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Electronic Supplementary Information for:

A simple small molecule as acceptor for fullerene-free organic solar cells with efficiency near 8%

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Measurements and instruments.

The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were taken on a Bruker AV400 Spectrometer. The melting point of the compounds were investigated by SGW X-4 melting point apparatus. 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. 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}. Atomic force microscopy (AFM) was performed using Multimode 8 atomic force microscope in tapping mode. The transmission electron microscopy (TEM) investigation was performed on Philips Technical G^2 F20 at 200 kV. The specimen for TEM measurement was prepared by spin casting the blend solution on ITO/PEDOT:PSS substrate, then floating the film on a water surface, and transferring to TEM grids. Grazing incidence X-ray diffraction (GIWAXS) characterization of the thin films was performed at beamline 7.3.3 Lawrence Berkeley National Lab.

The current density-voltage (*J-V*) curves of photovoltaic devices were obtained by a Keithley 2400 source-measure unit. All masked and unmasked tests gave consistent results with relative errors within 5%. The photocurrent was measured under illumination simulated 100 mW cm^{-2} AM 1.5G irradiation using an Oriel 96000 solar simulator, calibrated with a standard Si solar cell. The average PCE was obtained using 50 devices under the same conditions. External quantum efficiency (EQE) values of the devices were measured using Stanford Research Systems SR810 lock-in amplifier. The thickness of the active layers in the photovoltaic devices was measured on a Veeco Dektak 150 profilometer.

SCLC mobility was measured using a diode configuration of ITO/PEDOT:PSS/DR3TBDTT:PC$_{71}$BM/Au for hole and Al/ DR3TBDTT:PC$_{71}$BM /Al for electron by taking the dark current density in the range of 0-2 V and fitting the results to a space charge limited form, where SCLC is described by:

$$J = \frac{9\varepsilon_0\varepsilon_r\mu_0 V^2}{8L^3}$$

where J is the current density, L is the film thickness of the active layer, μ_0 is the hole or electron mobility, ε_r is the relative dielectric constant of the transport medium, ε_0 is the permittivity of free space (8.85×10^{-12} F m^{-1}), V (= V_{appl} - V_{bi}) is the internal voltage in the device, where V_{appl} is the applied voltage to the device and V_{bi} is the built-in voltage due to the relative work function difference of the two electrodes.

Organic photovoltaic device fabrication

The devices were fabricated with a structure of glass/ITO/PEDOT:PSS/PTB7-Th: DICTF/PDIN/Al. The ITO-coated glass substrates were cleaned by ultrasonic treatment in detergent, deionized water, acetone, and isopropyl alcohol under ultra-sonication for 15 minutes each and subsequently dried by a nitrogen blow. A thin layer (~ 40 nm) of PEDOT:PSS (Clevios P VP AI 4083, filtered at 0.45 μm) was spin-coated at 4000 rpm onto ITO surface. After baked at 150 °C for 20 minutes, the substrates were transferred into an argon-filled glove box. Subsequently, the PTB7-Th:DICTF active blend layer was prepared by spin-coating a mixed solvent of chloroform solution. The PDIN solution (1.5 mg/ml, dissolved in methanol (0.2% acetic acid)) was spin-coated on the top of active layers at 3000 rpm. Finally, 50 nm Al layer was deposited under high vacuum ($< 1.5\times10^{-4}$ Pa). The effective areas of cells were 4 mm^2 defined by shallow masks. The photocurrent was measured under illumination simulated 100 mW cm^{-2} AM 1.5G irradiation using an Oriel 96000 solar simulator, calibrated with a standard Si solar cell.

Materials

All starting materials were purchased from commercial suppliers and used without further purification. PTB7-Th was purchased from 1-Material Inc.

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 (2.04 g, 79%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, J = 7.8 Hz, 2H), 7.62 (dd, J = 1.6, 7.8 Hz, 2H), 7.56 (d, 2H), 7.39 (dd, J = 1.1, 3.6 Hz, 2H), 7.30 (dd, J = 1.1, 5.1 Hz, 2H), 7.11 (dd, J = 3.6, 5.1 Hz, 2H), 2.02 (m, 4H), 1.22-1.02 (m, 20H), 0.79 (t, J = 6.8 Hz, 6H), 0.68 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.7, 145.2, 140.2, 133.3, 128.1, 125.0, 124.6, 122.9, 120.2, 120.1, 55.3, 40.4, 31.8, 30.0, 29.3, 29.2, 23.8, 22.6, 14.1. 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), 7.79-7.74 (m, *4*H), 7.76 (d, *J* = 4.0 Hz, 2H), 7.70 (dd, *J* = 1.6, 7.9 Hz, 2H), 7.64 (d, *J* = 1.1 Hz, 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 182.7, 154.8, 152.2, 142.2, 141.6, 137.5, 132.4, 125.7, 124.0, 120.8, 120.7, 55.5, 40.2, 31.7, 29.9, 29.1, 29.1, 23.8, 22.6, 14.0. 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. (HPLC, 99.8%), Melting point: 109 ~ 110 °C.

Synthesis of compound **DICTF**

DCHOTF (300 mg, 0.492 mmol) and INCN (600 mg, 0.310 mmol) was dissolved in a dry $CHCl_3$ (50ml) solution, and then 1ml pyridine was added to the mixture under the protection of argon, and stirring at room temperature for 24h. 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 crude product was purified by silica gel using chloroform and petroleum (4:1) as eluent and then recrystallized from hexane and $CHCl_3$ mixture to afford DICTF as dark blue solid (430 mg, 91%).^{1}H NMR (400MHz, $CDCl_3$): δ 8.92 (s, 2H), 8.73 (dd, *J* = 1.4, 6.4 Hz, 2H), 7.98 (m, 2H), 7.91 (d, *J* = 4.2 Hz, 2H), 7.86 (dd, *J* = 1.4, 8.0 Hz, 2H), 7.76-7.80 (m, 8H) 7.62 (d, *J* = 4.2 Hz, 2H), 2.11-2.15 (m, 4H), 1.09-1.17 (m, 20H), 0.77 (t, *J* = 6.8 Hz, 6H), 0.68 (m, 4H);^{13}C NMR(100 MHz, CDCl3): δ 188.4, 160.8, 160.3, 152.5, 146.3, 142.3, 140.0, 138.0, 136.9, 136.4, 135.3, 134.6, 132.6, 126.2, 125.4, 125.0, 123.8, 122.6, 121.0, 120.8, 114.5, 114.4, 69.9, 55.9, 40.3, 31.7, 29.9, 29.2, 29.2, 23.9, 22.6, 14.0. MS (MALDI-TOF) m/z: calcd for $C_{63}H_{54}N_4O_2S_2$ [M^+], 963.37; found, 963.36. Anal. calcd. For $C_{63}H_{54}N_4O_2S_2$: C 78.55, H 5.65, N 5.82. Found: C 78.63, H 5.71, N 5.76. (HPLC, 99.9%), Melting point: 244 ~ 245 °C.

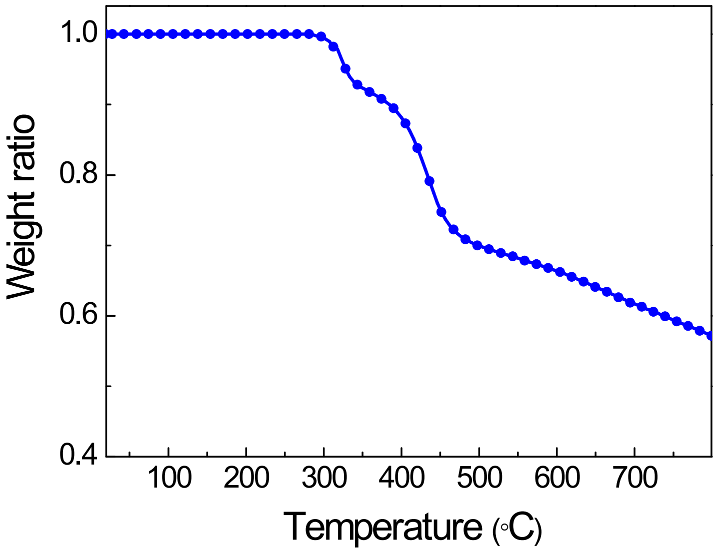

Fig. S1 TGA curve of DICTF with a heating rate of 10 ºC/min under N_2 atmosphere.

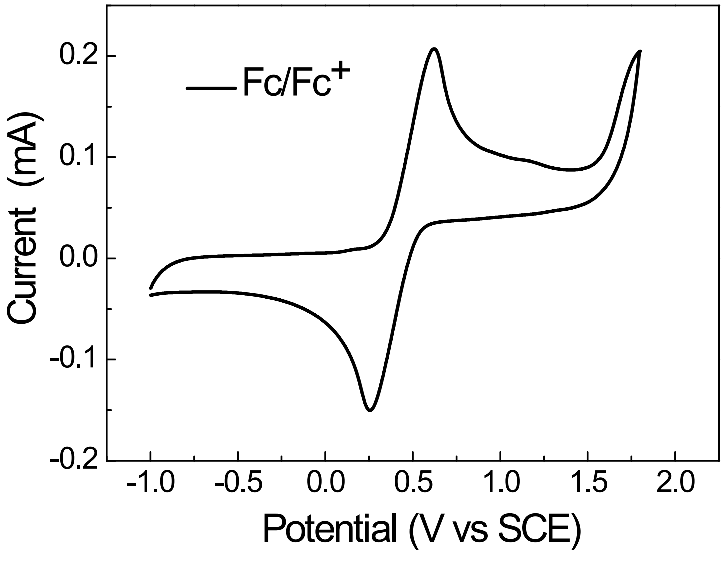

Fig. S2 Cyclic voltammogram of ferrocene/ferrocenium in a dichloromethane solution of 0.1 mol L^{-1} Bu_4NPF_6 with a scan rate of 100 mV s^{-1}.

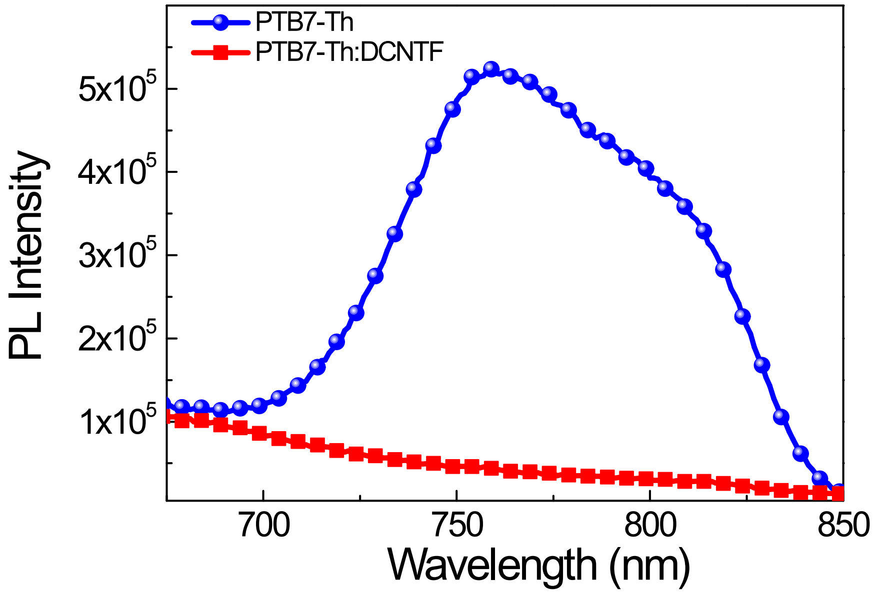

Fig. S3 Photoluminescence (PL) spectra of PTB7-Th neat film and PTB7-Th:DICTF blend films. The PL spectra was performed at an excitation wavelength of 470 nm.

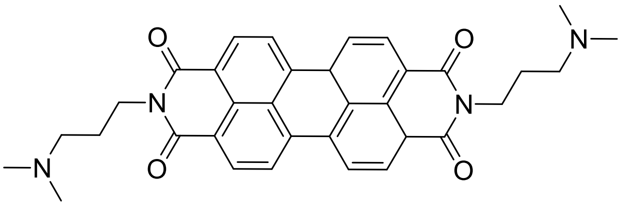

Fig. S4 The chemical structure of PDIN.

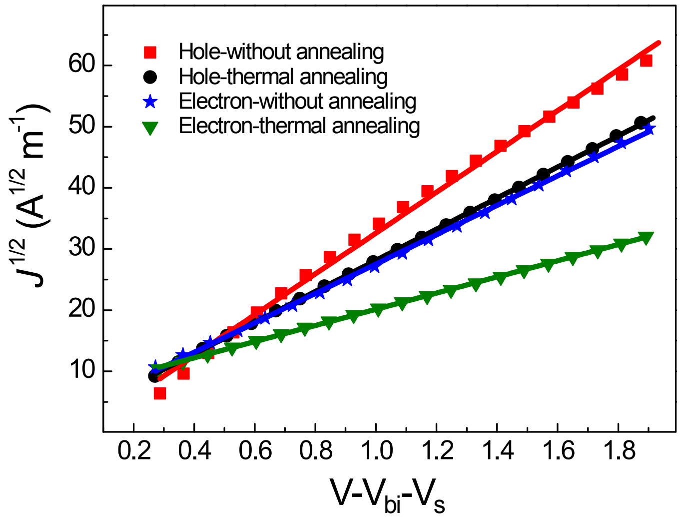

Fig. S5 *J-V* characteristics for the electron-only and hole-only devices fabricated from PTB7-Th:DICTF blend films with different treatment.

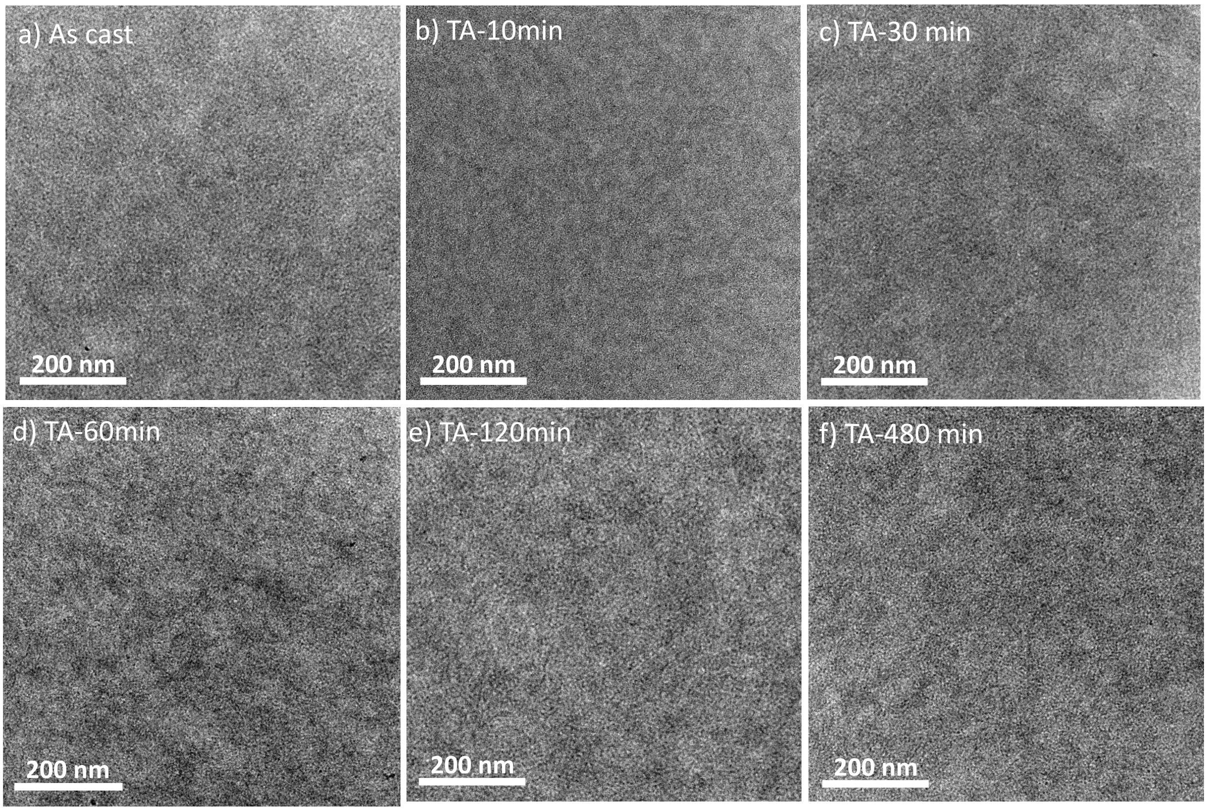

Fig. S6 TEM images of PTB7-Th:DICTF blend films without annealing and with thermal annealing for different time.

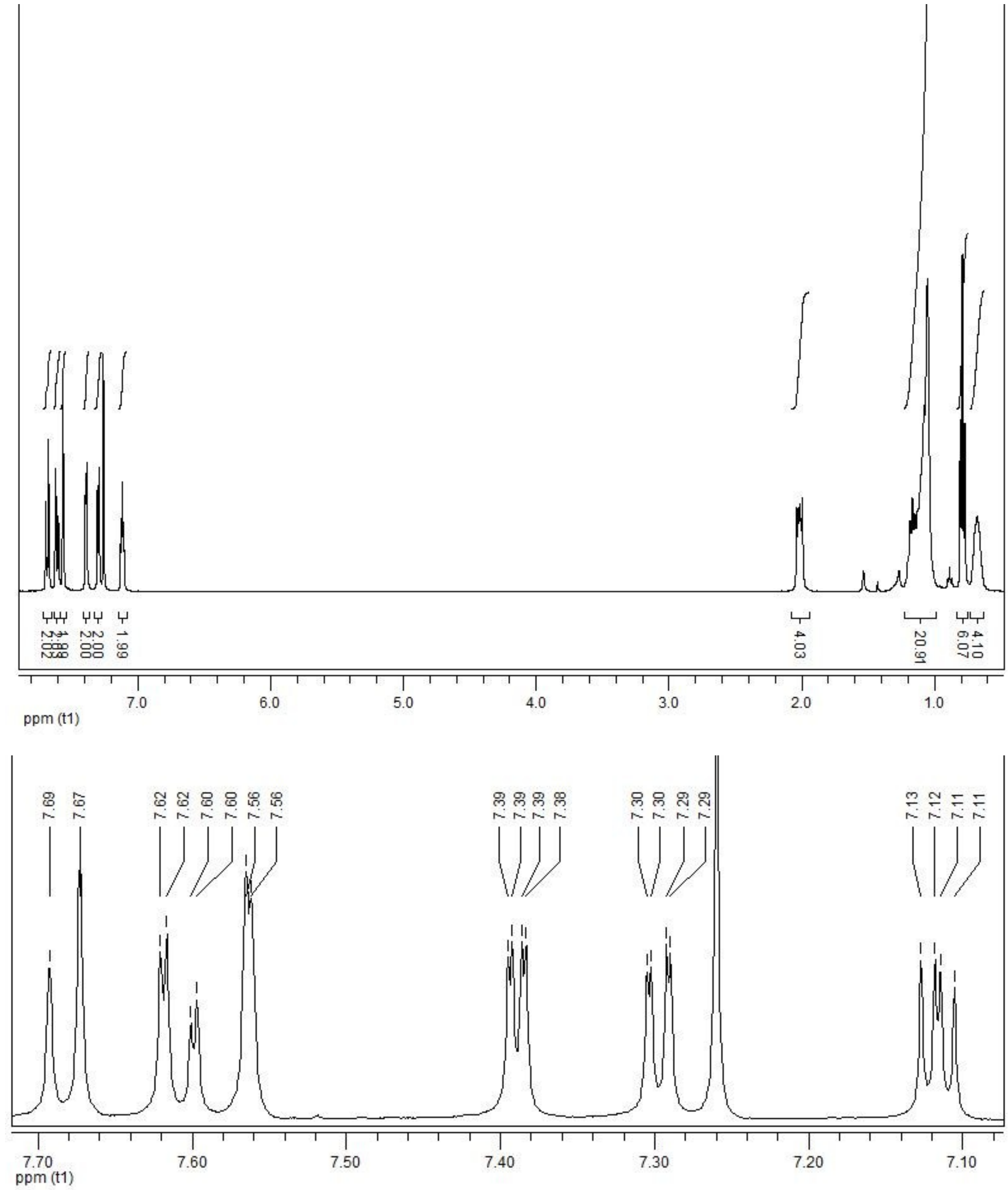

Fig. S7 ^{1}H NMR spectra of compound DTF at 300K in $CDCl_3$.

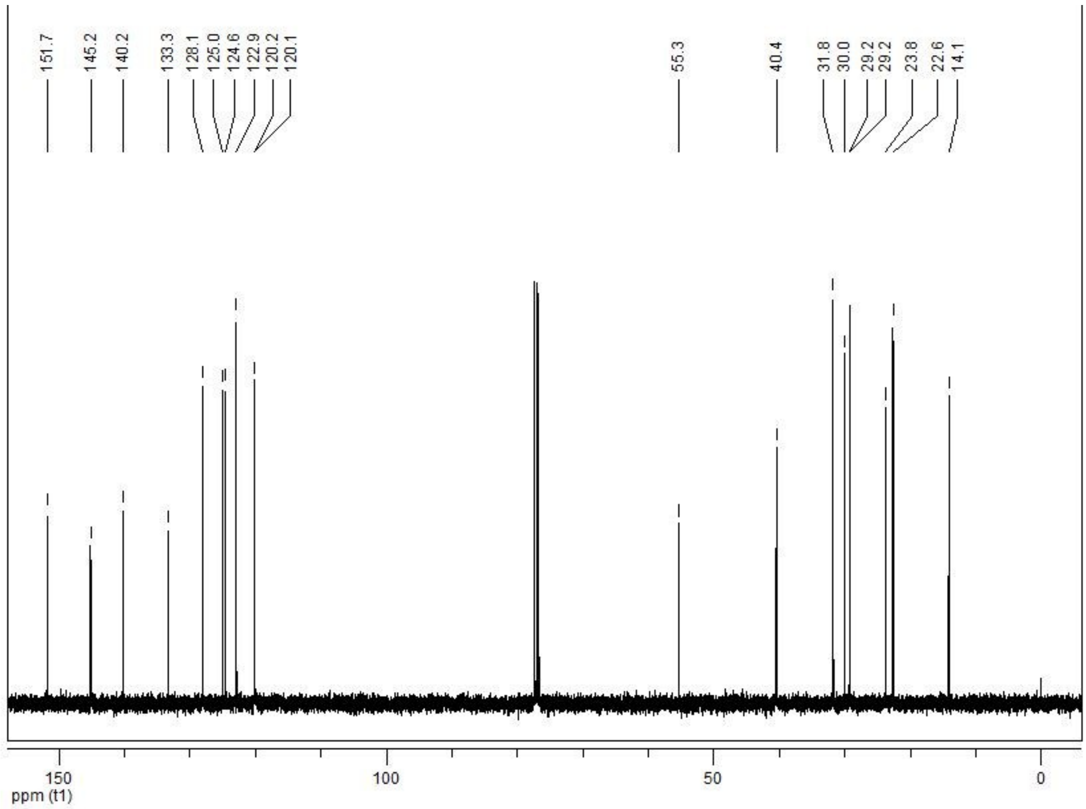

Fig. S8 ^{13}C NMR spectra of compound DTF at 300K in CDCl$_3$.

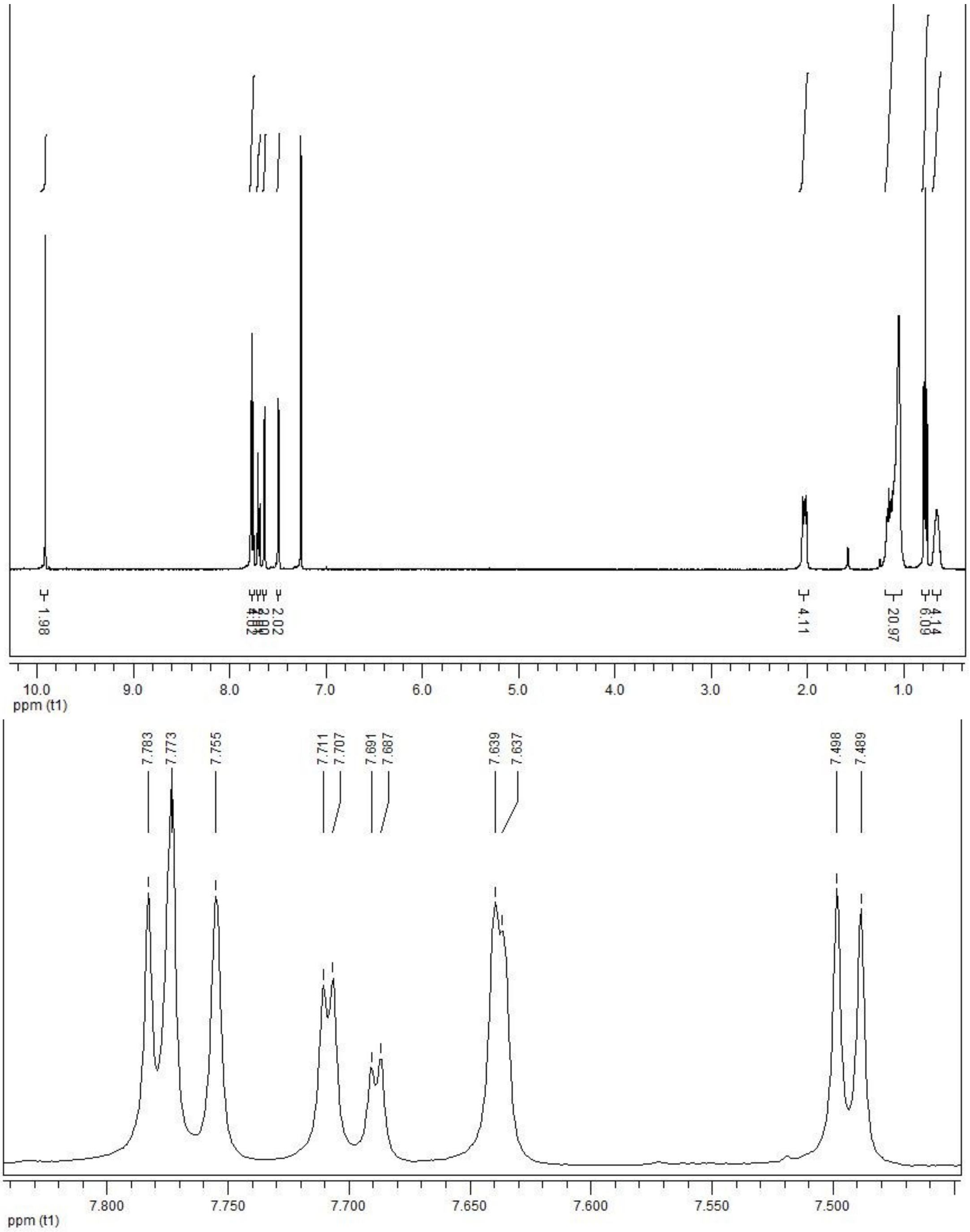

Fig. S9 ^{1}H NMR spectra of compound DCHOTF at 300K in $CDCl_3$.

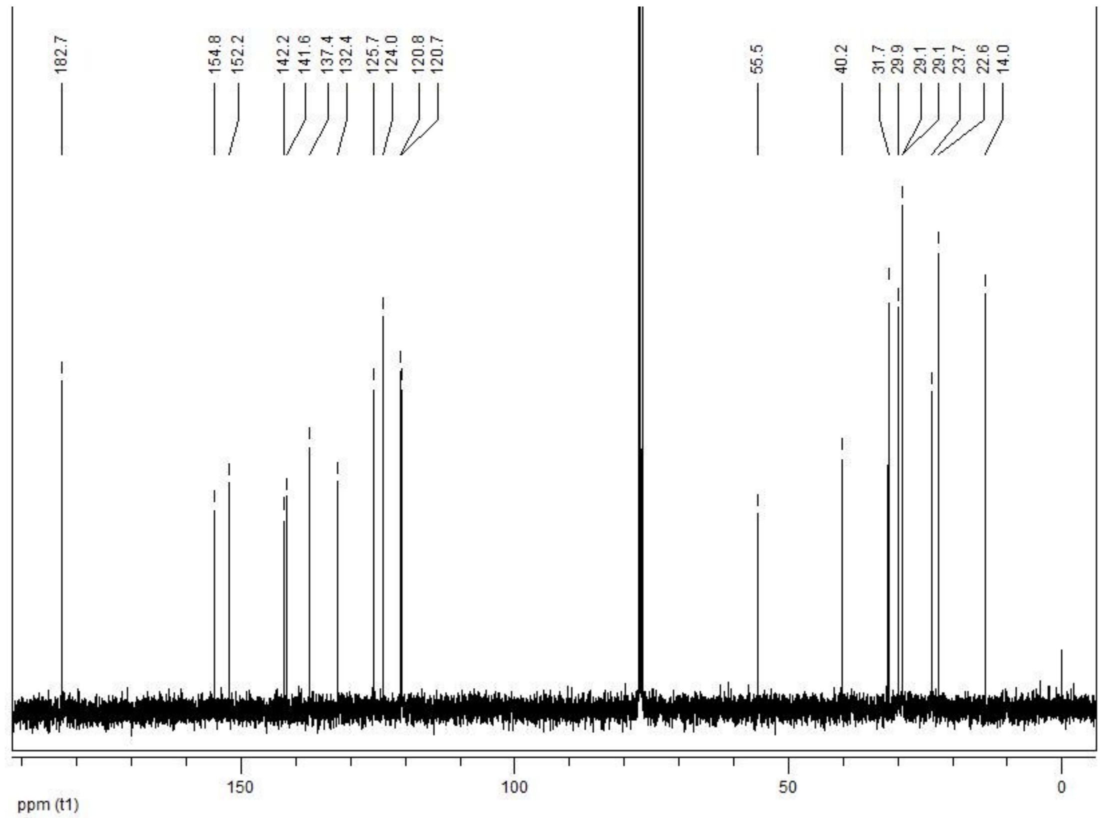

Fig. S10 ^{13}C NMR spectra of compound DCHOTF at 300K in $CDCl_3$.

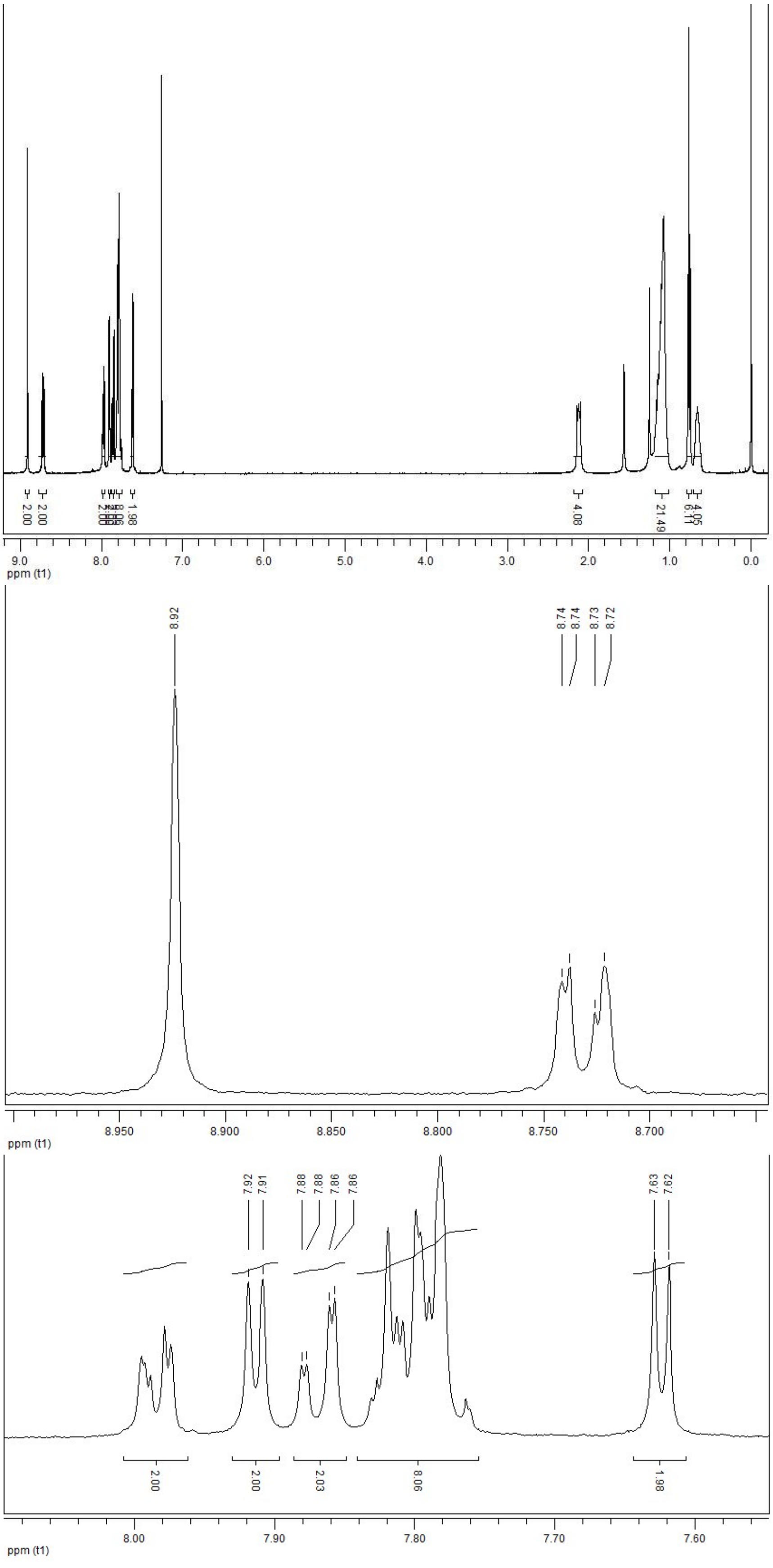

Fig. 11 ^{1}H NMR spectra of compound DICTF at 300K in $CDCl_3$.

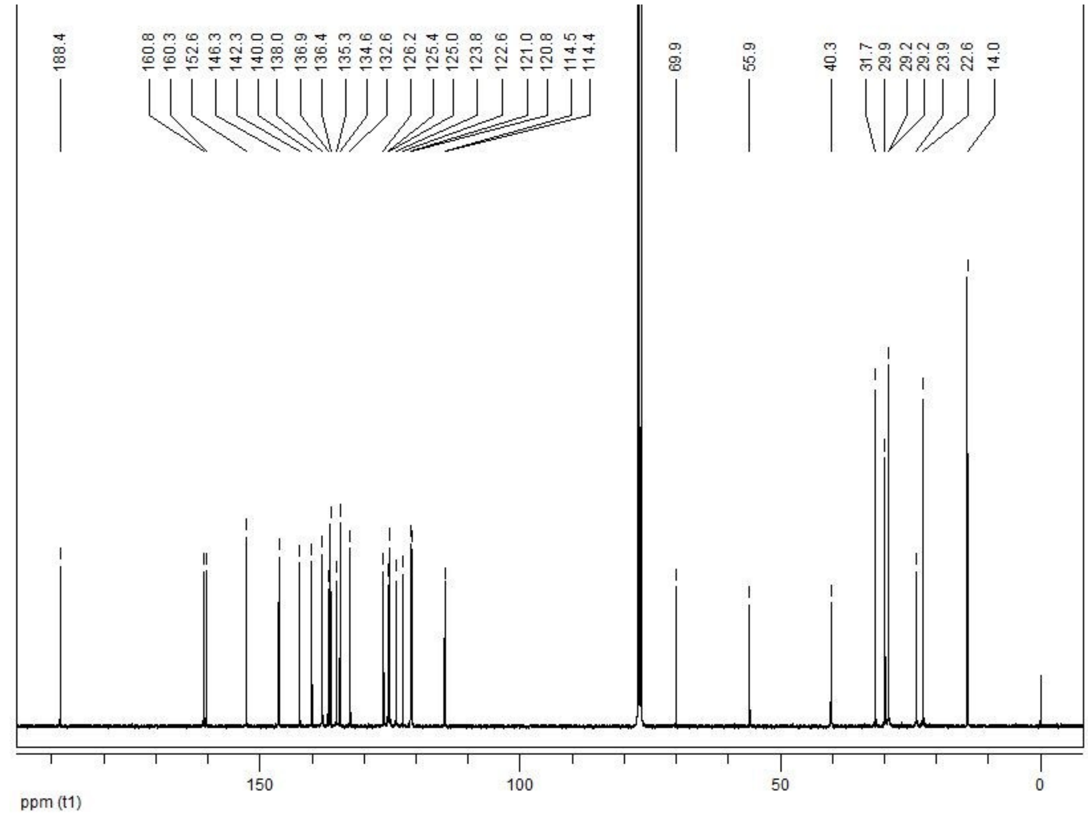

Fig. S12 ^{13}C NMR spectra of compound DICTF at 300K in $CDCl_3$.

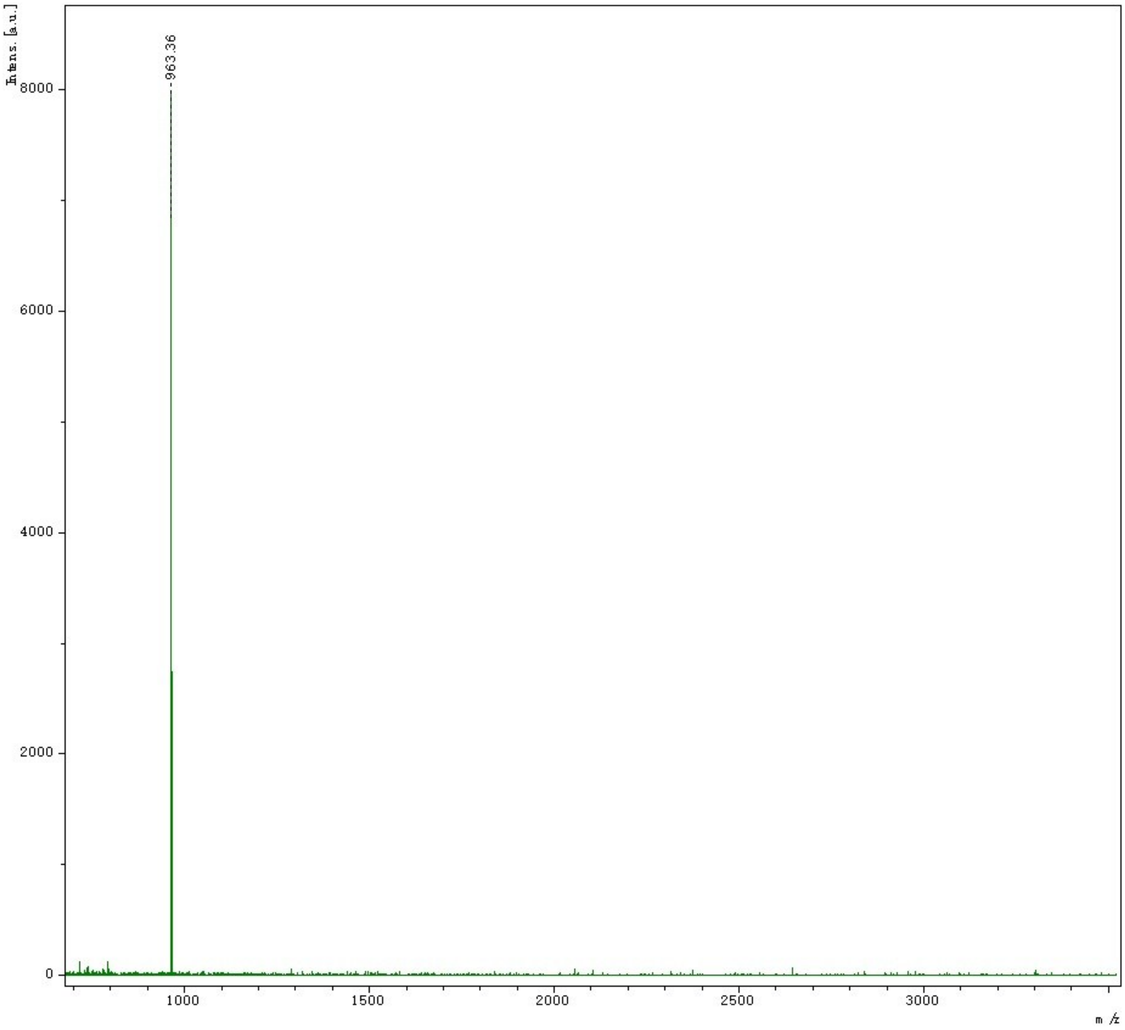

Fig. S13 MALDI-TOF plot of compound DICTF.

Photovoltaic performance.

Table S1 Photovoltaic performance of the solar cells based on PTB7-Th:DICTF blend films with different weight ratio under illumination of AM 1.5 G, 100 mW cm^{-2}.

Donor:Acceptor (w/w)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)
1:1	0.86±0.01	15.34±0.31	0.52±0.01	6.86±0.27
1:1.2	0.85±0.01	15.93±0.29	0.53±0.01	7.18±0.29
1:1.4	0.85±0.01	16.33±0.28	0.55±0.01	7.63±0.30
1:1.6	0.85±0.01	16.10±0.26	0.54±0.01	7.39±0.23

Table S2 The average device performance parameters for BHJ solar cells based on PTB7-Th:DICTF blend films (1:1.4, w/w) with different temperature thermal annealing for 10 min under illumination of AM 1.5 G, 100 mW cm^{-2}.

Treatment	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)
As cast	0.86±0.01	15.23±0.32	0.50±0.01	6.54±0.28
80°C	0.85±0.01	15.82±0.29	0.52±0.01	7.01±0.27
100°C	0.85±0.01	16.33±0.28	0.55±0.01	7.63±0.30
120°C	0.86±0.01	16.02±0.22	0.54±0.01	7.44±0.26

Table S3 The average device performance parameters for BHJ solar cells based on PTB7-Th:DICTF blend films (1:1.4 w/w) with different thermal annealing time under illumination of AM 1.5 G, 100 mW cm^{-2}.

Annealing time	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)
5 min	0.85±0.01	15.93±0.29	0.54±0.01	7.31±0.31
10 min	0.85±0.01	16.33±0.28	0.55±0.01	7.63±0.30
15 min	0.85±0.01	16.28±0.31	0.55±0.01	7.61±0.29

Table S4 The average device performance parameters for BHJ solar cells based on PTB7-Th:DICTF blend films (1:1.4 w/w) with different thermal annealing time under illumination of AM 1.5 G, 100 mW cm^{-2}.

Annealing time	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)
10 min	0.85±0.01	16.33±0.28	0.55±0.01	7.63±0.30
30 min	0.85±0.01	16.13±0.25	0.55±0.01	7.54±0.32
60 min	0.86±0.01	16.41±0.21	0.54±0.01	7.66±0.25
120 min	0.85±0.01	16.47±0.23	0.54±0.01	7.56±0.30
480 min	0.85±0.01	16.39±0.21	0.54±0.01	7.52±0.26