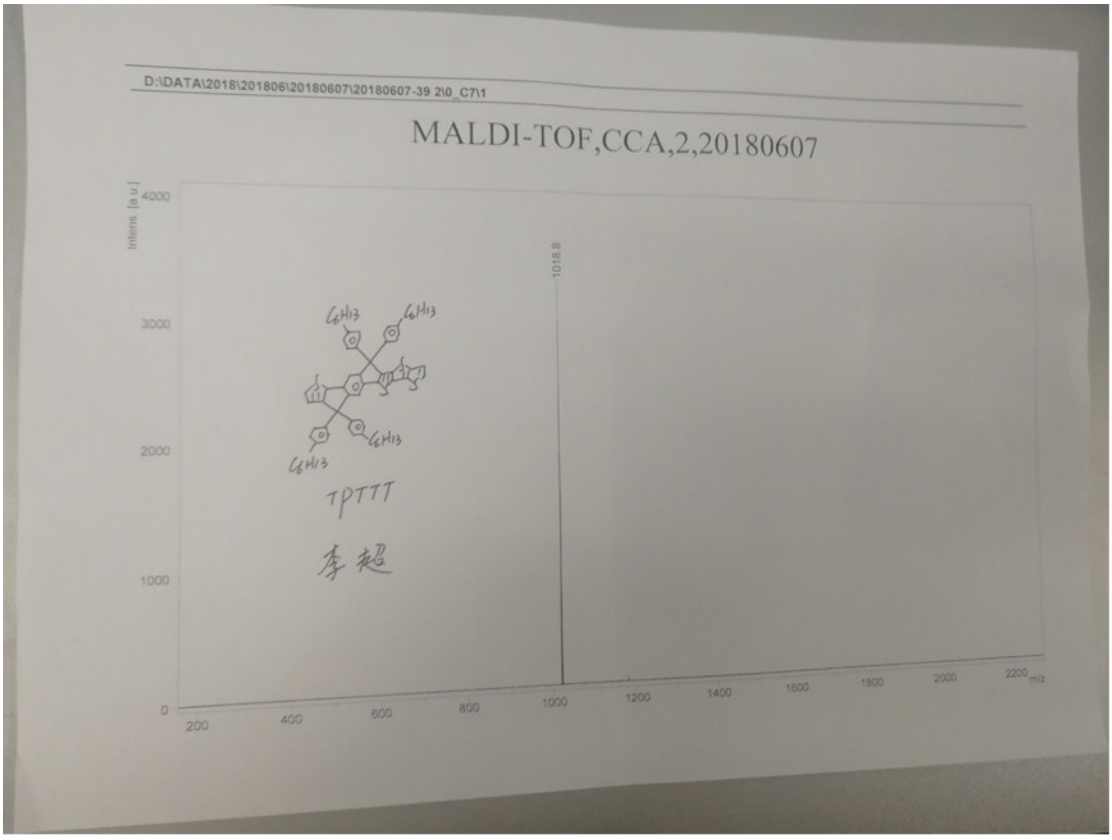


Figure S11. HR-MS spectrum of **TPTTT**.

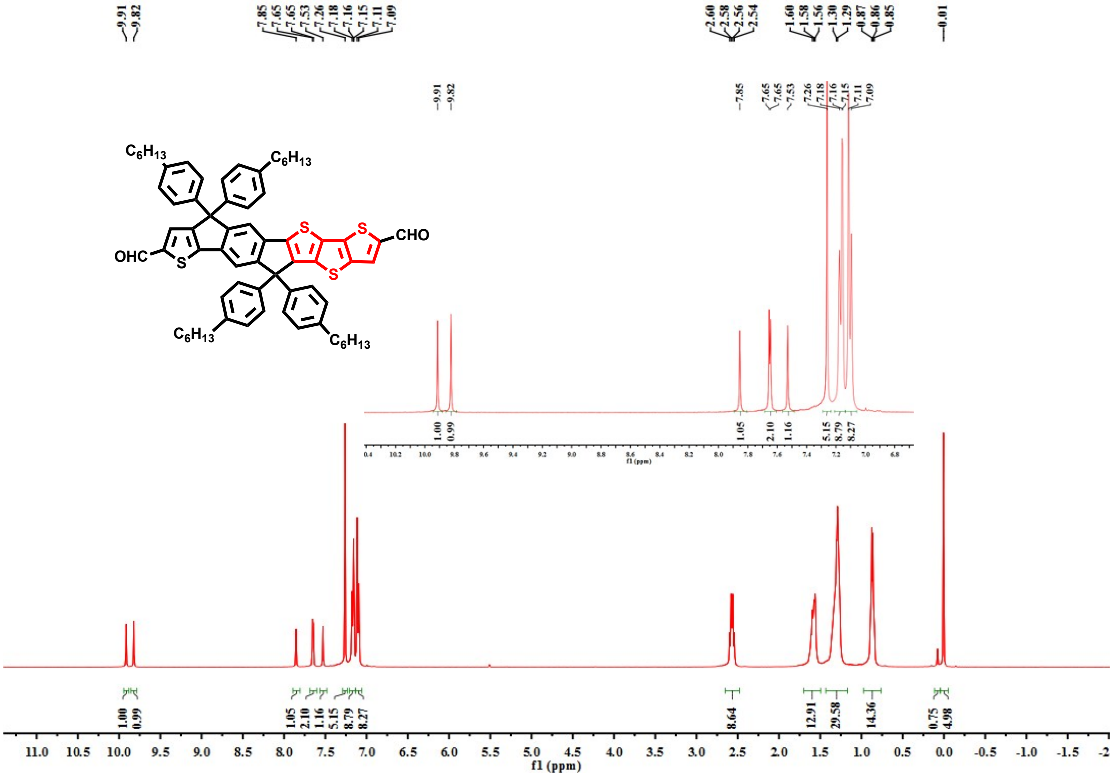


Figure S12. ^{1}H NMR spectrum of **TPTTT-CHO**.

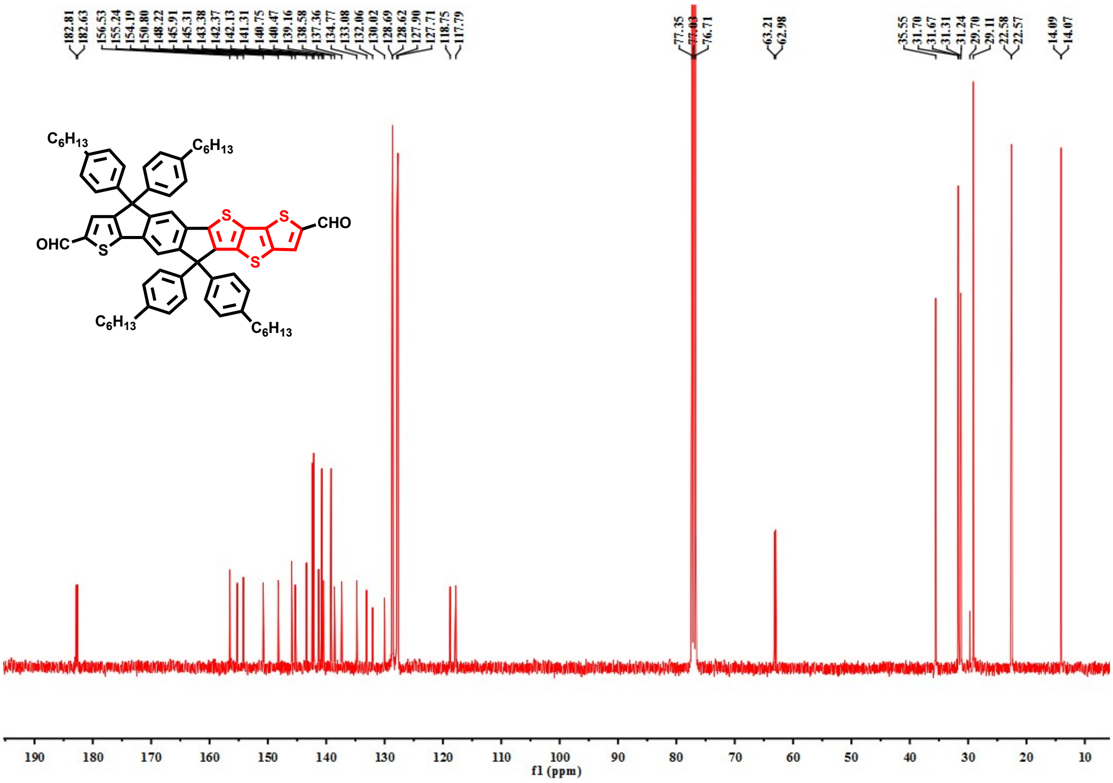
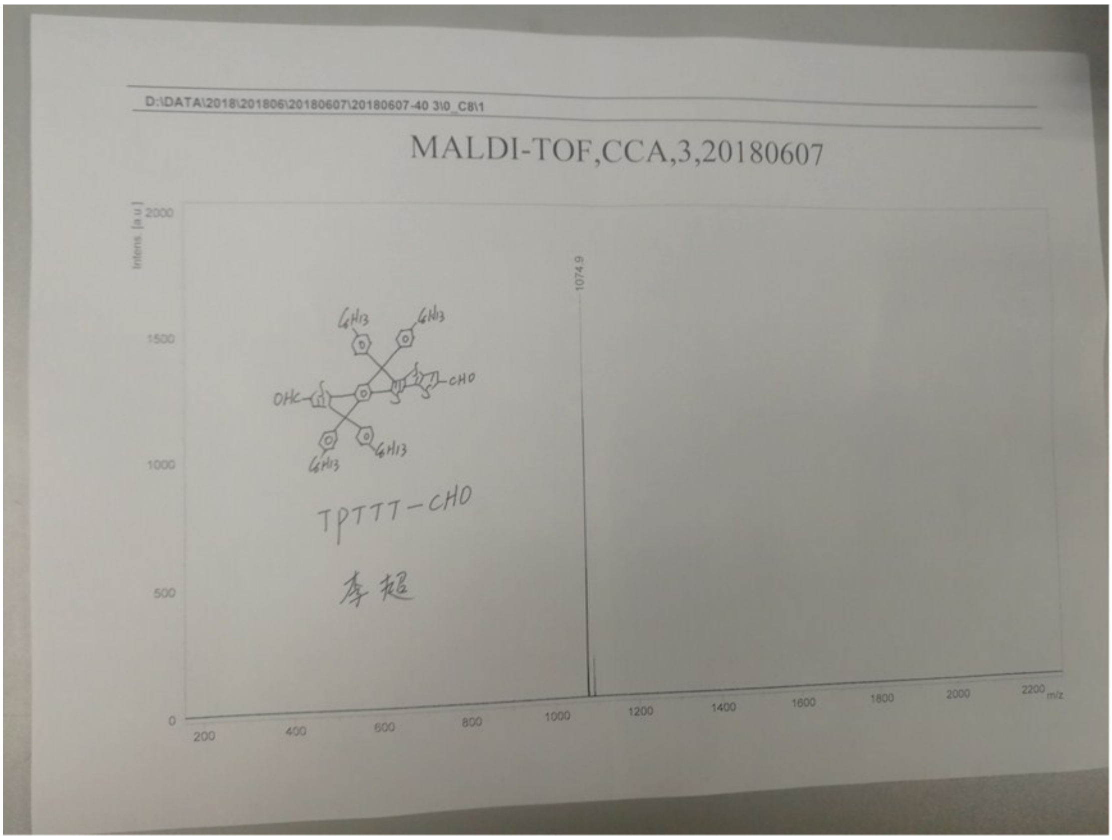


Figure S13. ^{13}C NMR spectrum of **TPTTT-CHO**.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MALDI-TOF,CCA,3,20180607

TPTTT-CHO

李超

Figure S14. HR-MS spectrum of **TPTTT-CHO**.

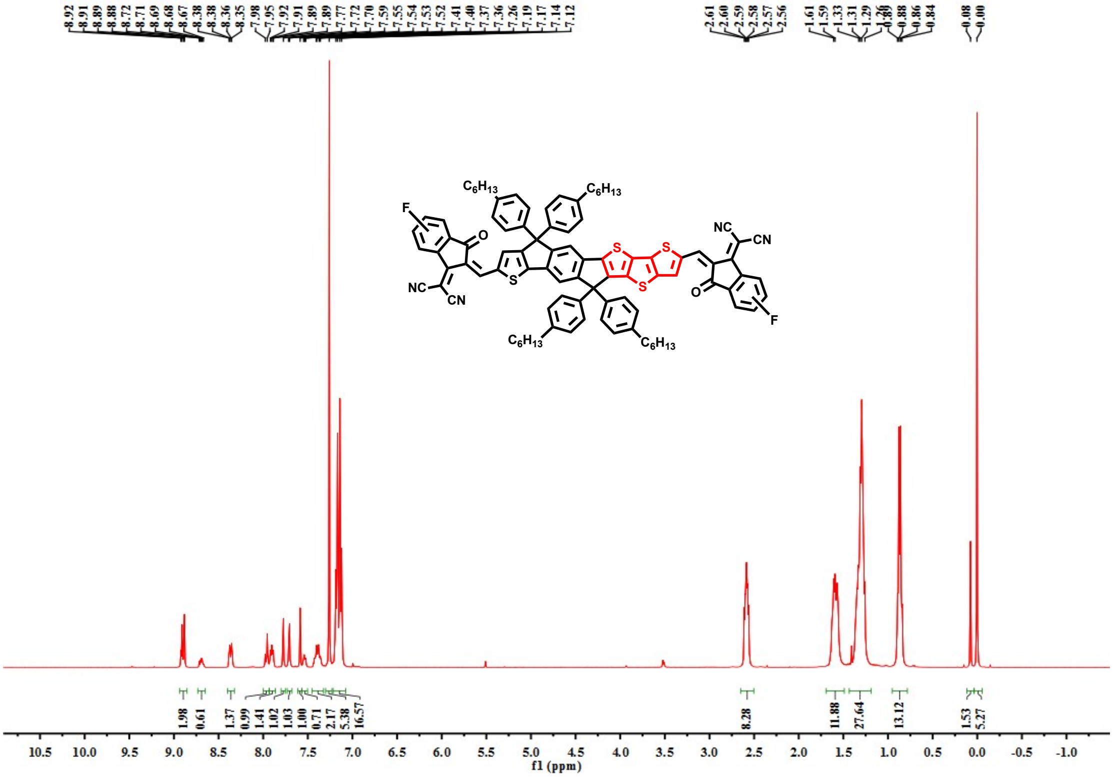

Figure S15. ^{1}H NMR spectrum of **TPTTT-2F**.

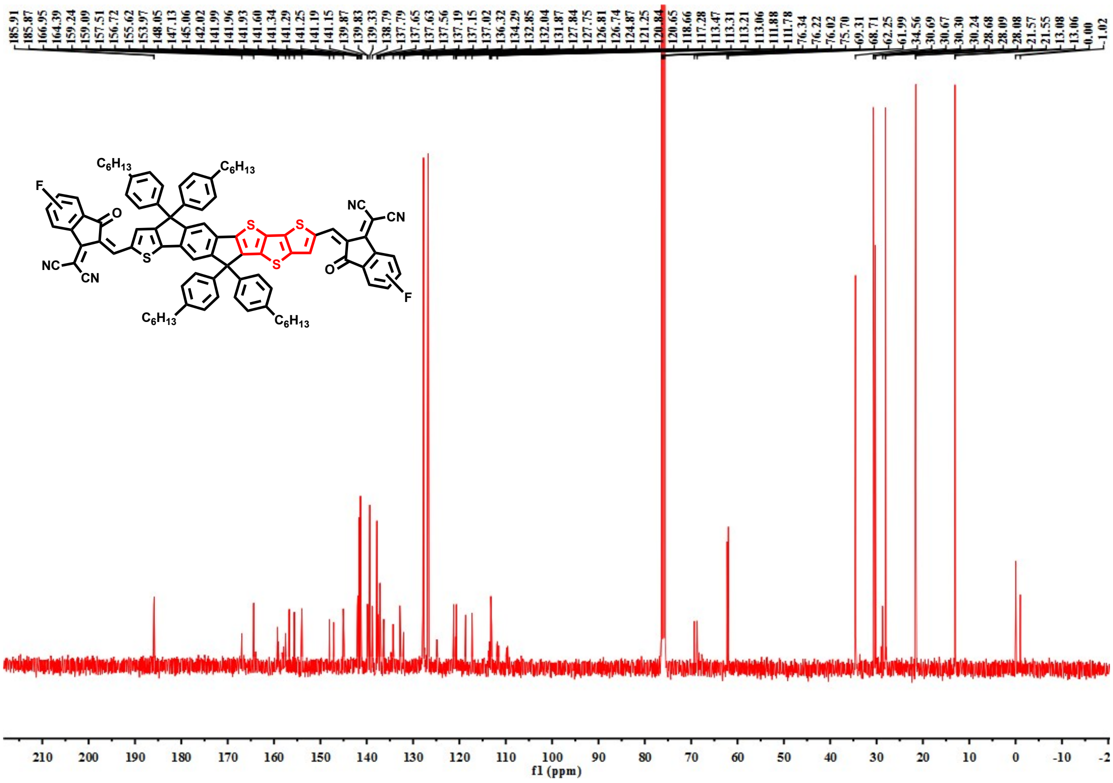

Figure S16. ^{13}C NMR spectrum of **TPTTT-2F**.

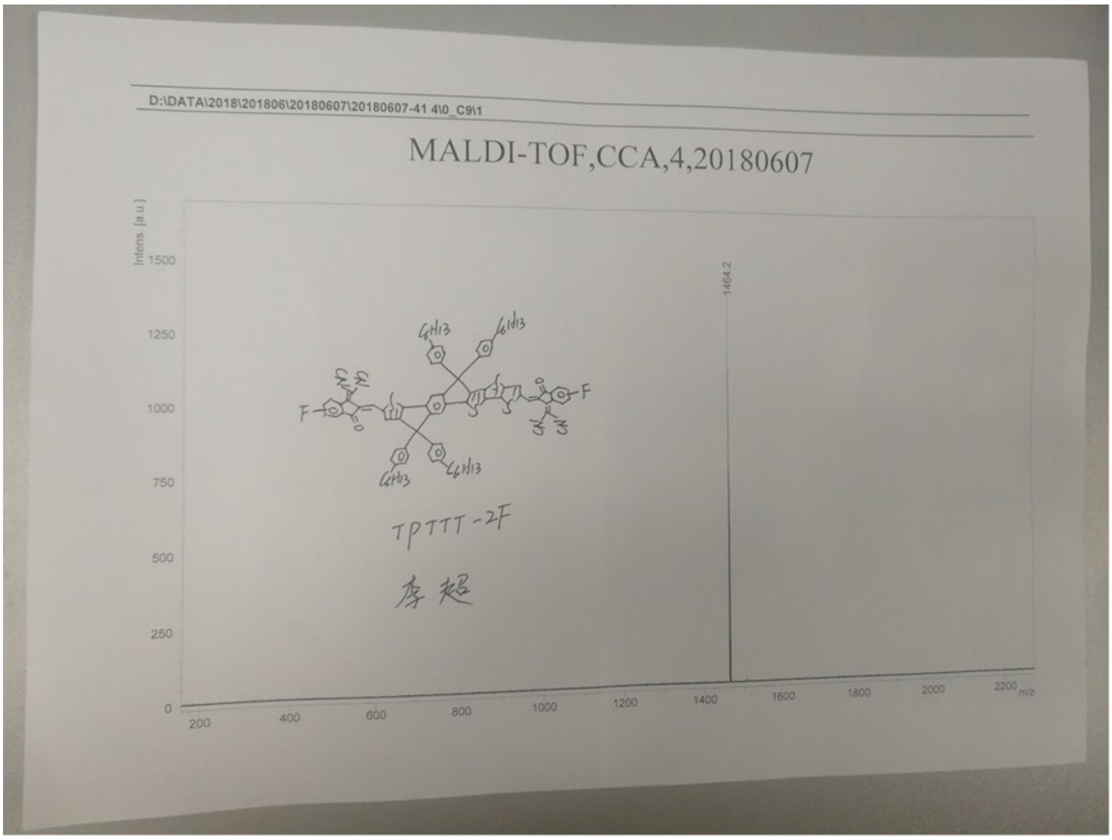

Figure S17. HR-MS spectrum of **TPTTT-2F**.

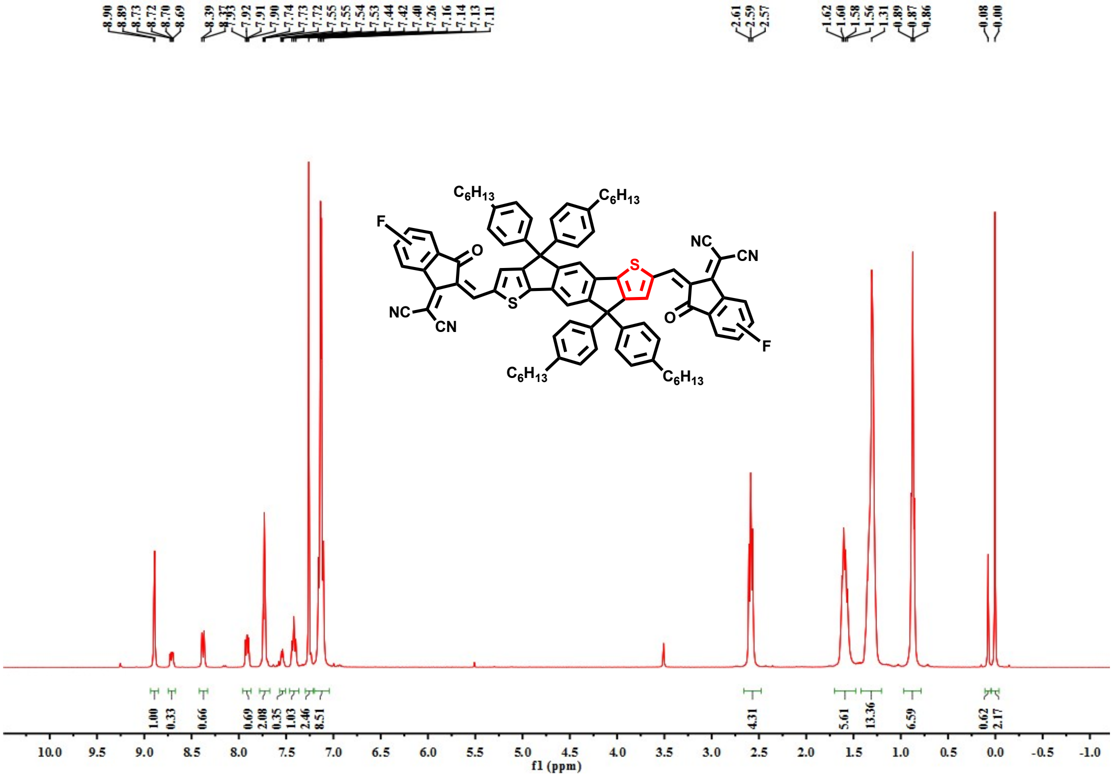

Figure S18. ^{1}H NMR spectrum of **TPT-2F**.

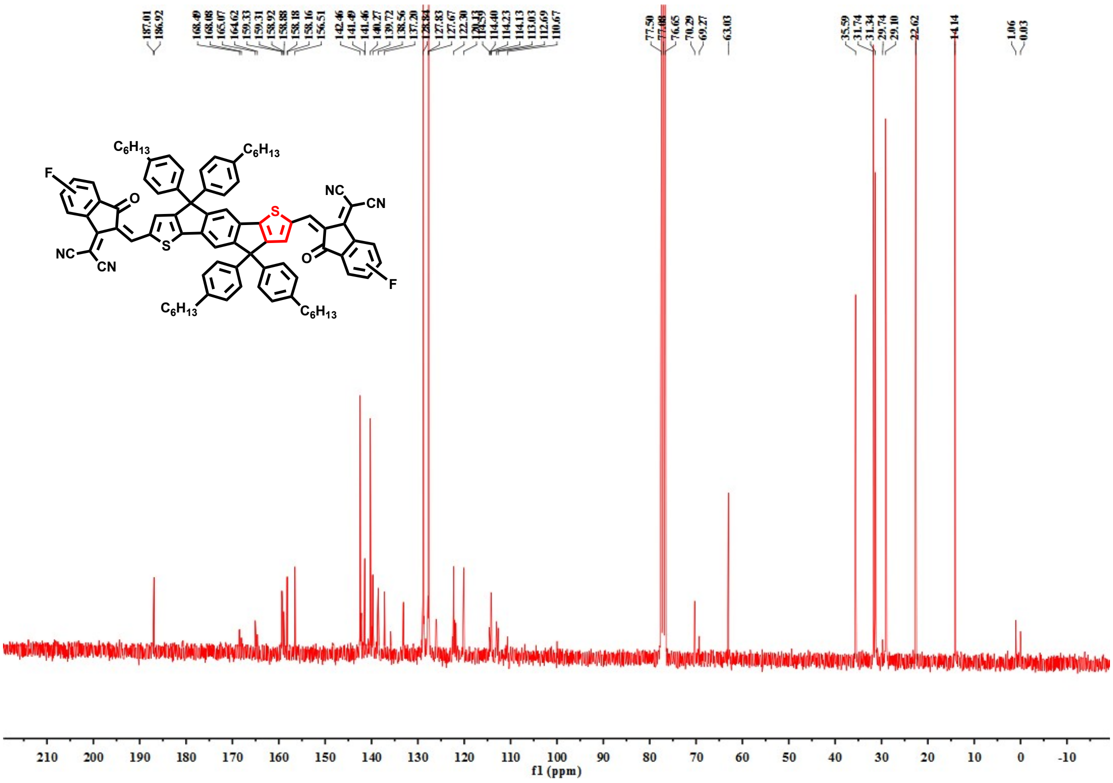

Figure S19. ^{13}C NMR spectrum of **TPT-2F**.

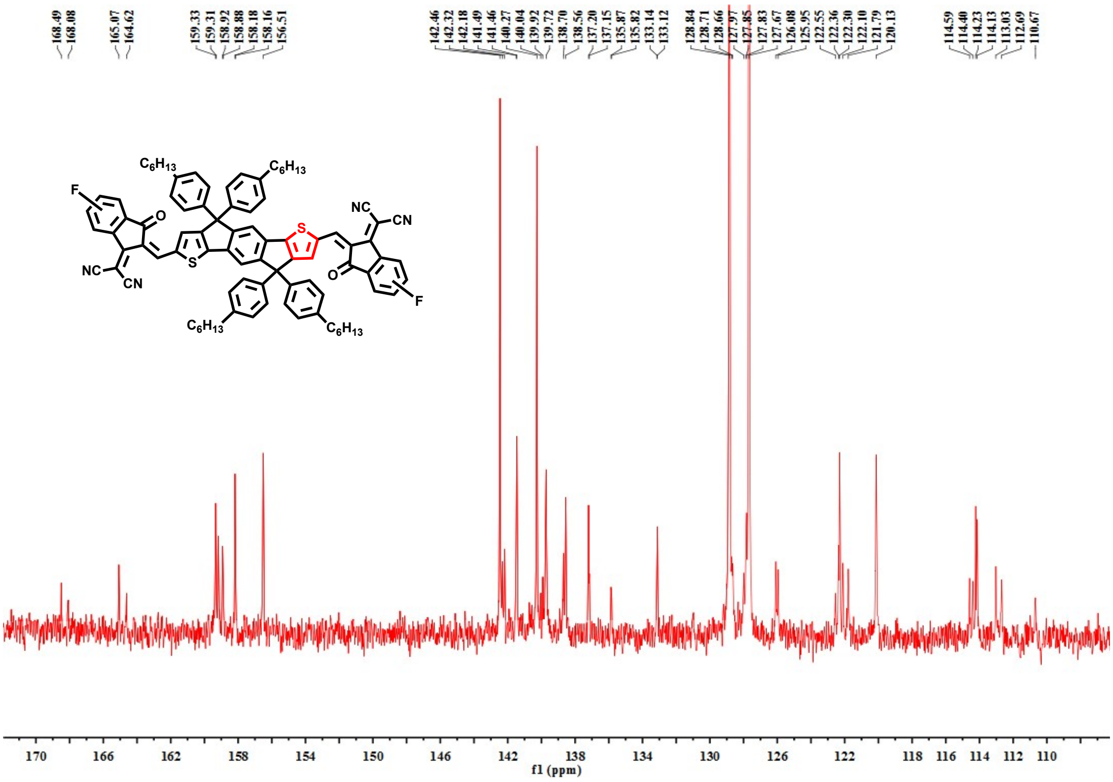

Figure S20. ^{13}C NMR spectrum of **TPT-2F** (partial spectrum).

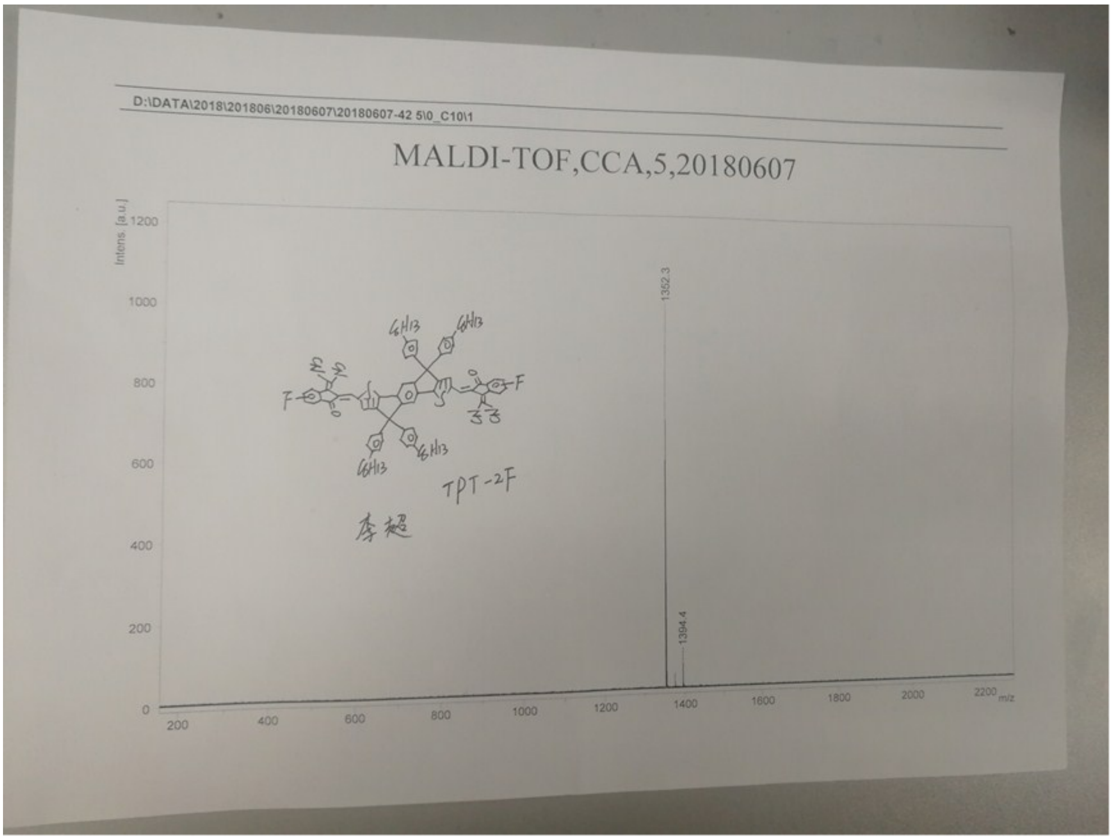

Figure S21. HR-MS spectrum of **TPT-2F**.

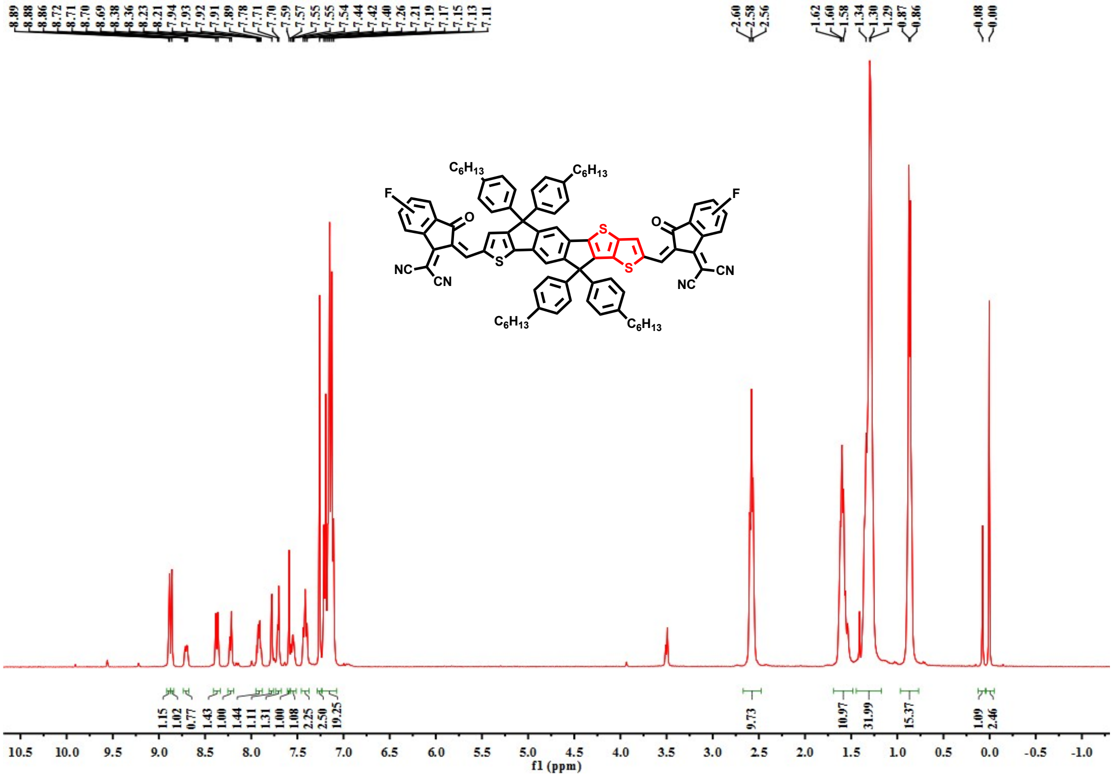

Figure S22. ^{1}H NMR spectrum of **TPTT-2F**.

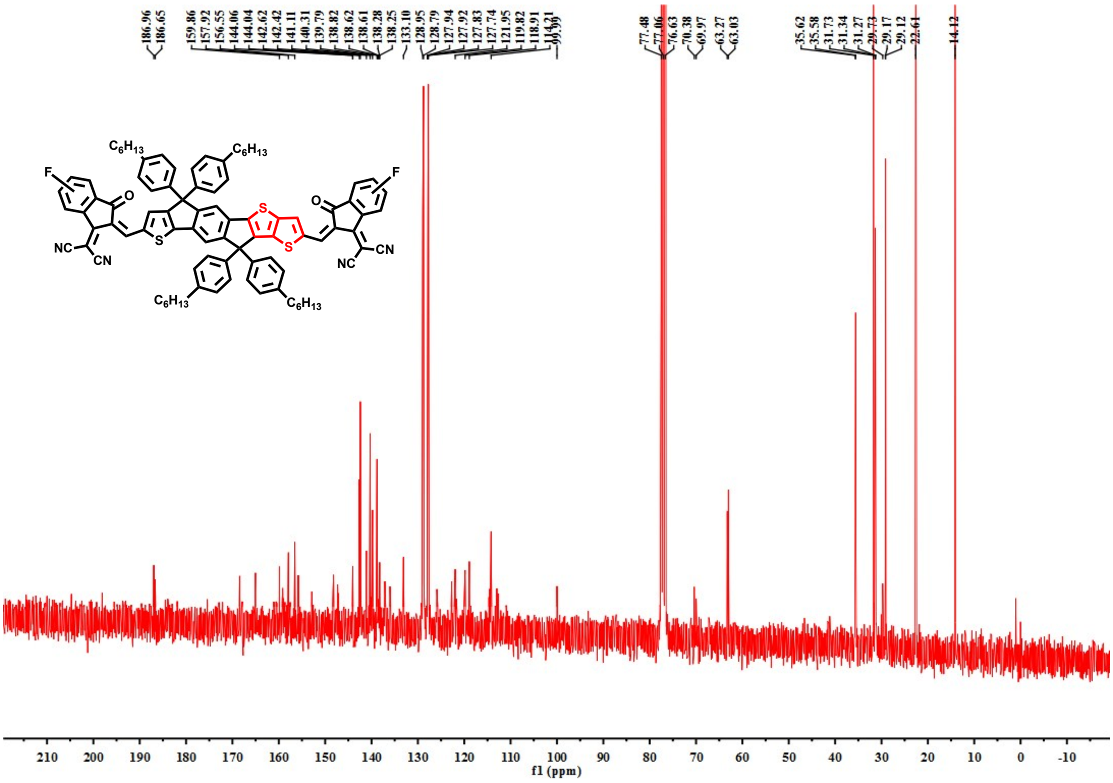

Figure S23. ^{13}C NMR spectrum of **TPTT-2F**.

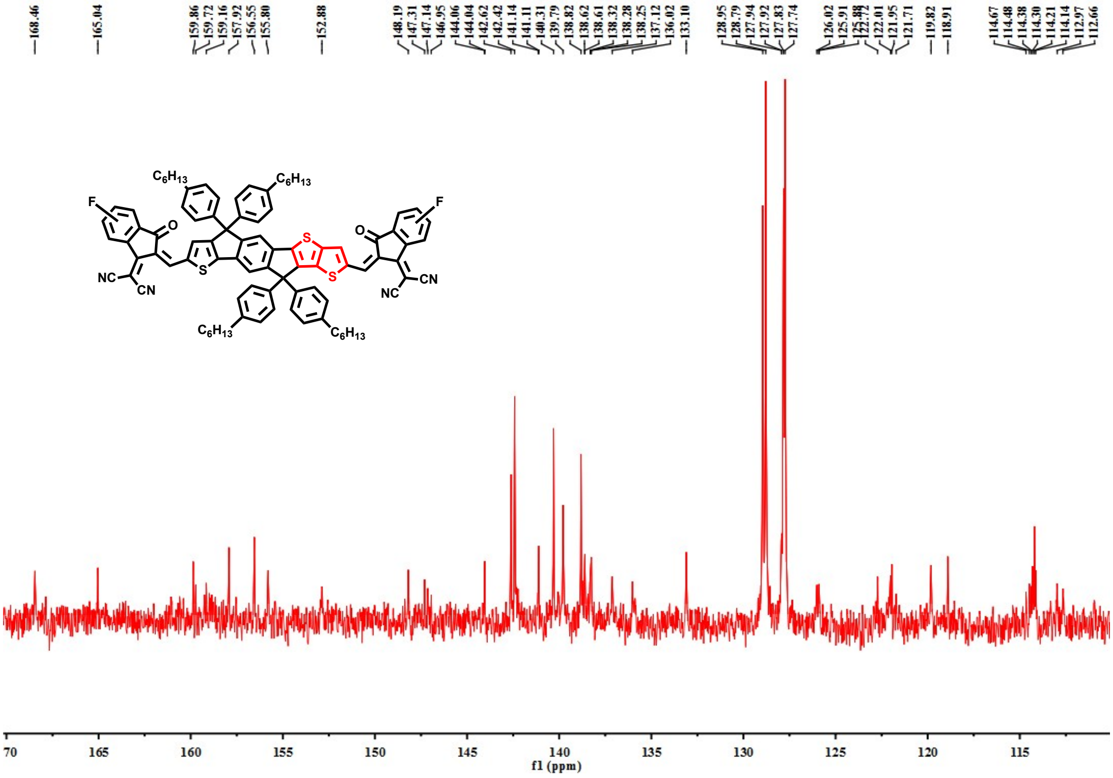

Figure S24. ^{13}C NMR spectrum of **TPTT-2F** (partial spectrum).

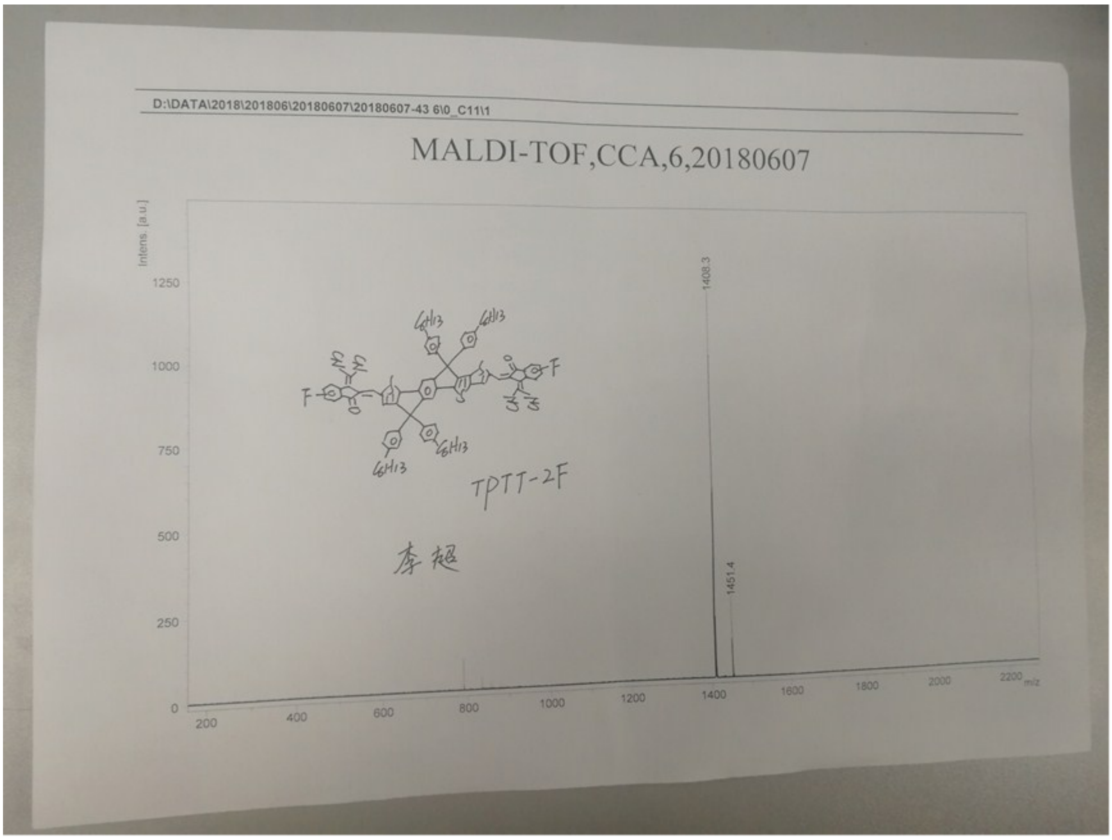

Figure S25. HR-MS spectrum of **TPTT-2F**.

S1.6 Reference

1. C. Li, Y. Xie, B. Fan, G. Han, Y. Yi and Y. Sun, *J. Mater. Chem. C*, 2018, **6**, 4873-4877.
2. E. Y. Ko, G. E. Park, J. H. Lee, H. J. Kim, D. H. Lee, H. Ahn, M. A. Uddin, H. Y. Woo, M. J. Cho and D. H. Choi, *ACS Appl. Mater. Interfaces*, 2017, **9**, 8838-8847.