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Electronic Supplementary Information

Asymmetric Selenophene-Based Non-Fullerene Acceptors for High-Performance Organic Solar Cells

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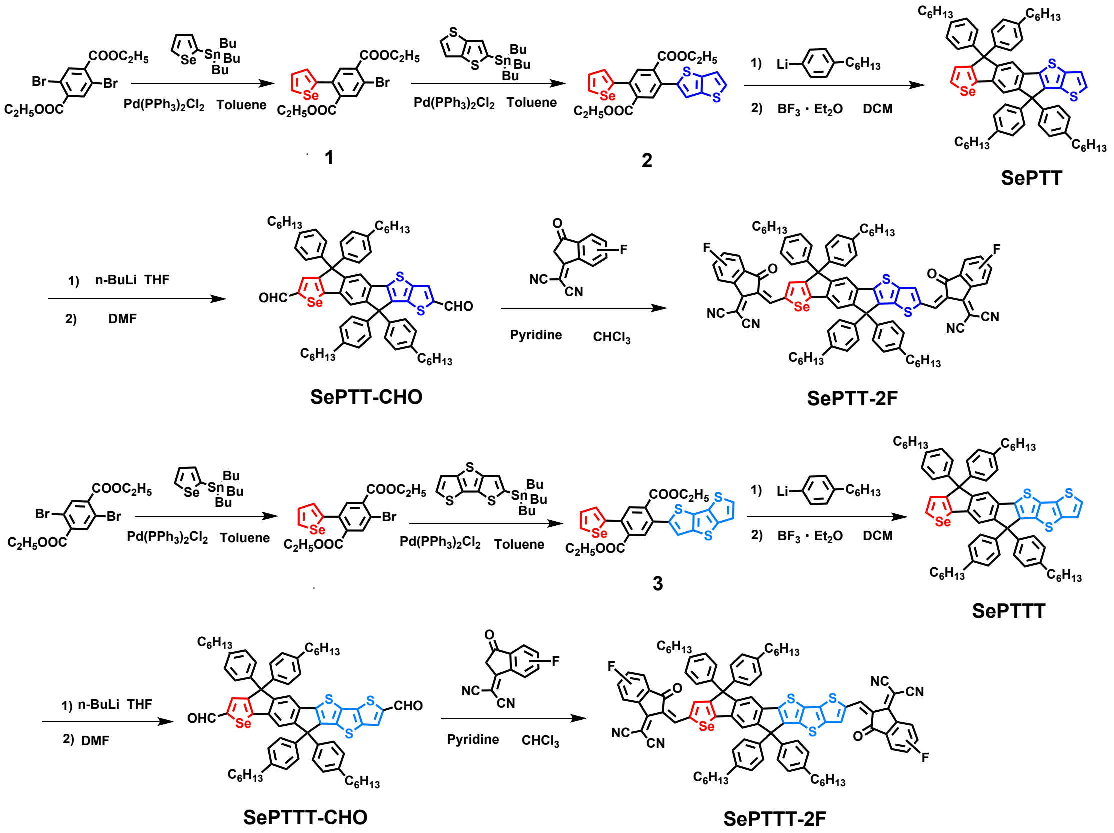
S1.1 Materials Synthesis

All the chemicals and reagents were purchased from commercial sources and used without further purification unless otherwise noted. Anhydrous THF was distilled from sodium/benzophenoneketyl prior to use. All the reactions were performed under nitrogen atmosphere unless otherwise stated. The detailed synthetic procedures for SePTT-2F and SePTTT-2F were listed below.



Scheme S1. Synthetic routes of SePTT-2F and SePTTT-2F.

Synthesis of diethyl 2-bromo-5-(selenophen-2-yl)terephthalate (**compound 1**):

Under the protection of nitrogen, n-BuLi (10.5 mL, 26.31 mmol) was added dropwise to a stirring solution of selenophene (3.44 g, 26.31 mmol) in dry THF (100 mL) at -78℃. After being kept stirring at -78 °C for 1.5 h, tri-n-butyltin chloride (9.42 g, 28.94 mmol) was then injected into the reaction mixture via a syringe. Then 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 2,5-dibromoterephthalate (10 g, 26.31 mmol), tributyl(selenophen-2-yl)stannane (11.02 g, 26.31 mmol) and anhydrous toluene (120 mL) was added $Pd(PPh_3)_2Cl_2$ (0.37 g, 0.53 mmol) under the protection of nitrogen. 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 colorless liquid (4.75 g, 42%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.09-8.08 (d, 1H), 7.79 (s, 1H), 7.84 (s, 1H), 7.31-7.28 (m, 1H), 7.20-7.19 (d, 1H), 4.45-4.39 (q, 2H), 4.23-4.18 (q, 4H), 1.43-1.39 (t, 3H), 1.17-1.14 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 166.56, 165.23, 145.61, 135.44, 135.04, 134.77, 134.44, 133.44, 132.61, 129.70, 129.48, 120.41, 62.10, 61.86, 14.21, 13.78. MS (MALDI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{16}H_{15}BrO_4Se$, 429.93; found, 430.7.

Synthesis of diethyl 2-(selenophen-2-yl)-5-(thieno[3,2-b]thiophen-2-yl)terephthalate (**compound 2**):

diethyl 2-bromo-5-(selenophen-2-yl)terephthalate (3 g, 6.97 mmol), tributyl(thieno[3,2-b]thiophen-2-yl)stannane (3.59 g, 8.37 mmol) and $Pd(PPh_3)_2Cl_2$ (98 mg, 0.14 mmol) were dissolved in anhydrous toluene (100 mL) under nitrogen atmosphere. The resulting solution was stirred at 115 ºC for 24 h. After cooling down to room temperature, the reaction mixture was poured into water (100 mL) and 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 an off-white solid (3.16 g, 92%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.10-8.09 (d, 1H), 7.85 (s, 1H), 7.82 (s, 1H), 7.40-7.39 (d, 1H), 7.33-7.31 (m, 1H), 7.28 (s, 2H), 7.24 (d, 1H), 4.26-4.20 (m, 4H), 1.18-1.10 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 167.67, 167.57, 146.29, 142.16, 139.87, 139.37, 135.91, 133.97, 133.88, 133.40, 132.48, 132.04, 131.85, 129.75, 129.40, 127.33, 119.44, 119.21, 61.78, 61.73, 13.85, 13.81. MS (MALDI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{22}H_{18}O_4S_2Se$, 489.98; found, 489.7.

Synthesis of **SePTT**:

To a stirring solution of 1-bromo-4-hexylbenzene (5.53 g, 22.92 mmol) in dry THF (100 mL) at -78℃ was added dropwise n-BuLi (9.17 mL, 22.92 mmol) under the protection of nitrogen. After being kept stirring at -78 ºC for 1.5 h, a solution of compound 2 (1.87 g, 3.82 mmol) in dry THF (10 mL) was added, then the resulting mixture was warmed to room temperature and stirred overnight. 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-6-ring **SePTT** building block as an orange solid (1 g, 26%). ^1H NMR (300 MHz, $CDCl_3$, δ): 7.89-7.87 (d, 1H), 7.47 (s, 1H), 7.43 (s, 1H), 7.26 (s, 2H), 7.22 (s, 1H), 7.20-7.15 (m, 8H), 7.08-7.05 (d, 2H), 2.58-2.53 (t, 8H), 1.58 (m, 8H), 1.29-1.28 (m, 24H), 0.87 (t, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 157.68, 153.15, 153.08, 145.95, 144.18, 143.43, 141.95, 141.74, 141.63, 141.47, 140.50, 137.91, 135.93, 133.88, 132.10, 128.49, 128.39, 128.16, 128.03, 126.31, 125.78, 120.41, 117.81, 116.93, 64.00, 63.02, 35.68, 31.83, 31.81, 31.43, 31.36, 29.81, 29.26, 22.70, 14.21. MS (MALDI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{66}H_{74}S_2Se$, 1010.44; found, 1010.3.

Synthesis of **SePTT-CHO**:

Under the protection of nitrogen, n-BuLi (1.6 mL, 4 mmol) was added dropwise to a stirring solution of SePTT (0.9 g, 0.89 mmol) in dry THF (60 mL) at -78 ºC. After being kept stirring at -78 ºC for 1 h, the reaction mixture was stirred at room temperature for another 1.5 h, which was then cooled to -78 ºC again and stirred for 10 mins, then anhydrous *N,N*-Dimethylformamide (DMF) (0.65 g, 8.9 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: ethyl acetate (9:1) as an eluent to afford an orange solid (0.56 g, 59%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 9.89 (s, 1H), 9.70 (s, 1H), 7.94 (s, 1H), 7.88 (s, 1H), 7.65 (s, 1H), 7.53 (s, 1H), 7.17-7.09 (m, 16H), 2.60-2.54 (t, 8H), 1.60-1.58 (m, 8H), 1.30-1.29 (m, 24H), 0.88-0.87 (t, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 183.96, 182.83, 158.35, 154.64, 154.41, 153.83, 151.46, 149.29, 146.98, 144.56, 142.35, 142.10, 141.92, 140.62, 140.14, 139.10, 137.90, 137.14, 135.15, 129.75, 128.73, 128.61, 127.80, 127.70, 119.46, 117.86, 64.24, 63.10, 35.55, 31.69, 31.67, 31.31, 31.23, 29.10, 22.58, 22.56, 14.08. MS (MALDI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{68}H_{74}O_2S_2Se$, 1066.40; found, 1066.3.

Synthesis of **SePTT-2F**:

Under nitrogen atmosphere, SePTT-CHO (100 mg, 0.094 mmol), 2-(6-fluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (80 mg, 0.375 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 stir at 55 ºC for 4 hours. After removal of solvent of reaction mixture, methanol was added and the precipitate was collected by filtration to get crude product, which was further purified by column chromatography on silica gel with petroleum ether: dichloromethane (1:1) as an eluent to afford black solid (86 mg, 63%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.86 (s, 1H), 8.73 (s, 1H), 8.71-8.67 (m, 0.5H), 8.38-8.35 (d, 1.5H), 8.23 (s, 1H), 7.94-7.87 (m, 2.5H), 7.73 (s, 1H), 7.56 (s, 1.5H), 7.41 (m, 2H), 7.22-7.09 (m, 16H), 2.60-2.55 (t, 8H), 1.62-1.55 (m, 8H), 1.30 (m, 24H), 0.87-

0.86 (t, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 187.52, 186.67, 168.04, 166.37, 165.46, 160.04, 159.19, 158.88, 155.97, 155.83, 153.01, 148.19, 147.31, 144.07, 143.76, 143.06, 142.62, 142.37, 141.45, 140.32, 139.78, 139.15, 138.86, 138.31, 137.12, 133.09, 128.94, 128.77, 127.84, 127.76, 125.93, 122.69, 122.05, 121.80, 121.63, 121.26, 120.42, 118.58, 114.33, 114.22, 114.15, 112.99, 112.74, 76.74, 70.36, 69.79, 64.19, 63.25, 35.63, 35.59, 31.72, 31.55, 31.27, 29.73, 29.19, 29.14, 22.61, 14.12. MS (MALDI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{92}H_{80}F_2N_4O_2S_2Se$, 1454.49; found, 1454.4.

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

Under the protection of nitrogen, n-BuLi (4.77 mL, 11.93 mmol) was added dropwise to a stirring solution of dithieno[3,2-b:2',3'-d]thiophene (2.34 g, 11.93 mmol) in dry THF (100 mL) at -78℃. After being kept stirring at -78 ºC for 1.5 h, tri-n-butyltin chloride (5.82 g, 17.88 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-(selenophen-2-yl)terephthalate (3.42 g, 7.95 mmol), tributyl(dithieno[3,2-b:2',3'-d]thiophen-2-yl)stannane (5.79 g, 11.92 mmol) and anhydrous toluene (120 mL) was added $Pd(PPh_3)_2Cl_2$ (0.28 g, 0.28 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 (4.03 g, 93%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.11-8.09 (m, 1H), 7.87 (s, 1H), 7.84 (s, 1H), 7.41-7.39 (d, 1H), 7.33-7.30 (m, 3H), 7.25-7.24 (m, 1H), 4.28-4.20 (m, 4H), 1.86-1.13 (q, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 167.59, 167.48, 146.20, 141.43, 141.38, 140.64, 135.96, 133.91, 133.86, 133.05, 132.50, 132.12, 131.81, 131.46, 130.83, 129.73, 129.41, 126.38, 120.74, 120.58, 61.82, 61.73, 29.68, 13.90, 13.79. MS (MALDI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{24}H_{18}O_4S_3Se$, 545.93; found, 545.9.

Synthesis of **SePTTT**:

To a stirring solution of 1-bromo-4-hexylbenzene (2.65 g, 10.99 mmol) in dry THF (60 mL) at -78℃ was added dropwise n-BuLi (4.4 mL, 10.99 mmol) under nitrogen atmosphere. After being kept stirring at -78℃ for 1 h, a solution of compound 3 (1 g, 1.83 mmol) in dry THF (10 mL) was added, then the resulting mixture was warmed to room temperature and stirred overnight. 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 **SePTTT** building block as an orange solid (0.52 g, 27%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.88-7.87 (d, 1H), 7.47 (s, 1H), 7.43 (s, 1H), 7.28 (d, 1H), 7.21-7.20 (d, 2H), 7.19-7.17 (m, 8H), 7.08-7.06 (d, 8H), 2.57-2.52 (q, 8H), 1.58-1.54 (m, 8H), 1.31-1.28 (m, 24H), 0.88-0.84 (t, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 157.66, 153.17, 153.08, 147.16, 144.01, 141.99, 141.79, 141.77, 141.42, 141.19, 140.11, 137.92, 136.05, 135.56, 132.45, 132.07, 131.67, 128.41, 128.30, 128.07, 127.92, 125.69, 125.36, 120.62, 117.64, 116.67, 63.91, 63.04, 35.57, 31.71, 31.69, 31.32, 31.26, 29.69, 29.15, 14.10, 14.08. MS (MALDI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{68}H_{74}S_3Se$, 1066.41; found, 1066.7.

Synthesis of **SePTTT-CHO**:

Under the protection of nitrogen, n-BuLi (0.68 mL, 1.69 mmol) was added dropwise to a stirring solution of SePTTT (0.45 g, 0.42 mmol) in dry THF (60 mL) at -78 ºC. 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) (0.31 g, 4.2 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 further purified by column chromatography on silica gel with petroleum ether : dichloromethane (1:1.5) as an eluent to afford an orange solid (0.21 g, 44%). ^1H NMR (300 MHz, $CDCl_3$, δ): 9.91 (s, 1H), 9.69 (s, 1H), 7.87-7.85 (d, 2H), 7.61 (s, 1H), 7.51 (s, 1H), 7.18-7.14 (m, 8H), 7.11-7.09 (d, 8H), 2.59-2.54 (q, 8H), 1.61-1.56 (m, 8H), 1.34-1.29 (m, 24H), 0.89-0.84 (t, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 183.95, 182.62, 158.18, 154.47, 154.22, 153.97, 151.21, 148.19, 145.39, 143.35, 142.34, 142.10, 141.28, 140.66, 140.47, 139.17, 138.58, 137.44, 137.34, 135.24, 133.07, 130.02, 128.67, 128.62, 127.90, 127.71, 119.33, 117.39, 64.24, 63.18, 35.55, 31.69, 31.66, 31.31, 31.24, 29.69, 29.11, 22.58, 22.56, 14.08, 14.07. MS (MALDI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{70}H_{74}O_2S_3Se$, 1122.40; found, 1122.6.

Synthesis of **SePTTT-2F**:

Under nitrogen atmosphere, SePTTT-CHO (70 mg, 0.062 mmol), 2-(6-fluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (40 mg, 0.187mmol) 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 stir at 55 ºC for 4 hours. After removal of solvent of reaction mixture, methanol was added and the precipitate was collected by filtration to get crude product, which was further purified by column chromatography on silica gel with petroleum ether: dichloromethane (1:1) as an eluent to afford black solid (80 mg, 85%). ^1H NMR (300 MHz, $CDCl_3$, δ): 8.95 (s, 1H), 8.92 (s, 1H), 8.71-8.68 (m, 0.5H), 8.38-

8.35 (d, 1.5H), 7.97-7.87 (m, 3.5H), 7.73 (s, 1H), 7.76 (s, 1.5H), 7.43-7.37 (t, 2H), 7.19-7.11 (m, 16H), 2.61-2.56 (t, 8H), 1.60-1.54 (m, 8H), 1.29-1.26 (m, 24H), 0.88-0.86 (t, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 187.53, 186.94, 168.02, 166.83, 165.46, 159.85, 158.91, 158.65, 156.08, 155.04, 149.10, 148.26, 146.14, 145.96, 143.48, 143.17, 143.04, 142.97, 142.66, 142.34, 142.18, 141.46, 140.40, 138.88, 138.75, 138.47, 138.20, 138.12, 137.40, 133.92, 132.98, 128.87, 128.78, 127.86, 127.81, 125.90, 122.29, 121.95, 121.01, 120.32, 118.01, 114.57, 114.39, 114.28, 114.13, 112.87, 112.71, 112.61, 70.35, 69.57, 64.19, 63.26, 35.61, 31.74, 31.71, 31.16, 31.29, 29.73, 29.15, 22.62, 22.60, 14.14, 14.12. MS (MALDI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{94}H_{80}F_2N_4O_2S_3Se$, 1510.46; found, 1510.4.

S1.2 Materials Characterization

^{1}H and ^{13}C spectra were recorded on a Bruker Avance 300 spectrometer with deuterated chloroform ($CDCl_3$) as the solvent and trimethylsilane (TMS) as the internal reference. UV-visible absorption spectra were measured on a Hitachi (model U-3010) UV–vis spectrophotometer. Mass spectra (MS) were recorded on Bruker Daltonics Biflex III MALDI-TOF Analyzer in the MALDI mode. Cyclic voltammetry (CV) measurements were performed under nitrogen at a scan rate of 100 mV s^{-1} using a Zahner IM6e Electrochemical workstation. A platinum plate coated with sample film, a platinum wire and a saturated Ag/AgCl electrode were employed as a working electrode, a counter electrode and a reference electrode, respectively. 0.1 M tetra-n-butylammonium hexafluorophosphate (Bu_4NPF_6) in anhydrous acetonitrile solution was employed as a supporting electrolyte and Ferrocene/ferrocenium (Fc/Fc^+) is used as an internal standard. Atomic force microscopy (AFM) measurements were performed using a Dimension Icon AFM (Bruker) in the tapping mode. TEM images were measured 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 an inverted device configuration of ITO/ZnO/PBT1-C:NFA/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 30 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:SePTT-2F with weight ratio of 1:0.9 in chlorobenzene, while the active layers were spin-coated from a solution of PBT1-C:SePTTT-2F with weight ratio of 1:1.1 in chlorobenzene. Solution with 0.3 % DIO was stirred overnight prior to cast. The active layers were allowed to heat at 80 °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. 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 performed by using a QEX10 Solar Cell IPCE measurement system (PV Measurements, Inc.).

S1.4 Space-Charge Limited Current Measurement

The charge transport properties were investigated by space charge limited current (SCLC) measurement. The hole-only devices and electron-only devices were fabricated with a structure of ITO/PEDOT:PSS/PBT1-C:NFA/MoO_3/Ag and ITO/ZnO/PBT1-C:NFA/ZrAcac/Al, respectively. The J–V curves of devices were fitted by using the Mott–Gurney equation: $J = 9\varepsilon_0\varepsilon_r\mu V^2/8L^3$, in which 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 hole mobility or electron mobility could be estimated from the slope of the $J^{0.5}$-V curve.

S1.5 Figures and Tables

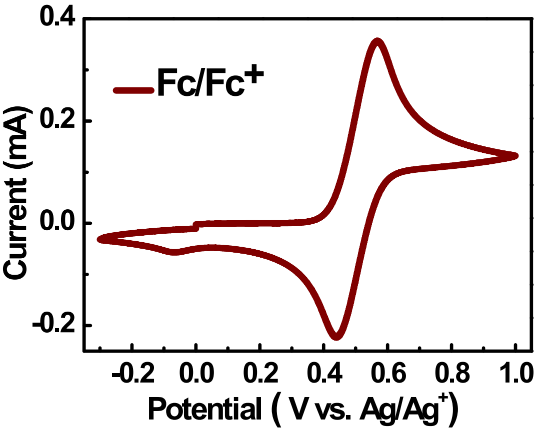


Fig. S1 Cyclic voltammograms of ferrocene external standard.

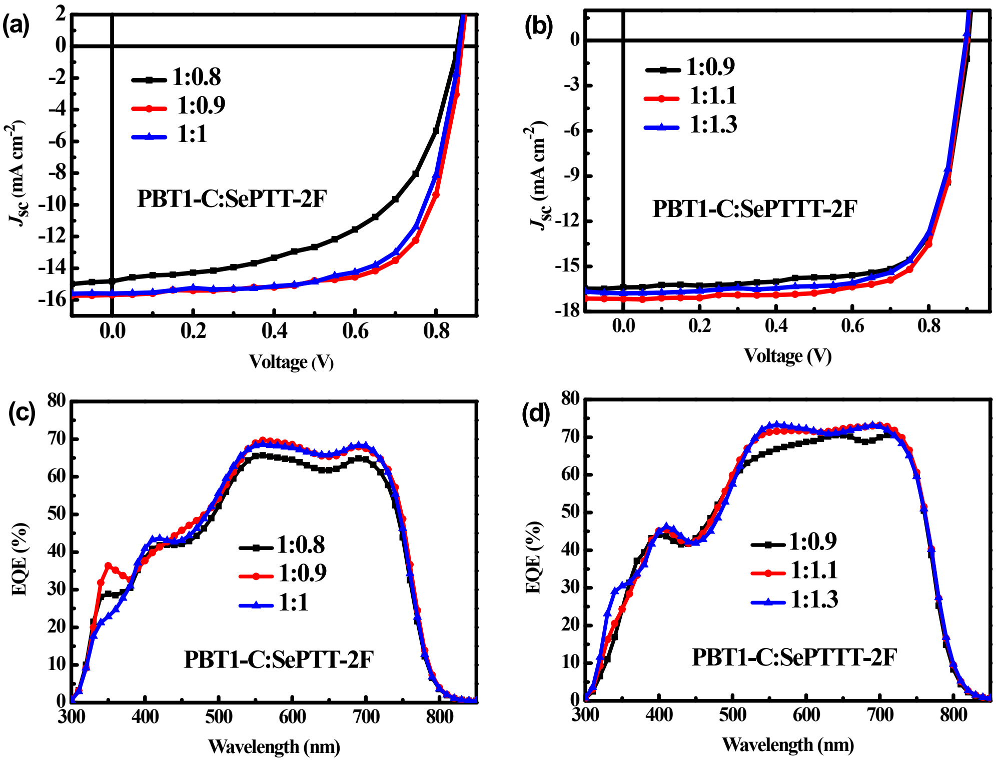


Fig. S2 *J-V* curves (a, b) and EQE spectra (c,d) of OSCs devices based on PBT1-C:NFAs blends with different D/A ratio.

Table S1. OSCs device data of OSCs based on PBT1-C:NFA blends 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] (%)
SePTT-2F	1:0.8	0.853	14.82	14.14	55.3	6.99
		(0.852±0.003)	(14.63±0.42)		(54.56±0.98)	(6.80±0.33)
	1:0.9	0.863	15.69	15.00	69.8	9.45
		(0.861±0.002)	(15.93±0.29)		(68.44±1.59)	(9.39±0.26)
	1:1	0.858	15.59	14.86	68.1	9.11
		(0.851±0.005)	(15.52±0.21)		(65.92±1.33)	(8.71±0.25)
SePTTT-2F	1:0.9	0.904	16.39	15.84	73.8	10.96
		(0.902±0.002)	(15.68±0.25)		(73.28±0.83)	(10.37±0.22)
	1:1.1	0.900	17.15	16.40	73.8	11.39
		(0.900±0.003)	(17.01±0.26)		(72.96±0.69)	(11.16±0.21)
	1:1.3	0.897	16.79	16.35	72.7	10.95
		(0.895±0.003)	(16.51±0.23)		(72.44±0.68)	(10.70±0.26)

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

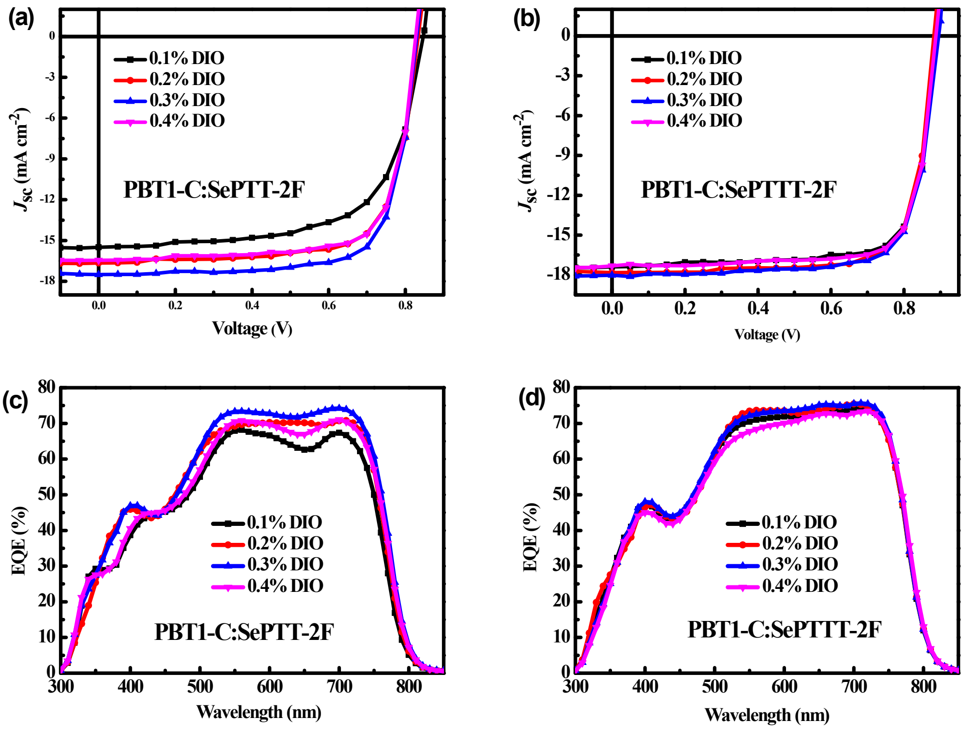


Fig. S3 *J-V* curves (a,b) and EQE spectra (c,d) of OSCs devices based on active layer with different DIO content.

Table S2. Device data of OSCs based on PBT1-C:NFA with different DIO content.

Active layer	DIO (v/v)	V_{oc} (V)	J_{sc} (mA cm^{-2})	$J_{sc,cal}$ (mA cm^{-2})	FF (%)	PCE$^{a)}$ (%)
PBT1-C:SePTT-2F=1:0.9	0.1%	0.847 (0.849±0.004)	15.49 (15.44±0.31)	14.87	65.1 (64.72±1.16)	8.54 (8.49±0.12)
	0.2%	0.834 (0.831±0.002)	16.65 (16.54±0.22)	16.06	73.1 (72.12±1.13)	10.15 (9.91±0.27)
	0.3%	0.830 (0.829±0.002)	17.51 (17.25±0.27)	16.72	75.0 (74.50±0.66)	10.90 (10.65±0.16)
	0.4%	0.827 (0.825±0.002)	16.45 (16.44±0.12)	15.79	74.7 (73.44±0.96)	10.16 (9.96±0.19)
PBT1-C:SePTTT-2F=1:1.1	0.1%	0.891 (0.885±0.005)	17.39 (16.93±0.28)	16.87	76.5 (74.98±1.34)	11.86 (11.23±0.27)
	0.2%	0.882 (0.881±0.003)	17.83 (17.33±0.25)	17.06	77.0 (75.96±1.79)	12.11 (11.59±0.36)
	0.3%	0.895 (0.896±0.002)	18.02 (17.62±0.19)	17.21	75.9 (75.94±0.35)	12.24 (11.99±0.13)
	0.4%	0.887	17.32	16.59	78.0	11.98

	(0.882±0.005)	(16.88±0.13)		(76.40±2.17)	(11.38±0.31)

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

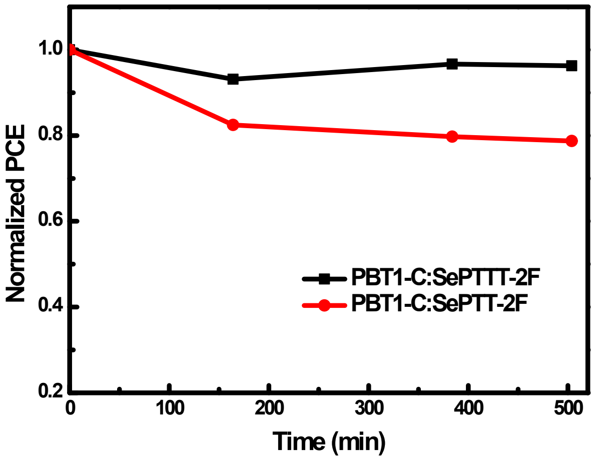


Fig. S4 The PCEs for the devices based on PBT1-C:SePTT-2F and PBT1-C:SePTTT-2F blended films after thermal treatment at 100 °C for various times.

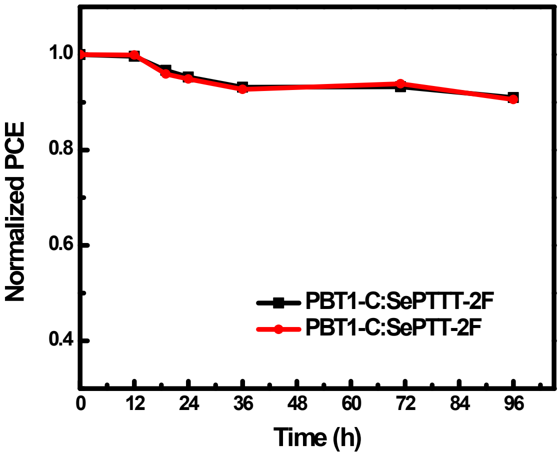


Fig. S5 The PCEs for the unencapsulated devices based on PBT1-C:SePTT-2F and PBT1-C:SePTTT-2F blended films after exposure to air for various time.

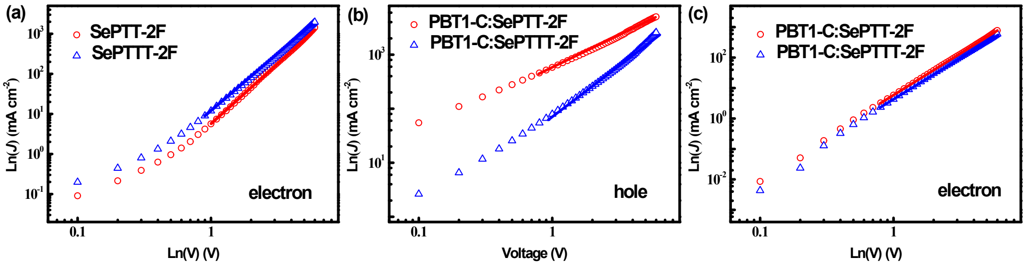


Fig. S6 Ln(*J*)-ln(*V*) characteristic curves and SCLC fittings curves of (a) electron-only device based on SePTT-2F and SePTTT-2F; (b) hole-only device of corresponding blend film, and (c) electron-only device of corresponding blend films.

Table S3. Charge transport properties of the neat and 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
SePTT-2F	-	5.14±0.65	-
SePTTT-2F	-	12.19±0.66	-
PBT1-C:SePTT-2F	7.46±1.15	2.49±0.13	3.00
PBT1-C:SePTT-2F	11.54±2.15	4.38±0.20	2.63

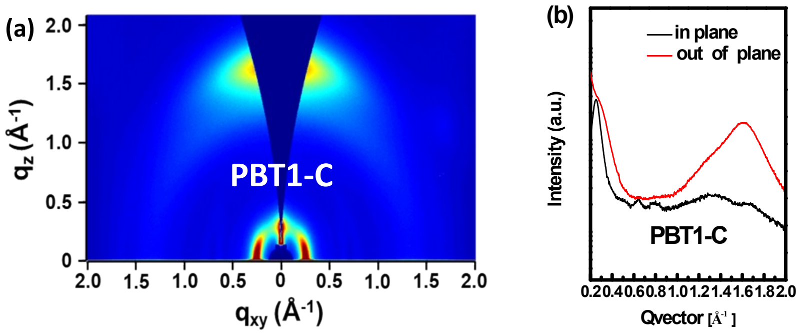


Fig. S7 (a) GIWAXR patterns of PBT1-C. (b) In-plane (black lines) and out-of-plane (red lines) line-cut profiles of PBT1-C film.

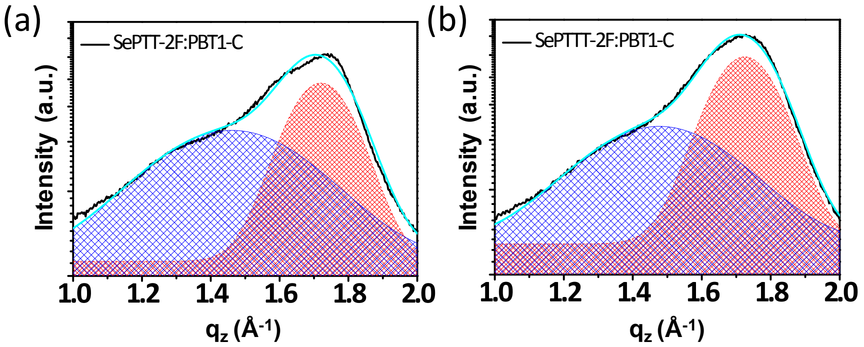


Fig. S8 Deconvoluted OOP (010) peaks by gaussian fitting of (a) SePTT-2F:PBT1-

C and (b) SePTTT-2F:PBT1-C blends.

Table S4. GIWAXS data of neat film (SePTT-2F and SePTTT-2F) and blend film (SePTT-2F:PBT1-C and SePTTT-2F:PBT1-C).

Films		q (010) (Å^{-1})	d-spacing (Å)	FWHM (Å^{-1})	Coherence length (Å)
SePTT-2F		1.46	4.30	0.537	10.5
SePTTT-2F		1.48	4.25	0.562	10.1
SePTT-2F:PBT1-C	1	1.46	4.30	0.483	11.7
	2	1.72	3.65	0.210	26.9
SePTTT-2F:PBT1-C	1	1.48	4.25	0.452	12.5
	2	1.72	3.65	0.219	25.8

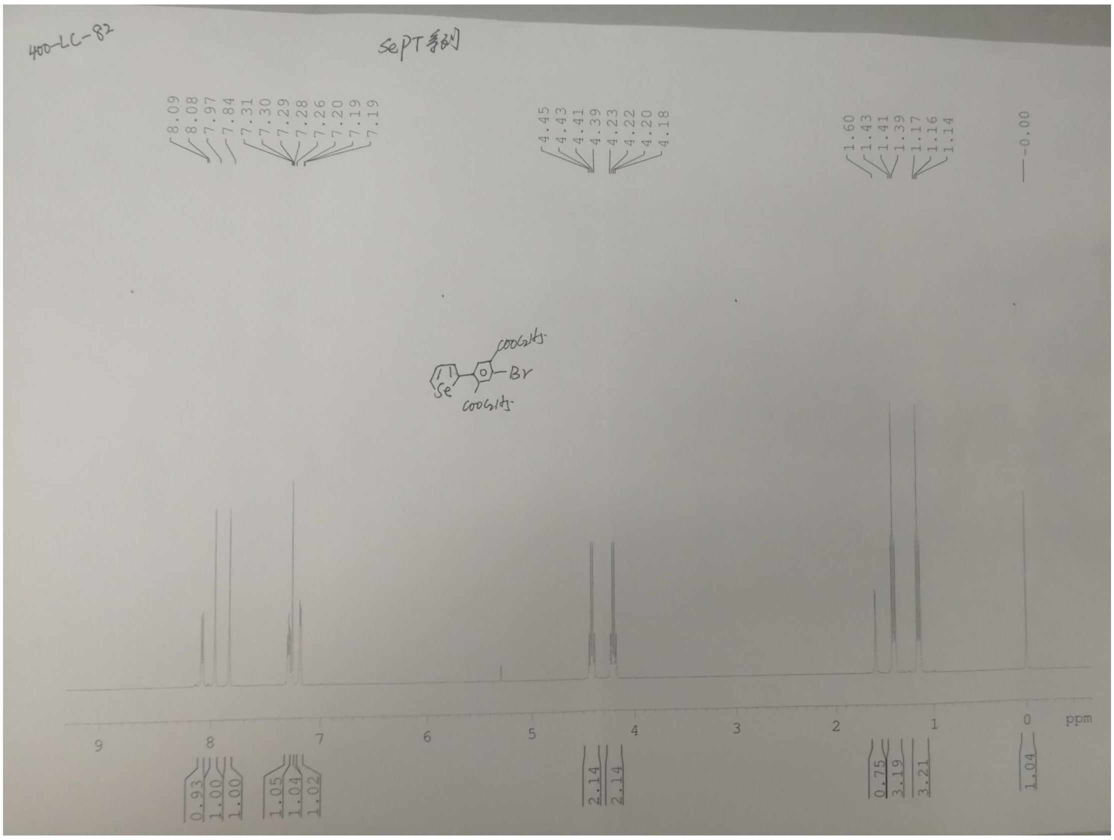


Fig. S9 ^{1}H NMR spectrum of compound **1**.

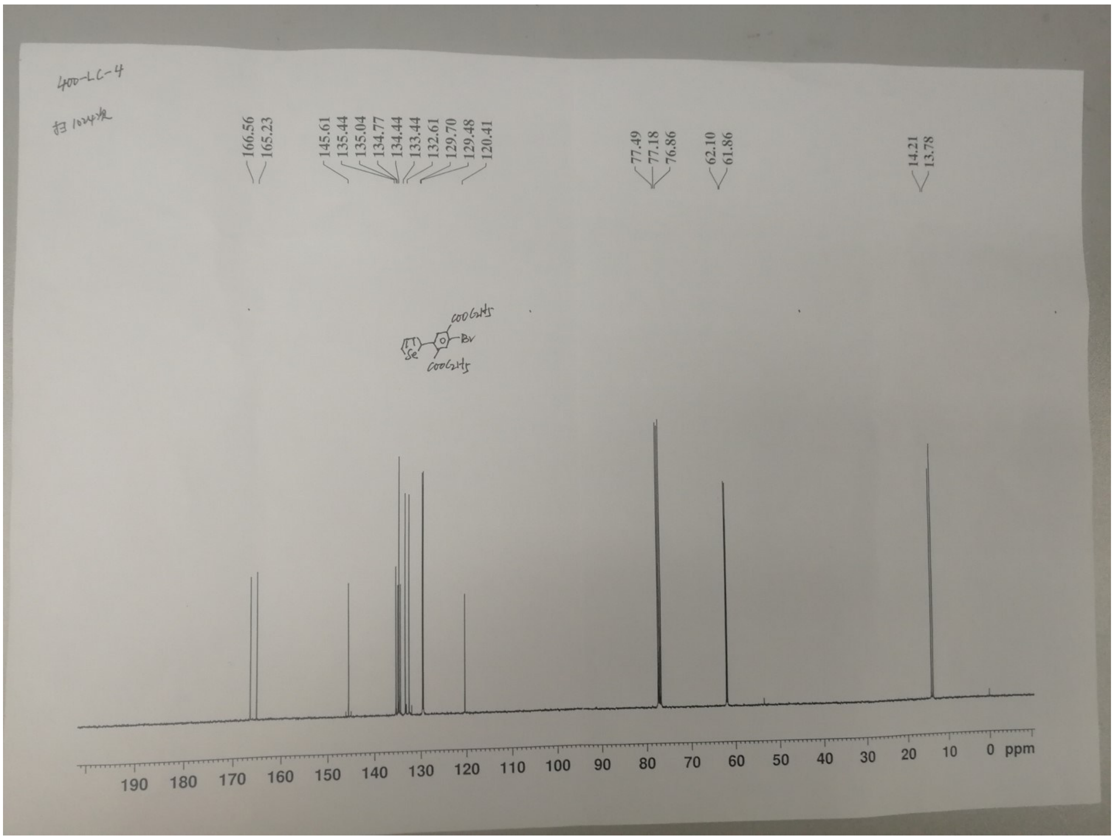


Fig. S10 ^{13}C NMR spectrum of compound **1**.

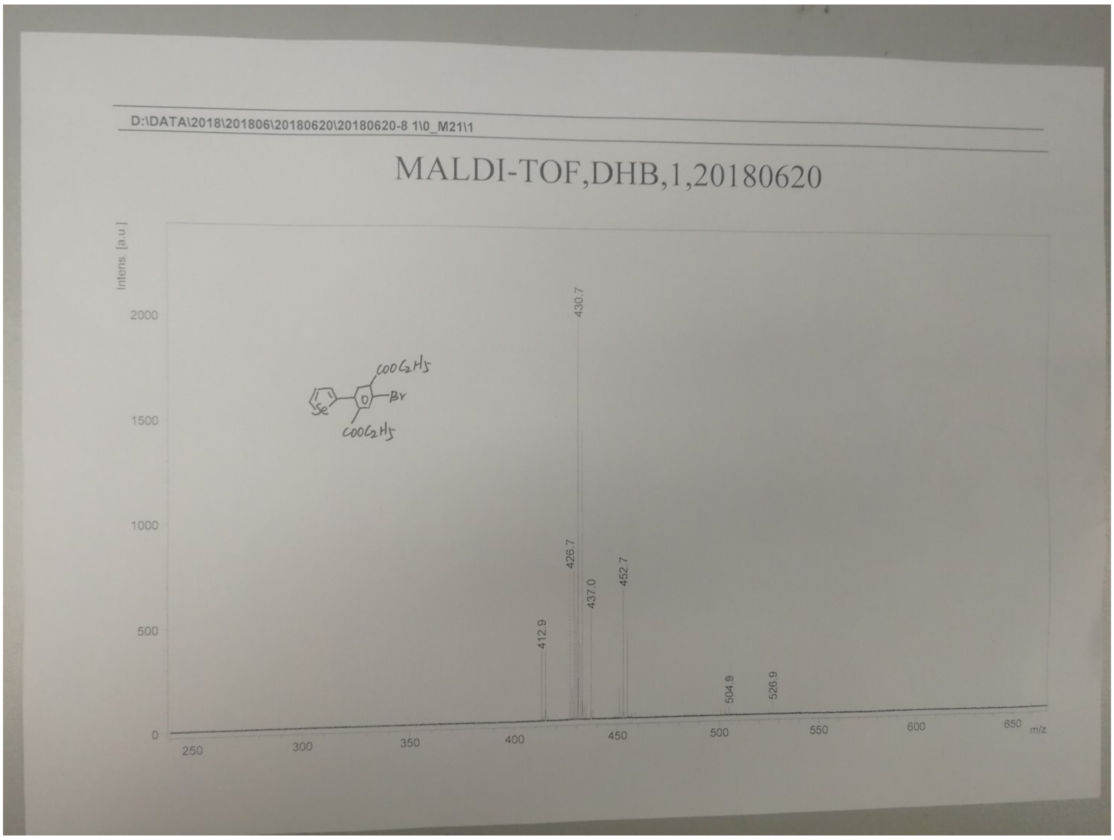


Fig. S11 MS spectrum of compound **1**.

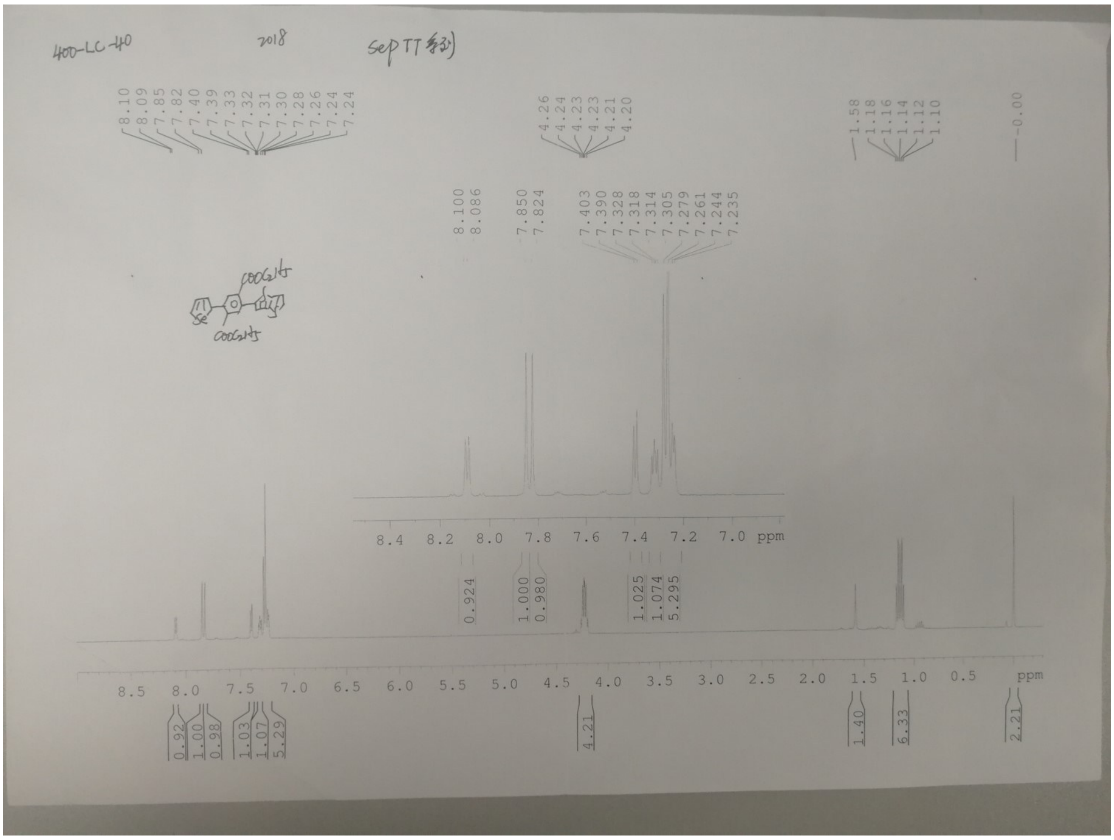


Fig. S12 ^{1}H NMR spectrum of compound **2**.

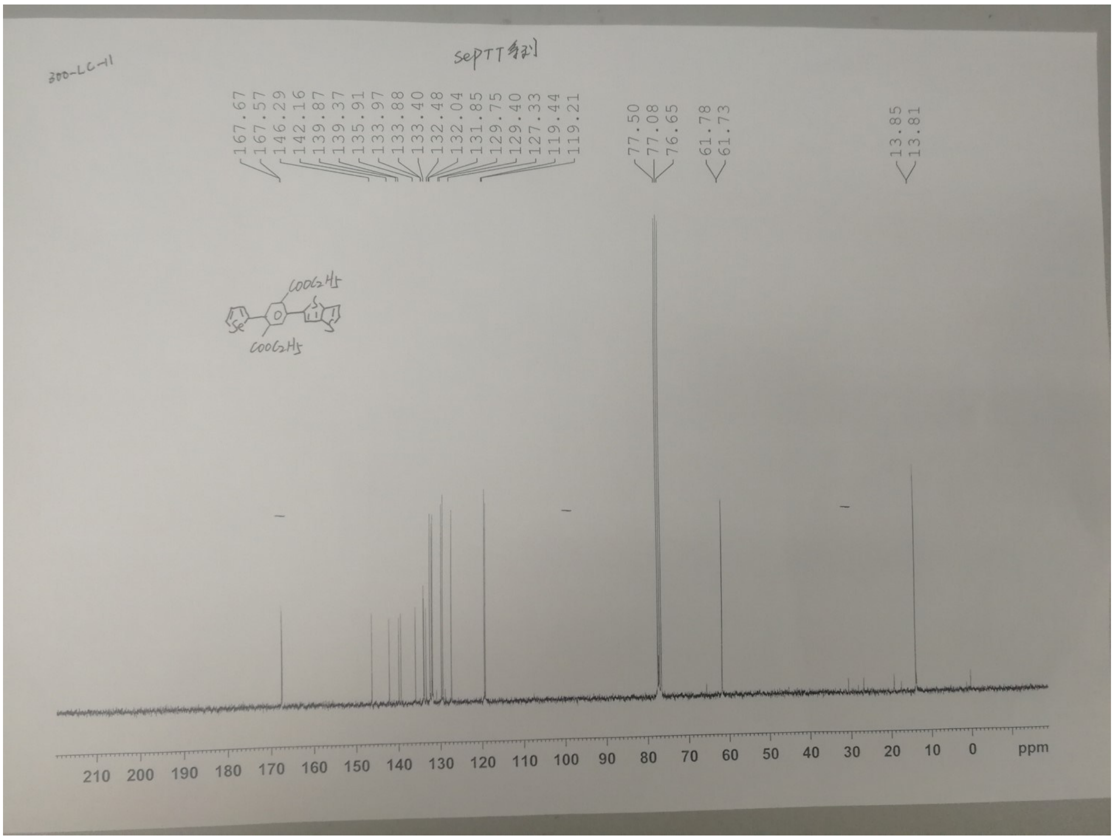


Fig. S13 ^{13}C NMR spectrum of compound **2**

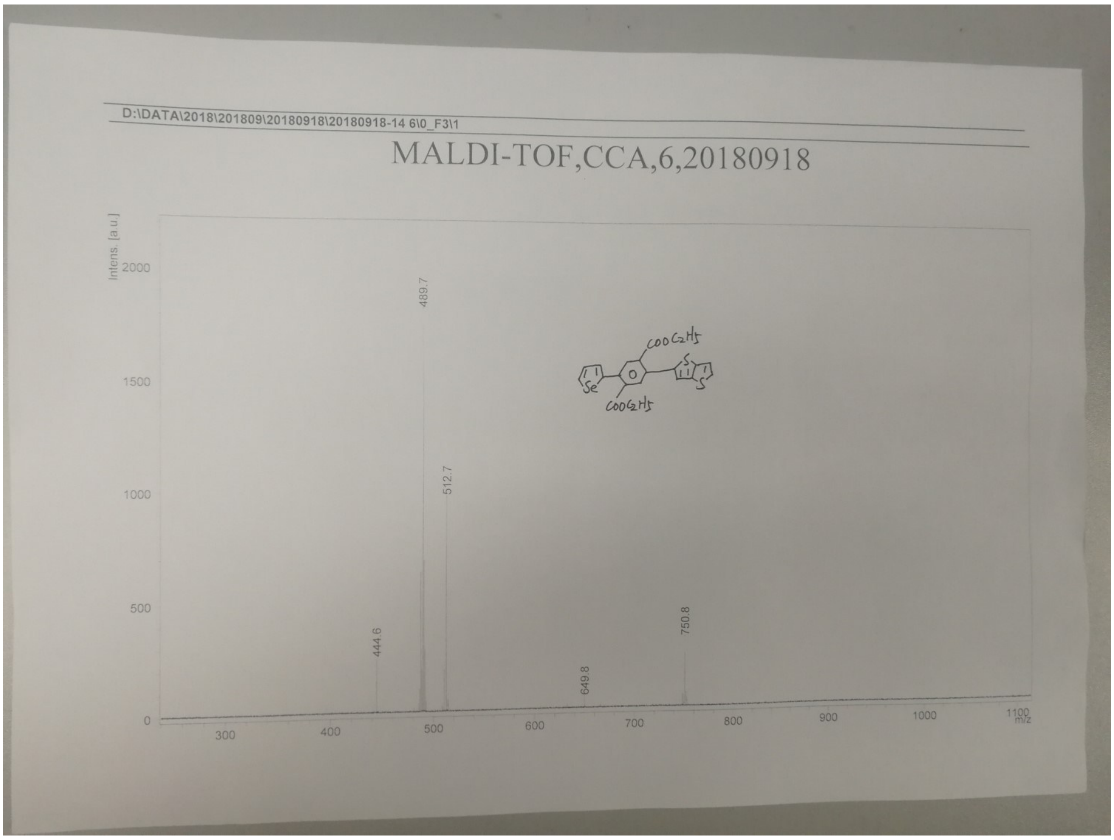


Fig. S14 MS spectrum of compound **2**.

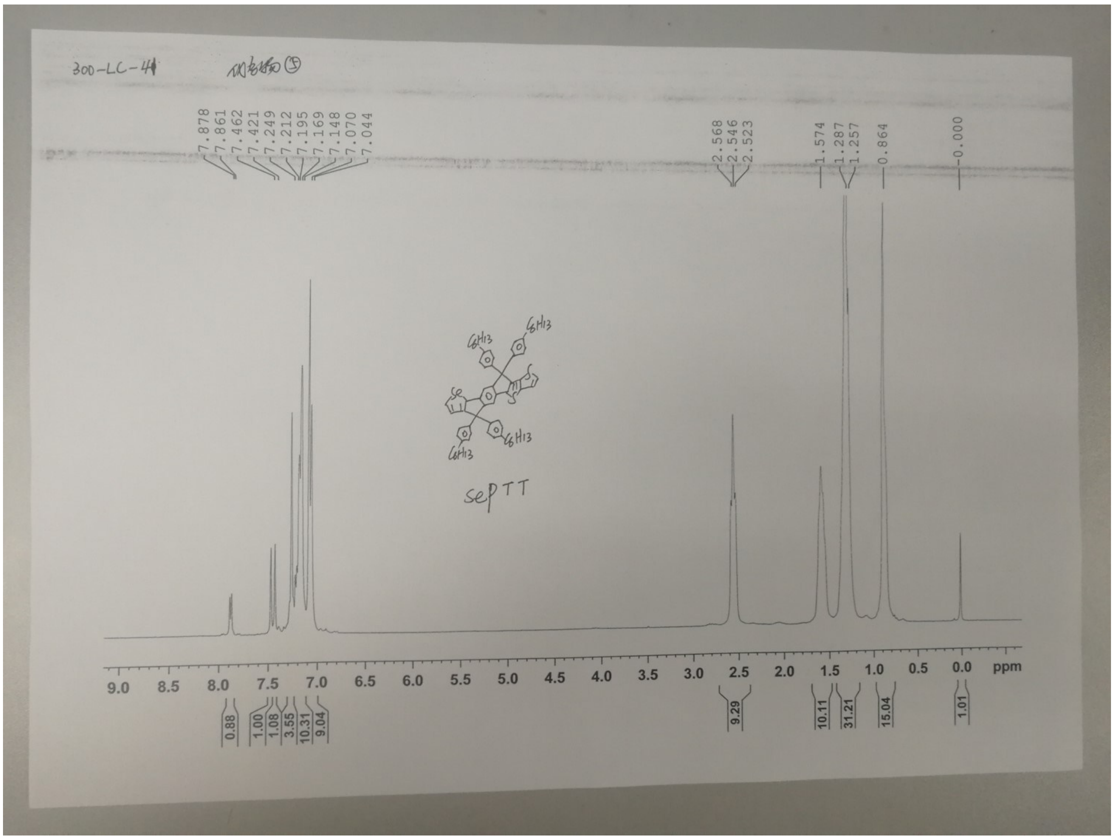


Fig. S15 ^{1}H spectrum of **SePTT**.

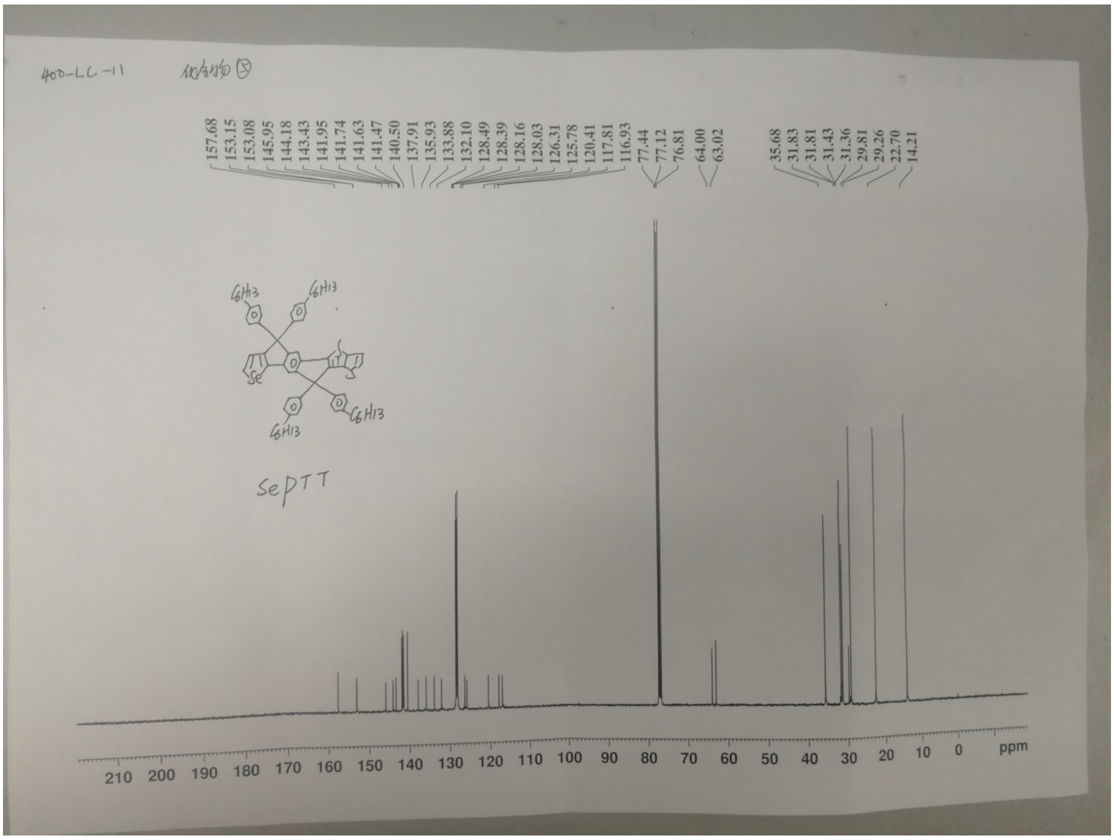


Fig. S16 ^{13}C spectrum of **SePTT**.

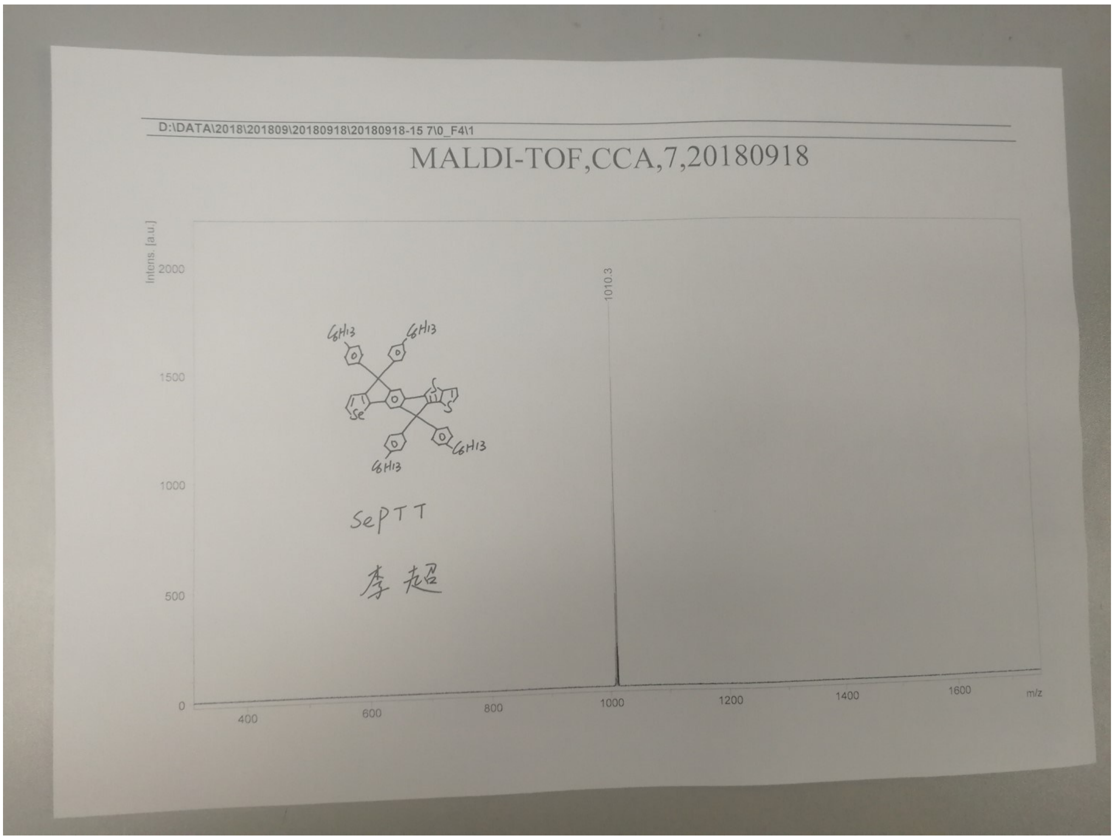


Fig. S17 MS spectrum of **SePTT**.

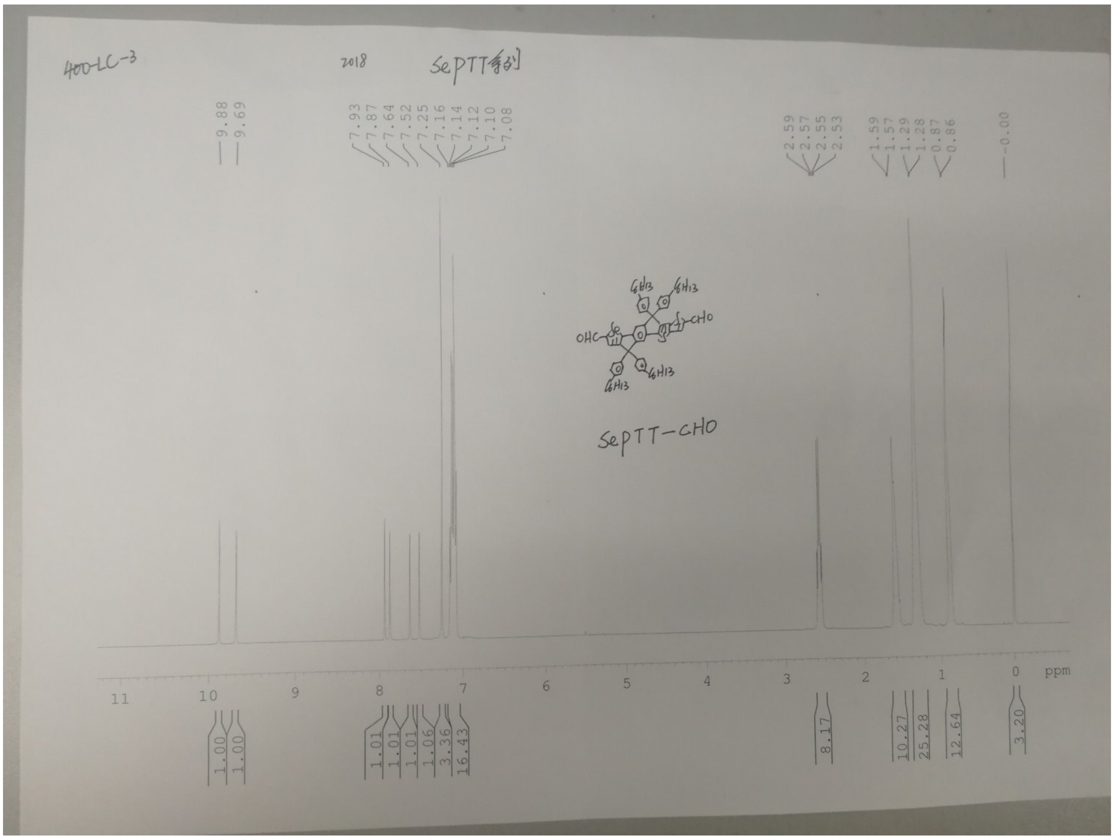


Fig. S18 ^{1}H spectrum of **SePTT-CHO**.

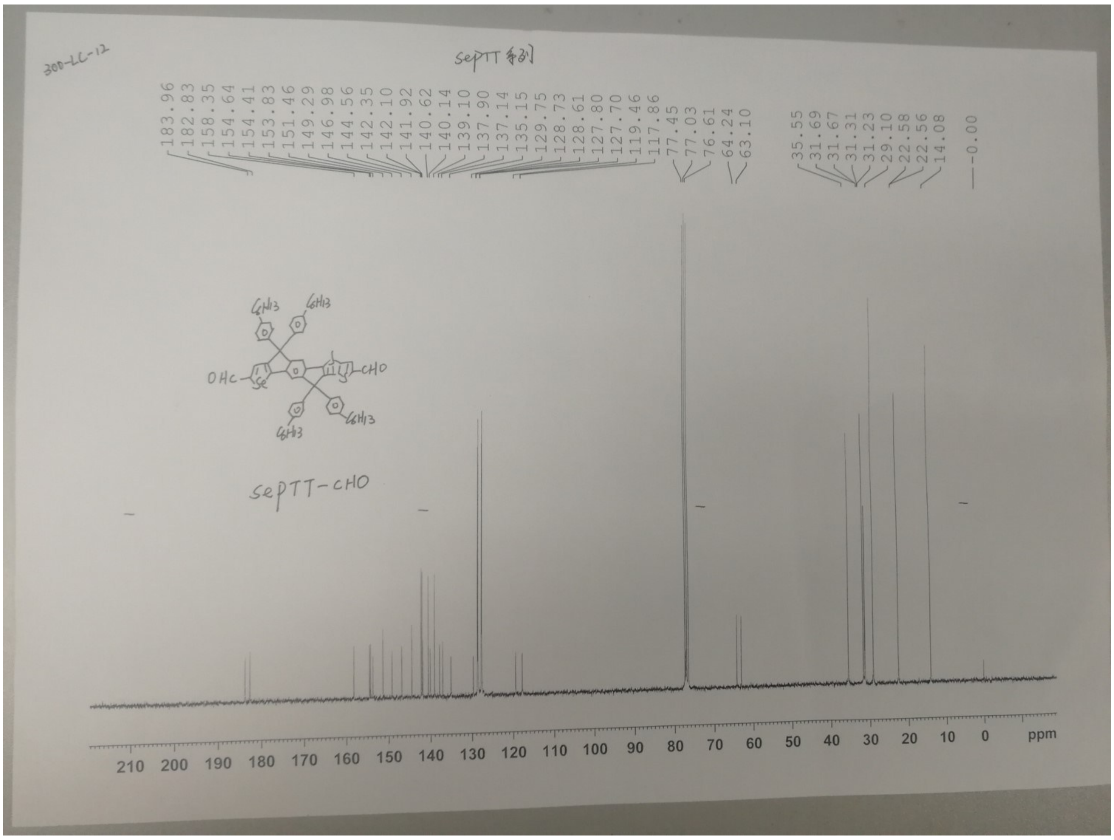


Fig. S19 ^{13}C spectrum of **SePTT-CHO**.

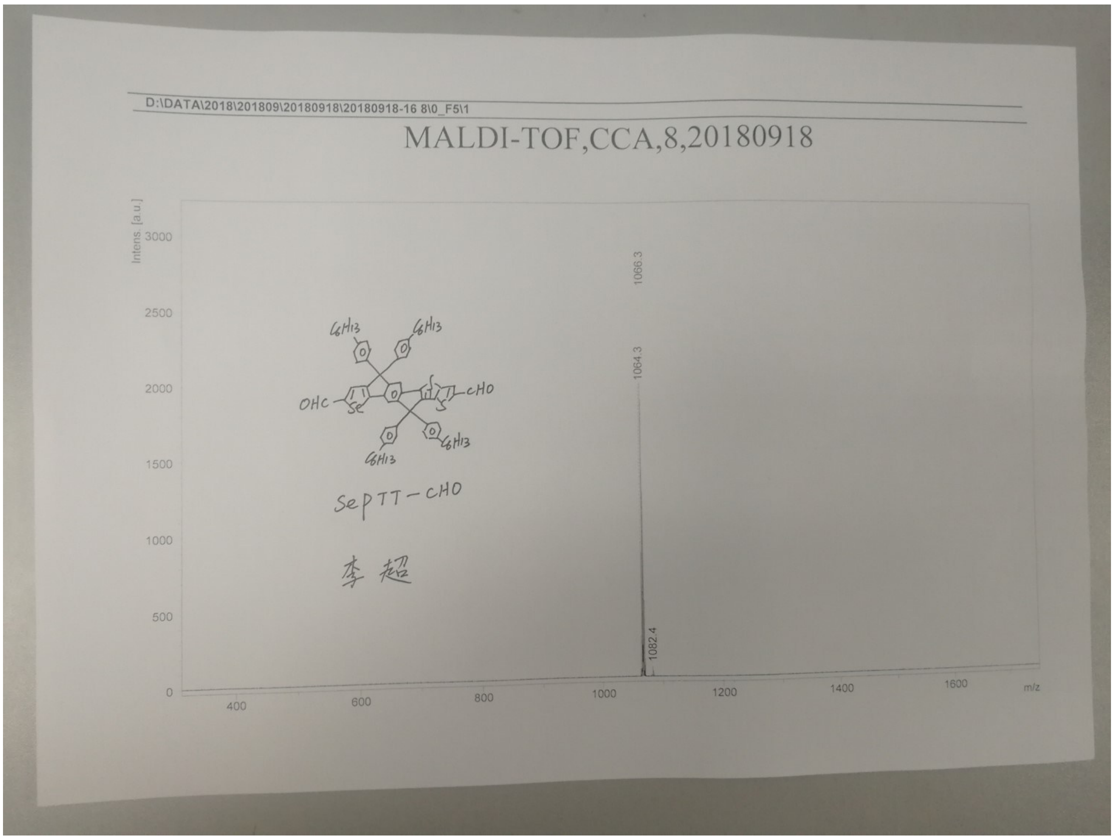


Fig. S20 MS spectrum of **SePTT-CHO**.

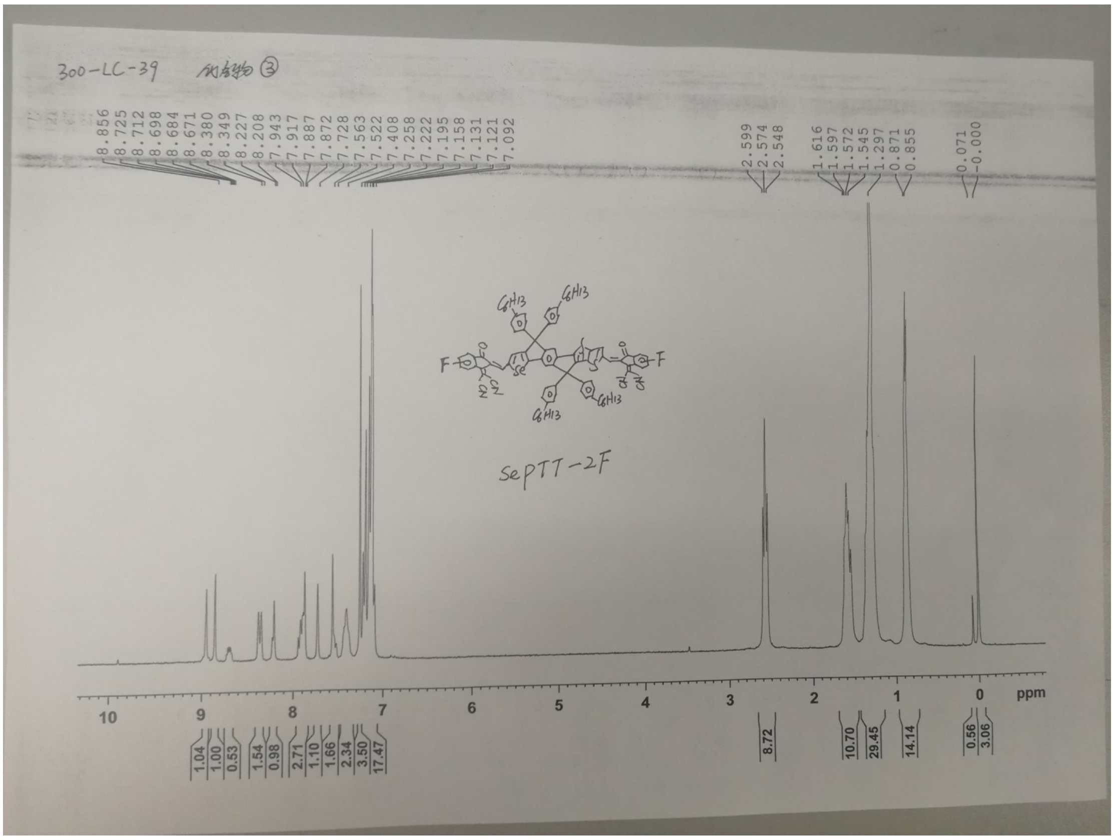


Fig. S21 ^{1}H spectrum of **SePTT-2F**.

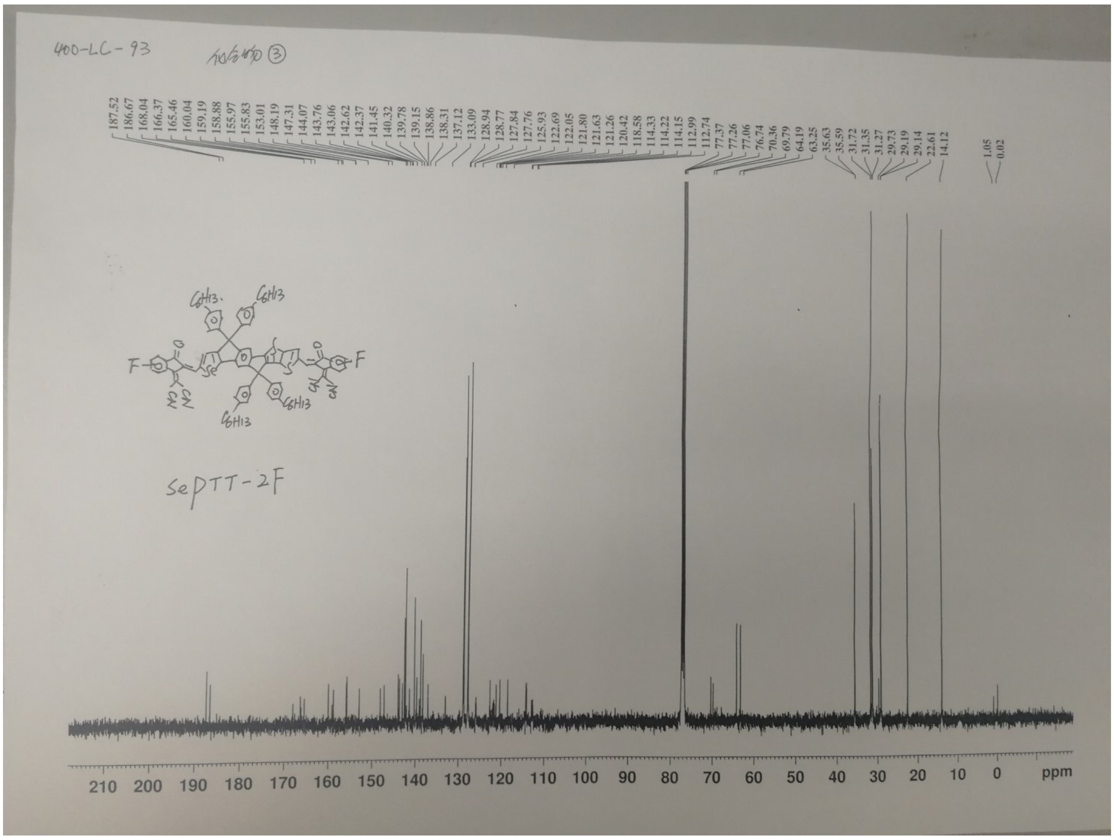


Fig. S22 ^{13}C spectrum of **SePTT-2F**.

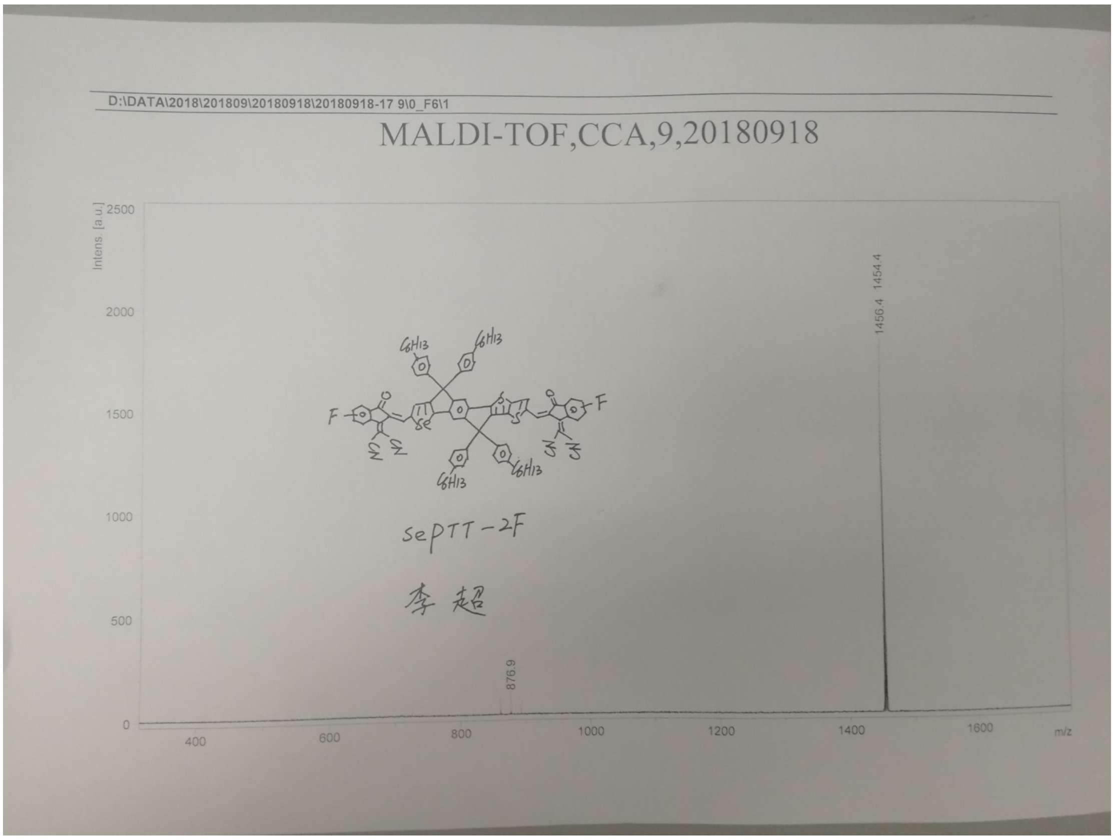


Fig. S23 MS spectrum of **SePTT-2F**.

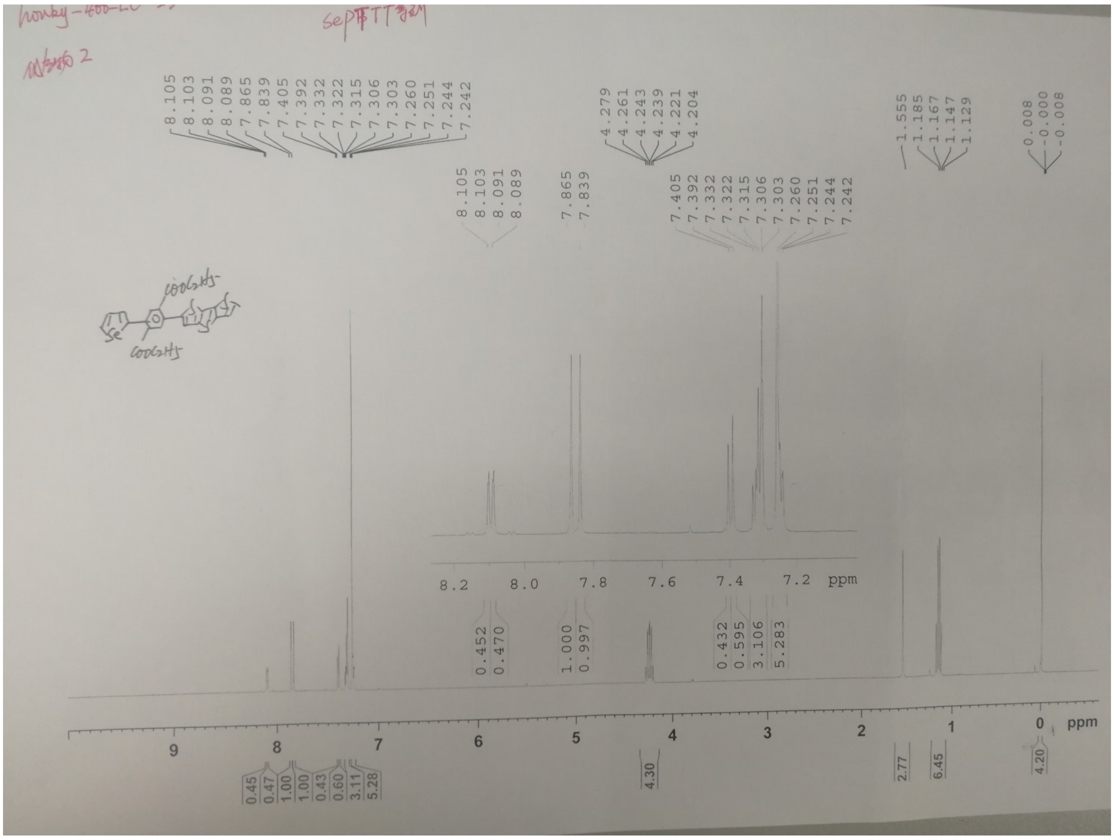


Fig. S24 ^{1}H spectrum of **compound 3**.

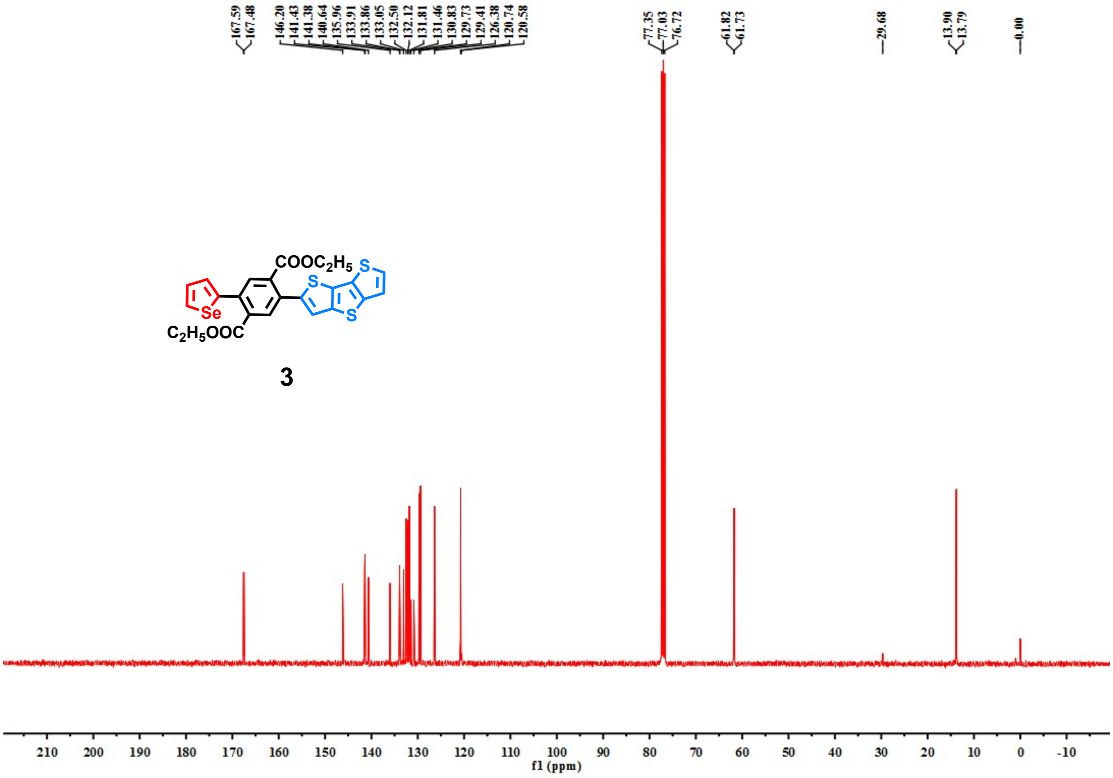


Fig. S25 ^{13}C spectrum of **compound 3**.

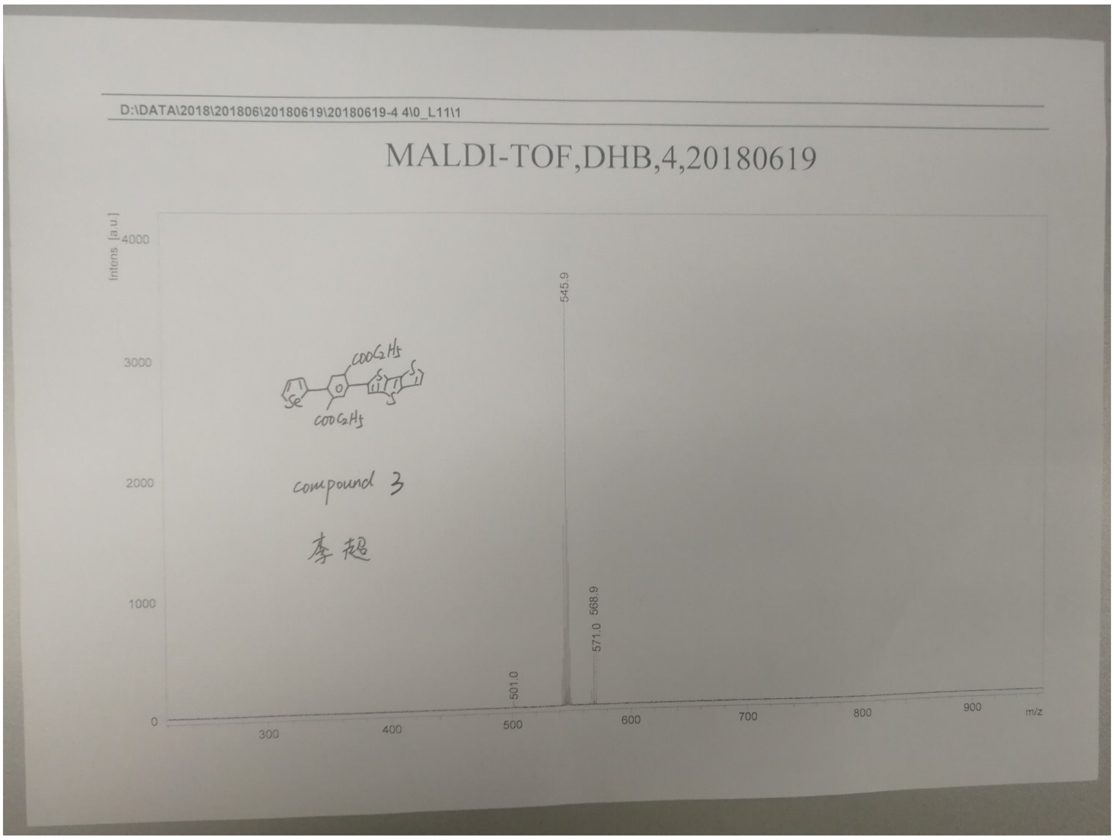


Fig. S26 MS spectrum of **compound 3**.

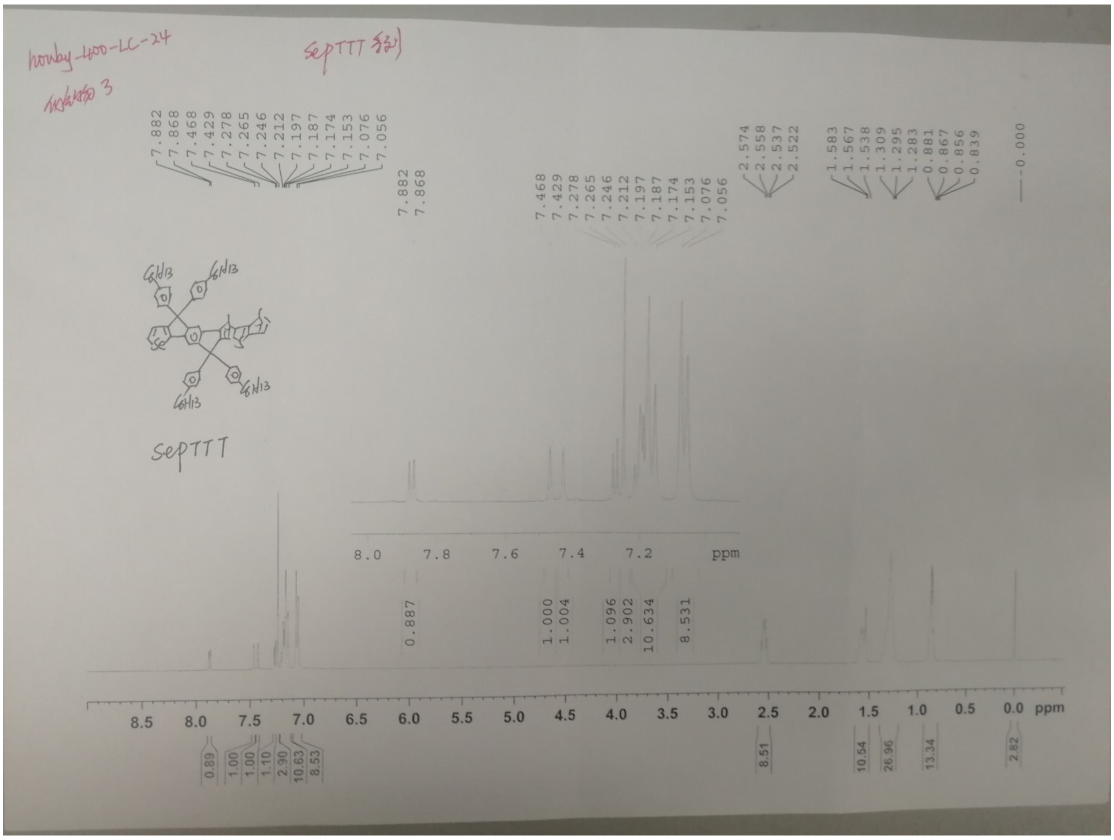


Fig. S27 ^{1}H spectrum of **SePTTT**.

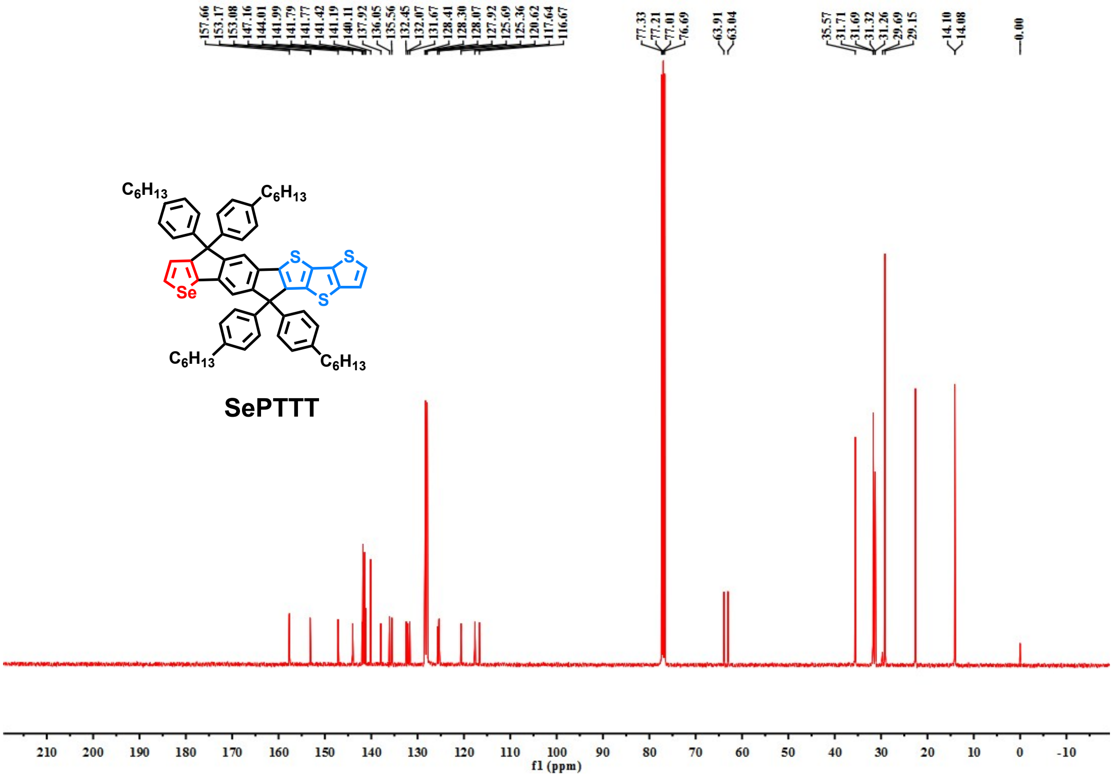


Fig. S28 ^{13}C spectrum of **SePTTT**.

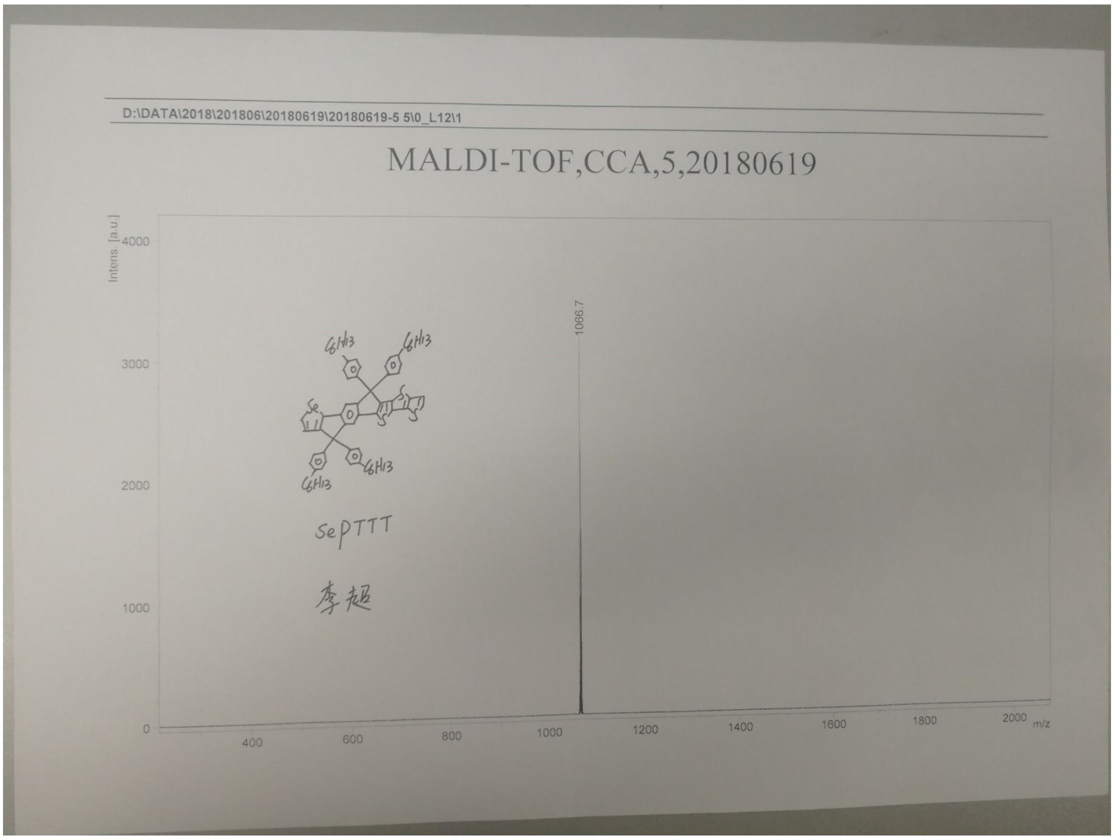


Fig. S29 MS spectrum of **SePTTT**.

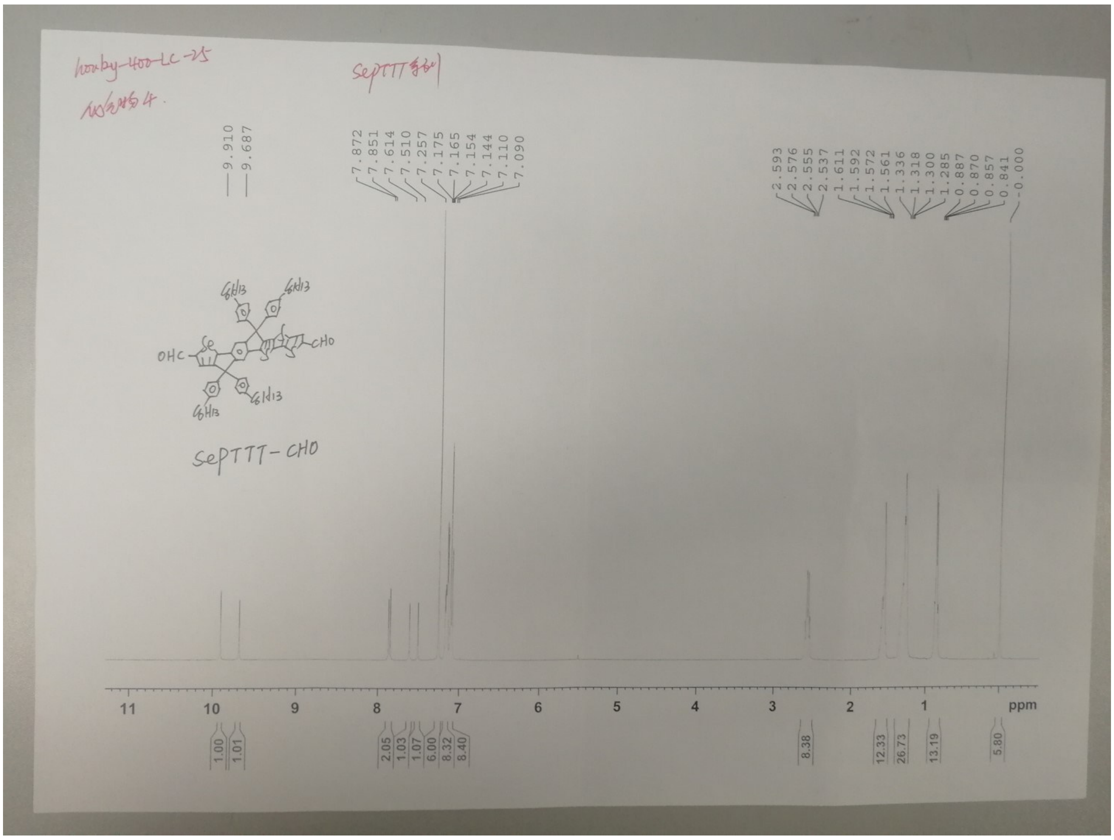


Fig. S30 ^{1}H spectrum of **SePTTT-CHO**.

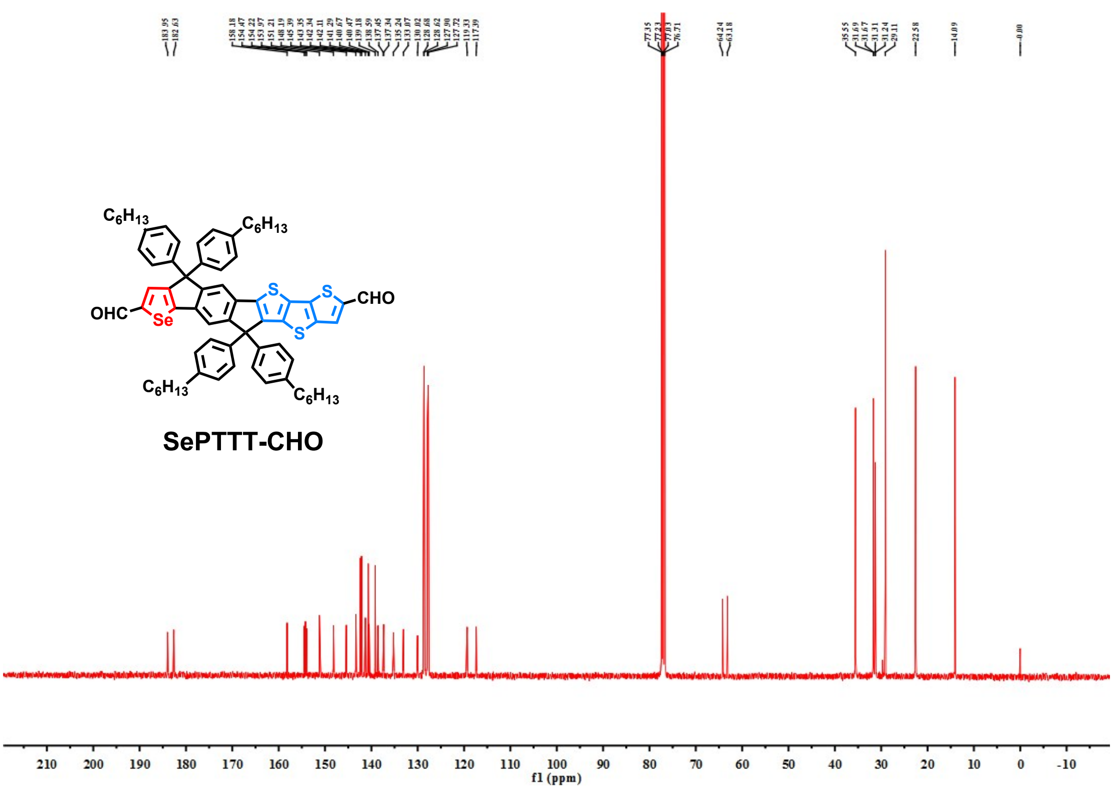


Fig. S31 ^{13}C spectrum of **SePTTT-CHO**.

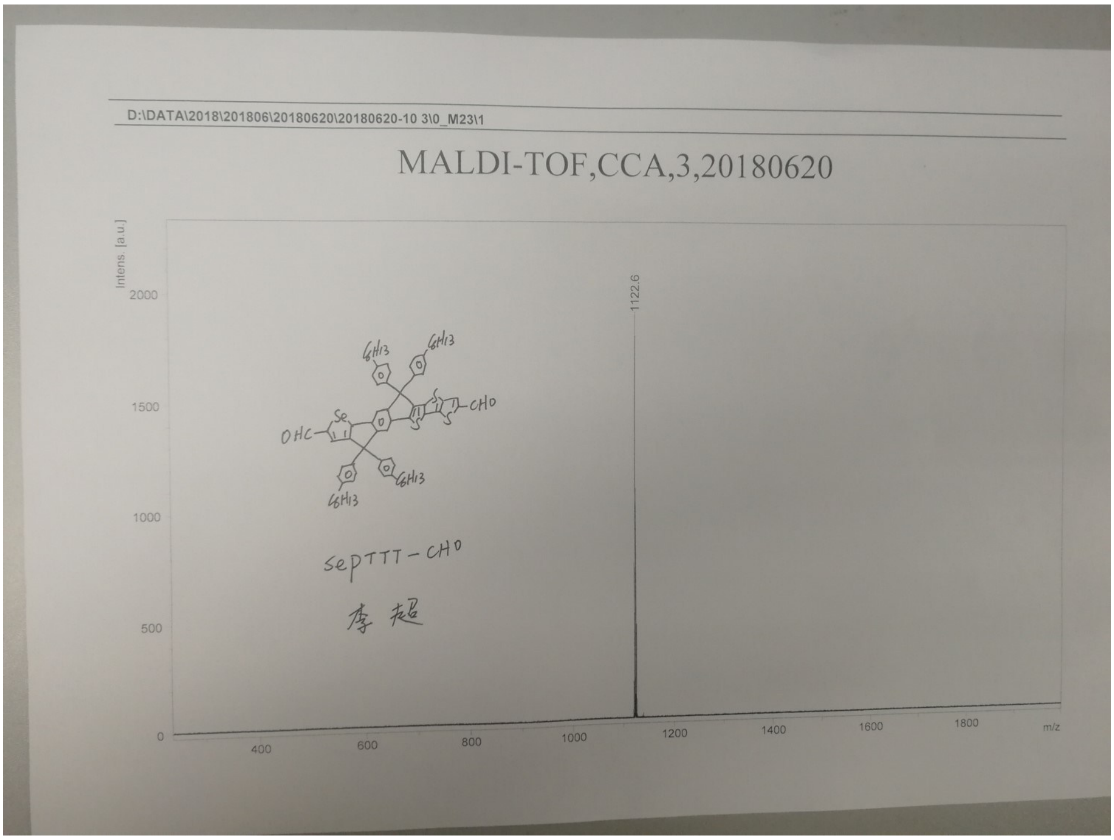


Fig. S32 MS spectrum of **SePTTT-CHO**.

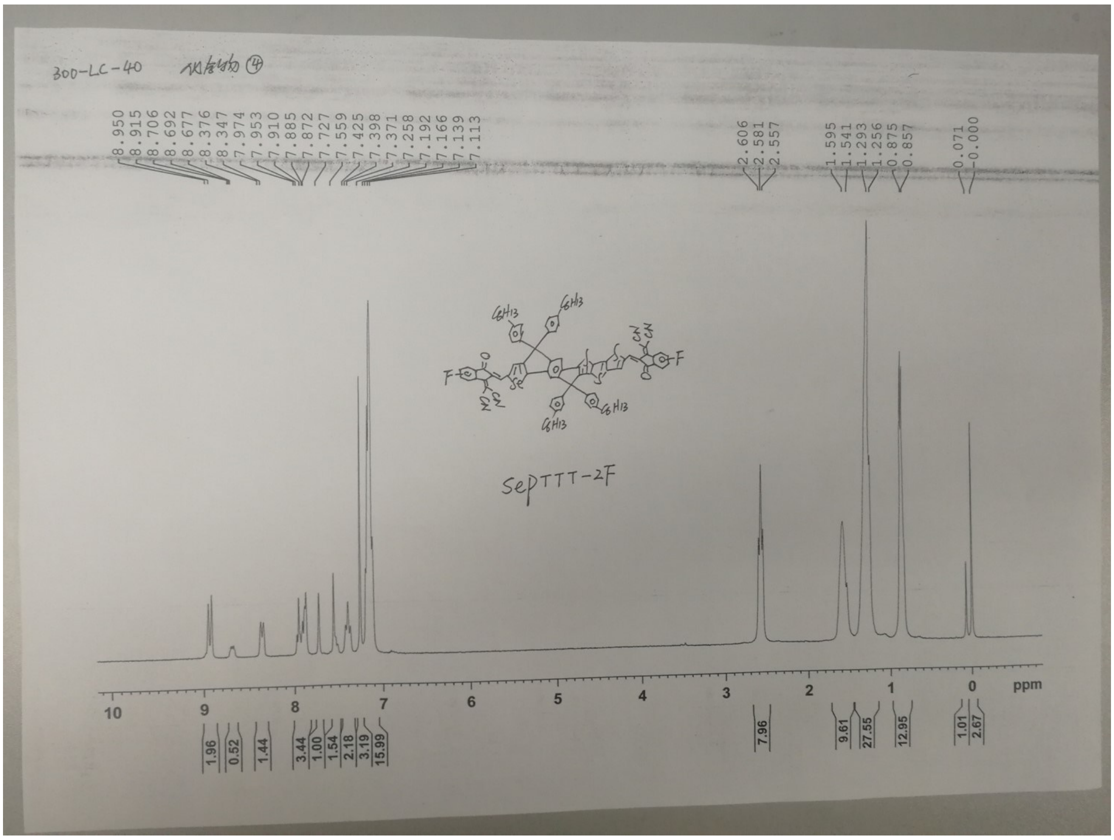


Fig. S33 ^{1}H spectrum of **SePTTT-2F**.

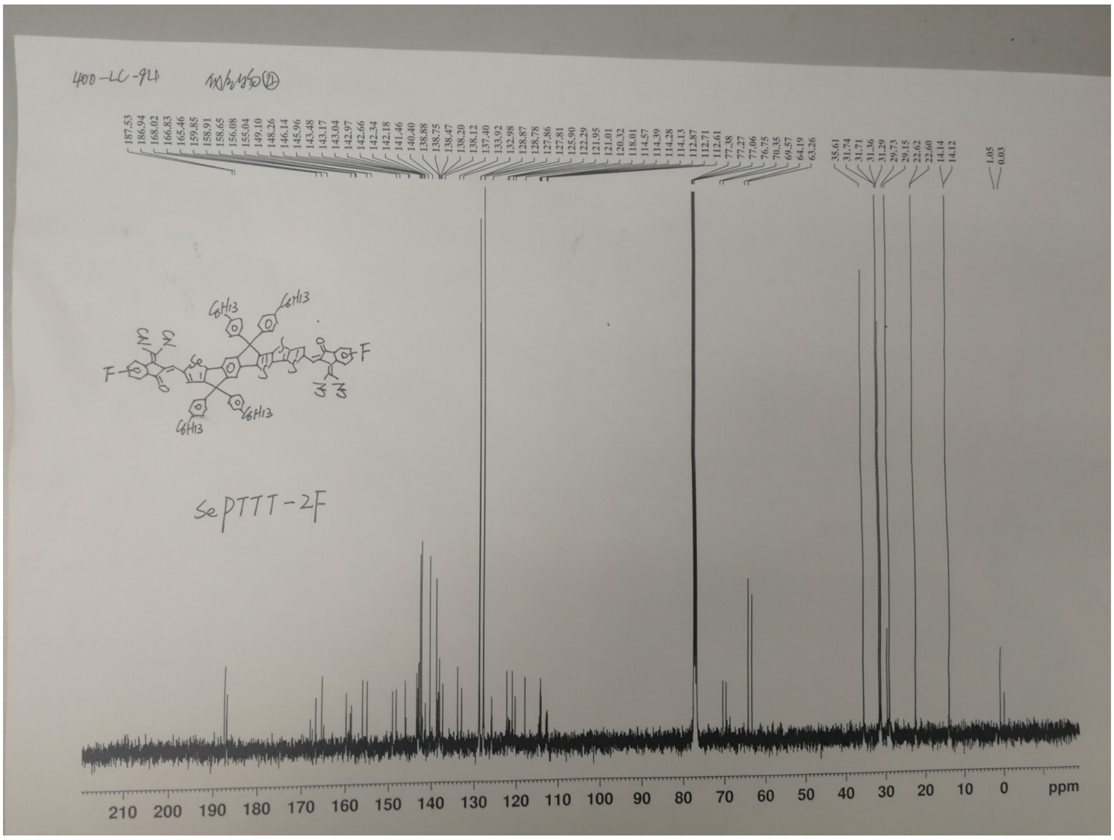


Fig. S34 ^{13}C spectrum of **SePTTT-2F**.

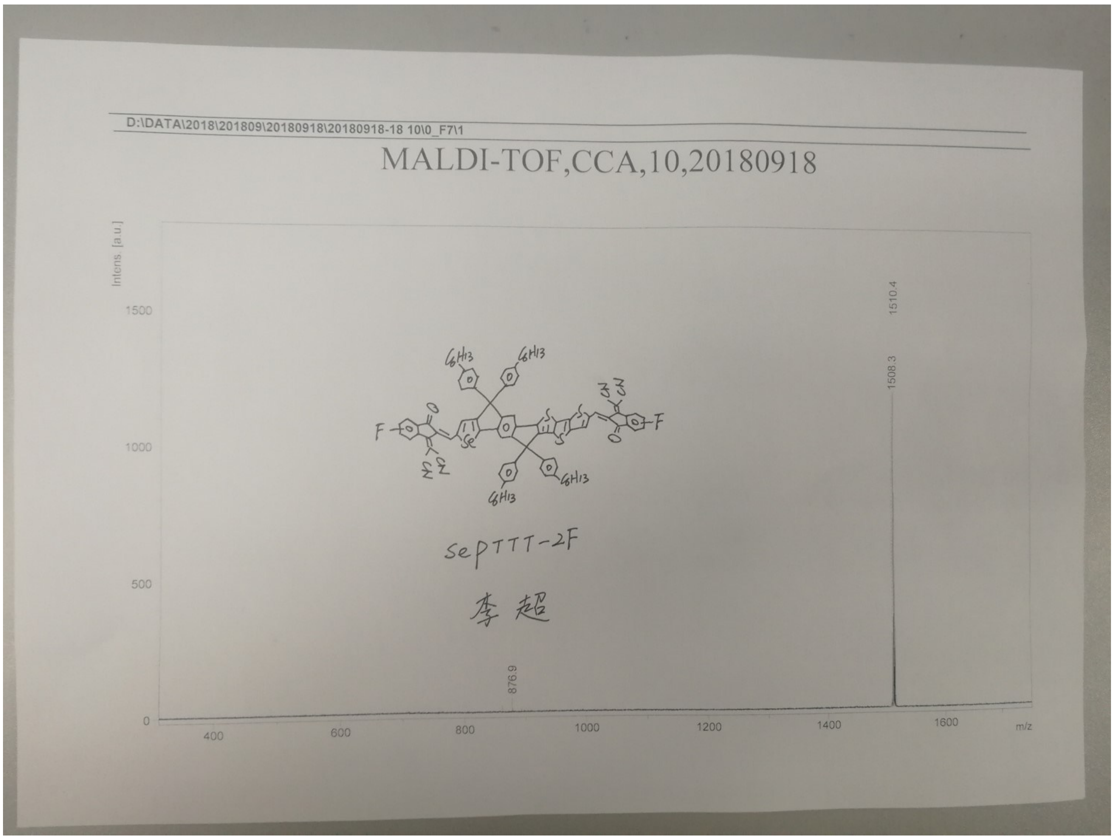


Fig. S35 MS spectrum of **SePTTT-2F**.