Electronic Supplementary Information for:

Fullerene-free small molecule organic solar cells with high open circuit voltage of 1.15V

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Materials: All reactions and manipulations were carried under argon atmosphere using standard Schlenk techniques. All starting materials were purchased from commercial suppliers and used without further purification.

Measurements and instruments: The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were taken on a Bruker AV400 Spectrometer. Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were performed on a Bruker Autoflex III instrument. The thermogravimetric analyses (TGA) were carried out on a NETZSCH STA 409PC instrument under purified nitrogen gas flow with a 10 °C min^{-1} heating rate. UV-vis spectra were obtained with a JASCO V-570 spectrophotometer. X-ray diffraction (XRD) experiments were performed on a Bruker D8 FOCUS X-ray diffractometer with Cu Kα radiation (λ = 1.5406 Å) at a generator voltage of 40 kV and a current of 40 mA. Atomic force microscope (AFM) investigation was performed using Bruker MultiMode 8 in "tapping" mode. Cyclic voltammetry (CV) experiments were performed with a LK98B II Microcomputer-based Electrochemical Analyzer in dichloromethane solutions. All CV measurements were carried out at room temperature with a conventional three-electrode configuration employing a glassy carbon electrode as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a Pt wire as the counter electrode. Dichloromethane was distilled from calcium hydride under dry argon immediately prior to use. Tetrabutylammonium phosphorus hexafluoride (Bu_4NPF_6, 0.1 M) in dichloromethane was used as the supporting electrolyte, and the scan rate was 100 mV s^{-1}. The current density-voltage (*J-V*) characteristics of photovoltaic devices were obtained by a Keithley 2400 source-measure unit. The photocurrent was measured under illumination simulated 100 mW cm^{-2} AM1.5G irradiation using a xeful-lamp-based solar simulator [Oriel 96000 (AM1.5G)] in an argon filled glove box. Simulator irradiance was characterized using a calibrated spectrometer and illumination intensity was set using a certified silicon diode. External quantum efficiency (EQE) value of the encapsulated device was obtained with a halogen-tungsten lamp, monochromator, optical chopper, and lock-in amplifier in air and photon flux was determined by a calibrated silicon photodiode.

Fabrication of organic solar cells: The photovoltaic devices were fabricated with a structure of glass/ITO/PEDOT:PSS/donor:acceptor /PDIN/Al. The ITO- coated glass substrates were cleaned subsequently by ultrasonic treatment in detergent, deionized water, acetone, and isopropyl alcohol under ultrasonication for 15 minutes each solvent and then dried by a nitrogen flow. A thin layer of PEDOT:PSS (Baytron P VP AI 4083, filtered at 0.45 μm) was spin-coated (3000 rpm, ca. 40 nm thick) onto ITO surface. After being baked at 150 °C for 20 min, the substrates were transferred into an argon-filled glove box. Then, the active layer was spin-coated from DR3TSBDT (10 mg/mL):DTBTF blend chloroform solution with different ratios at 1700 rpm for 20 s.

Subsequently, the methanol solution (0.2% acetic acid) of PDIN at a concentration of 1.5 mg mL^{-1} was spin-coated on top of the active layers. Thermal annealing was carried out on a digitally controlled hotplate at various temperatures after PDIN spin coating in an argon-filled glove box. Finally, 50 nm Al layer was deposited onto the surface of the PDIN layer under high vacuum ($< 2\times10^{-4}$ Pa). The thickness of active layers was measured using Dektak 150 profilometer. The effective area of each cell was 4 mm^2 defined by masks for the solar cell devices discussed in this work.

Synthesis:

Synthesis of compound DTF

A solution of compounds **1** (3.0 g, 4.66 mmol) and **2** (3.0 g, 18.40 mmol) in toluene (45 mL) and aqueous 2 M Na_2CO_3 (15 mL) was degassed twice with argon. Then $Pd(PPh_3)_4$ (50 mg, 0.043 mmol) was added and the mixture was stirred at 100 °C for 24 h under argon, after which the mixture was poured into water (200 mL), and extracted with chloroform. The organic layer was washed with water, and then dried over anhydrous Na_2SO_4. The solvent was removed by a rotating evaporator and the residue was purified by silica gel chromatography using a mixture of petroleum ether and dichloromethane (4:1) eluant to produce compound DTF (2.17 g, 84%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 8.0 Hz, 2H), 7.60 (s, 2H), 7.41 (s, 2H), 7.32 (d, J = 4.0

Hz 2H), 7.14 (d, *J* = 4.0 Hz, 2H), 2.05 (m, 4H), 1.25-1.05 (m, 20H), 0.82 (t, *J* = 6.8 Hz, 6H) , 0.70 (m, 4H). MS (MALDI-TOF): calcd for $C_{37}H_{46}S_2$ [M^+], 554.30; found: 554.32.

Synthesis of compound DCHOTF

A Vilsmeier reagent, which was prepared with $POCl_3$(1.48 ml, 16.20 mmol) in DMF (10 ml), was added to a solution of DTF (1.8 g, 3.24 mmol) in 1,2-dichloroethane (80 ml) at 0 °C. After being stirred at 65 °C for 12 h, the mixture was poured into ice water (300 ml), neutralized with Na_2CO_3, and then extracted with dichloromethane. The combined organic layer was washed with water and brine, dried over Na_2SO_4. After removal of solvent it was chromatographied on silica gel using a mixture of dichloromethane and petroleum ether (1:1) as eluant to afford DCHOTF (1.72 g, 87%) as a light yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.91 (s, 2H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 4.0 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.64 (s, 2H), 7.49 (d, *J* = 4.0 Hz, 2H), 2.04 (m, 4H), 1.20-1.00 (m, 20H), 0.79 (t, *J* = 6.8 Hz, 6H), 0.67 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.73, 154.76, 152.22, 142.20, 141.61, 137.49, 132.38, 125.71, 124.05, 120.77, 120.66, 55.53, 40.20, 31.73, 29.85, 29.11, 23.74, 22.57, 14.04. MS (MALDI-TOF): calcd for $C_{39}H_{46}O_2S_2$ [M^+], 610.29; found: 610.31. Anal. Calcd. For $C_{39}H_{46}O_2S_2$: C, 76.68; H, 7.59. Found: C, 76.72; H, 7.50.

Synthesis of compound DTBTF

DCHOTF (0.30 g, 0.49 mmol) was dissolved in a solution of dry $CHCl_3$ (60 mL), then thiobarbituric acid (0.60 g, 3.0 mmol) and three drops of piperidine were added, and the resulting solution was stirred at 25 °C for 12 h under argon. Then, the mixture was poured into water (200mL), and extracted with $CHCl_3$. The organic layer was washed with water, and then dried over Na_2SO_4, and evaporated. The residue was purified by silica gel chromatography using $CHCl_3$ as eluant, the crude solid was recrystallized from hexane and $CHCl_3$ mixture afford DTBTF (0.39 g, 82%). ^1H NMR (400 MHz, $CDCl_3$): 1H NMR (400 MHz, $CDCl_3$): δ 8.70 (s, 2H), 7.92 (d, J = 4.0 Hz, 2H), 7.87 (d, J = 8.0 Hz, 2H), 7.79 (d, J = 8.0 Hz, 2H), 7.77 (s, 2H), 7.63 (d, J = 4.0 Hz, 2H), 4.70-4.56 (m, 8H), 2.16-2.04 (m, 4H), 1.39 (t, J = 6.8 Hz, 6H), 1.34 (t, J = 6.8 Hz, 6H), 1.20-1.00 (m, 20H), 0.77 (t, J = 6.8 Hz, 6H) , 0.68-0.58 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.69, 161.94, 161.06, 160.01, 152.45, 149.64, 147.48, 142.32, 136.77, 132.70, 126.36, 125.12, 120.96, 110.14, 55.87, 44.03, 43.17, 40.28, 31.73, 29.86, 29.16, 23.79, 22.56, 14.04, 12.56, 12.40. MS (MALDI-TOF): calcd for $C_{55}H_{66}N_4O_4S_4$ [M^+], 975.40; found: 975.40. Anal. Calcd. For $C_{55}H_{66}N_4O_4S_4$: C, 67.73; H, 6.82; N, 5.74. Found: C, 67.89; H, 6.94; N, 5.64.

Table S1. Current density-voltage characteristics of the OPV devices based on DR3TSBDT:DTBTF blend films with different ratio under 100°C thermal annealing.

Weight ratio	V_{oc} [V]	J_{sc} [mA cm^{-}	FF	PCE [%]^{a,b}
1:0.3	1.14	6.12	0.41	2.71±0.15 (2.86)
1:0.5	1.15	7.42	0.45	3.64±0.20 (3.84)
1:0.8	1.15	7.19	0.44	3.47±0.16 (3.63)

a) Average values from 30 devices, b) The best PCEs are provided in parentheses.

Table S2. Current density-voltage characteristics of the OPV devices based on DR3TSBDT:DTBTF (w:w,1:0.5) blend films with different temperature thermal annealing.

Post treatment	V_{oc} [V]	J_{sc} [mA cm^{-}	FF	PCE [%]^{a,b}
80°C	1.15	6.50	0.42	2.98±0.16 (3.14)
100°C	1.15	7.42	0.45	3.64±0.20 (3.84)
120°C	1.15	7.02	0.44	3.38±0.17 (3.55)

a) Average values from 30 devices, b) The best PCEs are provided in parentheses.

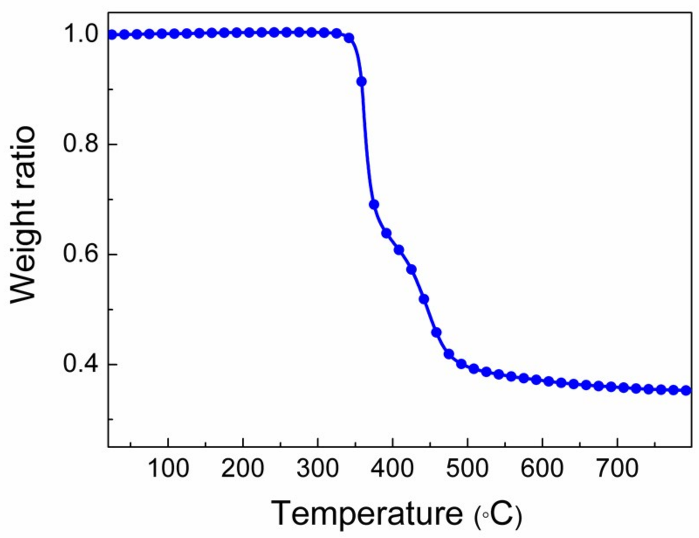

Fig. S1. TGA curve of DTBTF with a heating rate of 10 ºC/min under N_2 atmosphere.

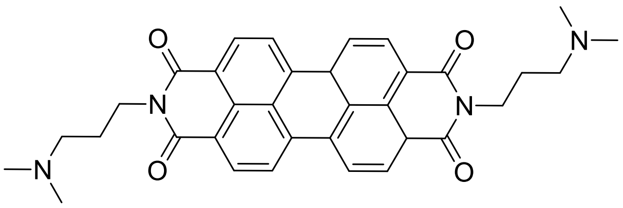

Fig. S2. Chemical structure of PDIN.

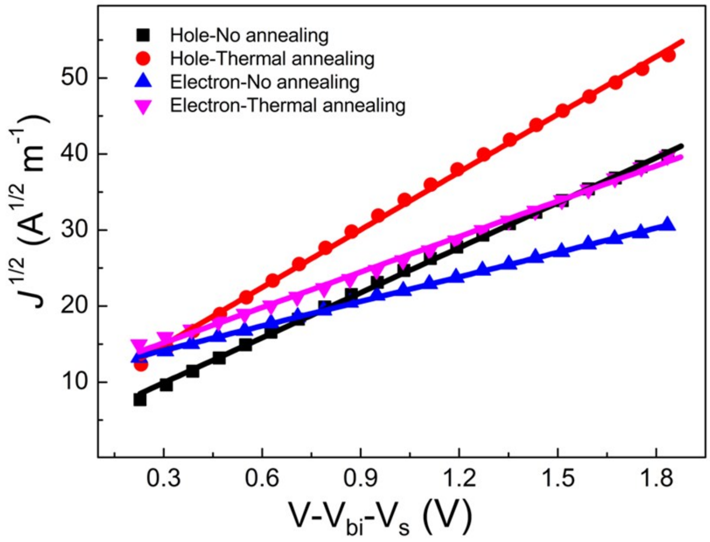

Fig. S3. *J-V* characteristics for the electron-only and hole-only devices fabricated from DR3TSBDT:DTBTF blend films with different treatment.

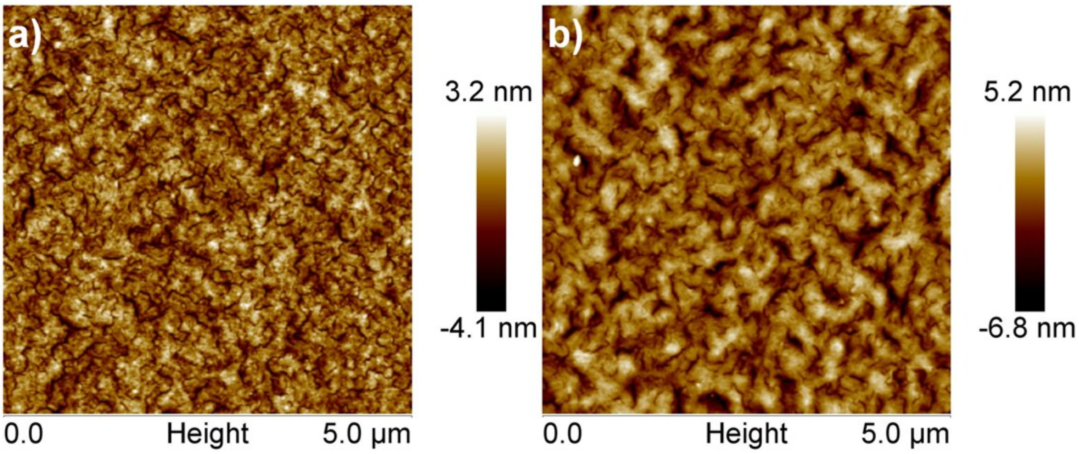

Fig. S4. AFM images of DR3TSBDT:DTBTF blend films (a) without annealing and (b) with thermal annealing.

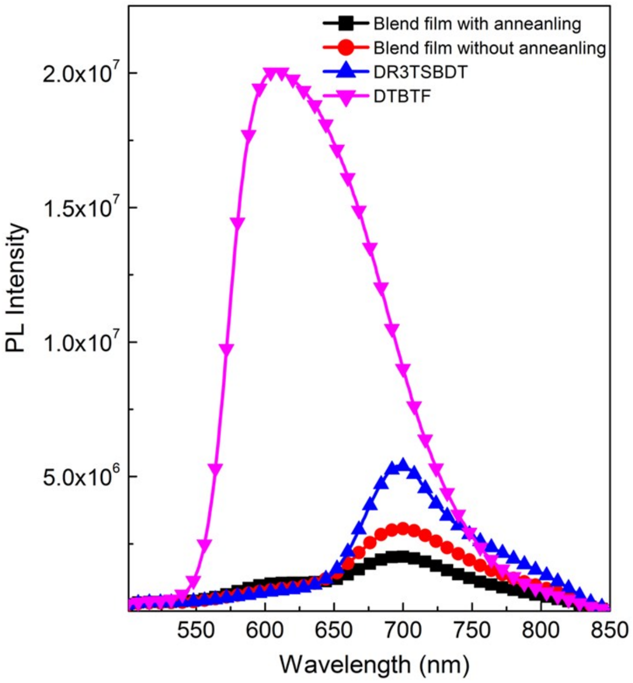

Fig. S5. Photoluminescence (PL) spectra of DR3TSBDT and DTBTF neat and blend films. The PL spectra was performed at an excitation wavelength of 450 nm.

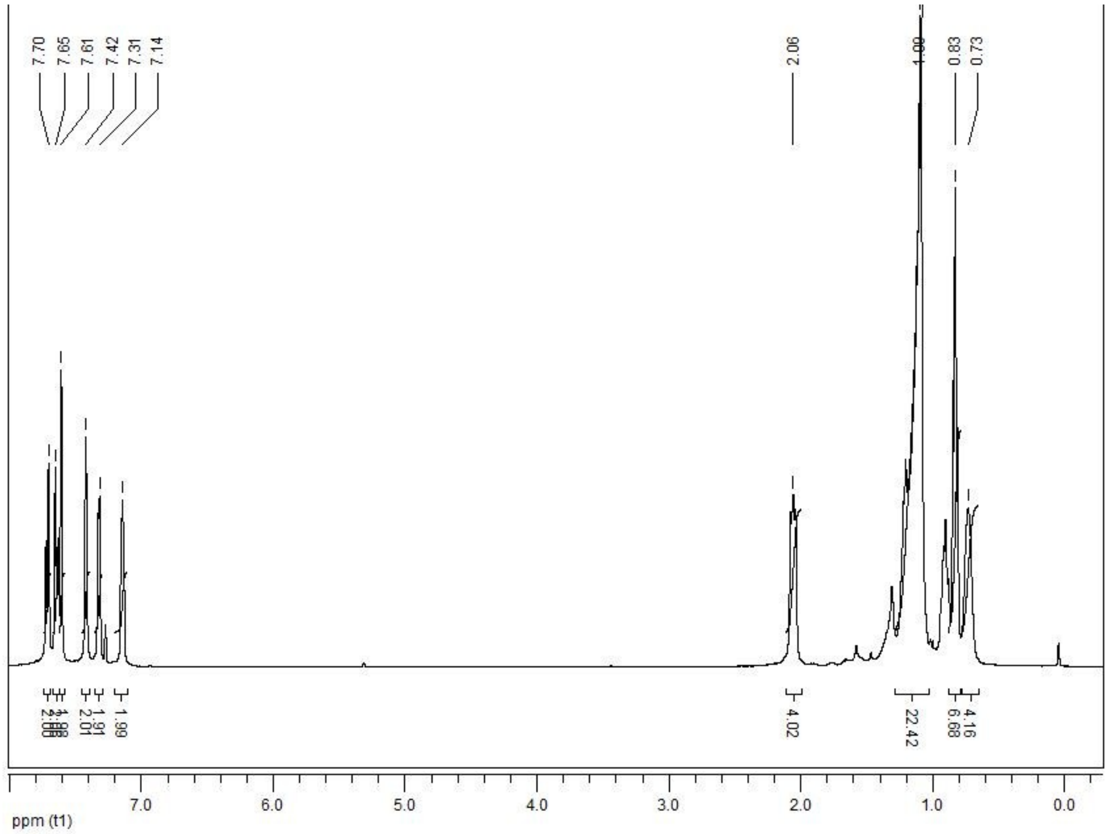

Fig. S6. ^{1}H NMR spectra of compound DTF at 300K in CDCl$_3$.

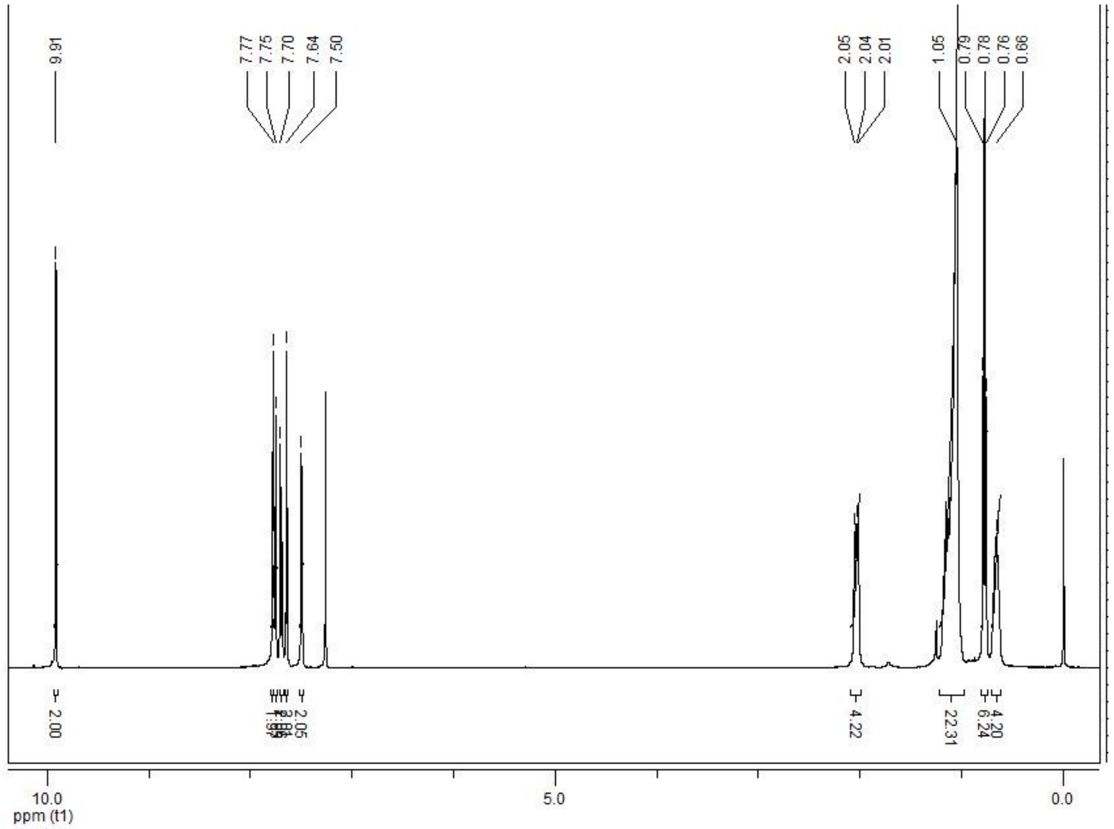

Fig. S7. ^{1}H NMR spectra of compound DCHOTF at 300K in CDCl$_3$.

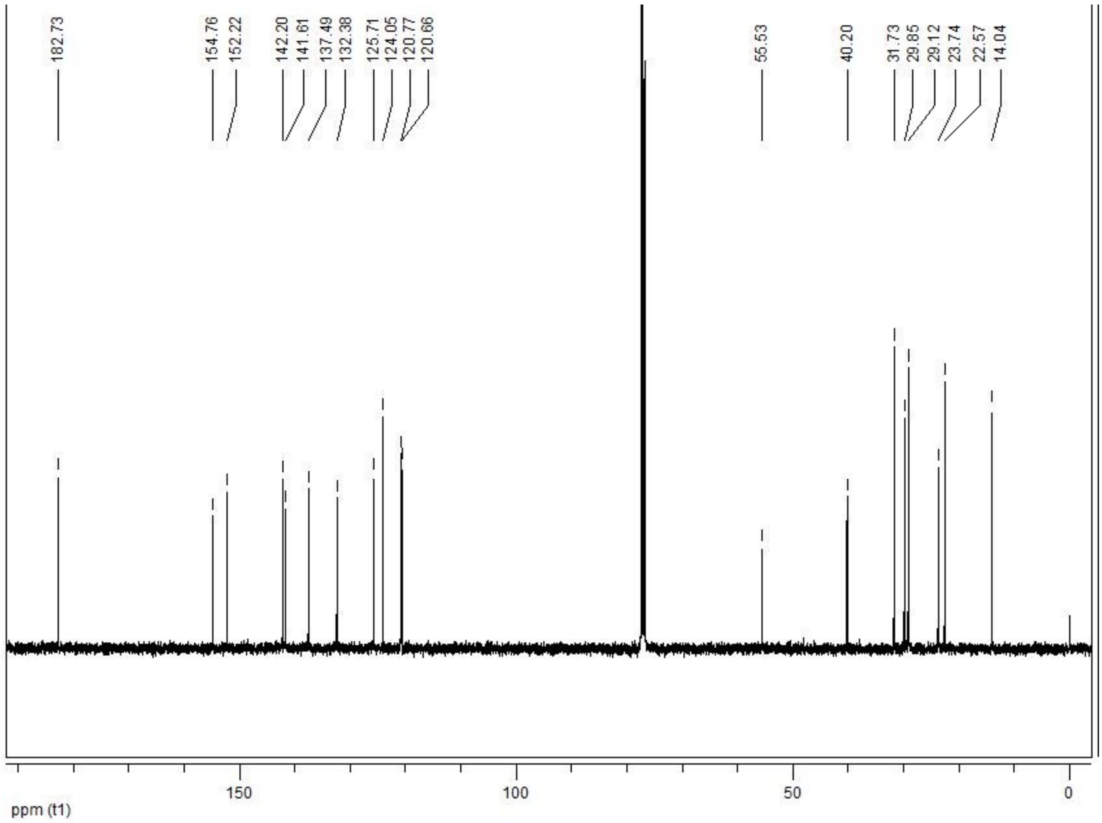

Fig. S8. ^{13}C NMR spectra of compound DCHOTF at 300K in CDCl$_3$.

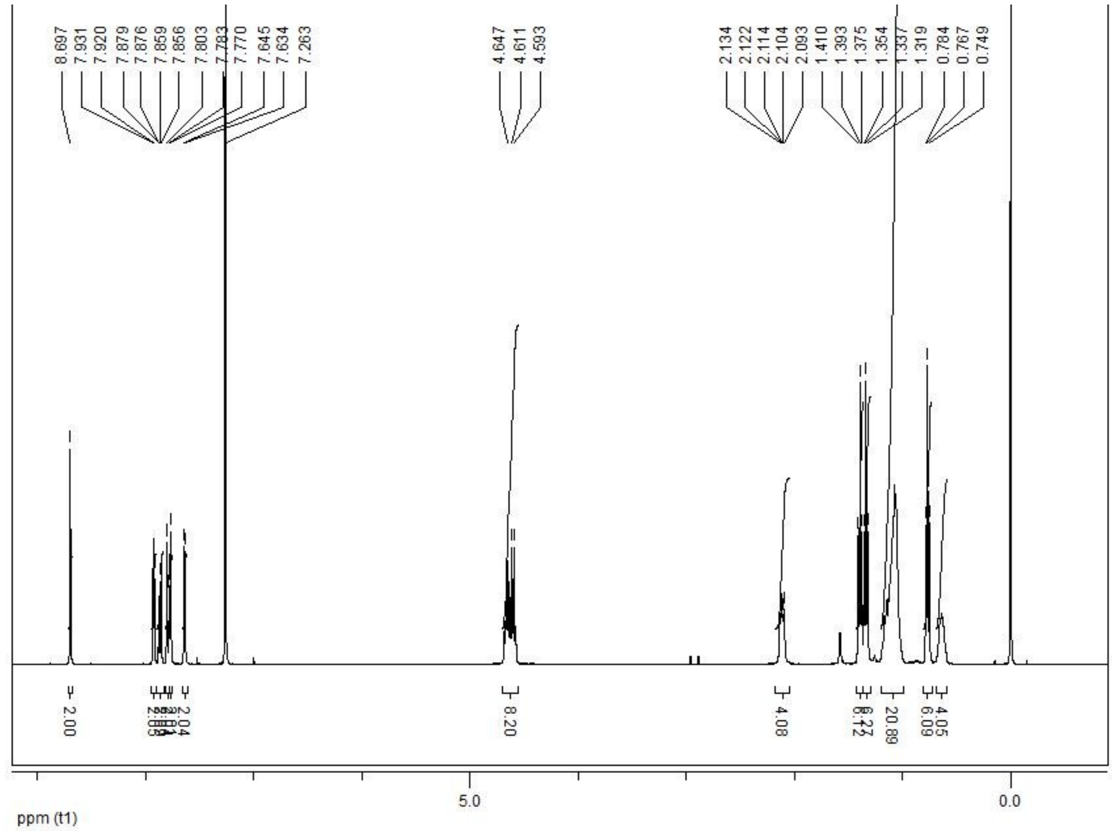

Fig. S9. ^{1}H NMR spectra of compound DTBTF at 300K in CDCl$_3$.

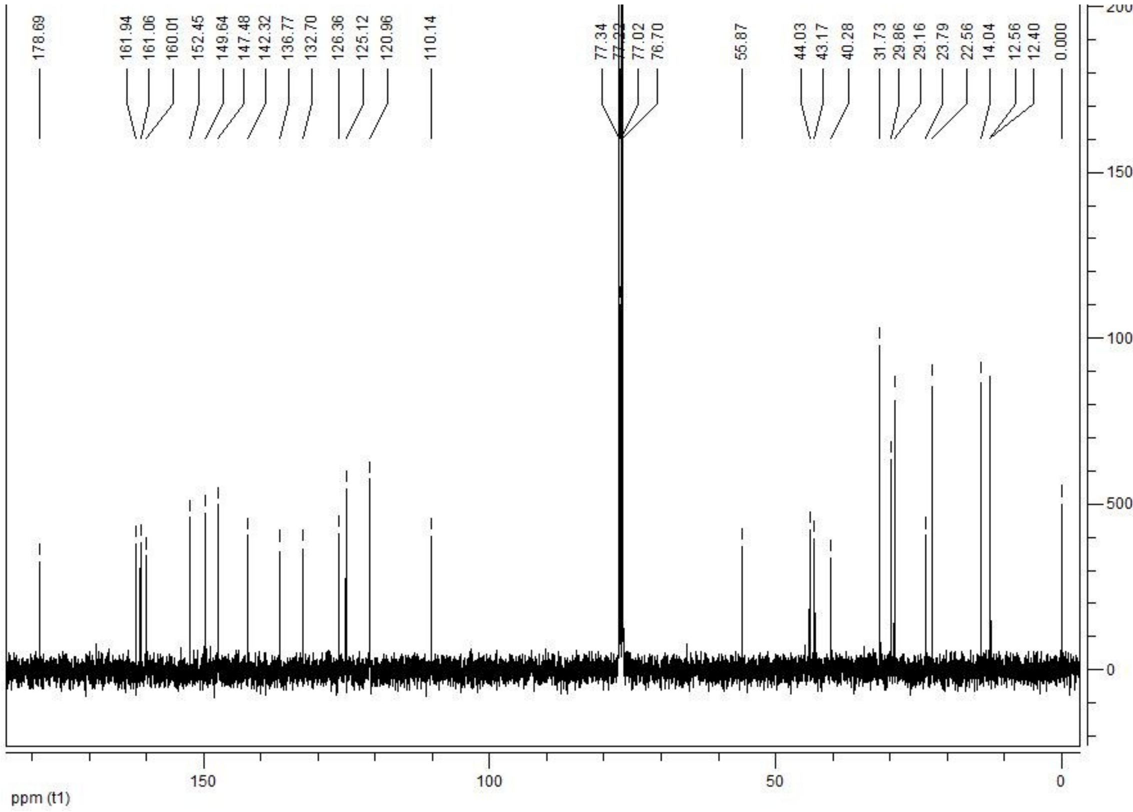

Fig. S10. ^{13}C NMR spectra of compound DTBTF at 300K in $CDCl_3$.

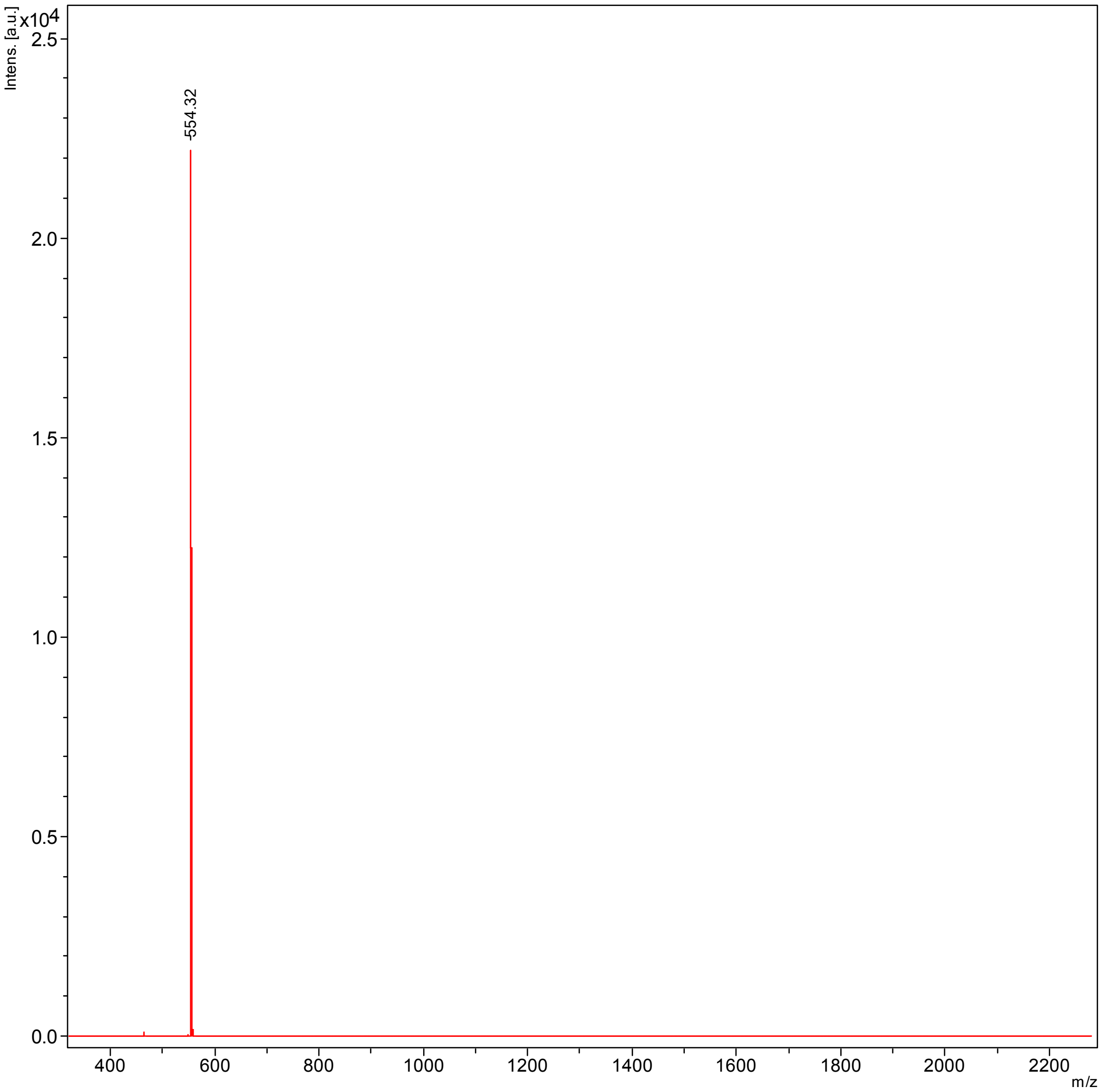

Fig. S11. MALDI-TOF plot of compound DTF.

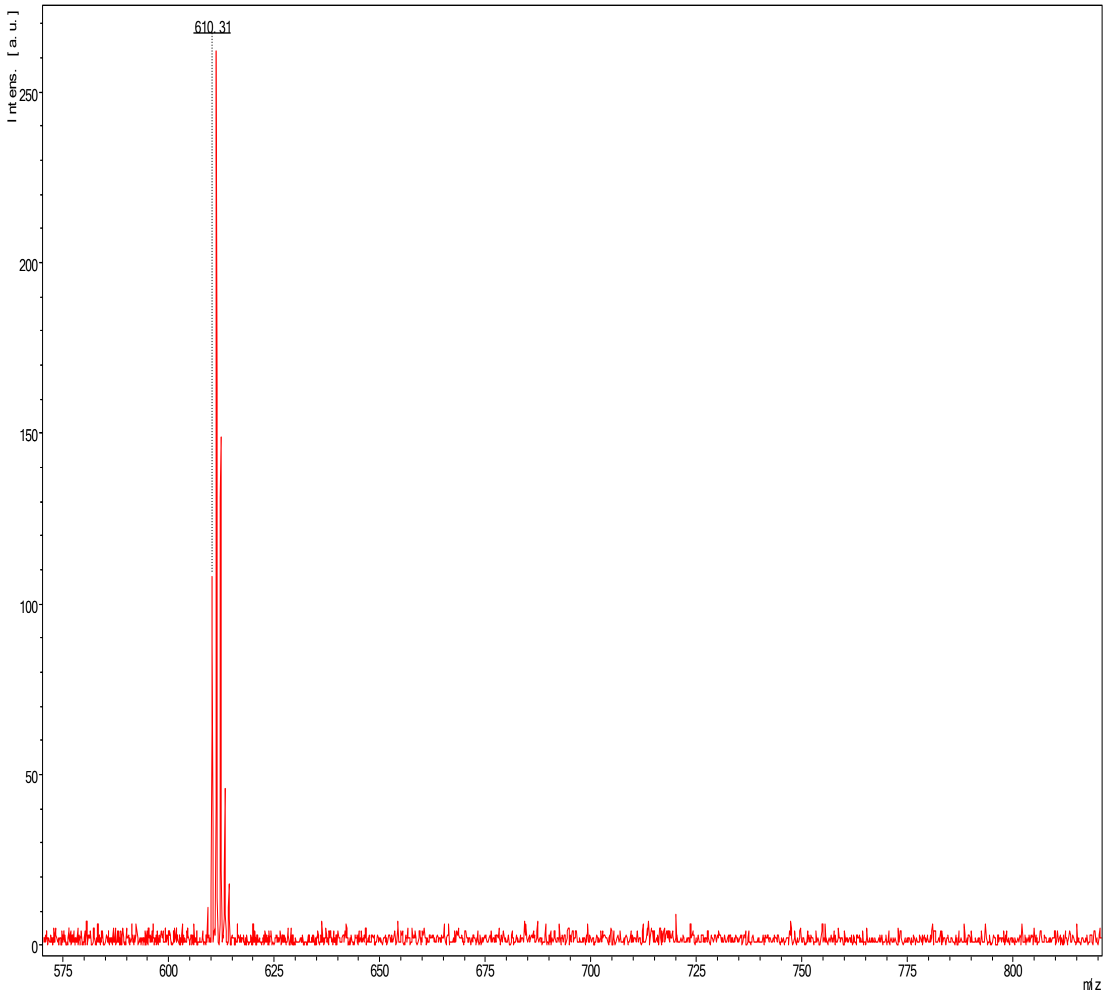

Fig. S12. MALDI-TOF plot of compound DCHOTF.

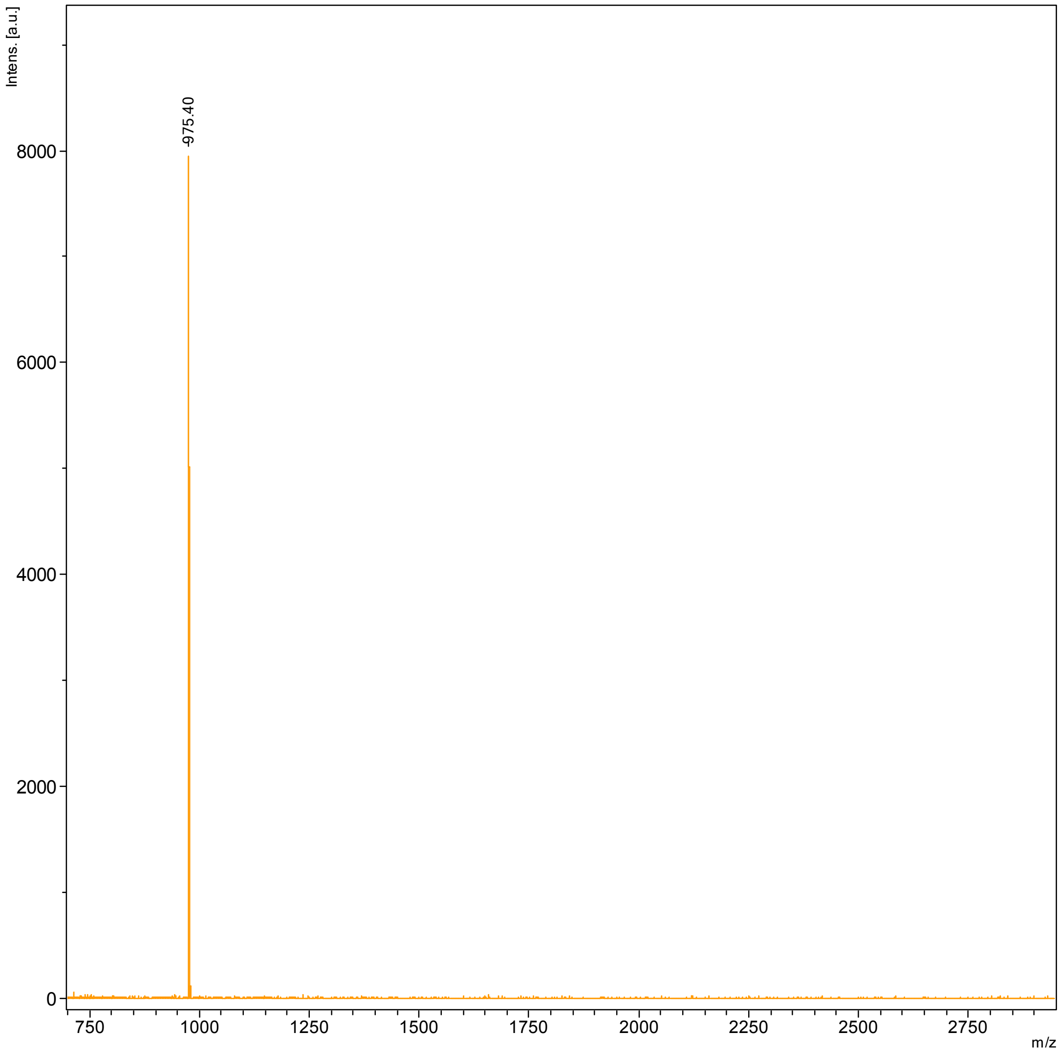

Fig. S13. MALDI-TOF plot of compound DTBTF.