Electronic Supplementary Information

Asymmetric A-D-π-A-Type Nonfullerene Small Molecule Acceptor for Efficient Organic Solar Cells

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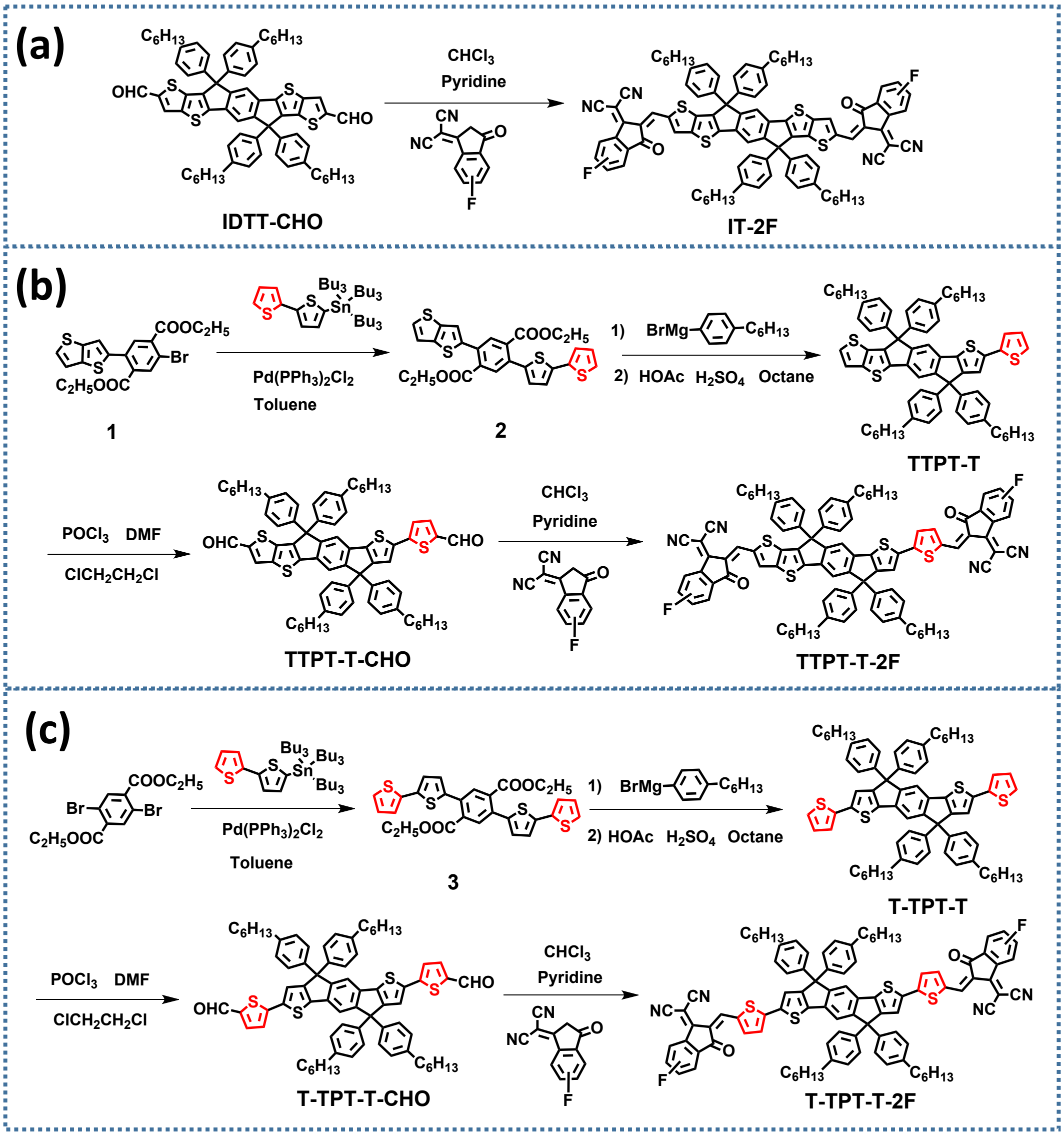
S1.1 Materials and Synthesis

All solvents and reagents were purchased from commercial sources and were used without further purification unless otherwise stated specially. Anhydrous THF was distilled from sodium benzophenone under nitrogen before use. Unless otherwise noted, all the reactions were conducted under the protection of nitrogen atmosphere. Diethyl 2-bromo-5-(thieno[3,2-b]thiophen-2-yl)terephthalate (compound 1) and IT-2F were synthesized according to corresponding literatures. [1,2] The detailed synthesis routes of TTPT-T-2F and T-TPT-T-2F were listed below.



Scheme S1. The synthetic routes of TTPT-T-2F and T-TPT-T-2F.

Synthesis of IT-2F

In a two-neck flask of 50 ml, to a solution of IDTT-CHO (100 mg, 0.093 mmol), 2-(6-fluoro-3-oxo-2, 3-dihydro-1H-inden-1-ylidene)malononitrile (78.9 mg, 0.37 mmol) and chloroform (30 mL) was added to pyridine (0.5 mL) under the protection of nitrogen atmosphere. And then the reaction mixture was allowed to stir 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 further purified by column chromatography on silica gel with petroleum ether: dichloromethane (1:1.5) as the eluent to obtain a dark black solid (108 mg, 79.35 %). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.85 (s, 2H); 8.72-8.69 (dd, *J* = 8.7, 3.9 Hz, 0.4H); 8.38-8.36 (d, *J* = 8.9 Hz, 1.6H); 8.24-8.22 (d, *J* = 7.4 Hz, 2H); 7.93-7.90 (dd, *J* = 8.2, 5.2 Hz, 1.5H); 7.64 (s, 2H); 7.56-7.54 (d, *J* = 6.1 Hz, 0.5H); 7.43-7.39 (t, J = 6.7 Hz, 2H); 7.22-7.12 (dd, *J* = 28.8, 8.1 Hz, 16H); 2.59-2.55 (t, *J* = 7.7 Hz, 8H); 1.61-1.56 (m, 8H); 1.36-1.26 (m, 24H); 0.87-0.84 (t, *J* = 6.3 Hz, 12H); ^{13}C NMR (300 MHz, $CDCl_3$, δ): 186.69, 168.43, 165.01, 164.57, 159.21, 158.93, 155.77, 153.35, 153.30, 147.73, 147.49, 147.34, 143.82, 142.58, 142.38, 142.24, 139.98, 139.54, 139.07, 138.89, 138.46, 138.35, 137.24, 137.02, 135.87, 133.06, 128.91, 127.89, 126.00, 125.86, 122.45, 122.04, 121.72, 118.64, 114.65, 114.43, 114.26, 114.19, 112.96, 112.61, 70.16, 69.14, 63.27, 35.63, 31.72, 31.29, 29.73, 29.21, 22.61, 14.12. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{94}H_{80}F_2N_4O_2S_4$, 1462.51; found, 1463.517.

Synthesis of compound 2

Under nitrogen atmosphere, n-BuLi (2.92 mL, 7.28 mmol) was added dropwise to a stirring solution of 2, 2'-bithiophene (1.21 g, 7.28 mmol) in dry THF (40 mL) at the temperature of -78℃. After being kept stirring at -78 °C for 2 h, tri-n-butyltin chloride (3.55 g, 10.92 mmol) was then injected into the reaction mixture via a syringe, and then the reaction mixture was moved 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 vacuum to give crude product, which was used in the next reaction without further purification. To a solution of diethyl 2-bromo-5-(thieno[3,2-b]thiophen-2-yl)terephthalate (2.0 g, 4.55 mmol) in anhydrous toluene (80 ml), [2,2'-bithiophen]-5-yltributylstannane (3.31 g, 7.28 mmol) and $Pd(PPh_3)_2Cl_2$ (0.16 g, 0.23 mmol) were added into the reaction system 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 was further 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 (2.21 g, 92.5%). ^1H NMR (300 MHz, $CDCl_3$, δ): 7.87-7.86 (d, J = 2.3 Hz, 2H), 7.41-7.39 (d, J = 5.1 Hz, 1H), 7.29-7.24 (m, 3H), 7.22-7.21 (d, J = 2.8 Hz, 1H), 7.16-7.15 (d, J = 3.6 Hz, 1H), 7.05-7.01 (dd, J = 7.8, 4.3 Hz, 2H), 4.31-4.21 (dq, J = 14.3, 7.2 Hz, 4H), 1.24-1.11 (dt, J = 24.9, 7.1 Hz, 6H); ^{13}C NMR (300 MHz, $CDCl_3$, δ): 167.61, 167.51, 142.09, 139.91, 139.39, 139.09, 138.79, 136.96, 134.13, 133.84, 133.54, 133.22, 132.11, 131.75, 127.95, 127.87, 127.39, 124.80, 124.04, 119.54, 119.27, 61.88, 61.83, 13.92, 13.87. MS (MALDI-TOF) m/z: $[M+H]^+$ calcd for $C_{26}H_{20}O_4S_4$, 524.02; found, 523.7.

Synthesis of TTPT-T

Under nitrogen atmosphere, 1-bromo-4-hexylbenzene (7.65 g, 31.71 mmol) was added dropwise into a stirring mixture of Mg (0.87 g, 35.68 mmol) and three grains of I_2 as initiator in dry THF (60 mL) at a two-neck flask at room temperature. When the reaction system turned into dark, all the reaction mixture was injected into a solution of compound 2 (2.08 g, 3.96 mmol) and dry THF (25ml). Then, the resulting mixture system was reacted at 70 °C overnight. After the reaction system was cooled to room temperature, the reaction mixture was poured into water and extracted with dichloromethane for three times. The combined organic phases was dried over with anhydrous $MgSO_4$ and filtered to obtain the filtrate, which was concentrated under reduced pressure. The resulting crude product was put in a two-neck flask of 250 ml, and then 60 ml octane, 10 ml acetic acid and 1 ml concentrated sulfuric acid were added successively. Afterwards, the reaction system was heated to 120 ºC for 12 h. When cooled to room temperature, the reaction mixture was poured into water and extracted with dichloromethane for three times. The combined organic phases was dried over with anhydrous $MgSO_4$ and filtered to obtain the filtrate, which was concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel with petroleum ether: dichloromethane (9:1) as an eluent to afford TTPT-T served as a novel asymmetrical A-D-π-A-based building block as yellow solid (0.797 g, 19.23 %). ^1H NMR (300 MHz, $CDCl_3$, δ): 7.45 (s, 1H), 7.42 (s, 1H), 7.26 (m, 3H), 7.21-7.15 (m, 10H), 7.09-7.08 (m, 8H), 7.00-6.99 (m, 1H), 2.59-2.52 (m, 8H), 1.57-1.54 (m, 8H), 1.29 (m, 24H), 0.87 (m, 12H); ^{13}C NMR (300 MHz, $CDCl_3$, δ): 156.44, 153.25, 153.17, 145.95, 143.29, 141.73, 141.63, 141.57, 140.35, 140.00, 139.81, 138.26, 135.95, 135.25, 133.81, 128.43, 128.40, 128.06, 127.97, 127.82, 126.34, 124.14, 123.22, 120.37, 119.69, 117.10, 117.03, 63.09, 62.95, 35.62, 31.75, 31.38, 31.30, 29.74, 29.20, 22.63, 14.13. MS (MALDI-TOF) m/z: $[M+H]^+$ calcd for $C_{70}H_{76}S_4$, 1044.48; found, 1044.2

Synthesis of TTPT-T-CHO

In a two-neck flask of 50 ml, POCl3 (1.78 mL, 19.13 mmol) was added dropwise to a stirring DMF (20 ml) at 0 ℃. And then the reaction mixture was moved to room temperature and stirred for another 30 min. A solution of TTPT-T (1 g, 0.96 mmol) in dichloroethane was added into the reaction mixture and the resulting mixture was heated to 80 ℃ and stirred overnight. The resulting mixture was poured into water, followed by extraction with dichloromethane for three times. The combined organic layers were dried with anhydrous $MgSO_4$ and the solvent was removed through evaporation to give crude product, which was further purified by column chromatography on silica gel with petroleum ether: ethyl acetate (9:1) as an eluent to afford an orange solid (0.70 g, 66.44 %). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 9.88 (s, 1H), 9.83 (s, 1H), 7.93 (s, 1H), 7.64-7.63 (d, J = 3.9 Hz, 1H), 7.54 (s, 1H), 7.50 (s, 1H), 7.26 (s, 1H), 7.23-7.22 (d, J = 3.9 Hz, 1H), 7.19-7.16 (m, 5H), 7.12-7.10 (m, 11H), 2.60-2.53 (dd, J = 13.6, 6.7 Hz, 8H), 1.58-1.55 (m, 8H), 1.29-1.26 (m, 24H), 0.95-0.87 (m, 12H); ^{13}C NMR (300 MHz, $CDCl_3$, δ): 182.85, 182.31, 157.59, 154.52, 154.01, 149.84, 147.70, 146.28, 144.20, 142.63, 142.29, 142.01, 141.56, 141.38, 141.06, 140.32, 139.39, 139.07, 137.34, 136.18, 135.63, 130.93, 129.90, 128.74, 127.86, 123.76, 122.00, 118.19, 117.64, 63.21, 63.10, 38.77, 35.61, 31.98, 31.75, 31.38, 31.30, 29.75, 29.41, 29.18, 23.04, 22.63, 14.14, 11.02. MS (MALDI-TOF) m/z: $[M+H]^+$ calcd for $C_{72}H_{76}O_2S_4$, 1100.47; found, 1100.2.

Synthesis of TTPT-T-2F

In a two-neck flask of 50 ml, to a solution of TTPT-T-CHO (100 mg, 0.091 mmol), 2-(6-fluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (57.8 mg, 0.272 mmol) and chloroform (30 mL) was added to pyridine (0.5 mL) under the protection of nitrogen atmosphere. And then the reaction mixture was allowed to stir at 65°C 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 further purified by column chromatography on silica gel with petroleum ether: dichloromethane (1:1.5) as the eluent to obtain a dark black solid (110 mg, 81 %). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.85-8.83 (d, J = 7.0 Hz, 2H), 8.73-8.69 (m, 0.5H), 8.38-8.35 (m, 1.5H), 8.20 (m, 1H), 7.93-7.91 (m, 1.5H), 7.75-7.74 (d, J = 3.7 Hz, 1H), 7.56-7.53 (m, 2.5H), 7.49 (s, 1H), 7.41 (m, 2H), 7.38 (m, 1H), 7.19-7.11 (m, 16H), 2.58-2.56 (m, 8H), 1.60-1.54 (m, 8H), 1.29-1.25 (m, 24H), 0.87-0.86 (m, 12H); ^{13}C NMR (300 MHz, $CDCl_3$, δ): 187.06, 186.71, 165.04, 158.86, 155.65, 154.67, 154.53, 153.91, 147.76, 147.17, 146.77, 144.68, 143.56, 142.49, 140.68, 139.75, 139.27, 139.06, 138.35, 137.53, 137.30, 136.94, 135.76, 133.05, 128.86, 128.71, 127.89, 127.82, 124.75, 123.36, 122.15, 121.80, 118.77, 117.99, 114.17, 112.60, 70.29, 69.86, 63.22, 35.61, 31.74, 31.72, 31.37, 31.28, 29.73, 29.21, 29.13, 22.61, 14.12. HRMS

(ESI) m/z: $[M+H]^+$ calcd for $C_{96}H_{82}F_2N_4O_2S_4$, 1488.97; found, 1489.531.

Synthesis of compound 3

Under N_2 atmosphere, n-BuLi (6.32 mL, 15.79 mmol) was added dropwise to a stirring solution of 2, 2'-bithiophene (2.62 g, 15.79 mmol) in dry THF (60 mL) at the temperature of -78℃. After being kept stirring at -78 ºC for 2 h, tri-n-butyltin chloride (7.71 g, 23.68 mmol) was then injected into the reaction mixture via a syringe, and then the reaction mixture was moved 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 MgSO4 and the solvent was removed in vacuum to give crude product, which was used in the next reaction without further purification. To a solution of diethyl 2, 5-dibromoterephthalate (2.0 g, 5.26 mmol) in anhydrous toluene (100 ml), [2, 2'-bithiophen]-5-yltributylstannane (7.19 g, 15.79 mmol) and $Pd(PPh_3)_2Cl_2$ (0.185 g, 0.263 mmol) were added into the reaction system under nitrogen atmosphere. The reaction mixture was refluxed for overnight and then cooled 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 was further 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 (2.78 g, 95.92%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.83 (s, 2H), 7.26-7.24 (d, J = 6.2 Hz, 2H), 7.21-7.20 (d, J = 2.8 Hz, 2H), 7.15-7.14 (d, J = 3.6 Hz, 2H), 7.05-7.00 (dd, J = 10.5, 3.7 Hz, 4H), 4.31-4.24 (q, J = 7.1 Hz, 4H), 1.24-1.20 (t, J = 7.1 Hz, 6H); ^{13}C NMR (300 MHz, $CDCl_3$, δ): 167.66, 139.13, 138.72, 136.98, 133.86, 132.95, 131.77, 127.95, 127.81, 124.78, 124.02, 61.87, 13.93. MS (MALDI-TOF) m/z: $[M+H]^+$ calcd for $C_{28}H_{22}O_4S_4$, 550.04; found, 549.7.

Synthesis of compound T-TPT-T

Under nitrogen atmosphere, 1-bromo-4-hexylbenzene (4.14 g, 17.15 mmol) was added dropwise into a stirring mixture of Mg (0.62 g, 25.42 mmol) and three grains of I_2 as initiator in dry THF (60 mL) at a two-neck flask at room temperature. When the reaction system turned into dark, all the reaction mixture was injected into a solution of compound 3 (2.00 g, 3.63 mmol) and dry THF (25ml). Then, the resulting mixture system was reacted at 70 ºC overnight. After the reaction system was cooled to room temperature, the reaction mixture was poured into water and extracted with dichloromethane for three times. The combined organic phases was dried over with anhydrous $MgSO_4$ and filtered to obtain the filtrate, which was concentrated under reduced pressure. The resulting crude product was put in a two-neck flask of 250 ml, and then 60 ml octane, 10 ml acetic acid and 1 ml concentrated sulfuric acid were added successively. Afterwards, the reaction system was heated to 120 ºC for 12 h. When cooled to room temperature, the mixture was quenched with 100 ml water and extracted with DCM for three times. The combined organic layers were dried with anhydrous MgSO4 and then concentrated under reduced pressure evaporation. The crude product was further purified by column chromatography on silica gel with petroleum ether: dichloromethane (9:1) as an eluent to afford T-TPT-T building block of luminous yellow solid (0.798 g, 20.50%). ^1H NMR (300 MHz, $CDCl_3$, δ): 7.37 (s, 2H), 7.26 (s, 2H), 7.19-7.16 (d, J = 8.0 Hz, 10H), 7.08-7.06 (m, 10H), 7.00-6.98 (m, 2H), 2.58-2.53 (t, J = 7.7 Hz, 8H), 1.59-1.54 (m, 8H), 1.30 (m, 24H), 0.87-0.85 (m, 12H); ^{13}C NMR (300 MHz, $CDCl_3$, δ): 156.41, 153.21, 141.76, 141.57, 140.05, 139.81, 138.27, 135.10, 128.41, 127.95, 124.15, 123.22, 119.69, 117.22, 63.06, 35.62, 31.77, 31.40, 29.20, 22.65, 14.16. MS (MALDI-TOF) m/z: $[M+H]^+$ calcd for $C_{72}H_{78}S_4$, 1070.7; found, 1070.1.

Synthesis of compound T-TPT-T-CHO

In a two-neck flask of 50 ml, $POCl_3$ (1.74 mL, 18.66 mmol) was added dropwise to a stirring DMF (20 ml) at 0 °C. And then the reaction mixture was moved to room temperature and stirred for another 30 min. A solution of T-TPT-T (1 g, 0.933 mmol) in dichloroethane was added into the reaction mixture and the resulting mixture was heated to 80 °C and stirred overnight. The resulting mixture was poured into water, followed by extraction with dichloromethane for three times. The combined organic layers were dried with anhydrous $MgSO_4$ and the solvent was removed through reduced pressure evaporation to give crude product, which was further purified by column chromatography on silica gel with petroleum ether: ethyl acetate (9:1) as an eluent to afford an orange solid (0.70 g, 66.44 %). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 9.83 (s, 2H), 7.64-7.63 (d, J = 3.8 Hz, 2H), 7.43 (s, 2H), 7.26 (s, 2H), 7.22 (m, 2H), 7.18-7.15 (d, J = 8.2 Hz, 8H), 7.10-7.07 (d, J = 8.1 Hz, 8H), 2.59-2.54 (t, J = 7.8 Hz, 8H), 1.59-1.56 (m, 8H), 1.30 (m, 24H), 0.87-0.85 (m, 12H); ^{13}C NMR (300 MHz, $CDCl_3$, δ): 182.30, 157.21, 153.84, 147.87, 142.92, 141.93, 141.23, 141.18, 138.62, 137.37, 135.26, 128.56, 127.83, 123.62, 122.02, 117.78, 63.15, 35.61, 31.75, 31.38, 29.18, 22.63, 14.14. MS (MALDI-TOF) m/z: $[M+H]^+$ calcd for $C_{74}H_{78}O_2S_4$, 1126.49; found, 1126.2.

Synthesis of compound T-TPT-T-2F

In a two-neck flask of 50 ml, Under nitrogen atmosphere, to a solution of T-TPT-T-CHO (100 mg, 0.089 mmol), 2-(6-fluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (56.7 mg, 0.267 mmol) and chloroform (30 mL) was added to pyridine (0.5 mL) under the protection of nitrogen atmosphere. And then the reaction mixture was allowed to stir at 65°C 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 further purified by column chromatography on silica gel with petroleum ether: dichloromethane (1:1.5) as the eluent to obtain a dark black solid (105 mg, 78.10%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.82 (s, 2H), 8.73-8.68 (m, 0.5H), 8.38-8.35 (m, 1.5H), 7.93-7.89 (dd, J = 8.1, 5.3 Hz, 1.5H), 7.75 (m, 2H), 7.55-7.53 (m, 0.5H), 7.49 (s, 4H), 7.43-7.40 (m, 2H), 7.38 (s, 2H), 7.19-7.10 (dd, J = 20.7, 8.1 Hz, 16H), 2.61-2.56 (t, J = 7.6 Hz, 8H), 1.60-1.54 (m, 8H), 1.30-1.25 (m, 24H), 0.87-0.85 (m, 12H); ^{13}C NMR (300 MHz, $CDCl_3$, δ): 187.06, 165.02, 158.86, 158.31, 154.88, 154.47, 146.84, 145.17, 142.39, 142.26, 142.09, 140.88, 139.09, 137.51, 135.93, 135.63, 133.04, 128.66, 127.83, 125.79, 124.60, 123.46, 121.97, 121.67, 121.59, 118.12, 114.27, 114.21, 112.95, 112.60, 63.18, 35.61, 31.74, 31.37, 29.14, 22.62, 14.13. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{98}H_{84}F_2N_4O_2S_4$, 1514.54; found, 1515.549.

S1.2 Characterization

The nuclear magnetic resonance (NMR) spectra were measured on a Bruker Avance 300/400 spectrometer using deuterated chloroform ($CDCl_3$) as the solvent and trimethylsilane (TMS) as the internal reference at room temperature. Solution and thin film (on a quartz substrate) UV-Vis absorption spectra were conducted on a Hitachi (model U-3010) UV–vis spectrophotometer. Mass spectra were measured utilizing a Bruker Daltonics Biflex Ⅲ MALDI-TOF Analyzer in the MALDI mode. Cyclic voltammetry (CV) measurements were carried out under nitrogen atmosphere in the anhydrous acetonitrile solution of tetra-n-butylammonium hexafluorophosphate (Bu_4NPF_6) (0.1 M) at a scan rate of 100 mV s^{-1} using a Zahner IM6e Electrochemical workstation, a platinum wire as a counter electrode, a saturated Ag/AgCl electrode as a reference electrode, and a platinum plate coated with sample film as a working electrode. Using ferrocene/ferrocenium (Fc/Fc^+) as an external standard, the onset oxidation potential of ferrocene external standard was determined to be 0.44 V in our lab. Therefore, the HOMO and LUMO energy levels could be calculated from the following equations: HOMO = – (E^{onset}_{ox} + 4.36) eV and LUMO = – (E^{onset}_{red} + 4.36) eV, where E^{onset}_{ox} and E^{onset}_{red} were the onset oxidation potential and onset reduction potential relative to Ag/AgCl, respectively. Atomic force microscopy (AFM) measurements were measured 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 performed at PLS-II 9A U-SAXS beamline of the Pohang Accelerator Laboratory in Korea.

S1.3 Organic Solar Cells Fabrication and Characterization

OSCs were fabricated with a structure of ITO/ZnO/Active Layer/MoO_3/Ag. The ITO-coated glass substrates were pre-cleaned by ultrasonic treatment in detergent, deionized water, acetone and isopropanol for 20 minutes, respectively. After drying for 3 hours in an air oven, ZnO electron transport layer was prepared by spin coating at 4000 rpm from the ZnO precursor solution. Then the ZnO substrates were immediately baked in air at 200 °C for 15 minutes. Blends of PBT1-C:NFA (IT-2F, TTPT-T-2F or T-TPT-T-2F) at different donor/acceptor (D/A) ratios after fully dissolved in chlorobenzene at a donor weight concentration of 7 mg/ml with/without different volume fractions of solvent additive (DIO) were spin-coated on the ZnO substrates. After the spin-coated films were treated with/without different temperatures of thermal annealing (TA), MoO_3 was deposited by sequentially thermal evaporation of 3 nm followed by thermal evaporation of 110 nm Ag. The optimal active layer thickness is around 100 nm. The device area of active portion is 4.00 mm^2. Current density-voltage (*J*-*V*) characteristics curves were recorded through a Keithley 2400 Source Measure Unit and under the solar simulator (Enli Technology Co., Ltd, SS-F5-3A) of 100 mW cm^{-2} under AM 1.5 G. Calibrated by a standard Si solar cell (SRC-2020, Enli Technology Co., Ltd). EQE spectra were recorded by using a solar-cell spectral-response measurement system (QE-R, Enlitech).

S1.4 Space Charge Limited Current (SCLC) Measurement[3]

Space charge limited current (SCLC) measurement was used to evaluate the charge transport properties. The electron-only and hole-only devices were fabricated with the structures: ITO/ZnO/Active Layer/ZrAcac/Ag for electrons and ITO/PEDOT: PSS/Active Layer/MoO_3/Al for holes. By fitting the current density-voltage curves through SCLC, electron/hole mobilities could be extracted from the *J*-*V* curves plotted as $J^{0.5}$ versus V using the Mott-Gurney equation: $J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu_e(\mu_h)\frac{V^2}{d^3}$, where J is the current density, ε_0 is the vacuum dielectric constant, ε_r is the relative permittivity of active layer, μ_e is the electron mobility, μ_h is the hole mobility and d is the thickness of active layer. V is the internal voltage, defined as: $V = V_{appl} - V_{bi}$, where V_{appl} is the applied voltage and V_{bi} is the offset voltage (V_{bi} is 0 here).

S1.5 Figures and Tables

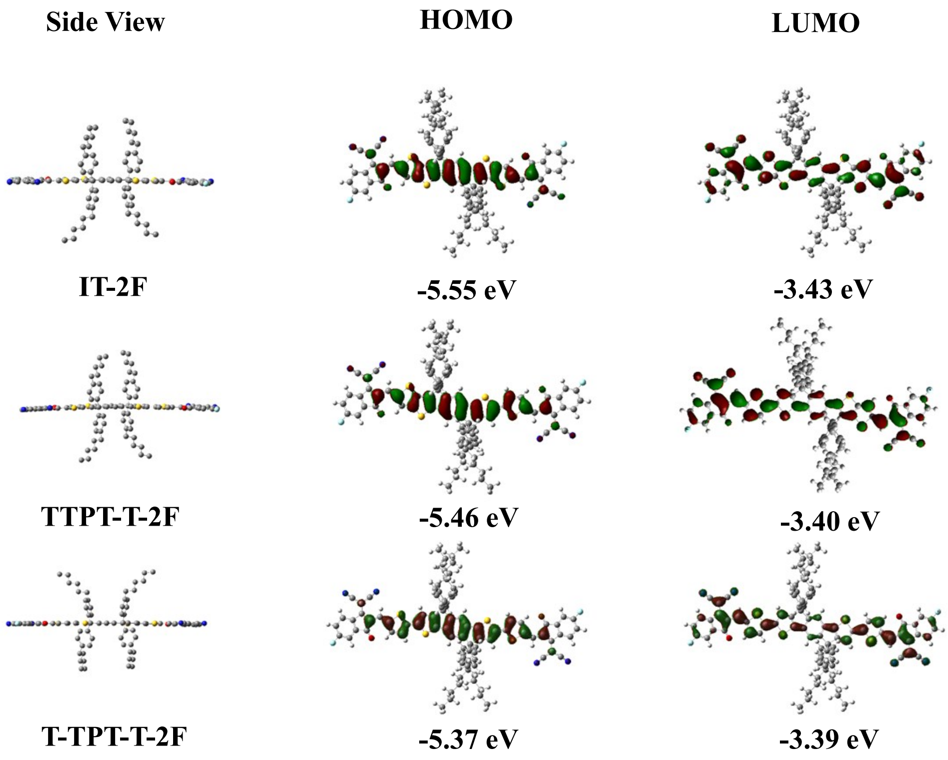


Figure S1. The side views and frontier molecular orbitals of the optimized molecular conformations obtained by DFT calculations for three nonfullerene SMAs.

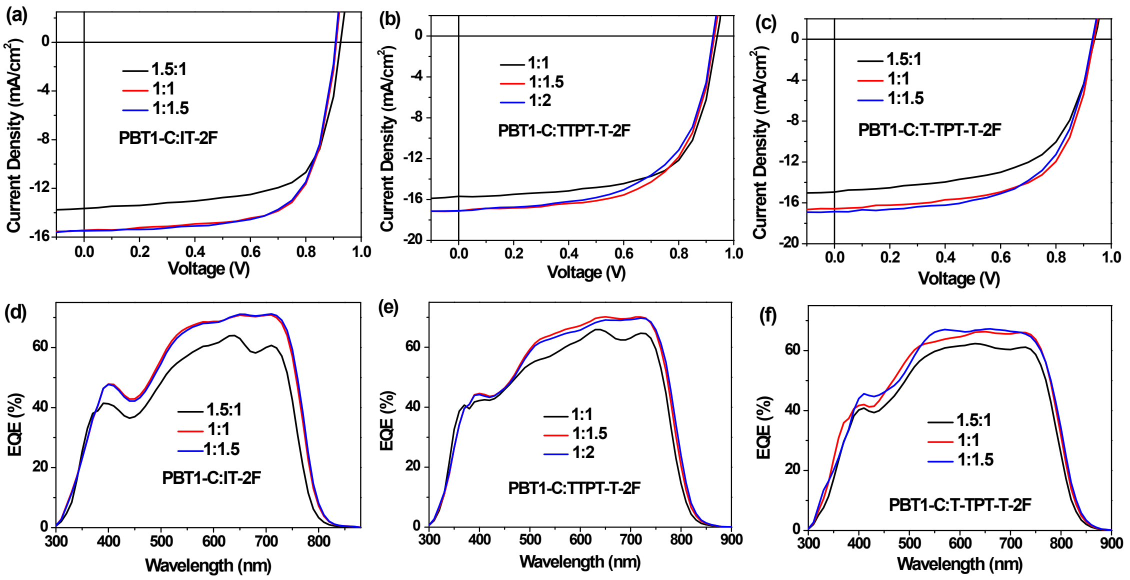


Figure S2. *J-V* curves (a, b, c) and EQE spectra (d, e, f) based on PBT1-C: SMA blends at different D/A ratios.

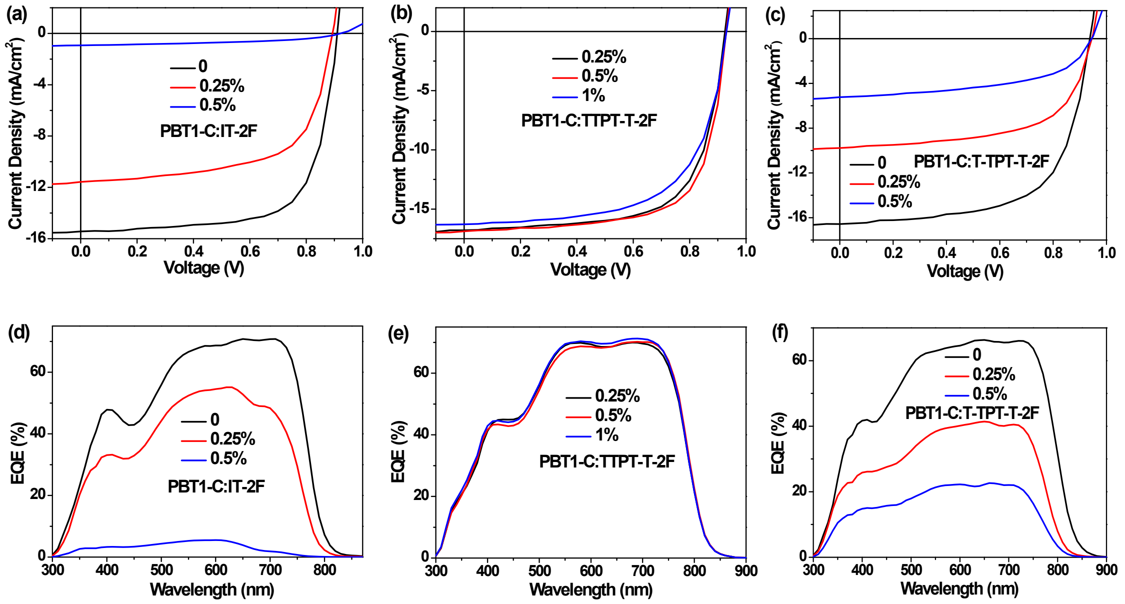


Figure S3. *J-V* curves (a, b, c) and EQE spectra (d, e, f) based on PBT1-C: SMA blends at different DIO content.

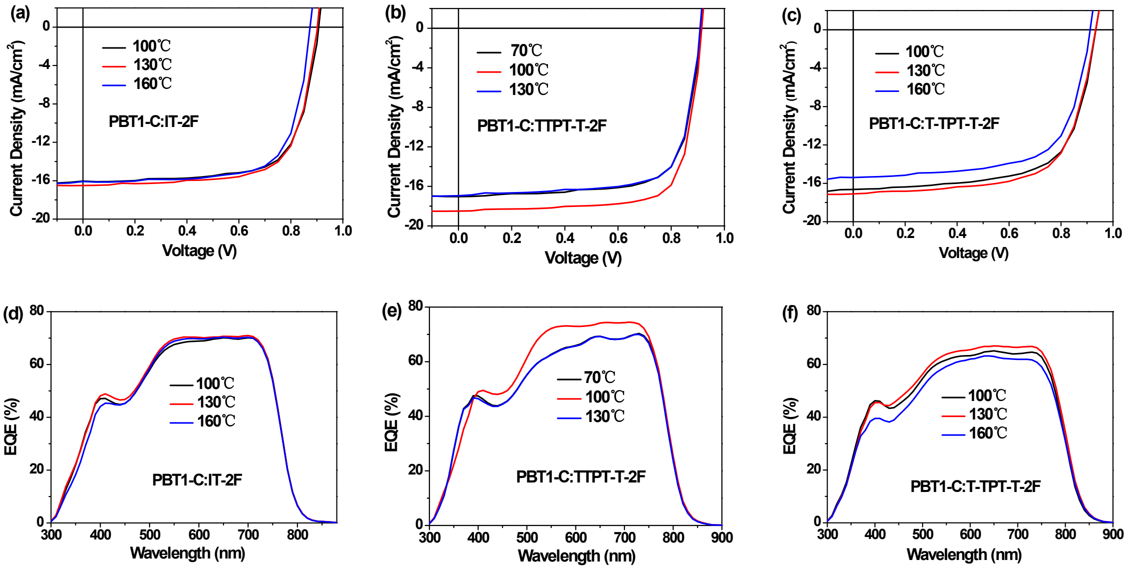


Figure S4. *J-V* curves (a, b, c) and EQE spectra (d, e, f) based on PBT1-C: SMA blends at different thermal annealing temperatures.

Table S1. Summary of photovoltaic parameters based on PBT1-C: SMA blends at different D/A ratios.

NFA	D/A (w/w)	V_{oc} (V)	J_{sc} (mA cm^{-2})	$J_{sc, cal}$ (mA cm^{-2})	FF (%)	PCE [a)] (%)
IT-2F	1.5:1	0.926 (0.923 ± 0.003)	13.65 (13.78 ± 0.21)	13.34	68.4 (67.5 ± 0.7)	8.65 (8.59 ± 0.06)
	1:1	0.910 (0.908 ± 0.003)	15.44 (15.37 ± 0.22)	15.72	70.2 (69.1 ± 0.9)	9.86 (9.64 ± 0.19)
	1:1.5	0.907 (0.908 ± 0.002)	15.49 (15.31 ± 0.18)	15.75	69.3 (68.0 ± 0.9)	9.74 (9.45 ± 0.17)
TTPT-T-2F	1:1	0.940 (0.939 ± 0.002)	15.69 (15.65 ± 0.09)	15.09	66.9 (65.5 ± 1.0)	9.87 (9.61 ± 0.18)
	1:1.5	0.930 (0.928 ± 0.002)	17.13 (17.09 ± 0.19)	16.47	62.8 (62.0 ± 0.7)	10.00 (9.83 ± 0.15)
	1:2	0.925 (0.923 ± 0.002)	17.10 (16.95 ± 0.15)	16.44	60.3 (59.0 ± 1.1)	9.54 (9.23 ± 0.20)
T-TPT-T-2F	1.5:1	0.940 (0.937 ± 0.003)	14.94 (14.45 ± 0.28)	14.95	60.3 (56.6 ± 2.5)	8.47 (7.67 ± 0.48)
	1:1	0.938 (0.937 ± 0.003)	16.57 (16.19 ± 0.28)	16.29	64.0 (63.7 ± 0.8)	9.94 (9.67 ± 0.17)
	1:1.5	0.932 (0.929 ± 0.004)	16.85 (16.47 ± 0.22)	16.51	61.6 (62.3 ± 1.3)	9.67 (9.49 ± 0.19)

a) All average values with standard deviations were calculated from 20 devices.

Table S2. Summary of photovoltaic parameters based on PBT1-C: SMA blends at different DIO content.

NFA	DIO (v/v)	V_{oc} (V)	J_{sc} (mA cm − 2)	$J_{sc, cal}$ (mA cm − 2)	FF (%)	PCE [a] (%)
IT-2F	0	0.910 (0.908 ± 0.003)	15.44 (15.37 ± 0.22)	15.72	70.2 (69.1 ± 0.9)	9.86 (9.64 ± 0.19)
	0.25	0.893 (0.896 ± 0.003)	11.57 (11.25 ± 0.29)	11.28	63.6 (62.6 ± 0.9)	6.57 (6.31 ± 0.22)
	0.5	0.921 (0.919 ± 0.003)	0.930 (0.909 ± 0.025)	0.90	45.3 (44.9 ± 0.7)	0.389 (0.375 ± 0.011)
TTPT-T-2F	0	0.930 (0.928 ± 0.002)	17.13 (17.09 ± 0.19)	16.47	62.8 (62.0 ± 0.7)	10.00 (9.83 ± 0.15)
	0.25	0.926 (0.923 ± 0.003)	16.79 (16.53 ± 0.21)	16.37	67.4 (66.1 ± 1.0)	10.48 (10.09 ± 0.25)
	0.5	0.930 (0.926 ± 0.003)	16.87 (16.50 ± 0.32)	16.31	69.2 (67.7 ± 1.0)	10.86 (10.35 ± 0.31)
	1.0	0.931 (0.930 ± 0.002)	16.29 (15.91 ± 0.25)	16.58	62.8 (62.4 ± 0.5)	9.52 (9.23 ± 0.17)
T-TPT-T-2F	0	0.938 (0.937 ± 0.003)	16.57 (16.19 ± 0.28)	16.29	64.0 (63.7 ± 0.8)	9.94 (9.67 ± 0.17)
	0.25	0.945 (0.945 ± 0.003)	9.776 (9.588 ± 0.132)	9.35	61.0 (60.6 ± 0.3)	5.635 (5.486 ± 0.092)
	0.5	0.944 (0.946 ± 0.003)	5.23 (5.15 ± 0.06)	5.04	52.9 (52.7 ± 1.0)	2.61 (2.57 ± 0.06)

[a] All average values with standard deviations were calculated from 20 devices.

Table S3. Summary of photovoltaic parameters based on PBT1-C: SMA blends at different thermal annealing temperatures.

NFA	T (°C)	V_{oc} (V)	J_{sc} (mA cm^{-2})	$J_{sc, cal}$ (mA cm^{-2})	FF (%)	PCE $^{a)}$ (%)
IT-2F	100	0.907 (0.904 ± 0.003)	16.04 (15.90 ± 0.12)	15.70	71.4 (69.4 ± 1.3)	10.39 (9.97 ± 0.25)
	130	0.902 (0.897 ± 0.006)	16.50 (16.23 ± 0.17)	15.97	70.8 (69.6 ± 1.3)	10.54 (10.13 ± 0.33)
	160	0.874 (0.874 ± 0.004)	16.08 (16.09 ± 0.06)	15.71	72.1 (70.6 ± 1.1)	10.13 (9.93 ± 0.14)
TTPT-T-2F$^{b)}$	70	0.911 (0.910 ± 0.002)	17.04 (16.79 ± 0.14)	16.38	72.8 (72.6 ± 0.7)	11.30 (11.10 ± 0.16)
	100	0.915 (0.910+0.004)	18.50 (18.32 ± 0.14)	17.70	75.1 (75.0 ± 0.6)	12.71 (12.51 ± 0.14)
	130	0.909 (0.907 ± 0.003	16.95 (16.58 ± 0.31)	16.30	73.5 (74.7 ± 1.2)	11.32 (11.22 ± 0.10)
T-TPT-T-2F	100	0.934 (0.931 ± 0.002)	16.64 (16.51 ± 0.37)	15.98	67.0 (65.6 ± 1.3)	10.41 (10.08 ± 0.25)
	130	0.933 (0.931 ± 0.001)	17.10 (17.21 ± 0.17)	16.57	67.1 (66.0 ± 1.0)	10.71 (10.58 ± 0.09)
	160	0.912 (0.913 ± 0.002)	15.40 (15.25 ± 0.22)	15.26	66.7 (66.1 ± 0.8)	9.37 (9.21 ± 0.13)

a) All average values with standard deviations were calculated from 20 devices.
b) PBT1-C:TTPT-T-2F blend film was processed with 0.5% DIO.

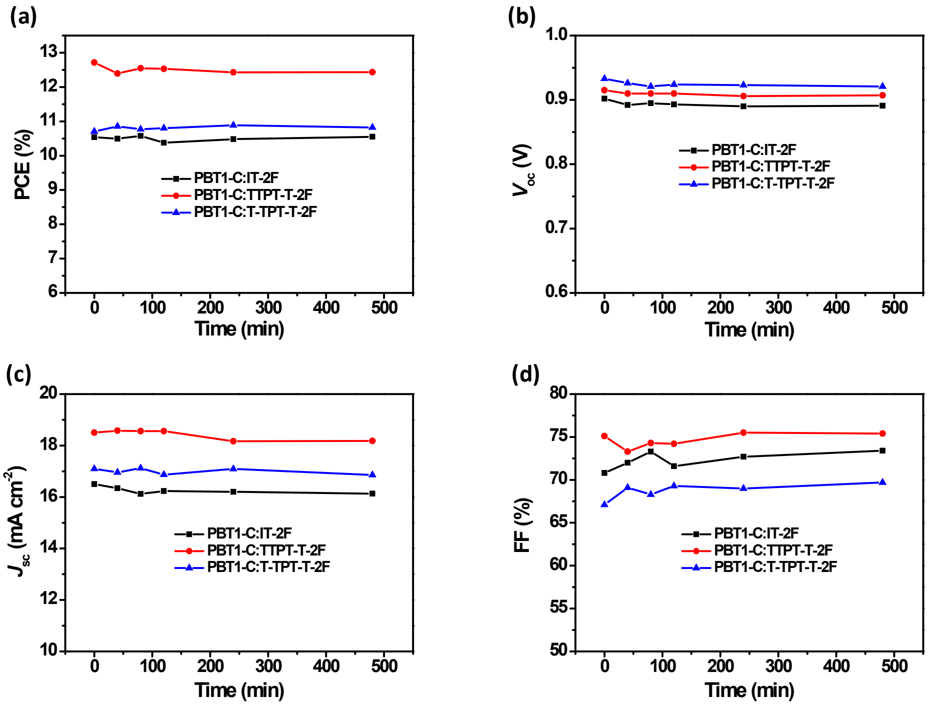


Figure S5. The device paramters of PBT1-C:IT-2F, PBT1-C:TTPT-T-2F, and PBT1-C:T-TPT-T-2F OSCs versus the heating time.

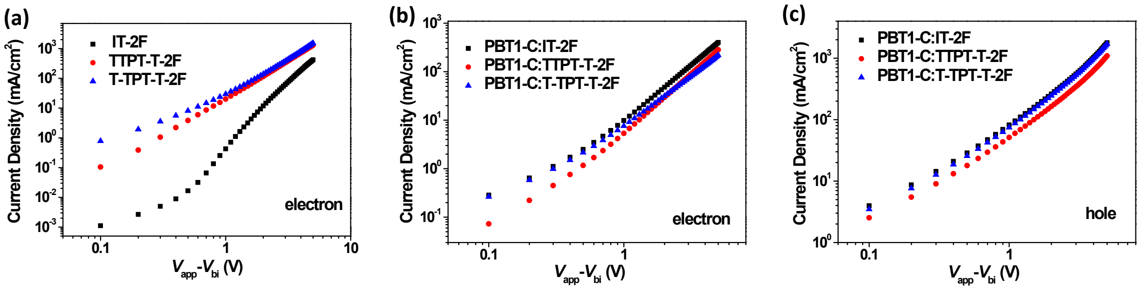
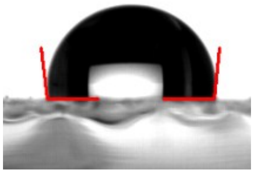
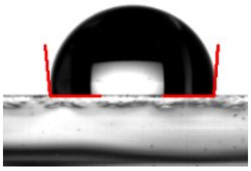
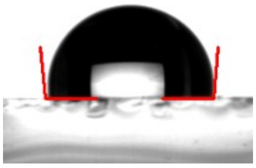
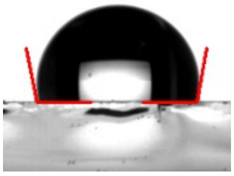
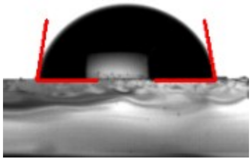
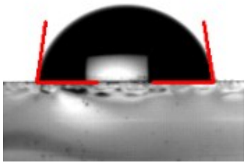
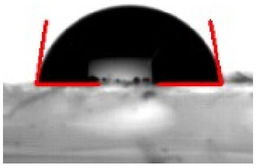
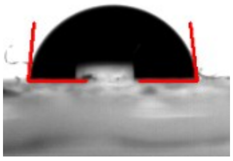


Figure S6. *J*-*V* plots of SCLC measurements for electron-only devices of (a) pure films based on three nonfullerene SMAs and (b) electron-only devices for blended films and (c) hole-only devices for blend films.

Table S4. Summary of carrier mobility.

Active layer	Hole mobility $(10^{-3} cm^2 V^{-1} s^{-1})$	Electron mobility $(10^{-4} cm^2 V^{-1} s^{-1})$	μ_h/μ_e
IT-2F	-	3.26 ± 0.21	-
TTPT-T-2F	-	6.59 ± 0.25	-
T-TPT-T-2F	-	7.72 ± 0.12	-
PBT1-C:IT-2F	0.85 ± 0.05	1.89 ± 0.09	4.50
PBT1-C:TTPT-T-2F	1.18 ± 0.05	3.55 ± 0.20	3.32
PBT1-C:T-TPT-T-2F	1.10 ± 0.02	1.16 ± 0.13	9.48

Table S5. Contact angles of water and glycerol of three SMAs and PBT1-C.

	IT-2F	TTPT-T-2F	T-TPT-T-2F	PBT1-C
θ_{water} (°)	95.95° 	94.74° 	95.32° 	100.51° 
θ_{Gl} (°)	79.91° 	81.58° 	79.91° 	83.31° 

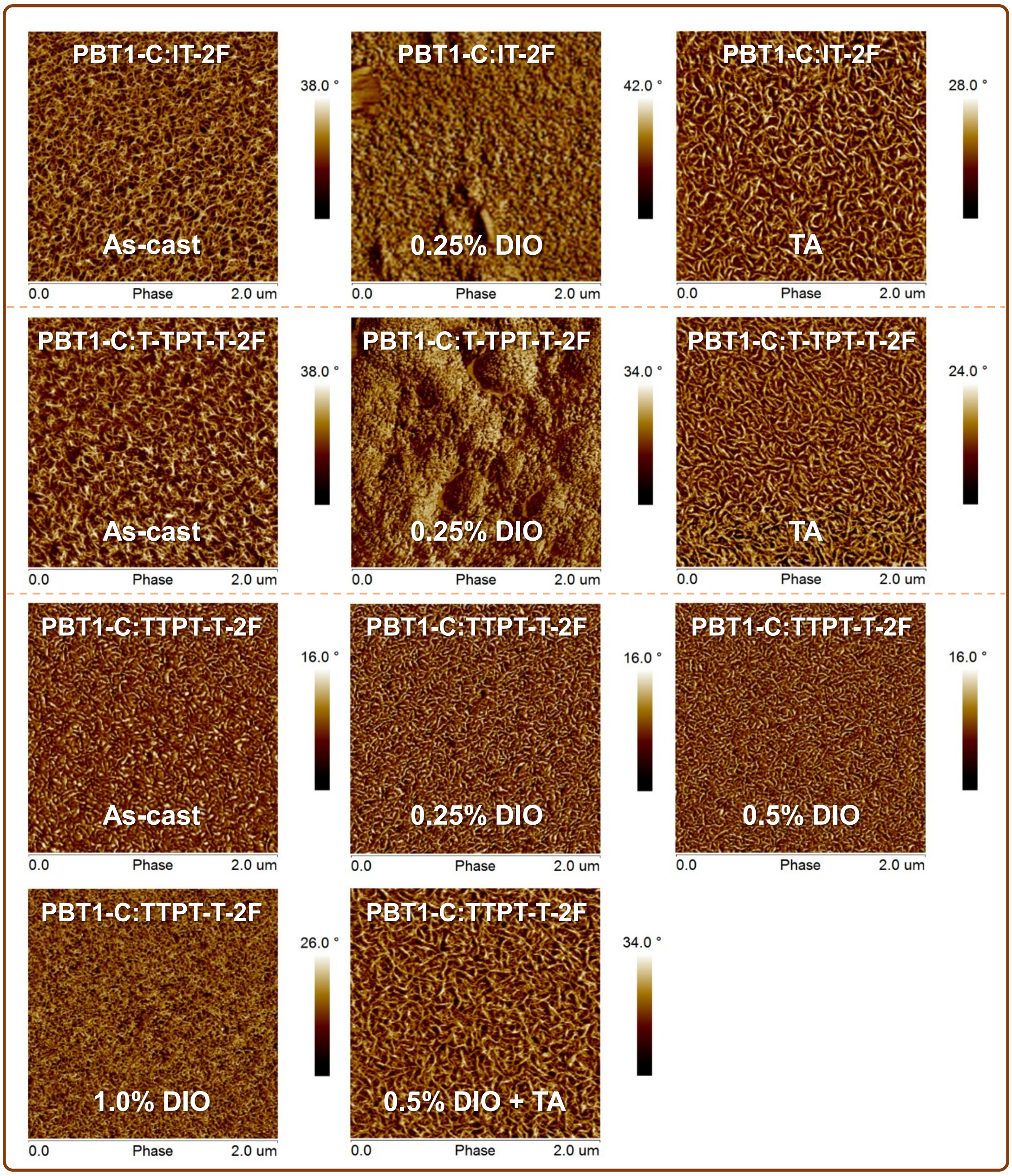


Figure S7. AFM phase images for three SMA-based blend films during different post-treatments.

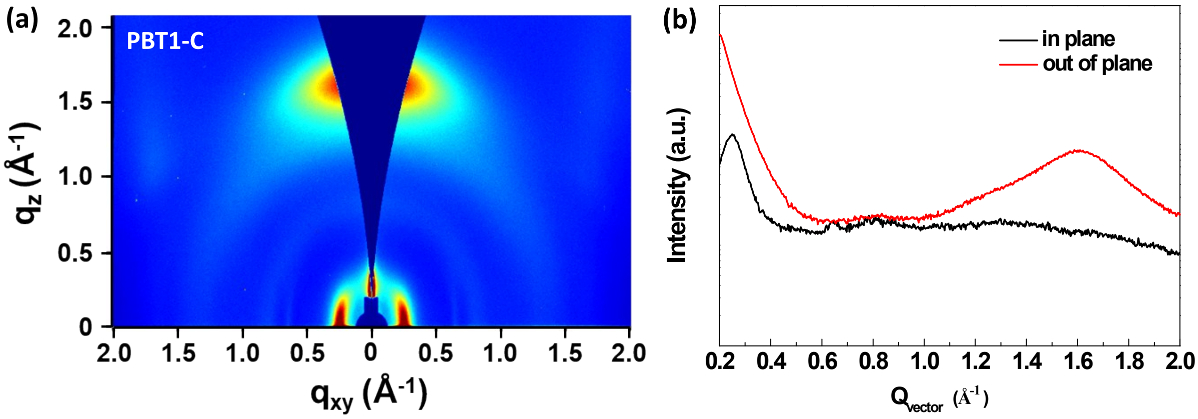


Figure S8. (a) 2D GIWAXS patterns and (b) corresponding scattering profiles of the polymer donor PBT1-C.

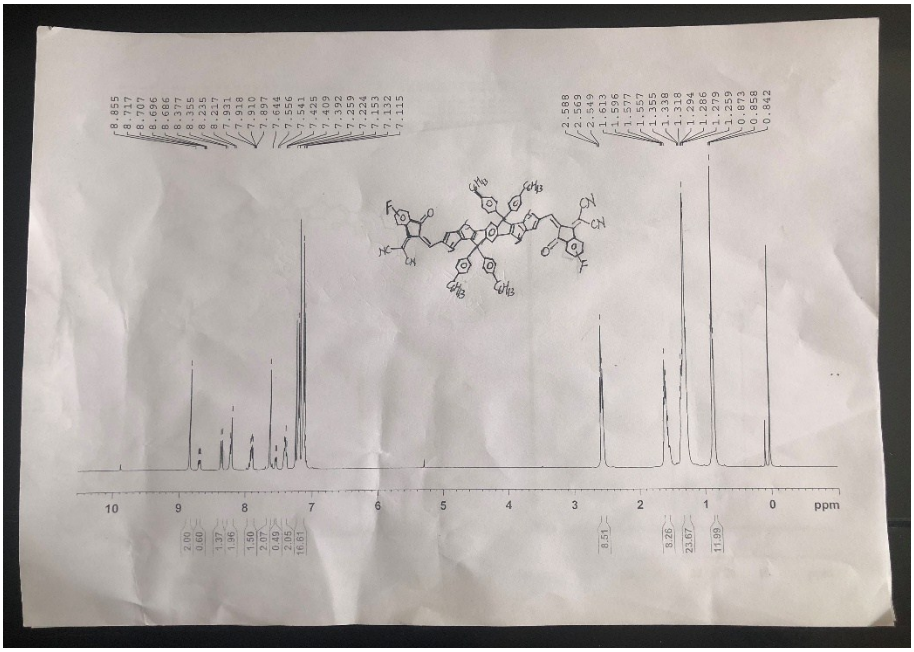


Figure S9. ^{1}H NMR spectrum of IT-2F.

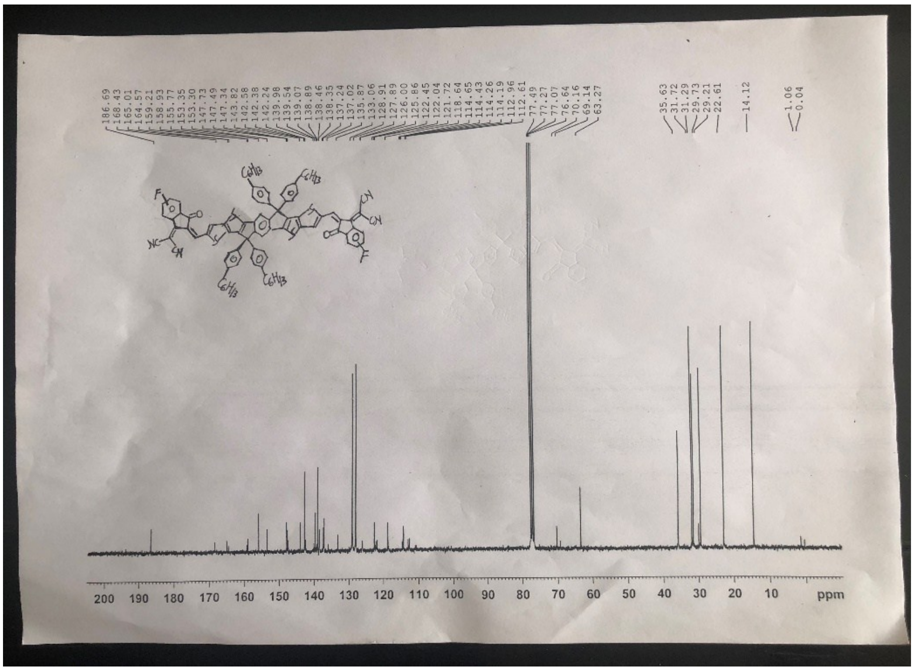
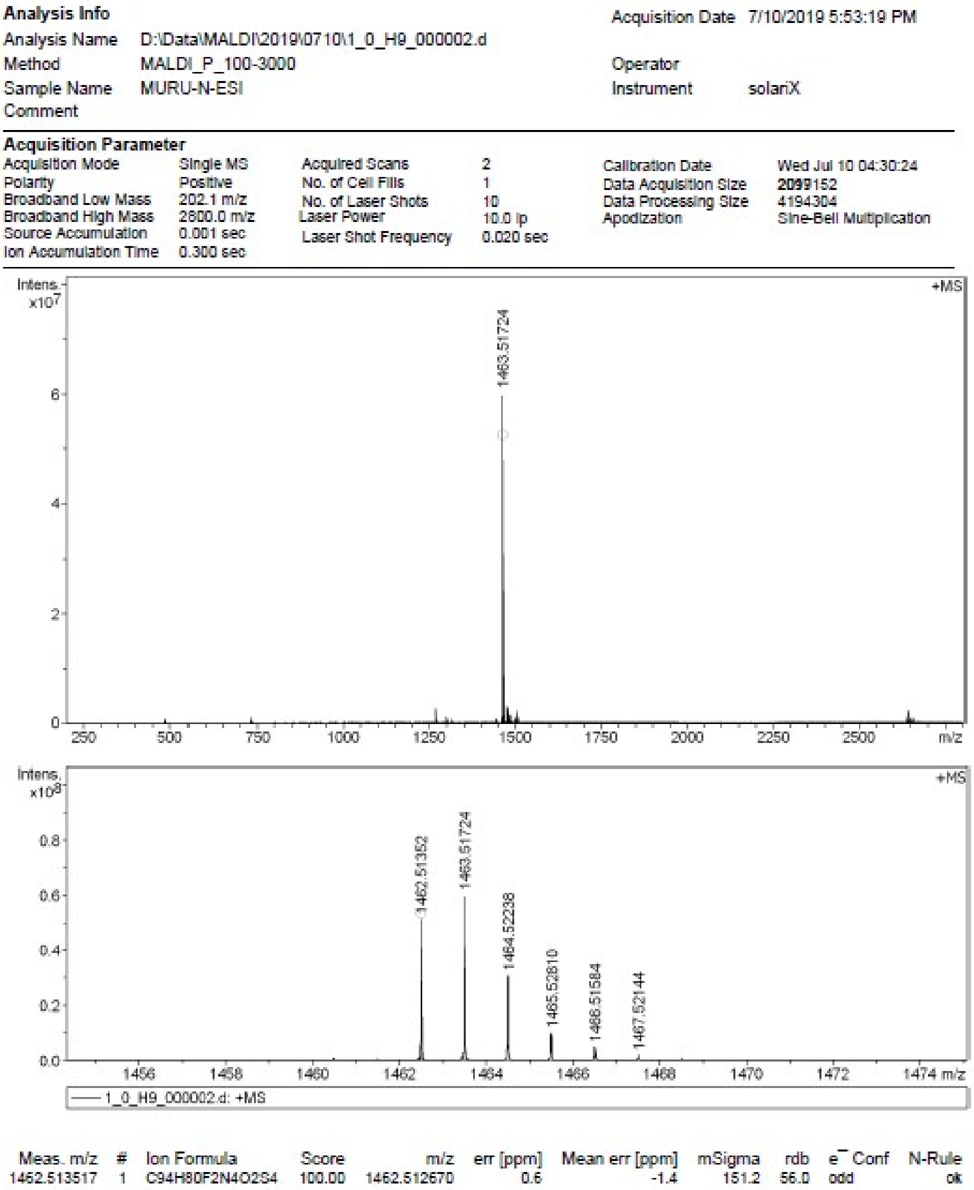


Figure S10. ^{13}C NMR spectrum of IT-2F.



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Ion Accumulation Time	0.300 sec				

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Figure S11. HR-MS spectrum of IT-2F.

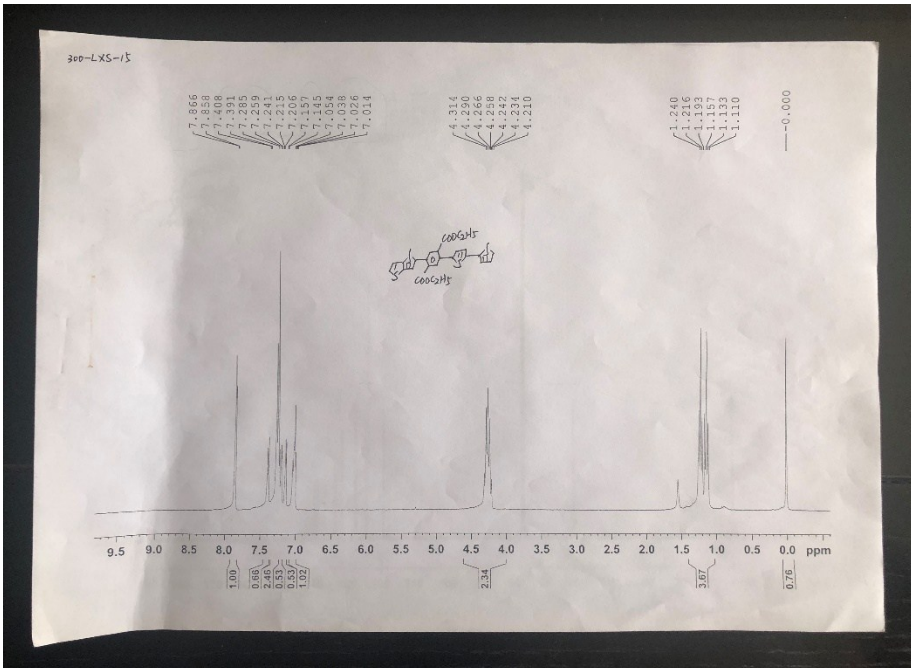

Figure S12. ^{1}H NMR spectrum of compound 2.

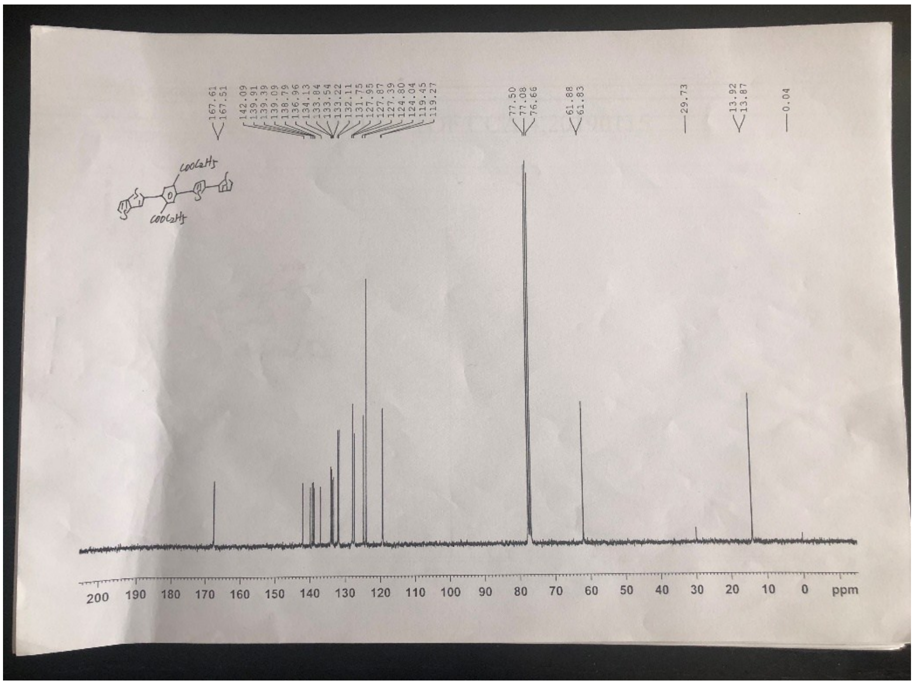

Figure S13. ^{13}C NMR spectrum of compound 2.

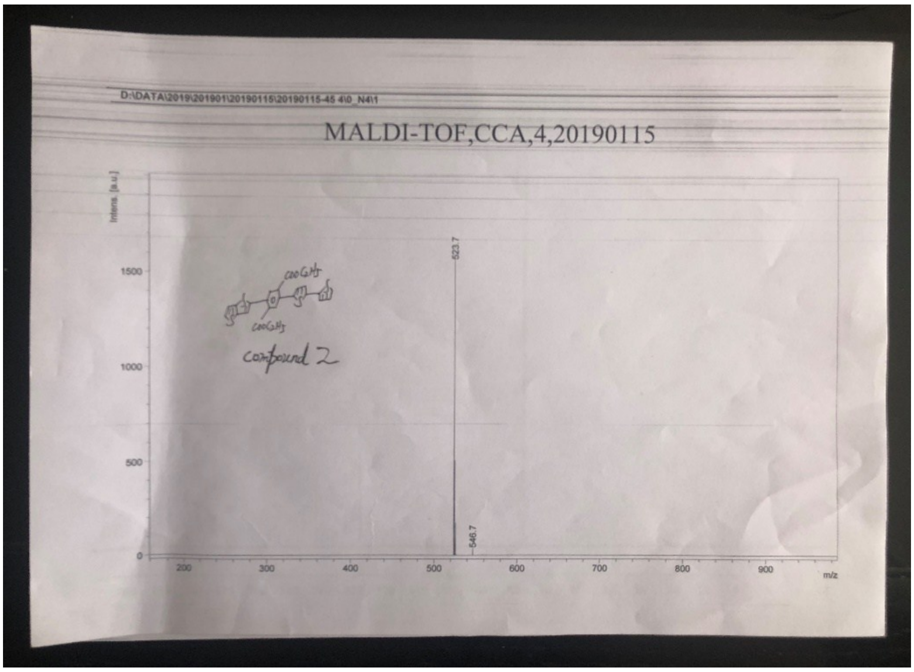

Figure S14. MS spectrum of compound 2.

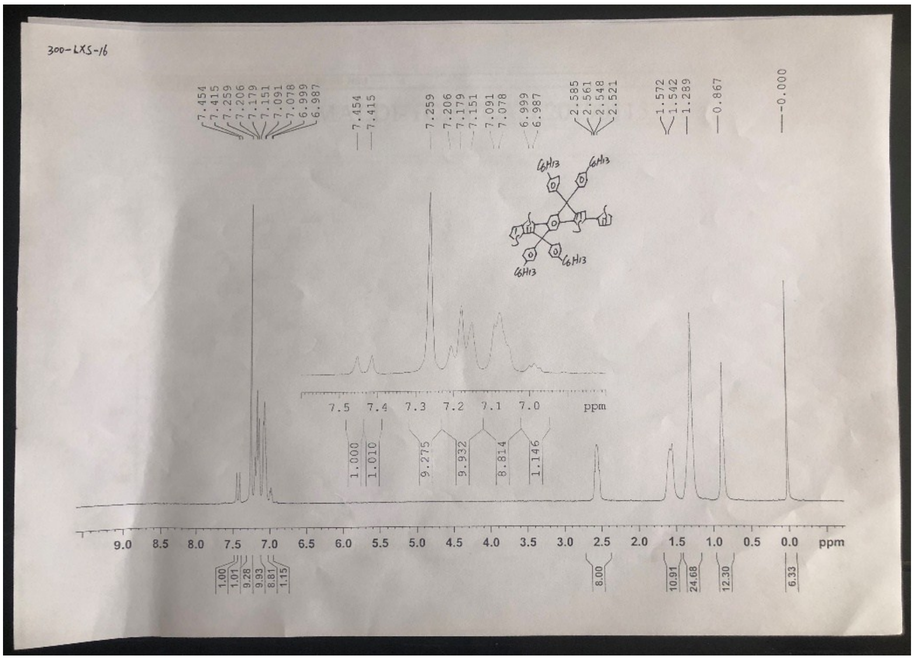

Figure S15. ^{1}H NMR spectrum of TTPT-T.

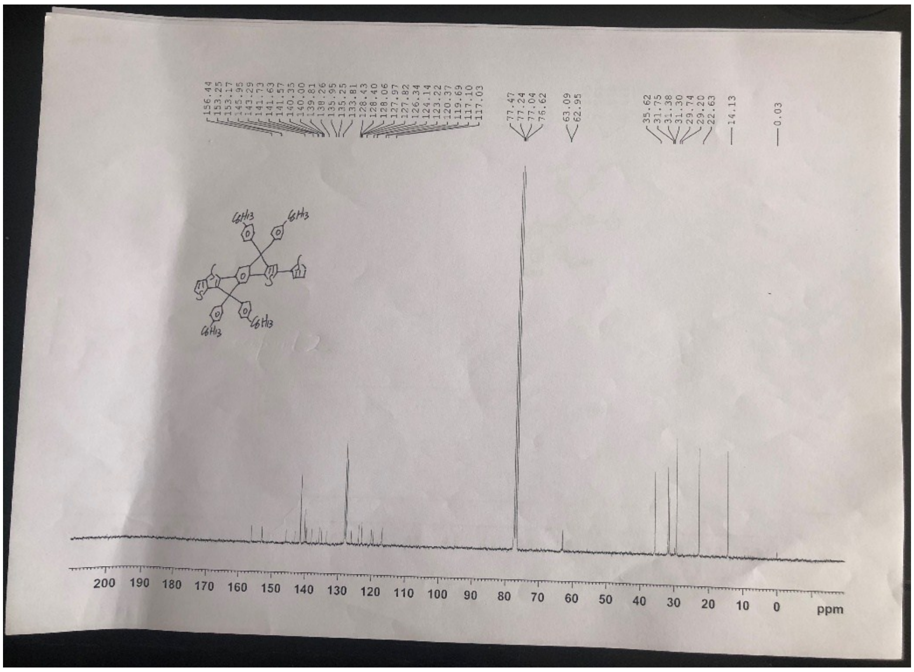

Figure S16. ^{13}C NMR spectrum of TTPT-T.

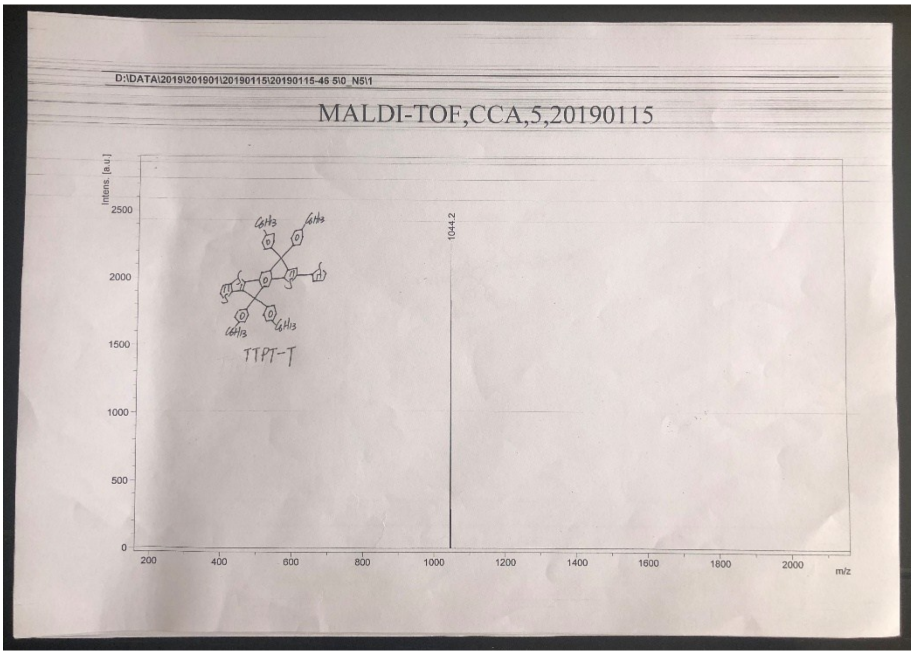

Figure S17. MS spectrum of TTPT-T.

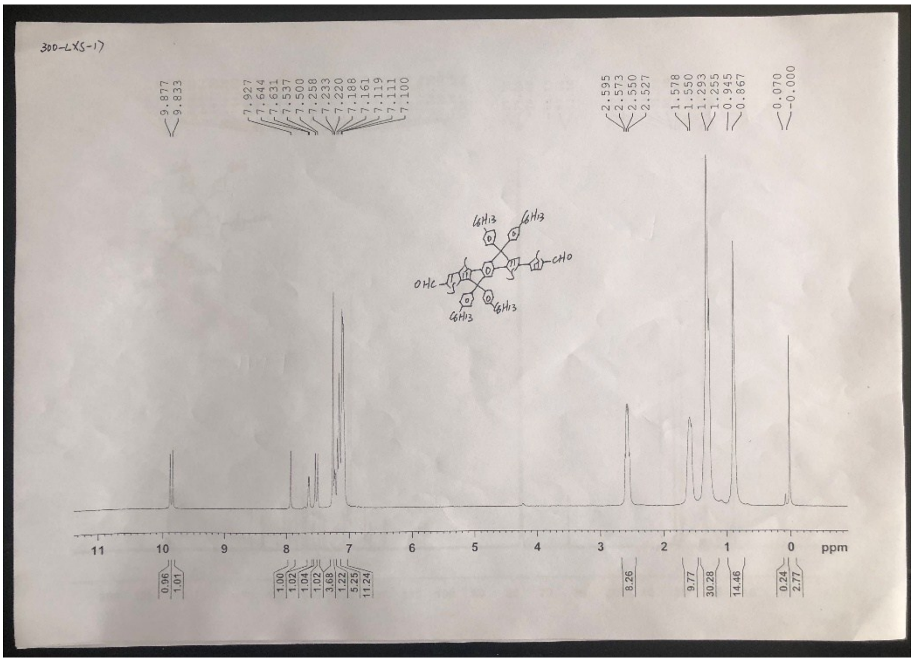

Figure S18. ^{1}H NMR spectrum of TTPT-T-CHO.

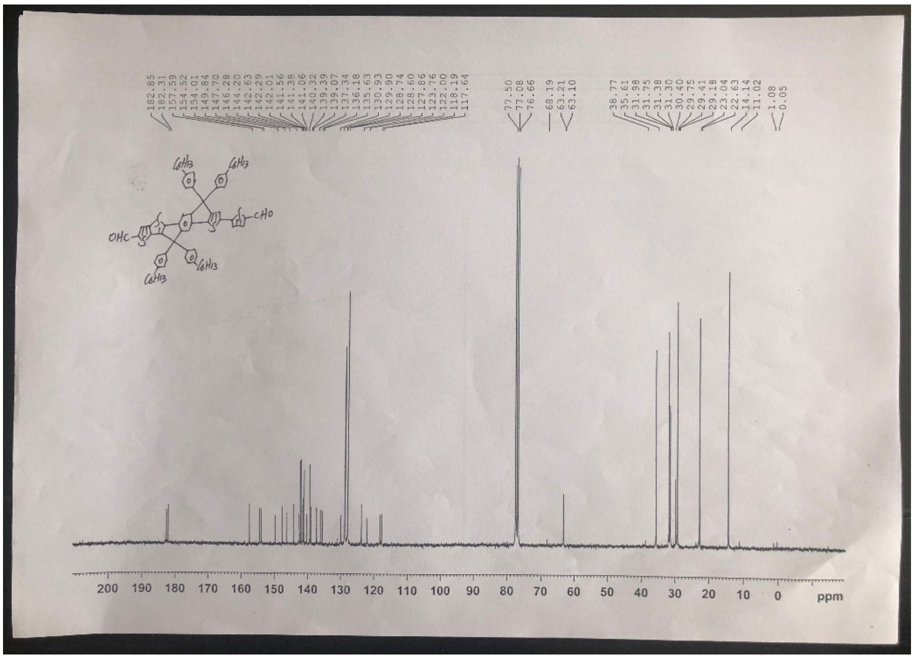

Figure S19. ^{13}C NMR spectrum of TTPT-T-CHO.

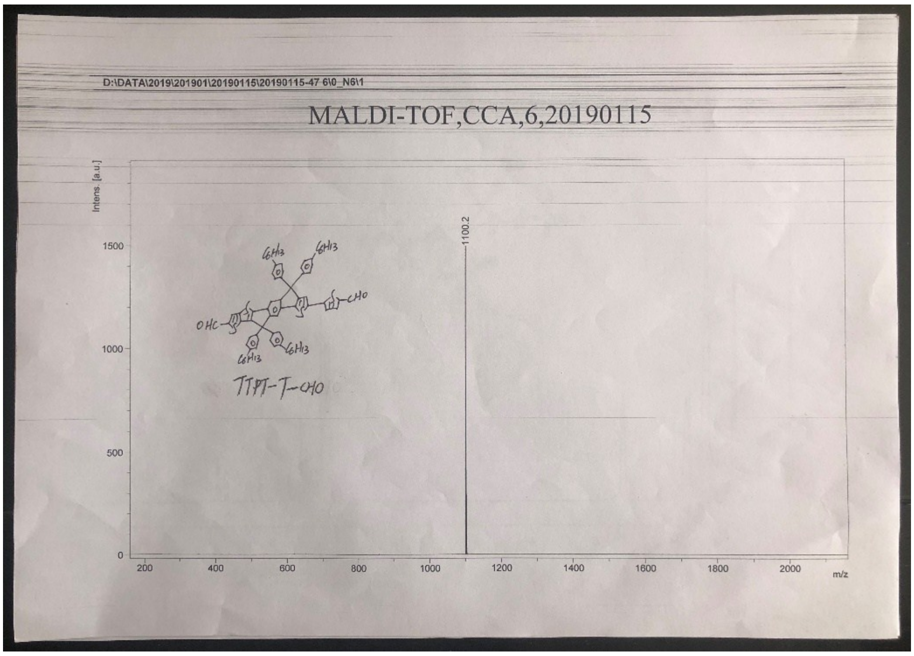

Figure S20. MS spectrum of TTPT-T-CHO.

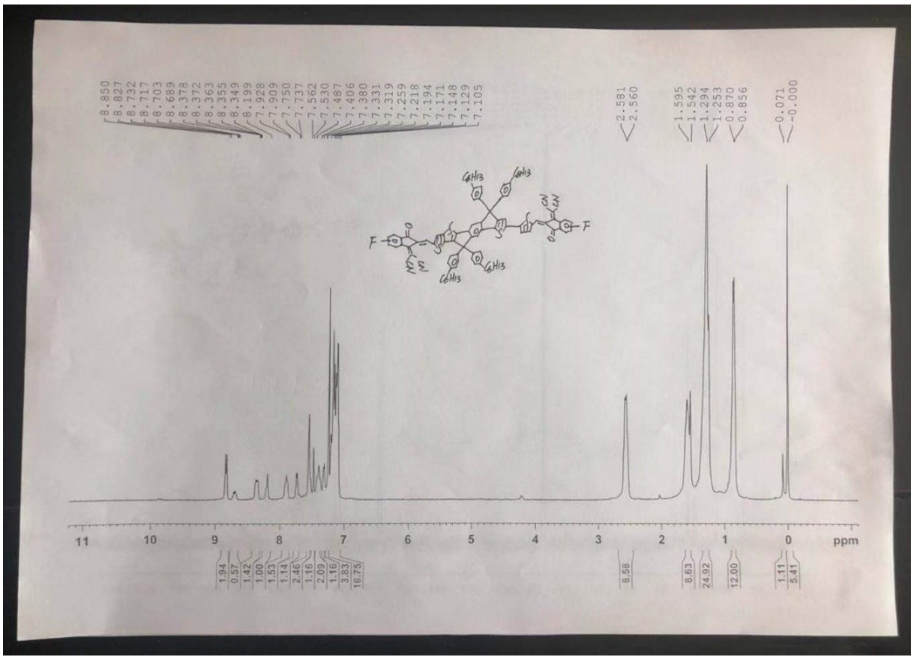

Figure S21. ^{1}H NMR spectrum of TTPT-T-2F.

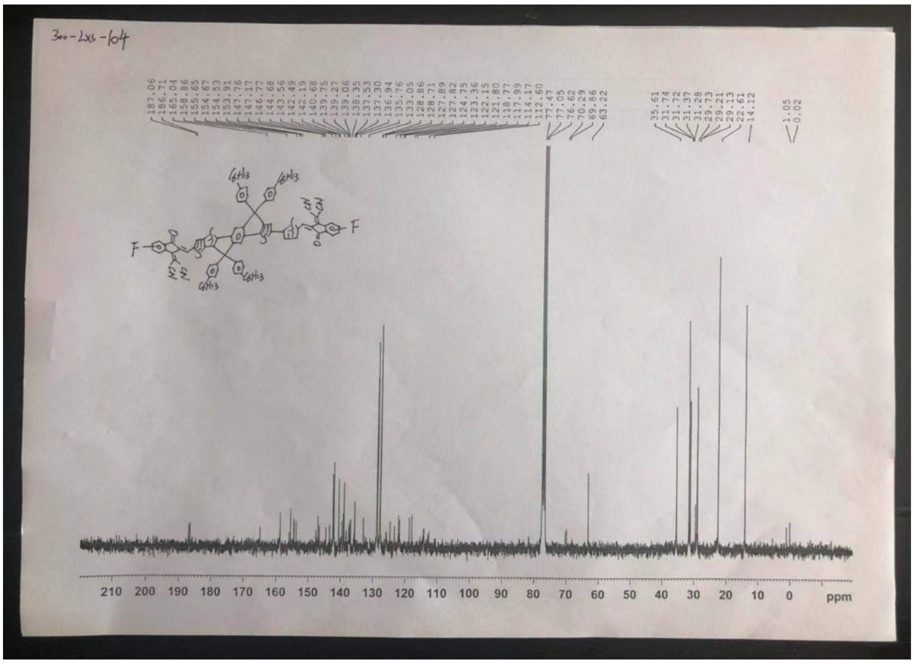

Figure S22. ^{13}C NMR spectrum of TTPT-T-2F.

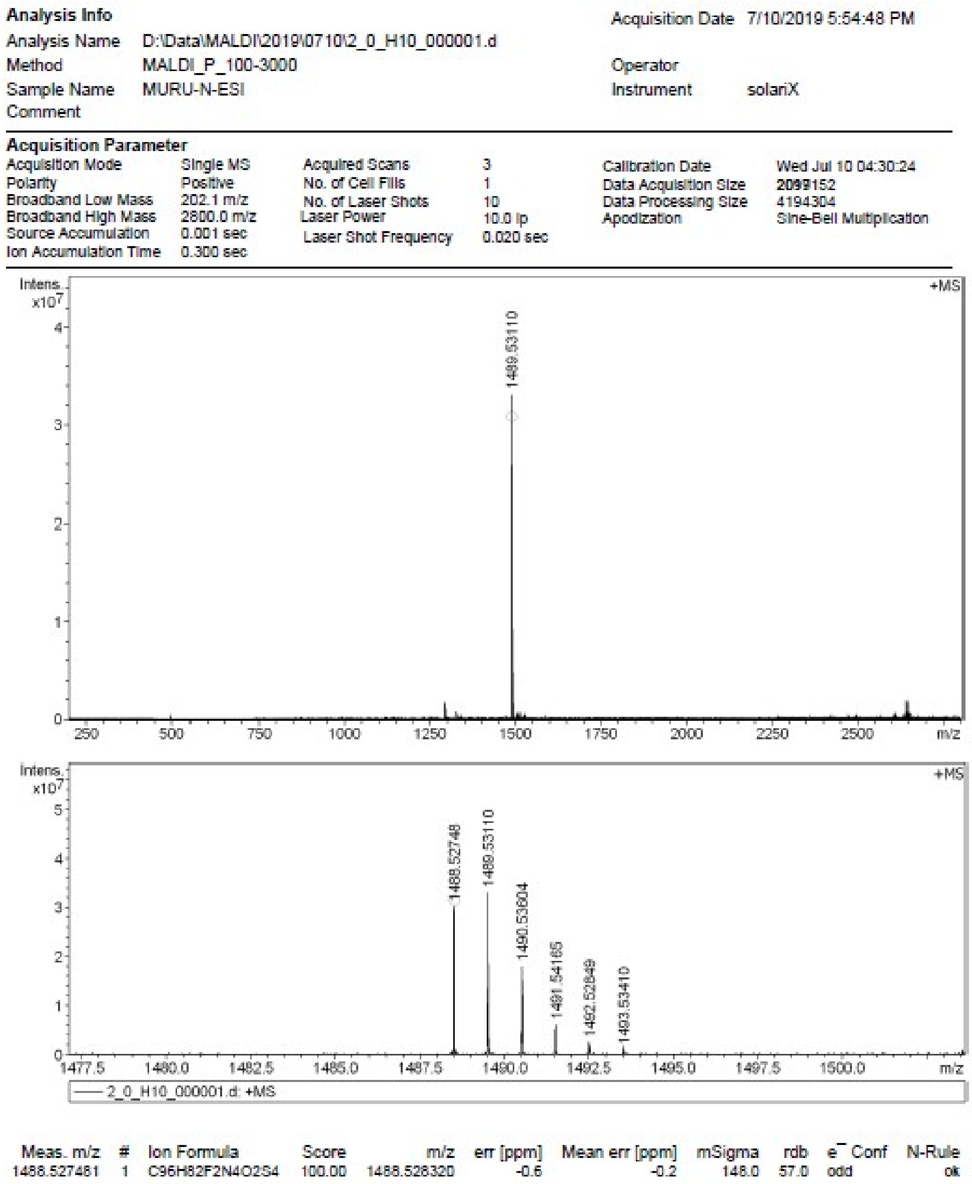

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Figure S23. HR-MS spectrum of TTPT-T-2F.

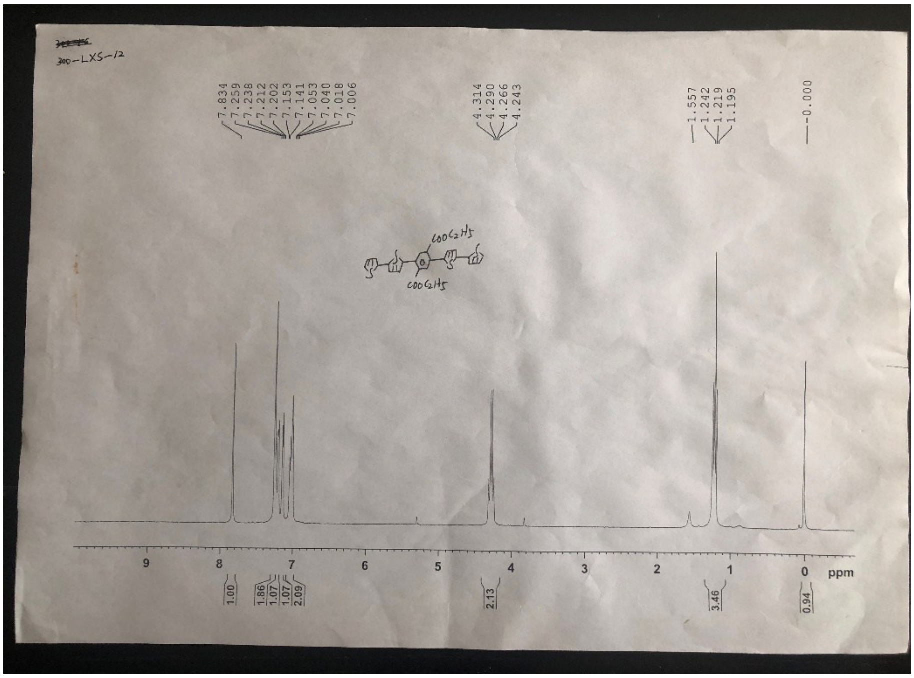


Figure S24. ^{1}H NMR spectrum of compound 3.

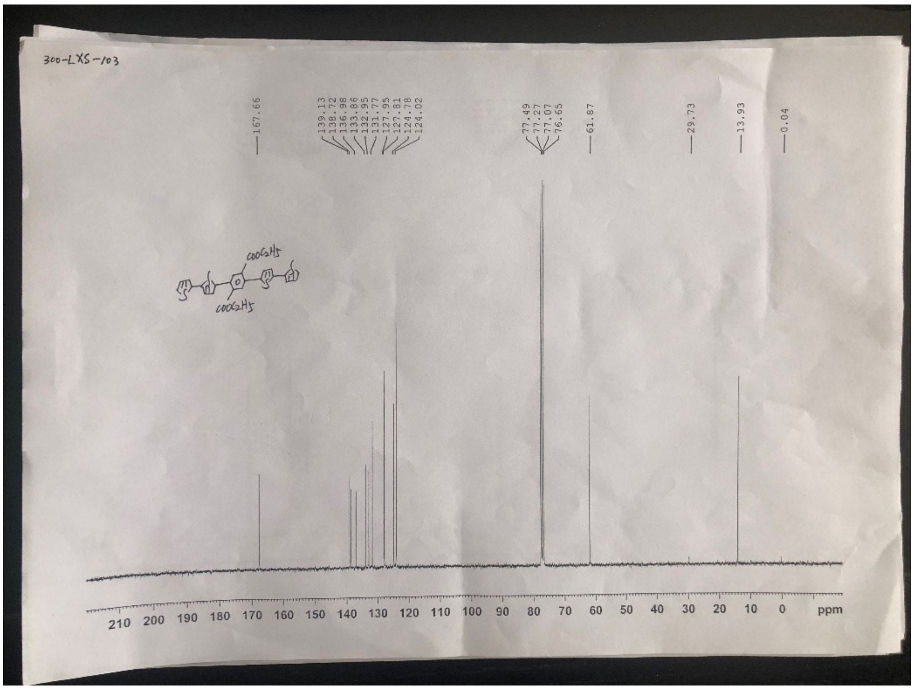


Figure S25. ^{13}C NMR spectrum of compound 3.

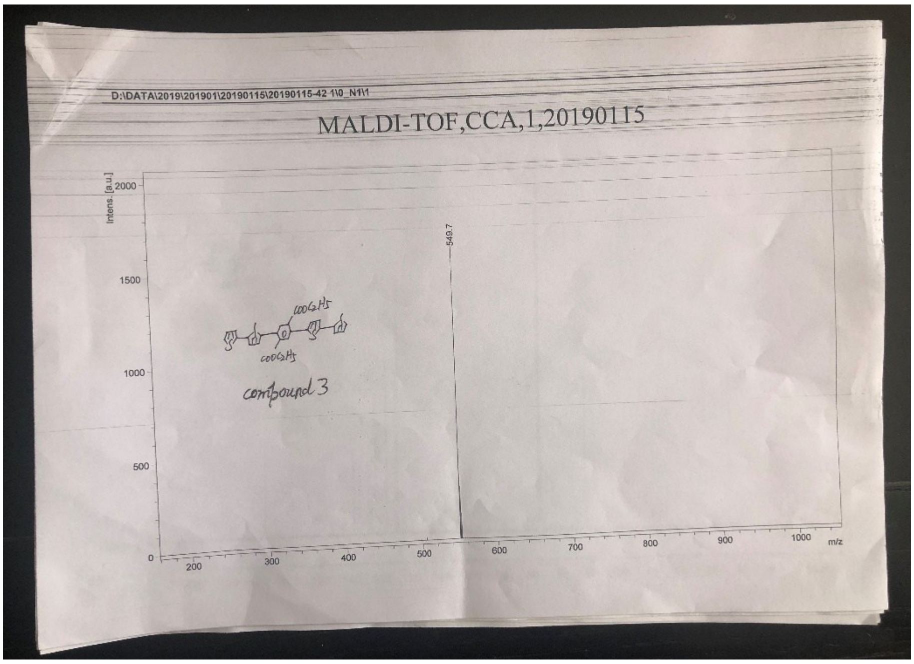


Figure S26. MS spectrum of compound 3.

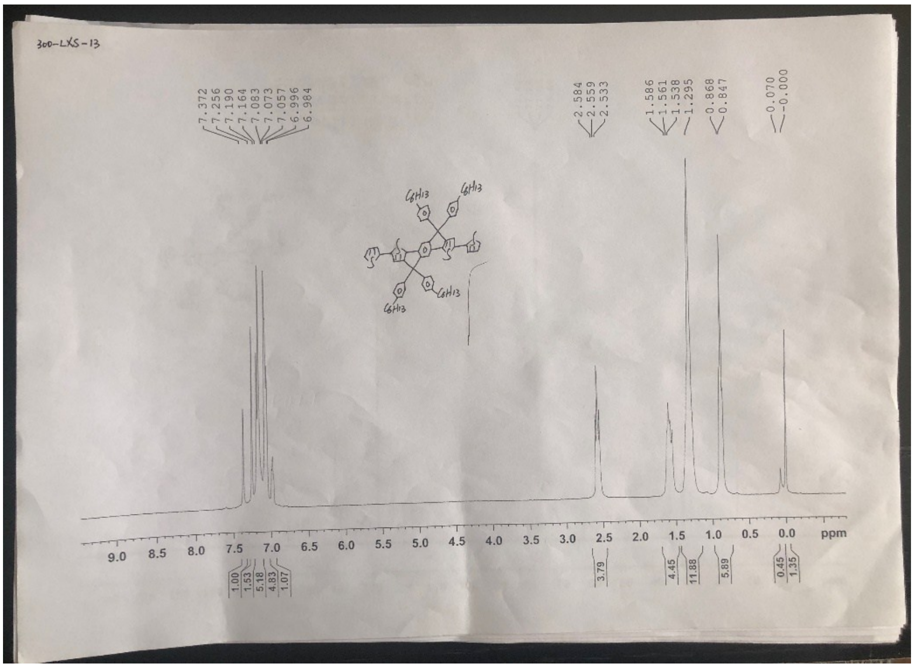


Figure S27. ^{1}H NMR spectrum of T-TPT-T.

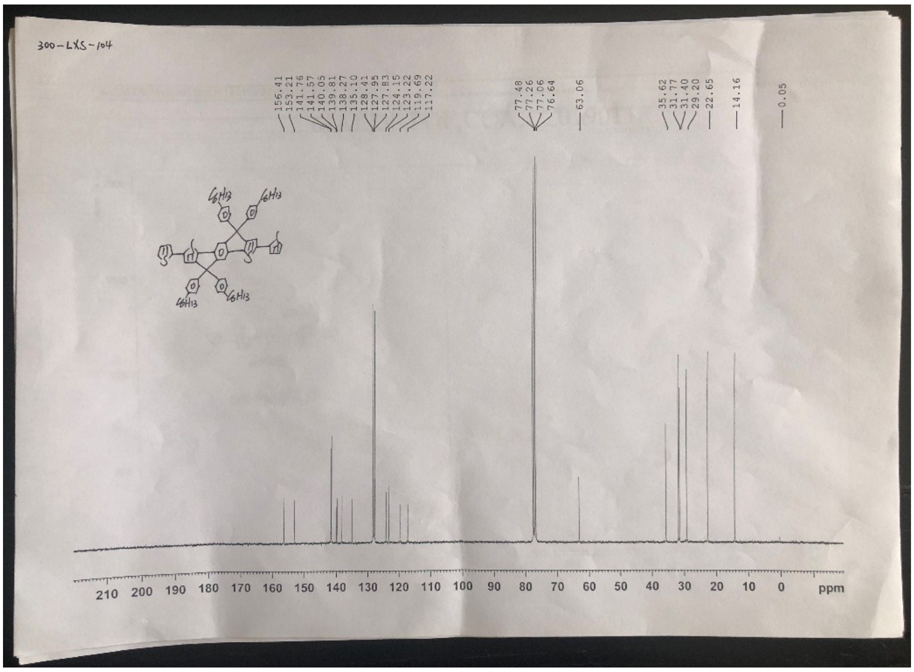


Figure S28. ^{13}C NMR spectrum of T-TPT-T.

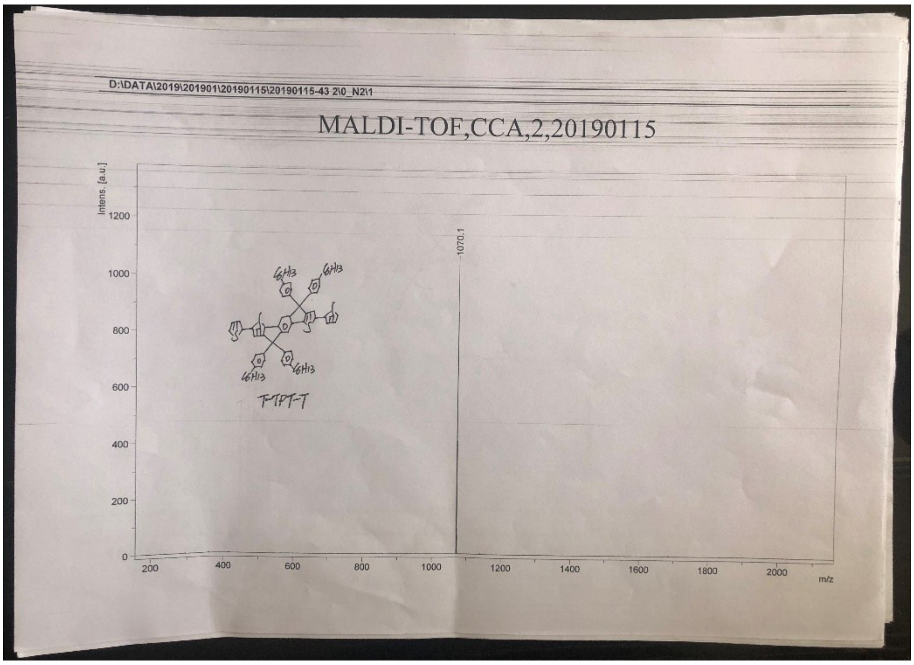


Figure S29. MS spectrum of T-TPT-T.

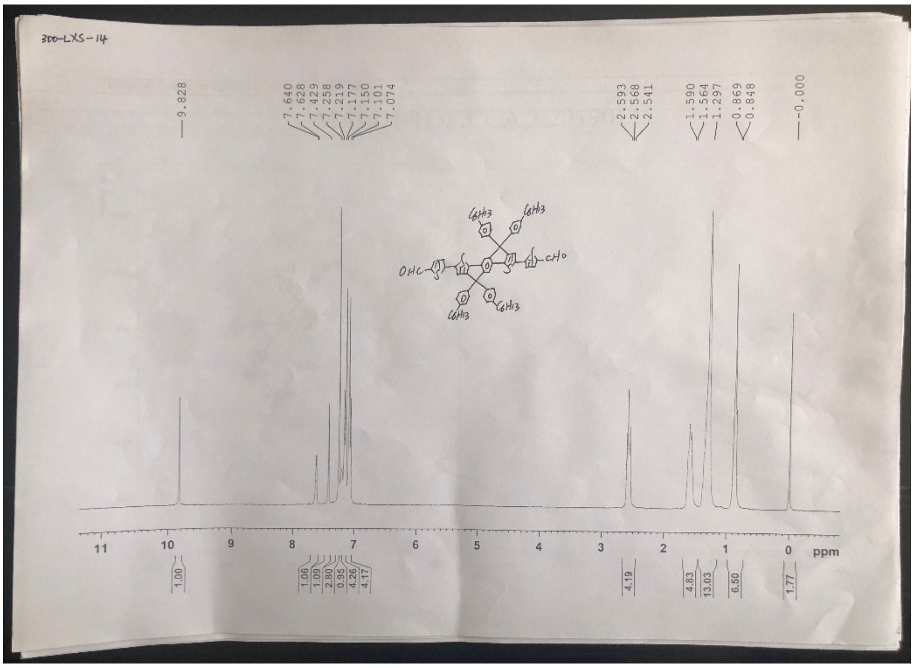


Figure S30. ^{1}H NMR spectrum of T-TPT-T-CHO.

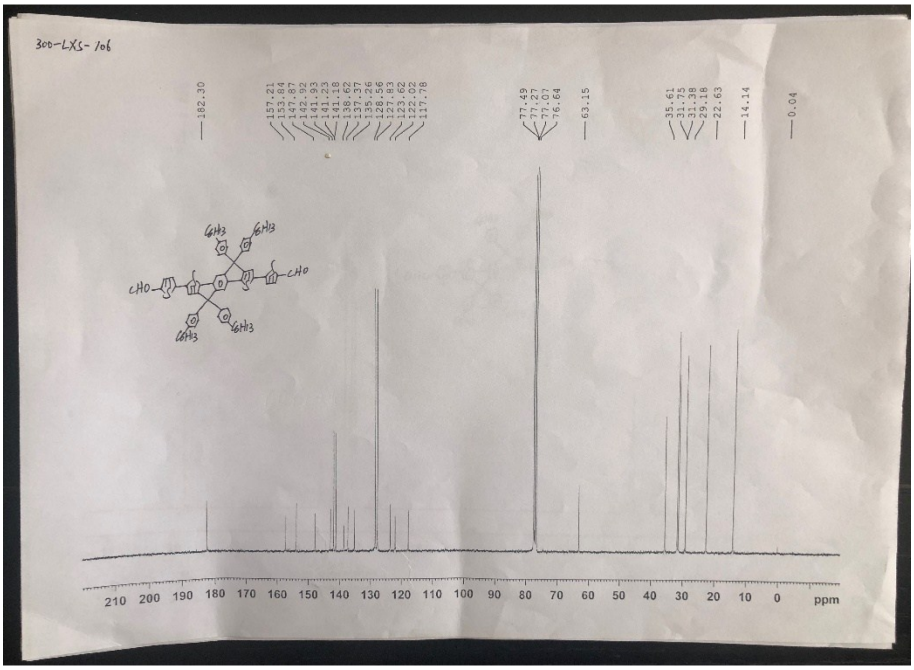


Figure S31. ^{13}C NMR spectrum of T-TPT-T-CHO.

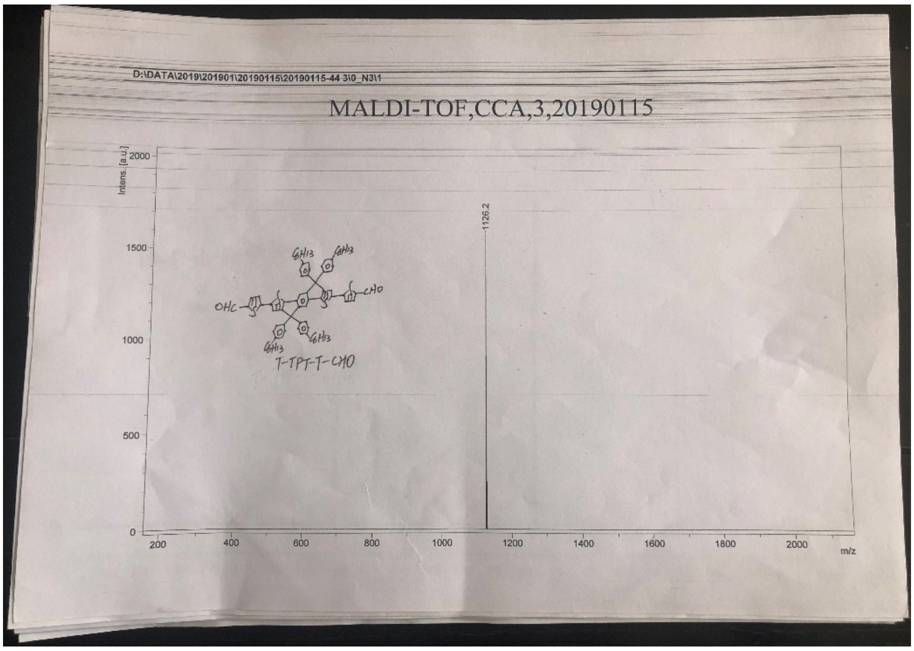


Figure S32. MS spectrum of T-TPT-T-CHO.

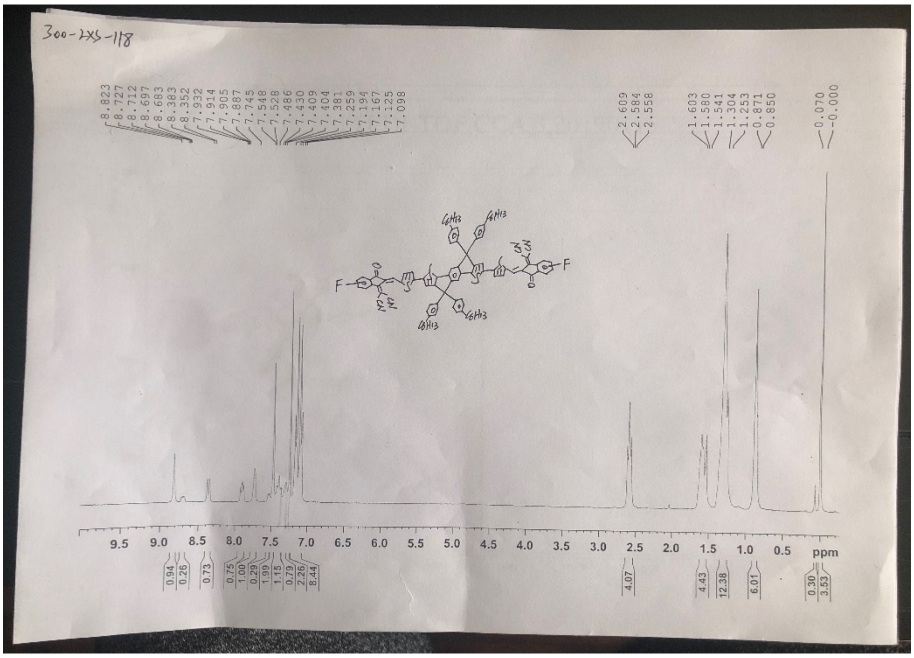


Figure S33. ^{1}H NMR spectrum of T-TPT-T-2F.

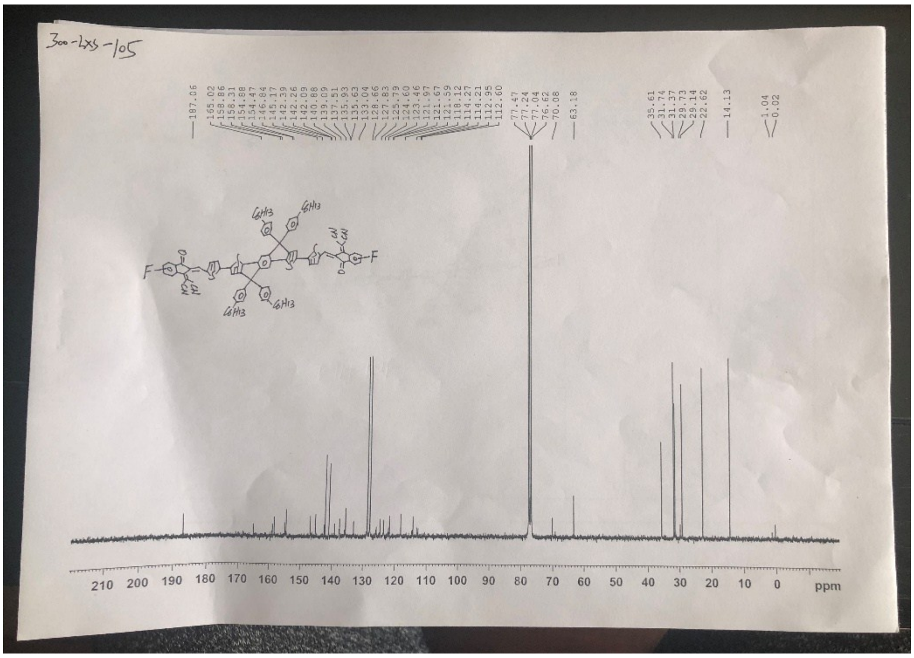
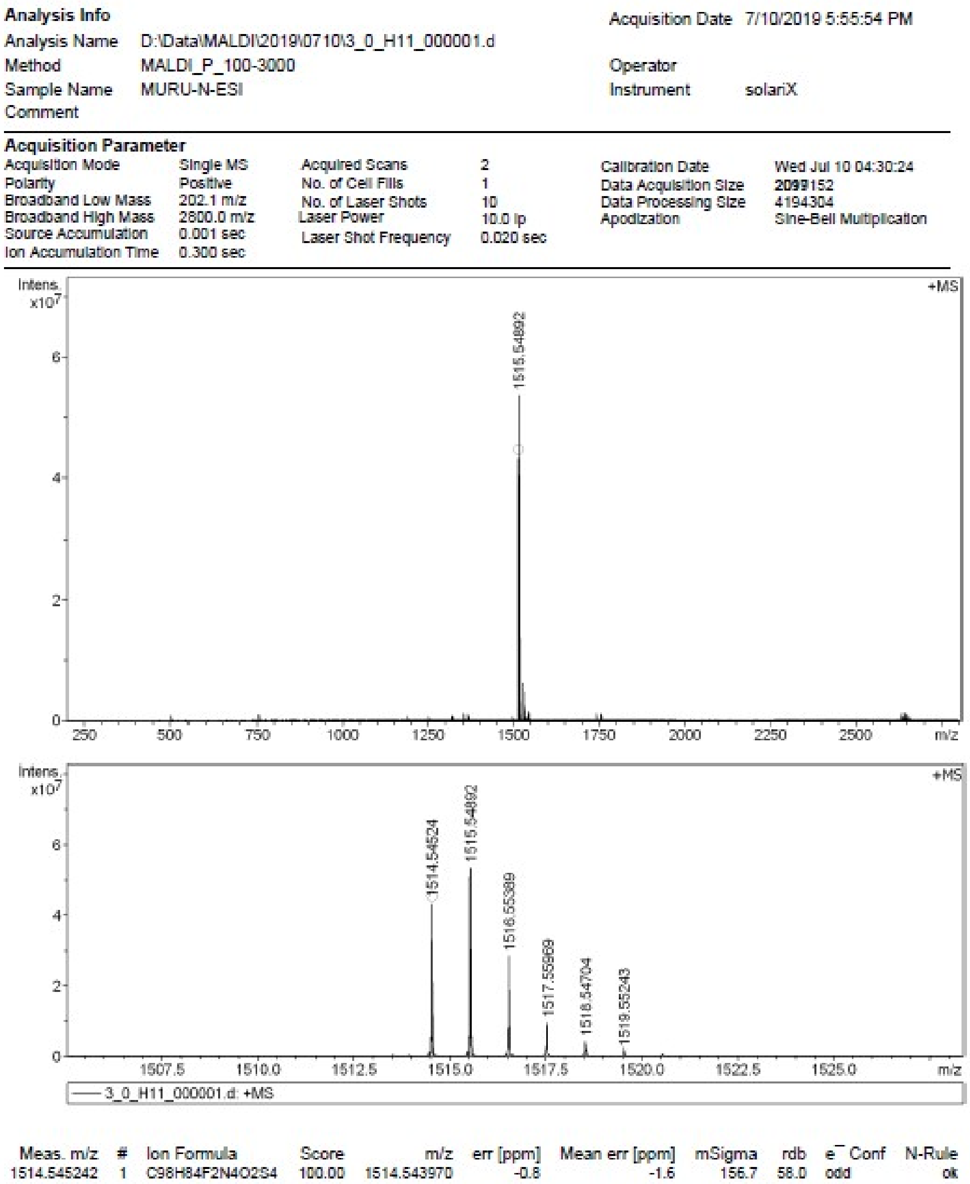


Figure S34. ^{13}C NMR spectrum of T-TPT-T-2F.



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Analysis Name	D:\Data\MALDI\2019\0710\3_0_H11_000001.d		
Method	MALDI_P_100-3000	Operator	
Sample Name	MURU-N-ESI	Instrument	solariX
Comment			

Acquisition Parameter

Acquisition Mode	Single MS	Acquired Scans	2	Calibration Date	Wed Jul 10 04:30:24
Polarity	Positive	No. of Cell Fills	1	Data Acquisition Size	2099152
Broadband Low Mass	202.1 m/z	No. of Laser Shots	10	Data Processing Size	4194304
Broadband High Mass	2800.0 m/z	Laser Power	10.0 lp	Apodization	Sine-Bell Multiplication
Source Accumulation	0.001 sec	Laser Shot Frequency	0.020 sec		
Ion Accumulation Time	0.300 sec				

Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1514.545242	1	C98H84F2N4O2S4	100.00	1514.543970	-0.8	-1.6	156.7	58.0	odd	ok

Figure S35. HR-MS spectrum of T-TPT-T-2F.

S1.6 References

1. C. Li, J. Song, L. Ye, C. Koh, K. Weng, H. Fu, Y. Cai, Y. Xie, D. Wei, H. Y. Woo, Y. Sun, *Solar RRL,* **2019**, 3, 1800246.
2. F. Yang, C. Li, W. Lai, A. Zhang, H. Huang, W. Li, *Mater. Chem. Front.* **2017**, 1, 1389-1395.
3. G. G. Malliaras, J. R. Salem, P. J. Brock, C. Scott, *Phys. Rev. B,* **1998**, 58, R13411-R13414.