Fluorene-Fused Ladder-Type Non-Fullerene Small Molecular Acceptors for High-Performance Polymer Solar Cells

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General Information

^{1}H NMR and ^{13}C NMR spectra of all compounds were recorded on a Bruker Advanced II (400 MHz) spectrometer using *d*-chloroform as solvent. The high resolution mass spectra (HRMS) were recorded on Thermo Scientific LTQ Orbitrap XL using ESI, and matrix-assisted laser desorption ionization-time of flight mass spectrometry (MALDI-TOF MS) were performed on 5800 MALDI-TOF/TOF mass spectrometry (AB SCIEX, USA) in positive mode. UV-vis spectra were measured using a Shimadzu UV-2700 recording spectrophotometer. Cyclic voltammetry (CV) measurements were conducted on a CHI voltammetric analyzer in acetonitrile solution with Pt disk, Pt plate, and standard calomel electrode (SCE) as working electrode, counter electrode, and reference electrode, respectively, in 0.1 M tetrabutylammonium hexafluorophosphate (*n*-Bu$_4$NPF$_6$) as supporting electrolyte at room temperature by using a scan rate of 100 mV s^{-1}. The CV curves were recorded versus the potential of SCE, which was calibrated by the ferrocene-ferrocenium

(Fc/Fc$^+$) redox couple (4.8 eV below the vacuum level). Atomic force microscopy (AFM) images were obtained by using a NanoMan VS microscope in the tapping-model. Transmission electron microscopy (TEM) images of films were obtained by using a JEOL JEM-1400 transmission electron microscope operated at 80 kV. The wave functions were obtained using Gaussian09 program at B3LYP/6-31G(d) level.

Device Fabrication and Characterization

PSCs were fabricated with device structure of ITO/PEDOT:PSS/active layer/PDIN/Ag Al, where ITO (indium tin oxide) and Al was anode and cathode; PEDOT: PSS (poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate)) and PDIN (N,N′-bis-(propylenedimethylamine)-3,4,9,10-perylenediimide) served as hole and electron transport layers (HTL and LTL), respectively. The cleaned ITO substrates were treated by oxygen plasma for 1 min to improve its work function and clearance. PEDOT:PSS solution was spin-coated on the ITO substrates at 5000 RPM for 40 s and then baked at 150℃ for 15 min in air. The donor of PBDB-T was purchased from Solarmer Materials Inc.. The PBDB-T: FTTCN and PBDB-T-2F: FTTCN-M with 1:1 weight ratio were dissolved in chlorobenzene (adding 1% v/v of 1,8-diiodooctane, DIO) to prepare 20 mg/mL binary blend solutions, respectively. After heated and stirred at 60℃ for ~3 h, the prepared blend solutions were spin-coated on PEDOT:PSS at 2000 rpm for 40 s in high-purity nitrogen-filled glove box. Then the active layers were annealed at 100℃ for 10 min . The methanol solution (0.3% acetic acid) of PDIN at a concentration of 2 mg/mL was prepared to fabricate LTL. The

prepared PDIN solution was spin-coated onto active layers at 5000 RPM for 40 s. Finally, 100 nm Al was deposited by thermal evaporation with a shadow mask and the effective area of cell is 3.8 mm^2, which is defined by the vertical overlap of ITO anode and Al cathode.

Current-voltage (I-V) curves of PSCs were measured using a Keithley 2400 source meter in high-purity nitrogen-filled glove box. The AM 1.5 illumination with light intensity of 100 mW/cm2 was provided by a XES-40S2-CE (SAN-EI Electric Co., Ltd.) solar simulator (AAA class, 40×40 mm2 effective irradiated area). This light intensity was calibrated by standard silicon solar cells purchased from Zolix INSTRUMENTS CO., LTD. The different light intensity was obtained by a set of neutral optical filters with transmission of 10%, 25%, 50% and 79%, respectively. External quantum efficiency (EQE) spectra of PSCs were measured by a Zolix Solar Cell Scan 100.

Synthesis of compound 1:

To a 250 mL two-necked round bottom flask, 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene (1.6 g, 2.73 mmol), ethyl 2-bromothieno[3,2-b]thiophene-3-carboxylate (1.75 g, 6.0 mmol), anhydrous K_2CO_3 (3.7 g, 27.3 mmol), Aliquat 336 (2 drops) and $Pd(PPh_3)_4$ (315 mg, 0.27 mmol) were dissolved in deoxygenated toluene/H_2O (120 mL, v/v = 5:1). Then the reaction mixture was refuxed for 24 h. After cooling to room temperature, 100 mL water was added, then the mixture was extracted with dichloromethane (DCM), and the organic layer was collected, washed with water and dried with anhydrous Na_2SO_4. After removal of the

solvent under reduced pressure, the residue was purified by column chromatography on silica gel using a mixture solvent (petroleum ether/dichloromethane, v/v = 1/1) as eluent to give a yellow solid (1.69 g, 82%). ^{1}H NMR (400 MHz, CDCl$_3$), δ (ppm): 7.76~7.78 (d, 2H), 7.54~7.59 (m, 4H), 7.45~7.47 (d, 2H), 7.25~7.28 (d, 2H), 4.26~4.33 (m, 4H), 1.98~2.03 (m, 4H), 1.24~1.28 (m, 6H), 1.09~1.10 (m, 12H), 0.75~0.87 (m, 10H); ^{13}C NMR (100 MHz, CDCl$_3$), δ (ppm): 162.27, 153.96, 150.91, 141.20, 140.78, 135.89, 132.88, 129.15, 128.47, 124.69, 120.80, 119.42, 118.85, 60.88, 55.39, 40.19, 31.51, 29.74, 23.84, 22.63, 14.23, 14.07; HRMS (ESI) m/z: [M + H]$^+$ calcd. for C$_{43}$H$_{47}$O$_4$S$_4^+$, 755.23517, found 755.23541.

Synthesis of compound 2:

To a stirring solution of compound 2 (1.2 g, 1.59 mmol) in dry THF (30 mL) under argon condition was added dropwise (4-hexylphenyl) magnesium bromide which was prepared from 1-bromo-4-hexylbenzene (5.75 g, 23.8 mmol) and magnesium (630 mg, 26.2 mmol) in THF (20 mL). Then the mixed solution was heated to reflux for 16 h. After cooling to room temperature, the solution was poured into water and extracted with ethyl acetate, then washed with saturated salt water several times and dried with anhydrous Na$_2$SO$_4$. After removal of the solvent under reduced pressure, the crude product was obtained and then used in the next step without further purification. The crude product was dissolved in glacial acetic acid (100 mL), and 1 mL concentrated sulfuric acid in 5 mL glacial acetic acid was dropwise added into the solution, then the mixture was heated to 85°C for 2 h. After cooling to room temperature, the mixture was extracted with dichloromethane and washed with water. The collected organic

layer was dried with anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel using a mixture solvent as eluent (petroleum ether/dichloromethane, v/v = 15/1) to give a yellow solid (1.14 g, 56%). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.59~7.62(d, 2H), 7.38~7.41(d, 2H), 7.27~7.30(d, 2H), 7.22~7.25(d, 2H), 7.15~7.18(d, 8H), 7.06~7.09(d, 8H), 2.53~2.56(m, 8H), 2.02~2.05(m, 4H), 1.48~1.51(m, 12H), 1.20~1.23(m, 24H), 1.01~1.03(m, 12H) 0.69~0.80(m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 152.47, 151.34, 146.18, 143.49, 141.59, 141.52, 140.72, 139.53, 137.02, 128.45, 128.20, 126.29, 120.41, 117.22, 113.64, 62.98, 54.62, 40.68, 35.67, 31.78, 31.70, 31.58, 31.31, 29.87, 29.30, 24.04, 22.71, 22.68, 14.18, 14.13; MALDI-TOF-MS m/z: [M] calcd. for $C_{87}H_{102}S_4$, 1274.69, found 1274.94.

Synthesis of compound 3:

To a dry 100 mL two-necked round bottom flask, 20 mL anhydrous N, N-dimethylformamide (DMF) was added, and the solution was cooled to $0^{o}C$ and stirred when 4 mL phosphorous oxychloride ($POCl_3$) was added by syringe under argon protection. The mixture was kept at $0^{o}C$ for 1.5h, and then compound 2 (800 mg, 0.63 mmol) in dry 1, 2-dichloroethane (30 mL) was added. Then the mixture solution was allowed to reflux overnight. After cooling to room temperature, 100 mL water was added, then the mixture was extracted with dichloromethane (DCM), and the organic layer was collected, washed with water and dried with anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using a mixture solvent as eluent (petroleum

ether/dichloromethane, v/v = 3/2) to give a yellow solid (676 mg, 81%). ^{1}H NMR (400 MHz, CDCl$_3$), δ (ppm): 9.81(s, 2H), 7.88(s, 2H), 7.58(s, 2H), 7.39(s, 2H), 6.99~7.06(m, 16H), 2.44~2.49(m, 8H), 1.96~1.98 (m, 16H), 1.48~1.51(m, 12H), 1.20~1.23(m, 24H), 1.01~1.03(m, 12H) 0.69~0.80(m, 18H); ^{13}C NMR (100 MHz, CDCl$_3$), δ (ppm): 182.89, 153.67, 151.84, 150.17, 146.34, 144.00, 142.06, 141.35, 140.68, 140.49, 139.67, 136.32, 129.94, 128.86, 127.93, 117.68, 114.66, 63.03, 54.75, 40.54, 35.59, 31.70, 31.48, 31.24, 29.74, 29.19, 24.00, 22.62, 22.59, 14.10, 14.04; MALDI-TOF-MS m/z: [M] calcd. for C$_{89}$H$_{102}$O$_2$S$_4$, 1330.68, found 1331.22.

Synthesis of FTTCN:

To a 100 mL round bottom flask, compound 3 (200 mg, 0.15 mmol), 2-(6-oxo-5,6-dihydro-4H-cyclopenta[c]thiophen-4-ylidene)malononitrile (120 mg, 0.60 mmol), chloroform (30 ml) were added under argon protection and stirred for a while when pyridine (1 mL) was added. The mixture was kept stirring at 70°C for 12 h. After removal of chloroform of reaction mixture under reduced pressure, 100 mL methanol was added and the precipitate was collected by filtration. The residue was purified by column chromatography on silica gel using a mixture solvent as eluent (petroleum ether/dichloromethane, v/v = 1/1) to give a dark solid (211 mg, 83%). ^{1}H NMR (400 MHz, CDCl$_3$), δ (ppm): 8.78(s, 2H), 8.34(s, 2H), 8.11(s, 2H), 7.91(s, 2H), 7.66(s, 2H), 7.52(s, 2H), 7.10~7.20(m, 16H), 2.52~2.57(m, 8H), 2.06~2.11(m, 4H), 1.48~1.51(m, 12H), 1.20~1.23(m, 24H), 1.01~1.03(m, 12H) 0.69~0.80(m, 18H); ^{13}C NMR (100 MHz, CDCl$_3$), δ (ppm): 181.38, 156.21, 154.83, 154.32, 152.34, 148.08, 147.22, 143.39, 142.52, 142.25, 141.59, 139.58, 139.36, 139.24, 137.28, 137.26, 136.34,

128.78, 128.27, 127.97, 127.54, 117.98, 115.23, 114.40, 67.24, 63.11, 54.85, 35.60, 31.70, 31.50, 31.23, 29.74, 29.24, 24.07, 22.59, 14.09, 14.03; MALDI-TOF-MS m/z: [M] calcd. for $C_{109}H_{106}N_4O_2S_6$, 1694.66, found 1695.36.

Synthesis of FTTCN-M:

To a 100 mL round bottom flask, compound 3 (200 mg, 0.15 mmol), 2-(1-methyl-6-oxo-5,6-dihydro-4H-cyclopenta[c]thiophen-4-ylidene)malononitrile (128 mg, 0.60 mmol), chloroform (30 ml) were added under argon protection and stirred for a while when pyridine (1 mL) was added. The mixture was kept stirring at 70°C for 12 h. After removal of chloroform of reaction mixture under reduced pressure, 100 mL methanol was added and the precipitate was collected by filtration. The residue was purified by column chromatography on silica gel using a mixture solvent as eluent (petroleum ether/dichloromethane, v/v = 1/1) to give a dark solid (202 mg, 78%). ^{1}H NMR (400 MHz, CDCl$_3$), δ (ppm): 8.71(s, 2H), 8.12(s, 2H), 8.08(s, 2H), 7.65(s, 2H), 7.51(s, 2H), 7.11~7.21(m, 16H), 2.79(s, 6H), 2.53~2.58(m, 8H), 2.07~2.12(m, 4H), 1.48~1.51(m, 12H), 1.20~1.23(m, 24H), 1.01~1.03(m, 12H) 0.69~0.80(m, 18H); ^{13}C NMR (100 MHz, CDCl$_3$), δ (ppm): 182.28, 156.03, 154.70, 153.79, 152.27, 147.55, 144.49, 143.37, 142.22, 142.19, 141.48, 139.47, 139.09, 138.96, 137.07, 136.79, 136.31, 129.16, 128.80, 127.99, 124.83, 117.94, 115.19, 114.56, 66.66, 63.16, 54.84, 35.61, 31.70, 31.52, 31.22, 29.77, 29.25, 22.59, 14.09, 14.04, 13.62; MALDI-TOF-MS m/z: [M] calcd. for $C_{111}H_{110}N_4O_2S_6$, 1722.70, found 1723.54.
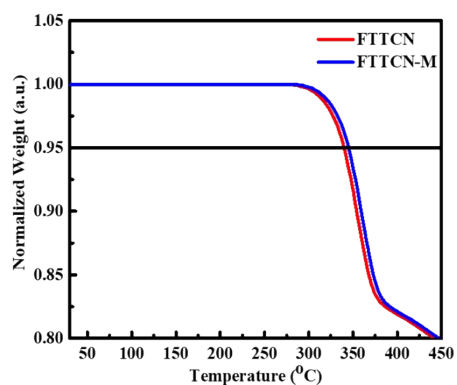
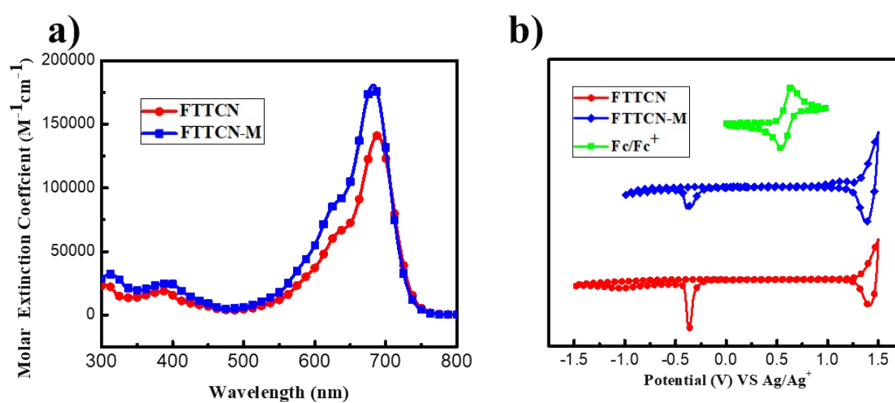Figure S1. TGA curve for FTTCN and FTTCN-M.

Figure S2. a) Absorption spectrum in dilute CF solution (1×10^{-5}M) of two SMAs; b) CV curves of two SMAs and Fc/Fc$^+$.
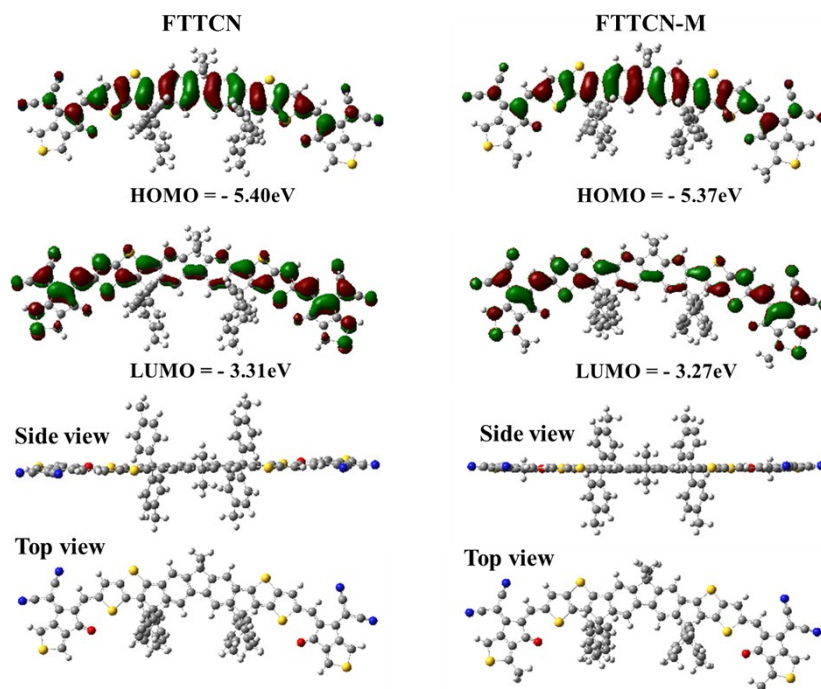

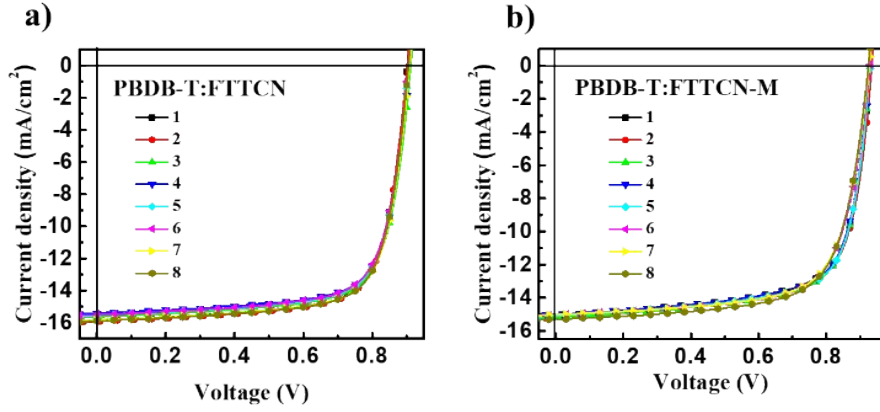**Figure S3.** Optimized geometry of FTTCN and FTTCN-M and its frontier molecular orbitals.

Figure S4. *J-V* curves of PBDB-T: FTTCN and PBDB-T: FTTCN-M for 8 devices.

Table S1. The devices photovoltaic parameters of PSCs based on PBDB-T:FTTCN (1:1 w/w) and PBDB-T:FTTCN-M (1:1 w/w) with 1.0 vol % DIO addition under illumination of AM 1.5 G at 100 mW cm^{-2}.

Active Layer	V_{oc} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)
PBDB-T:FTTCN	0.91	15.64	73.13	10.41
	0.91	15.42	72.89	10.23
	0.91	15.53	72.89	10.30
	0.90	15.48	73.35	10.22
	0.91	15.85	73.04	10.53
	0.90	15.89	73.82	10.56
	0.90	15.84	73.55	10.48
	0.90	15.93	73.38	10.52
PBDB-T:FTTCN-M	0.93	15.20	70.76	10.00
	0.93	15.07	70.78	9.92
	0.93	15.11	71.52	10.05
	0.93	15.19	71.37	10.08
	0.93	15.00	71.38	9.96
	0.93	15.03	70.60	9.87
	0.93	15.01	70.41	9.83
	0.92	15.30	70.70	9.95

Table S2. Photovoltaic parameters calculated from the J_{ph}-V_{eff} curves of PBDB T: FTTCN (1:1 w/w) and PBDB-T: FTTCN-M (1:1 w/w) with 1% DIO addition.

Active layer	J_{sat} (mA cm^{-2})	$J_{ph}^{\#}$ (mA cm^{-2})	J_{ph}^{*} (mA cm^{-2})	$\eta^{\#}$ (%)	η^{*} (%)
PBDB-T: FTTCN	16.92	15.89	14.29	93.9	84.5
PBDB-T: FTTCN-M	16.37	15.19	13.13	92.8	80.2

J_{sat} is the J_{ph} values at V_{eff} = 3.0 V; $J_{ph}^{\#}$ and J_{ph}^{*} are the J_{ph} values under the short circuit and maximum power output conditions, respectively. $\eta^{\#} = J_{ph}^{\#} /J_{sat}$, $\eta^{*} = J_{ph}^{*}/J_{sat}$.
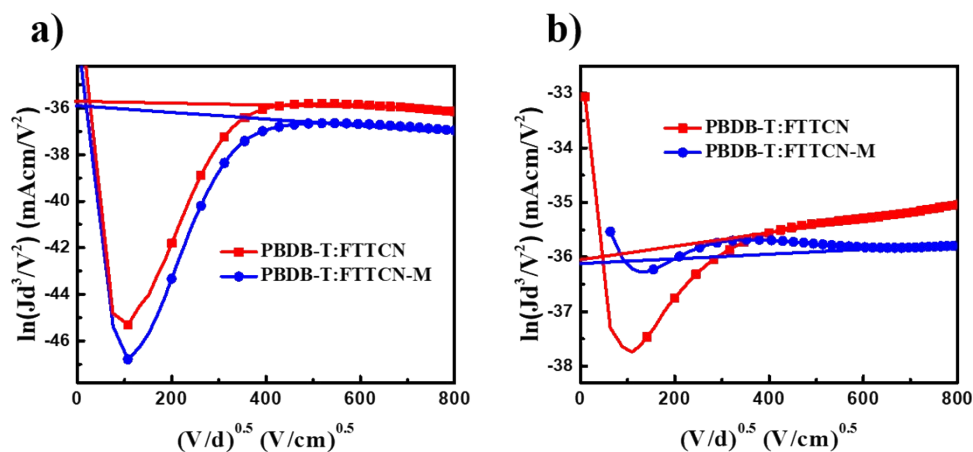
Figure S5. The $\ln(Jd^3/V^2)$ versus $(V/d)^{0.5}$ curves of (a) electron-only devices, (b) hole-only devices.

Table S3. Hole and electron mobility.

Active layer	μ_h (cm^{2}V^{-1}s^{-1})	μ_e (cm^{2}V^{-1}s^{-1})	μ_h/μ_e
PBDB-T: FTTCN	8.12×10^{-4}	6.60×10^{-4}	1.23
PBDB-T: FTTCN-M	7.49×10^{-4}	5.55×10^{-4}	1.35
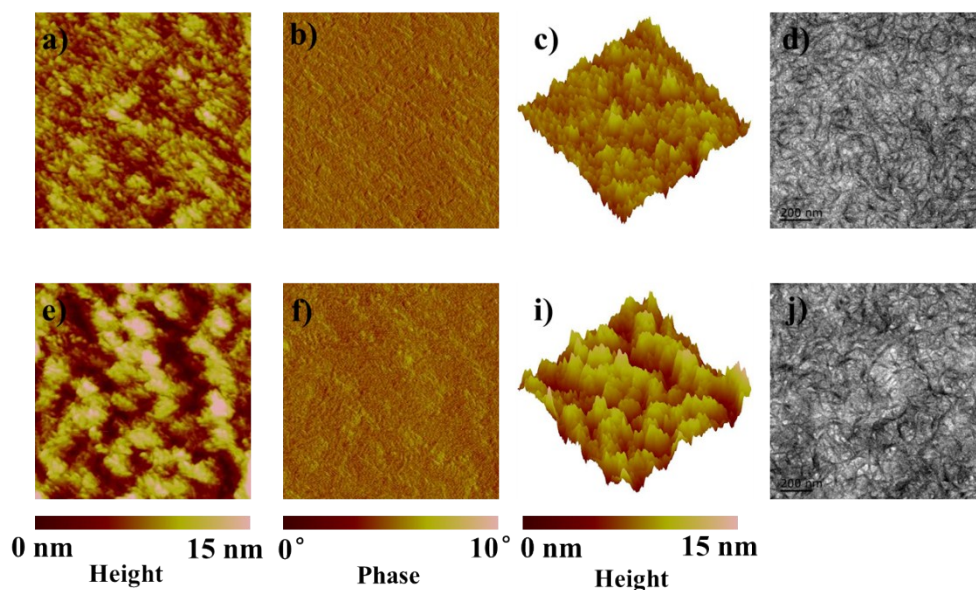
Figure S6. AFM height (a), phase (b) and 3D image (c) of PBDB-T:FTTCN; AFM height (e), phase (f) and 3D image (i) of PBDB-T:FTTCN-M. TEM image of PBDB-

T:FTTCN (d) and PBDB-T:FTTCN-M (j) (**2 um x 2 um**).

Table S4. Collections of photovoltaic data obtained from PSCs with fluorene-based SMAs as the blended acceptor materials.

SMAs	Donors	FFs	PCEs (%)	Ref.
DTBTF	DR3TSBDT	0.45	3.64	1
BAF-2HDT	PffBT4T-2OD	0.64	7.13	2
FRD$_2$	PTB7-Th	0.723	9.4	3
BAF-4CN	PffBT4T-2OD	0.707	8.40	4
FRdCN$_2$	PTB7-Th	0.719	10.70	5
FBM	PCE10	0.51	5.0	6
PMI-F-PMI	PTZ1	0.635	5.70	7
DCF-2HT	PBDB-T	0.495	5.71	8
F8-DPPTCN	PBDB-T	0.39	2.37	9
FTIC-C6C8	PBDB-T	0.647	11.12	10
DICTF	PTB7-Th	0.55	7.63	11
FDICTF	PBDB-T	0.66	9.81	12
FTTCN	PBDB-T	0.738	10.56	This Work

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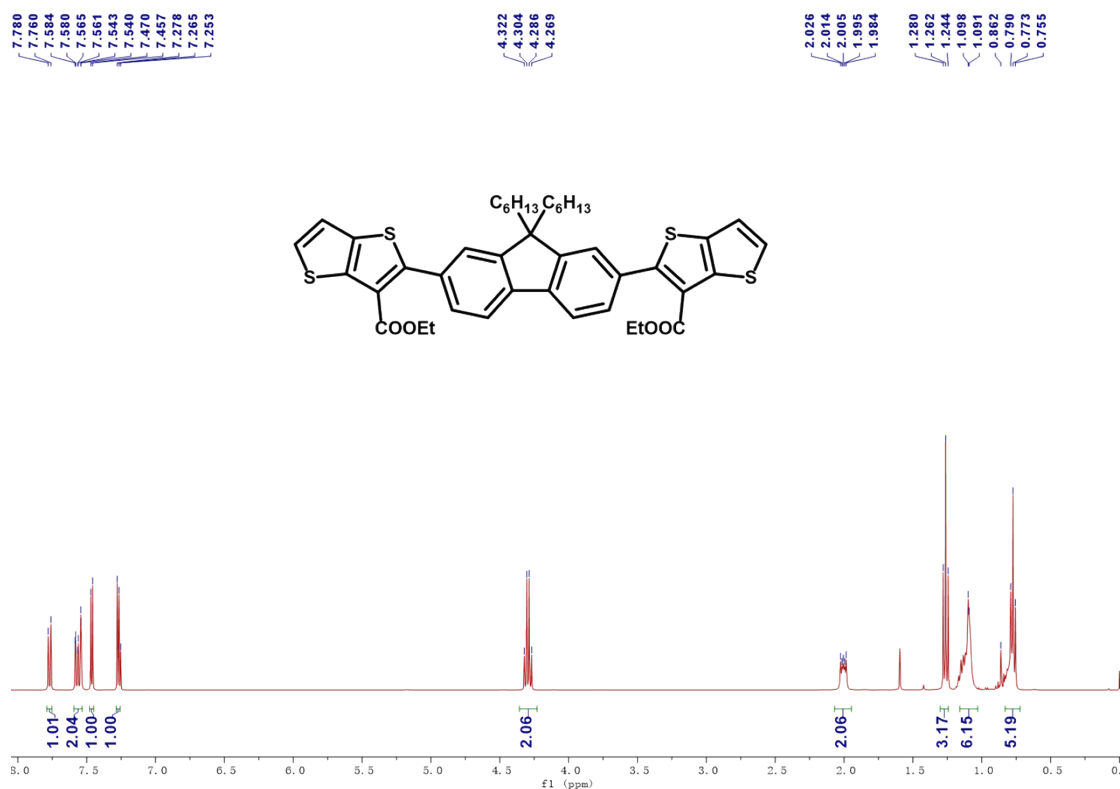
Figure S7. The ^{1}H NMR spectrum of compound 1 in CDCl$_3$.
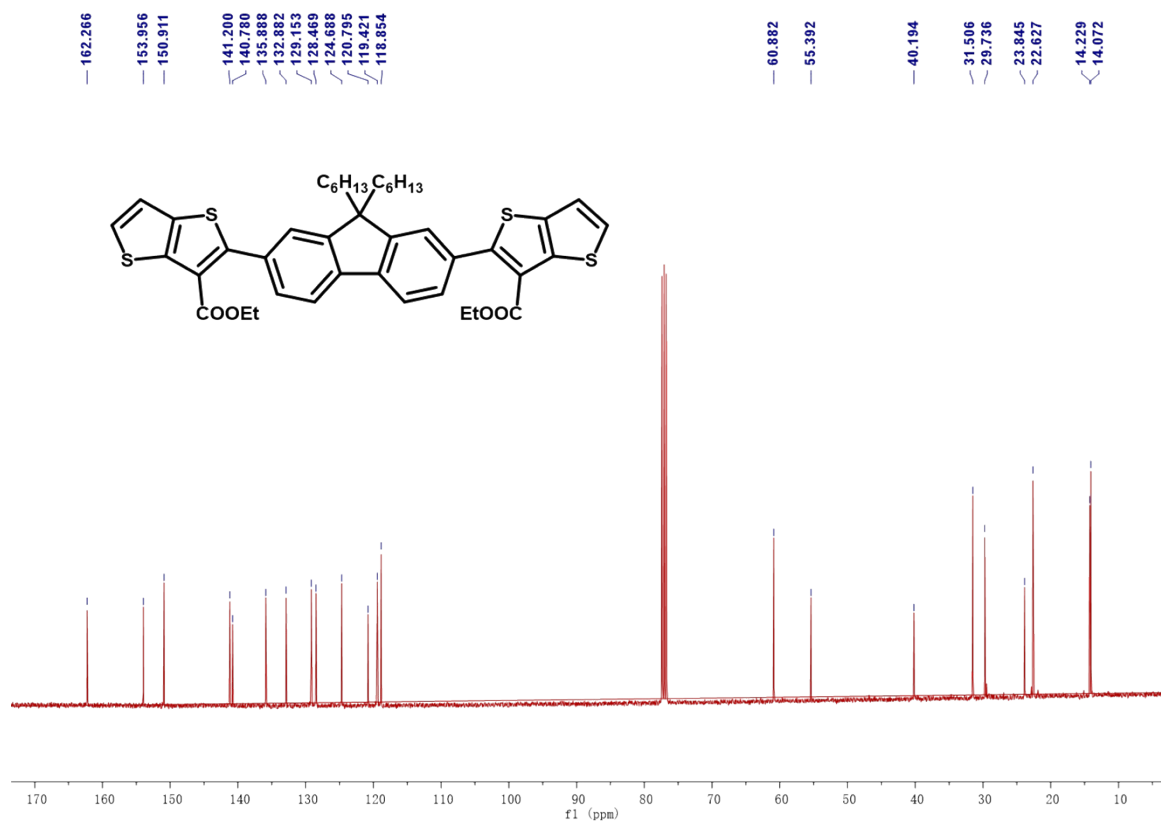
Figure S8. The ^{13}C NMR spectrum of compound 1 in CDCl$_3$.
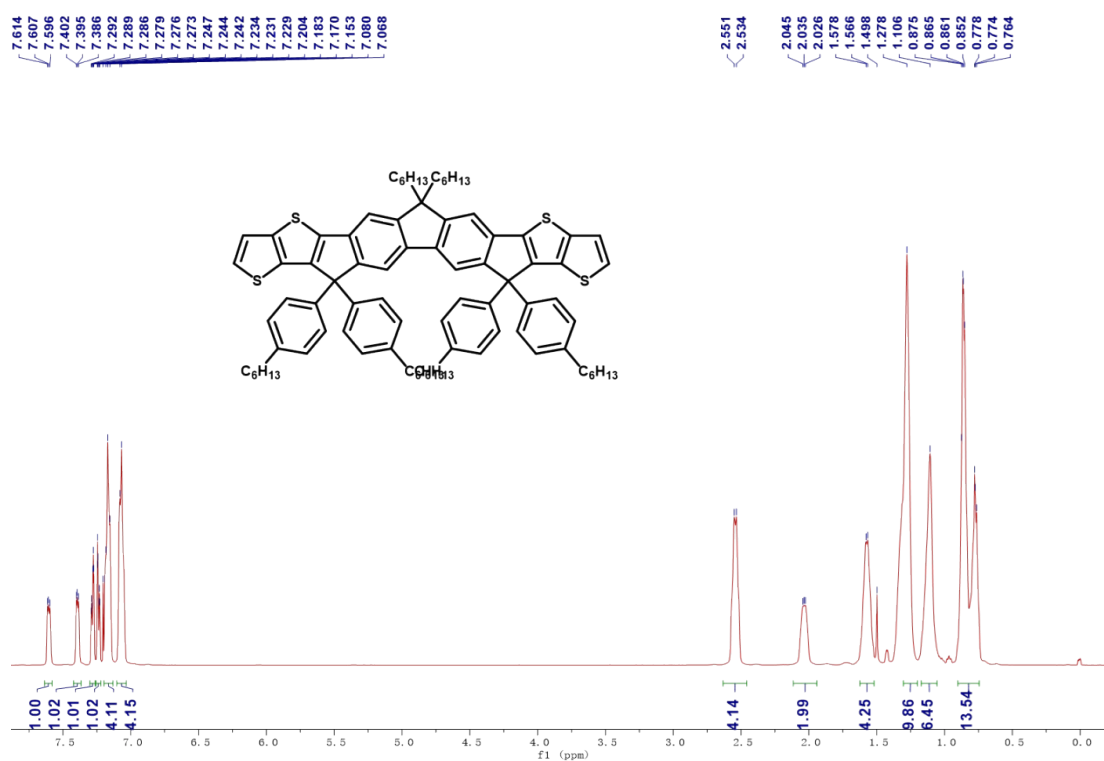
Figure S9. The ^1H NMR spectrum of compound 2 in CDCl$_3$.
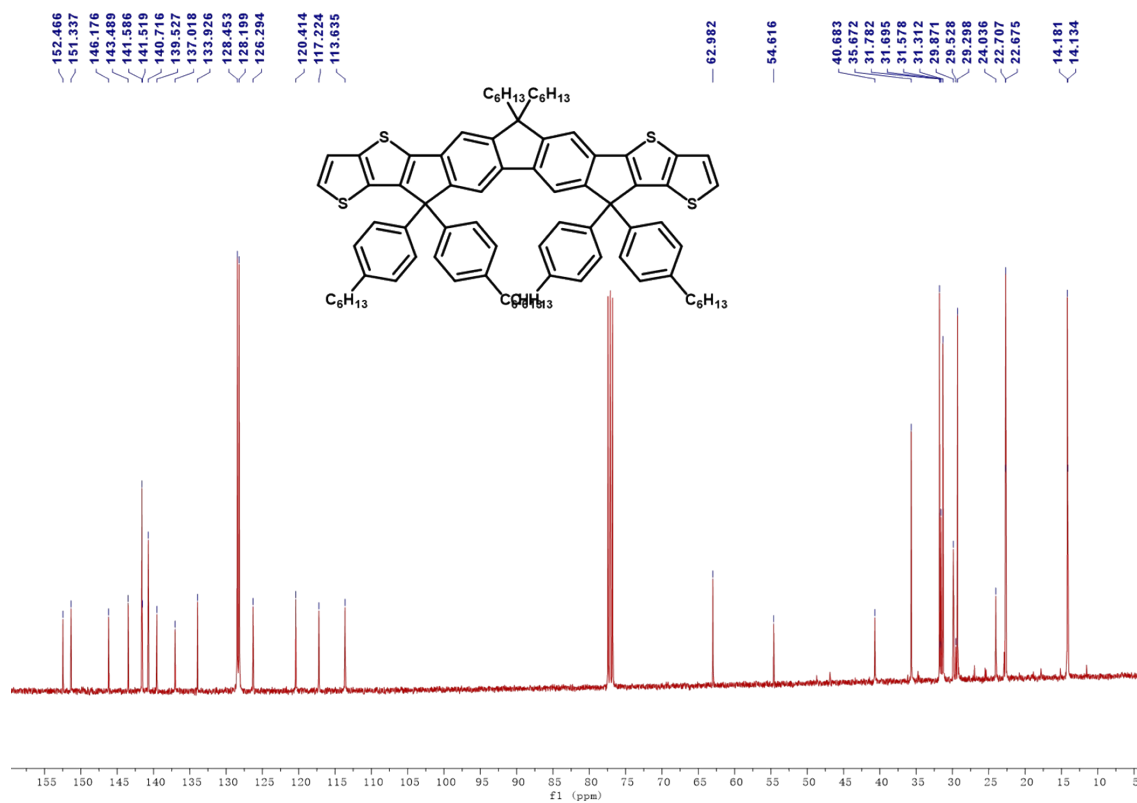
Figure S10. The ^{13}C NMR spectrum of compound 2 in CDCl$_3$.
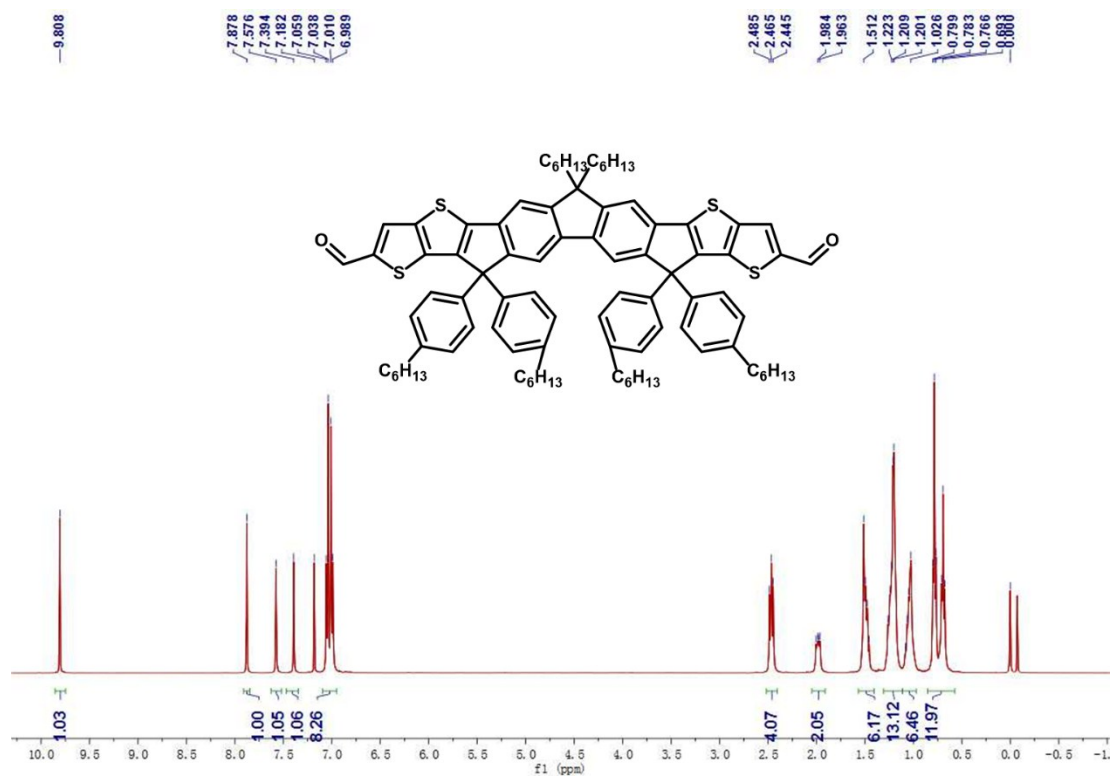
Figure S11. The ^{1}H NMR spectrum of compound 3 in CDCl$_3$.
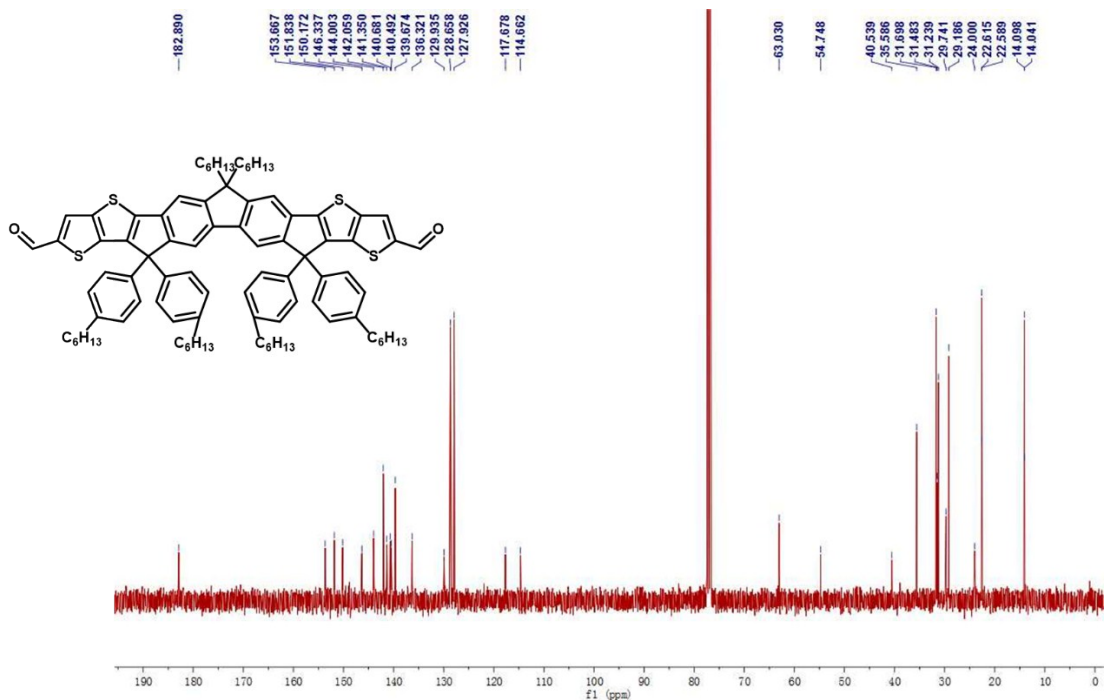
Figure S12. The ^{13}C NMR spectrum of compound 3 in CDCl$_3$.
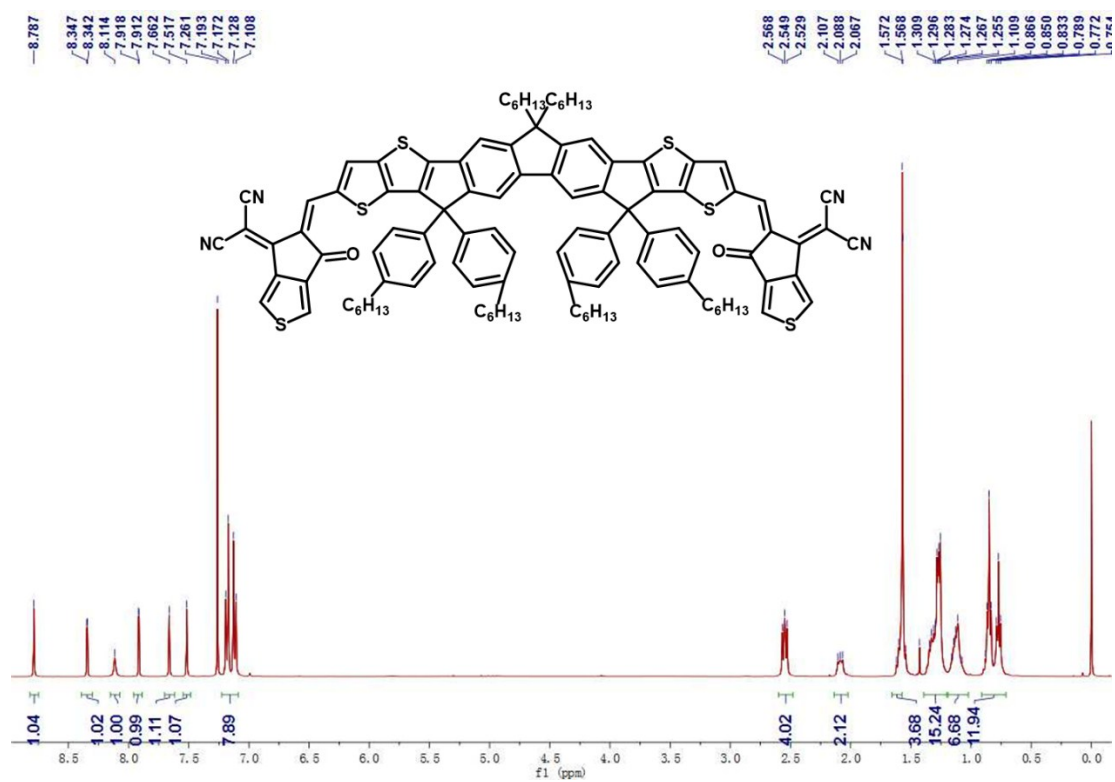
Figure S13. The ^{1}H NMR spectrum of FTTCN in CDCl$_3$.
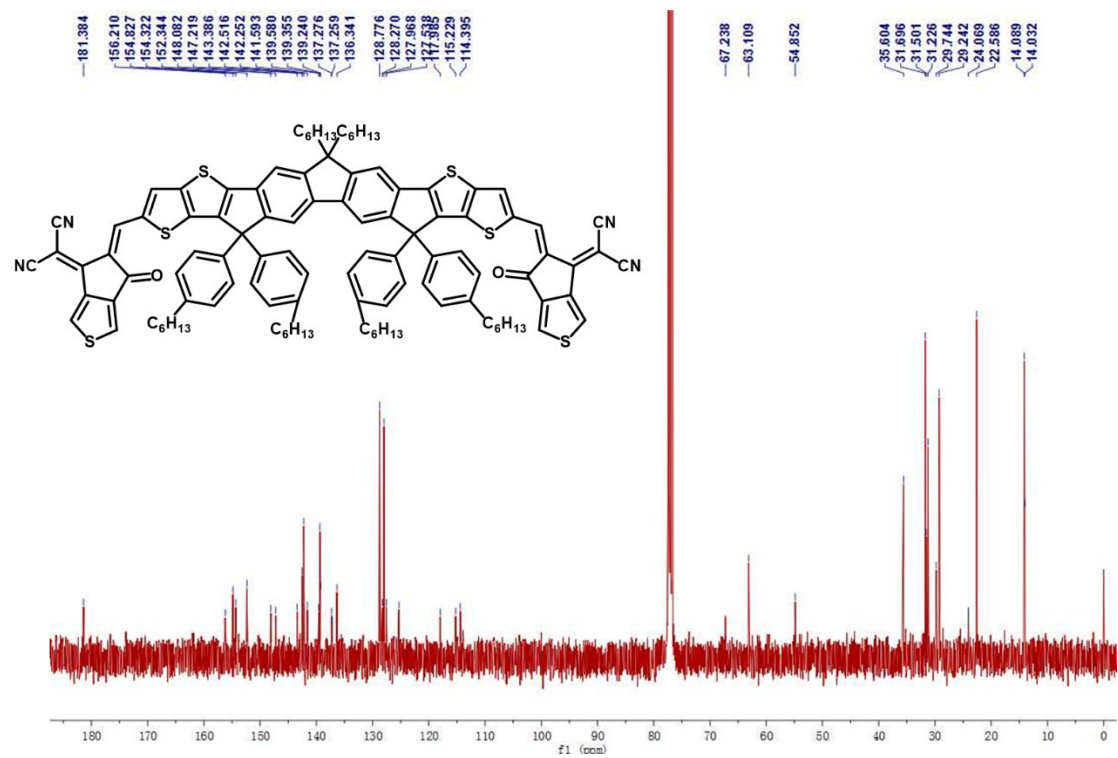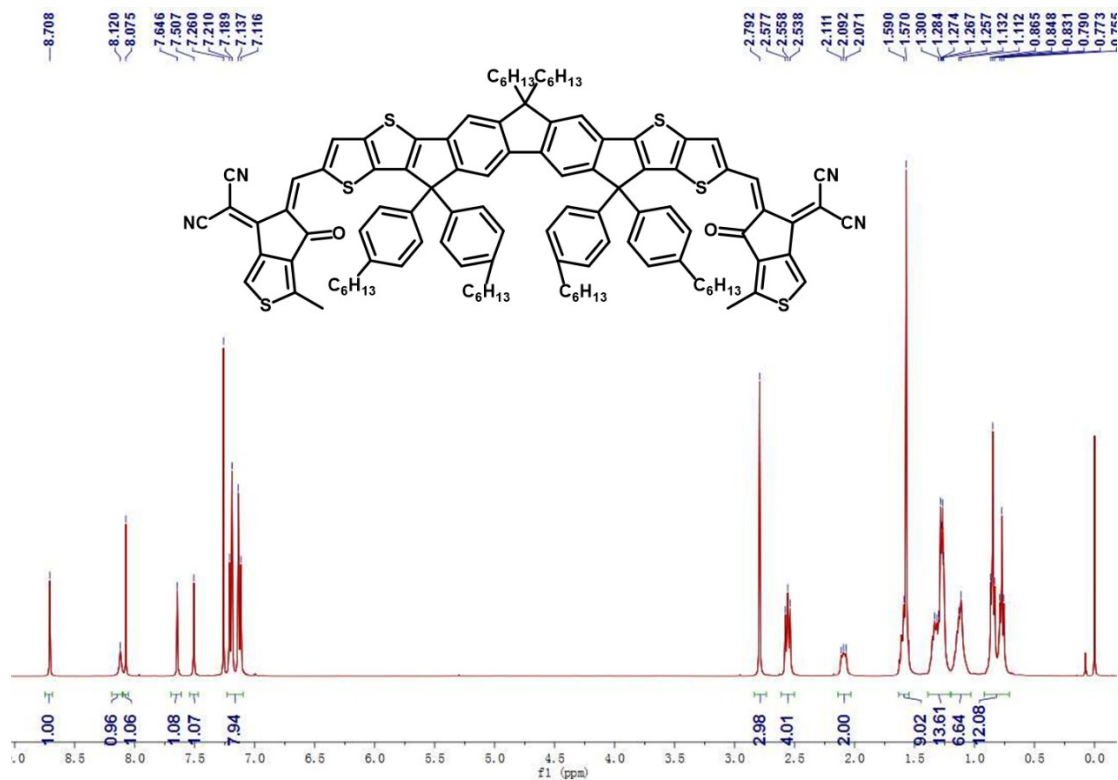
Figure S14. The ^{13}C NMR spectrum of FTTCN in CDCl$_3$.

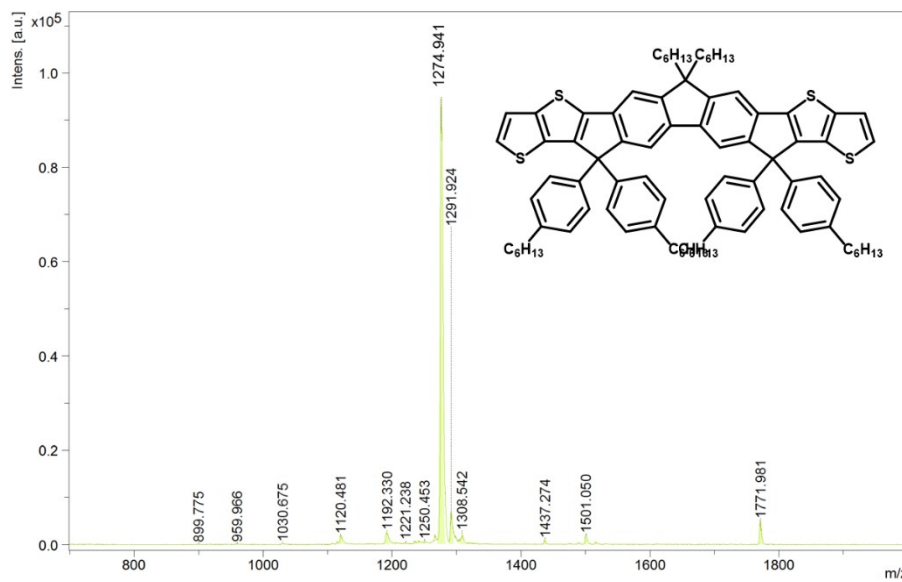**Figure S15.** The ^{1}H NMR spectrum of FTTCN-M in CDCl$_3$.
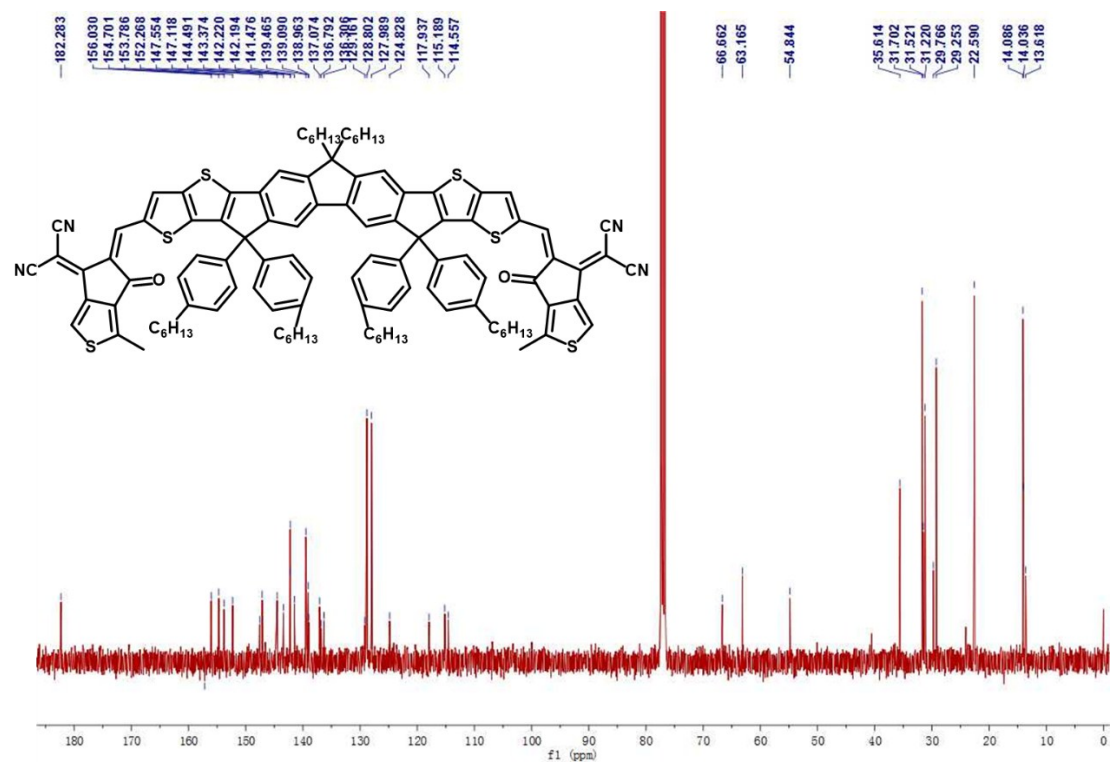
Figure S16. The ^{13}C NMR spectrum of FTTCN in CDCl$_3$.
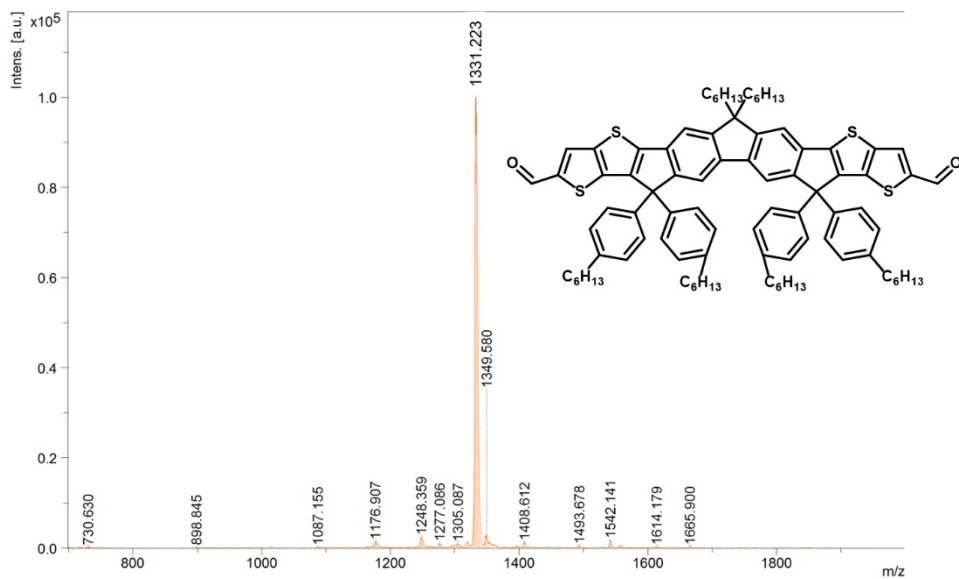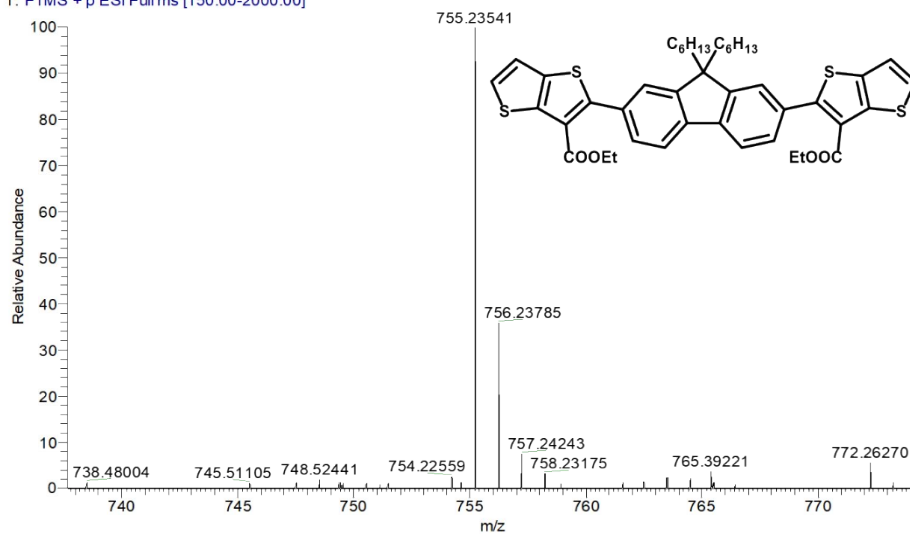
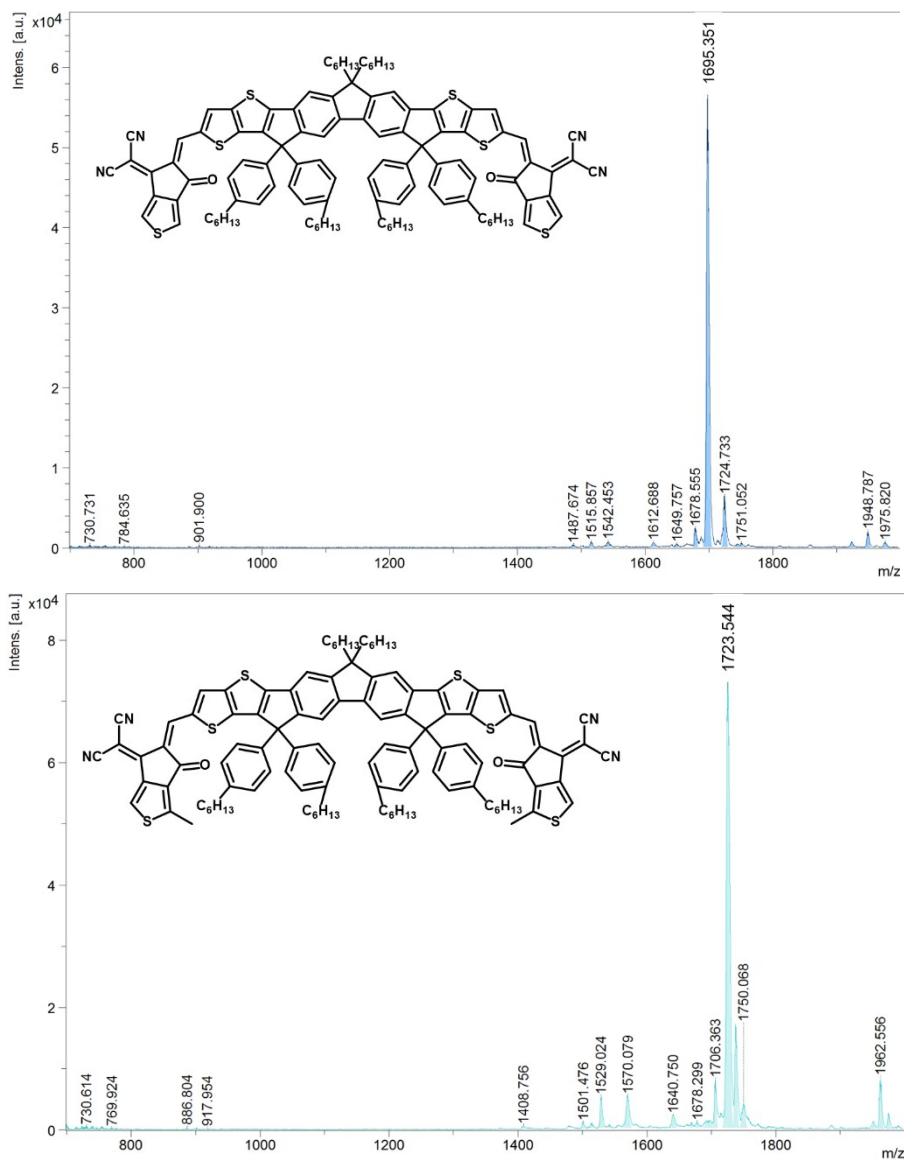**Figure S17.** The HRMS/MALDI-TOF-MS figures for compound 1, compound 2, compound 3, FTTCN, and FTTCN-M, respectively.