Supporting Information

Dithienocoronenediimide (DTCDI)-Derived Triads for High-Performance Air-Stable, Solution-Processed Balanced Ambipolar Organic Field-Effect Transistors

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Content

1. Synthesis of dithienocoronenediimide (DTCDI)-derived triads

Synthesis of parent DTCDI

PDI-BT [1] (220 mg, 0.175 mmol), I_2 (91.7 mg, 0.361 mmol) was dissolved in benzene (125 mL), and stirred for 18h with exposure in UV-light (302 nm). After the reaction was done, the solvent was evaporated in vacuum. The crude was washed with acetone and methanol, purified by column chromatography (Silica gel, hexane:dichloroform (2:1), v/v)) to afford the pure product (66 mg, 30%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.42 (s, 2H), 8.24 (s, 2H), 8.86-8.77 (m, 4H), 4.16 (m, 4H), 2.02 (m, 4H), 1.50-1.19 (m, 82H), 0.83 (m, 12H).

Synthesis of DTCDI-BT

The dibromo intermediate DTCDI-2Br (200 mg, 0.14 mmol), 2-(tributyl)stannylthiophene (211 mg, 0.57 mmol), $Pd_2(dba)_3$ (4.67 mg, 0.005 mmol), P(*o*-Tolyl)$_3$ (6.93 mg, 0.0228 mmol) were dissolved in dry chlorobenzene (27 mL) under nitrogen, and the reaction mixture was heated at 135 °C for 20 h. After cooling to room temperature, the reaction mixture was quenched with water, and extracted with toluene. The solvent was evaporated to dryness to give a solid crude product. The crude was purified by recrystallized from a large amount of chloroform to give the desired compound as a red-purple solid (0.160 g, 80% yield). IR: ν = 1700 (C=O), 1658 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 9.16 (s, 2H), 8.95 (s, 2H), 8.80 (s, 2H), 7.56-7.54 (m, 6H), 4.17 (m, 4H), 2.01

(m, 4H), 1.50-1.12 (m, 82H), 0.80 (m, 12H). ^{13}C NMR spectra was not obtained due to its limited solubility. MALDI-TOF m/z: 1416.4610, calcd 1416.1392. Anal. Calcd for $C_{90}H_{114}N_2O_4S_4$: C, 76.33; H, 8.11; N, 1.98; S, 9.06. Found: C, 76.32; H, 8.12; N, 1.98; S, 9.05.

Synthesis of DTCDI-BBT

The synthetic procedure is similar as described for **DTCDI-BT.** Reagent used were 2-(tributyl)stannylbenzo[*b*]thiophene (168.58 mg, 0.57 mmol), $Pd_2(dba)_3$ (4.67 mg, 0.005 mmol), P(*o*-Tolyl)$_3$ (6.93 mg, 0.0228 mmol) and chlorobenzene (27 mL). After workup, the product was red-purple solid (161 mg, 75% yield). IR: ν = 1700 (C=O), 1658 (C=O) cm^{-1}. ^{1}H NMR and ^{13}C NMR spectra were not obtained due to its limited solubility. MALDI-TOF m/z: 1516.5774, calcd 1516.2565. Anal. Calcd for $C_{98}H_{118}N_2O_4S_4$: C, 77.63; H, 7.84; N, 1.85; S, 8.46 Found: C, 77.64; H, 7.83; N, 1.85; S, 8.43.

Synthesis of DTCDI-BNT

The synthetic procedure is similar as described for **DTCDI-BT**. Reagent used were 2-(tributyl)stannylnaphtho[2,3-b]thiophen (196.96 mg, 0.57 mmol), $Pd_2(dba)_3$ (4.67 mg, 0.005 mmol), P(*o*-Tolyl)$_3$ (6.93 mg, 0.0228 mmol) and chlorobenzene (27 mL). After workup, the product was red-purple solid (167 mg, 73% yield). IR: ν = 1700 (C=O), 1658 (C=O) cm^{-1}. ^{1}H NMR and ^{13}C NMR spectra were not obtained due to its limited solubility. MALDI-TOF m/z: 1616.5951, calcd 1616.3739. Anal. Calcd

for $C_{106}H_{122}N_2O_4S_4$: C, 78.76; H, 7.61; N, 1.73; S, 7.94 Found: C, 78.77; H, 7.63; N, 1.72; S, 7.92.

2. Thermal gravimetric analysis (TGA)

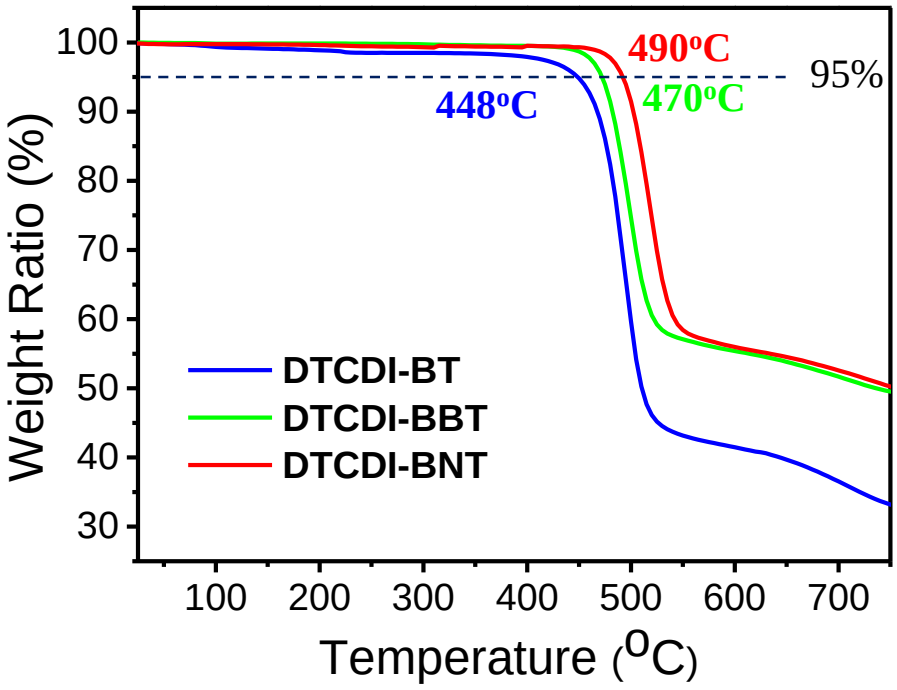

Fig. S1 TGA plots of compounds **DTCDI-BT, DTCDI-BBT** and **DTCDI-BNT** under a nitrogen flow with a heating rate of 20 ºC/min.

3. Differential Scanning Calorimetry (DSC) Measurements

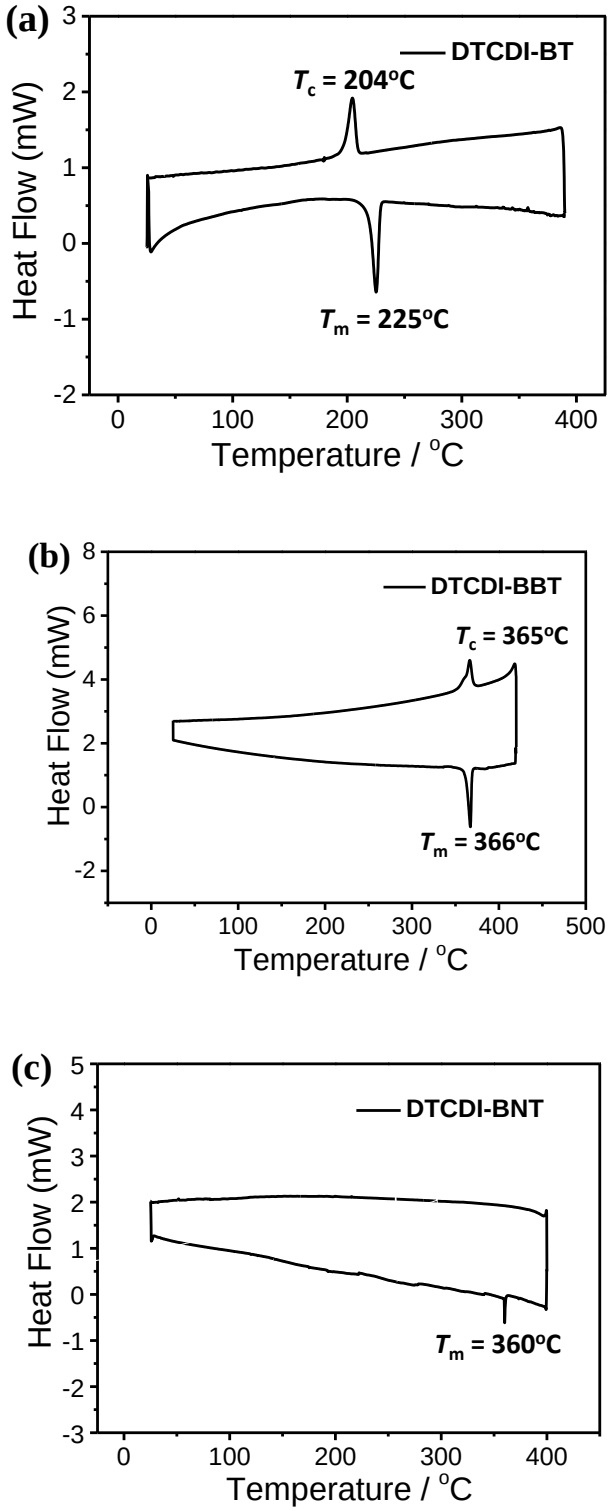

Fig. S2 DSC curves of **DTCDI-BT** (a), **DTCDI-BBT** (b) and **DTCDI-BNT** (c) in the second heating-cooling cycle under a nitrogen flow with a heating rate of 10 ºC/min.

4. Photoelectron yield spectroscopy (PESA) mesurement

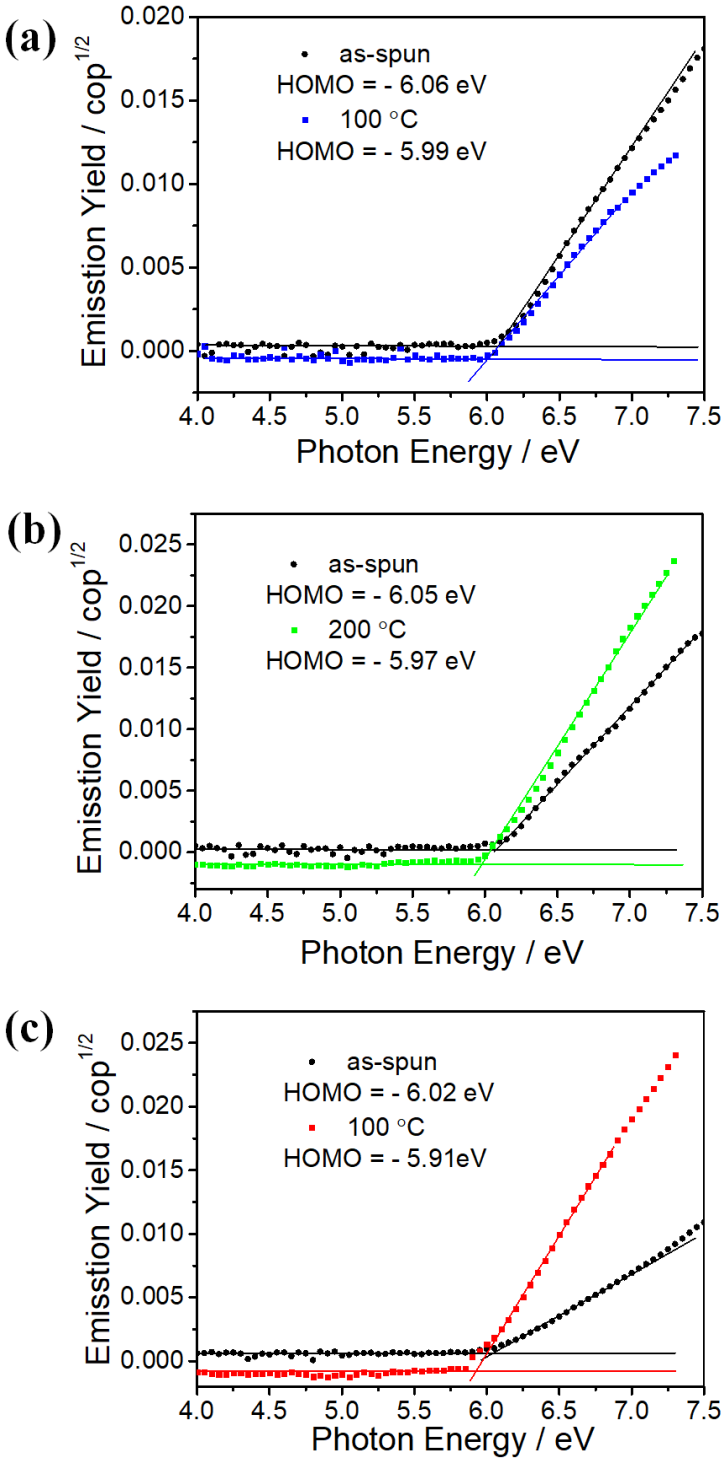

Fig. S3 Photoelectron yield spectroscopy in air (PESA) spectra of **DTCDI-BT** (a), **DTCDI-BBT** (b) and **DTCDI-BNT** (c) in a spin-coated film on a precleaned ITO substrate annealed along with that of as-spun film.

5. OFET Fabrication and Measurement

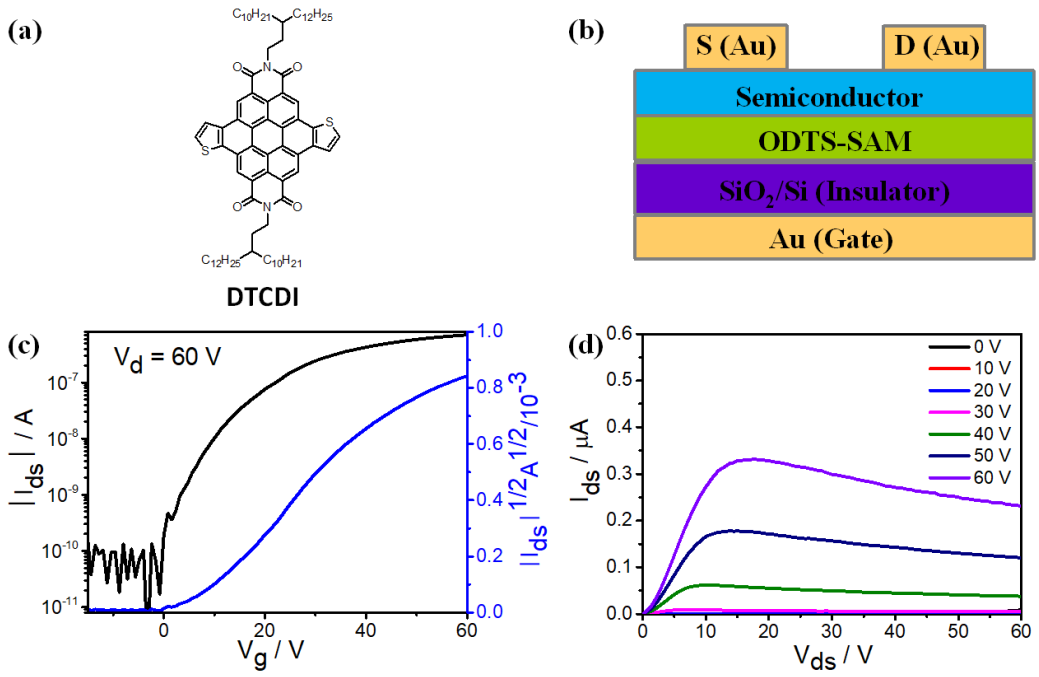

Fig. S4 (a) Chemical structures of **DTCDI**; (b) Schematic representation of bottom-gate top-contact device architecture used in this work; Transfer and output characteristics for EFTs with **DTCDI**-based as-spun thin film (c, d) evaluated under ambient conditions.

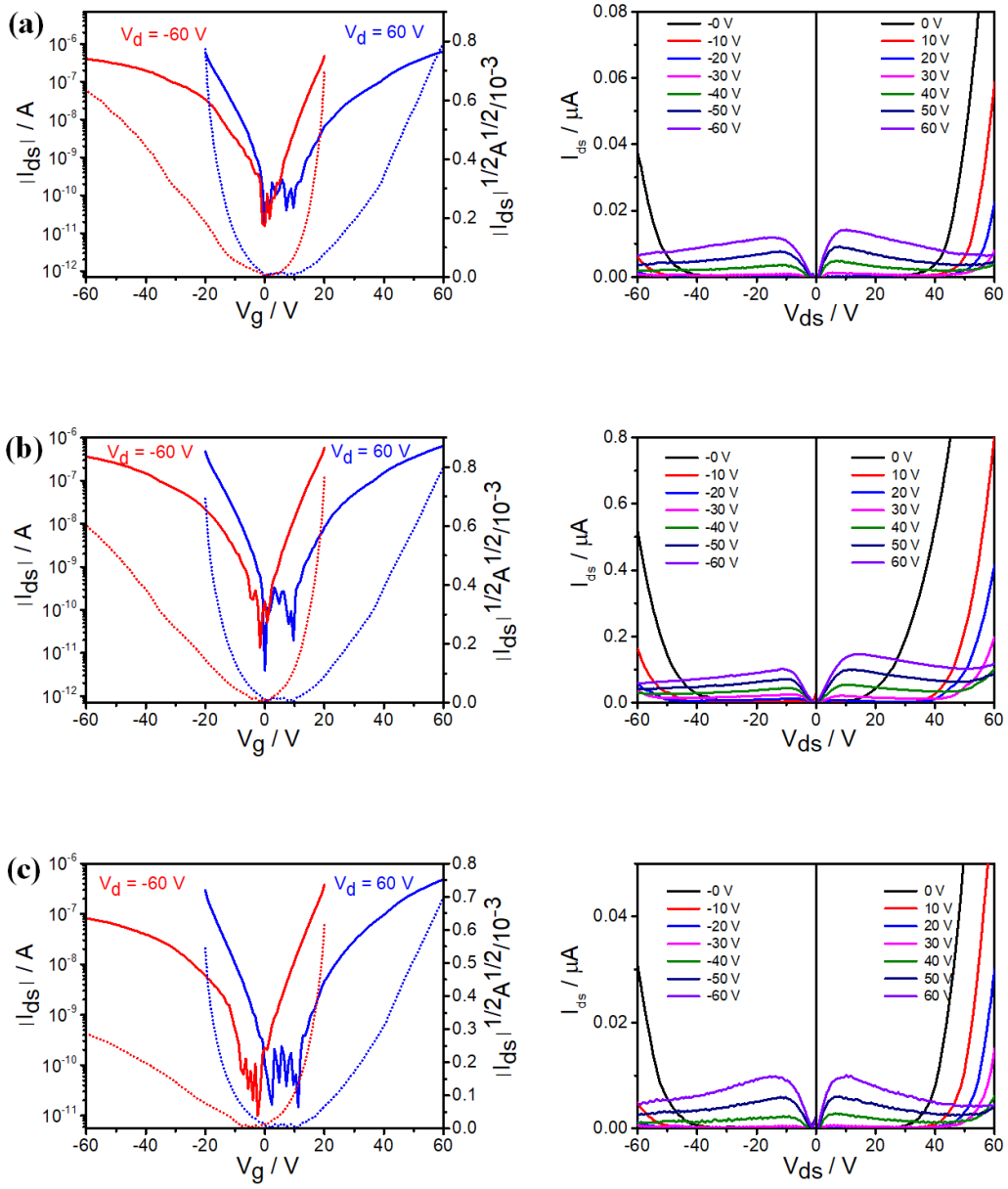

Fig. S5 Transfer (left) and output (right) characteristic curves of BGTC transistors based on **DTCDI-BT** evaluated under ambient conditions at different thermal annealing temperatures together: (a) 100°C; (b) 150°C; (c) 200°C.

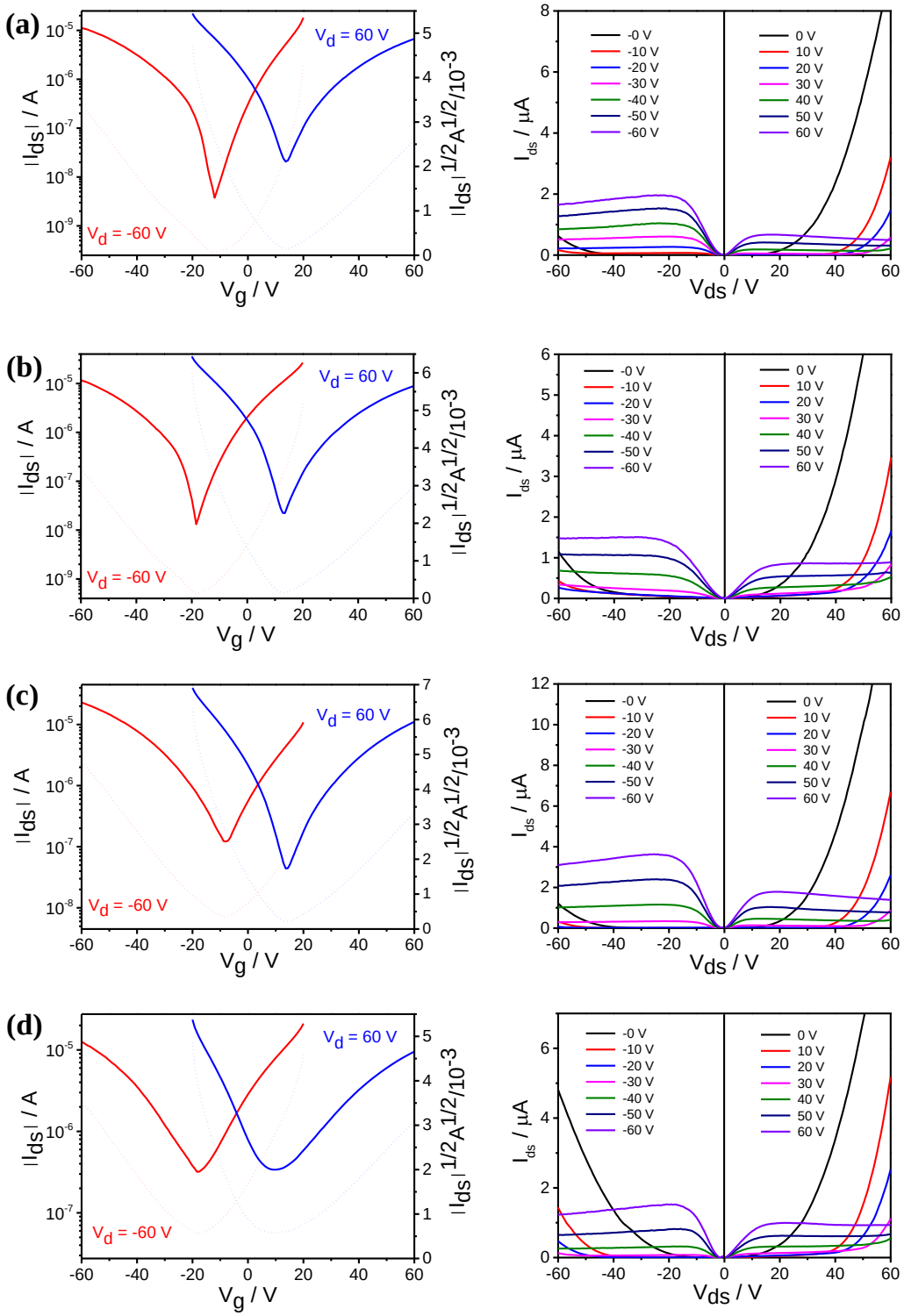

Fig. S6 Transfer (left) and output (right) characteristic curves of BGTC transistors based on **DTCDI-BBT** evaluated under ambient conditions at different thermal annealing temperatures together: (a) 100°C; (b) 150°C; (c) 200°C; (d) 250°C.

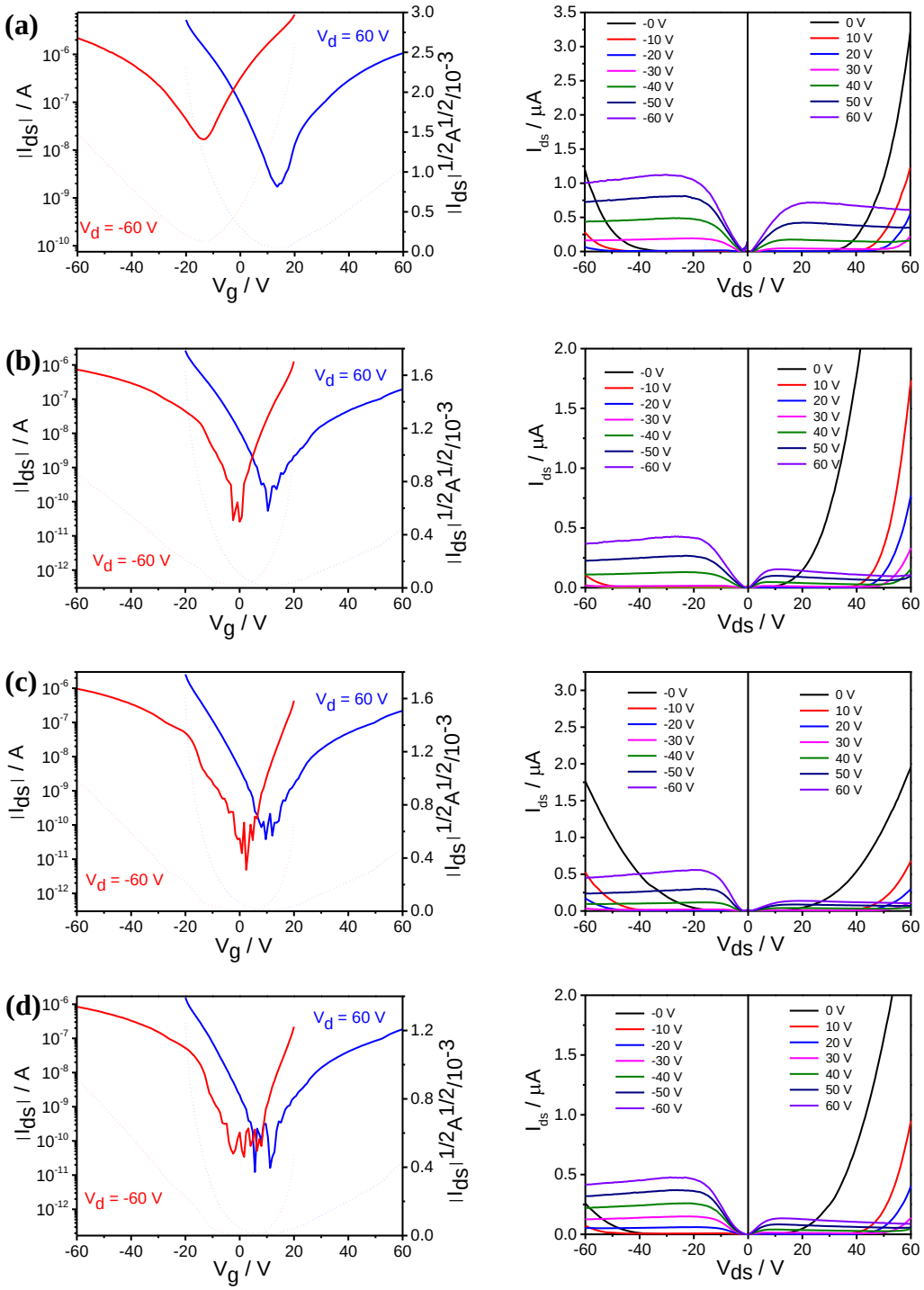

Fig. S7 Transfer (left) and output (right) characteristic curves of BGTC transistors based on **DTCDI-BNT** evaluated under ambient conditions at different thermal annealing temperatures together: (a) 100°C; (b) 150°C; (c) 200°C; (d) 250°C.

6. NMR spectra

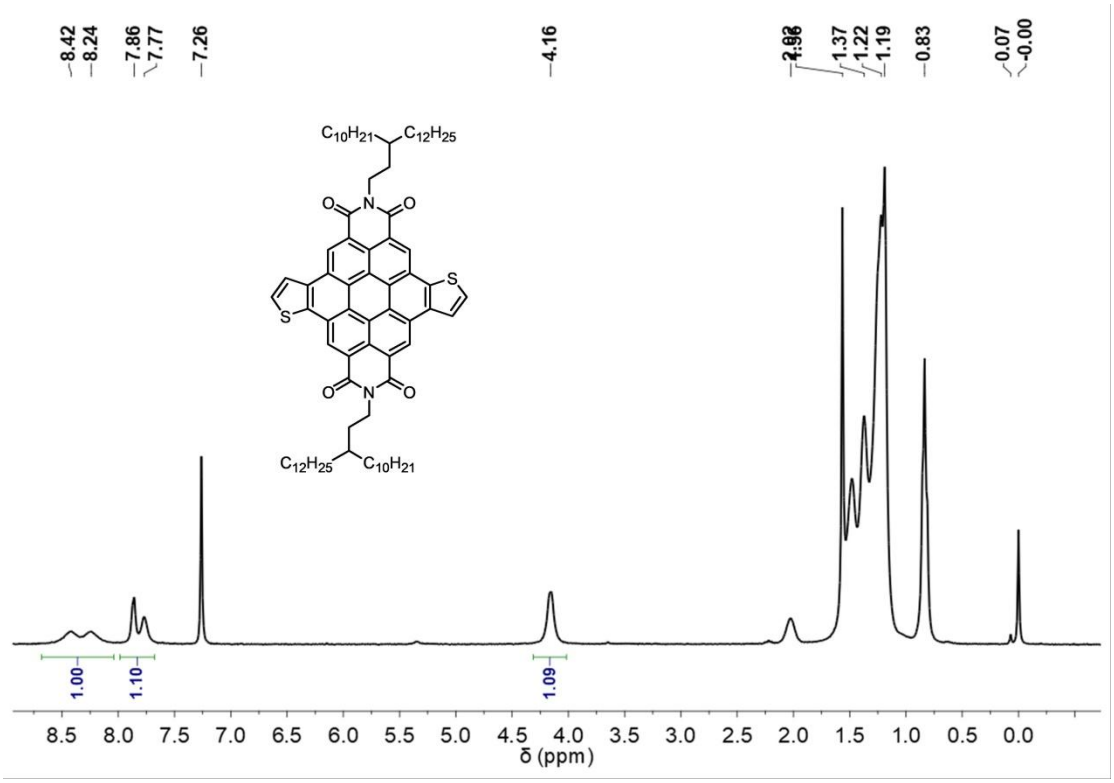

Fig. S8 ^{1}H NMR spectrum of **DTCDI** (400 MHz, $CDCl_3$, r.t.)

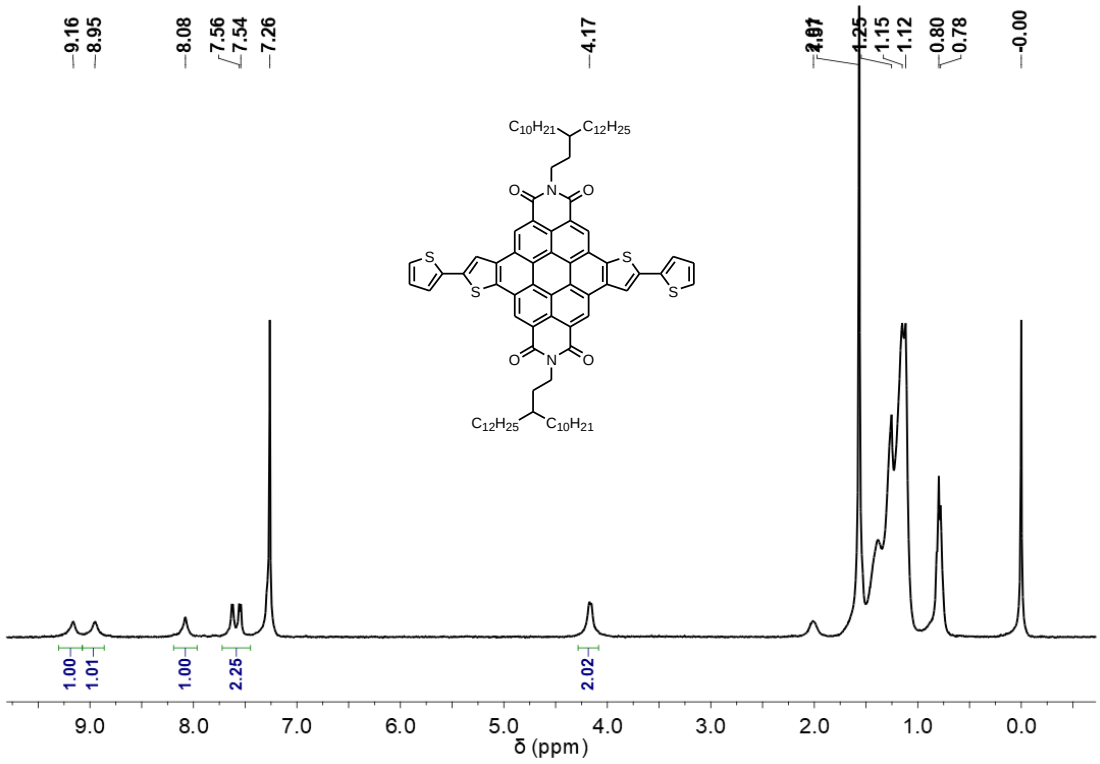

Fig. S9 ^{1}H NMR spectrum of **DTCDI-BT** (400 MHz, $CDCl_3$, r.t.)

7. Mass spectra

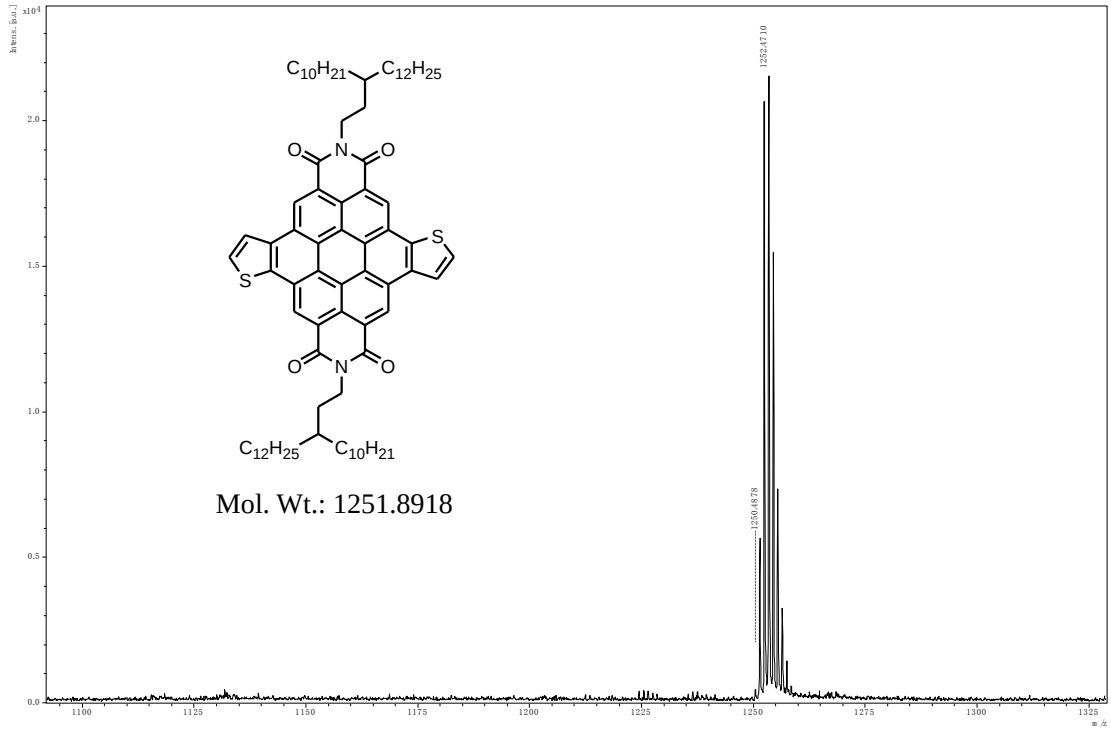

Fig. S10 Mass spectra of **DTCDI**.

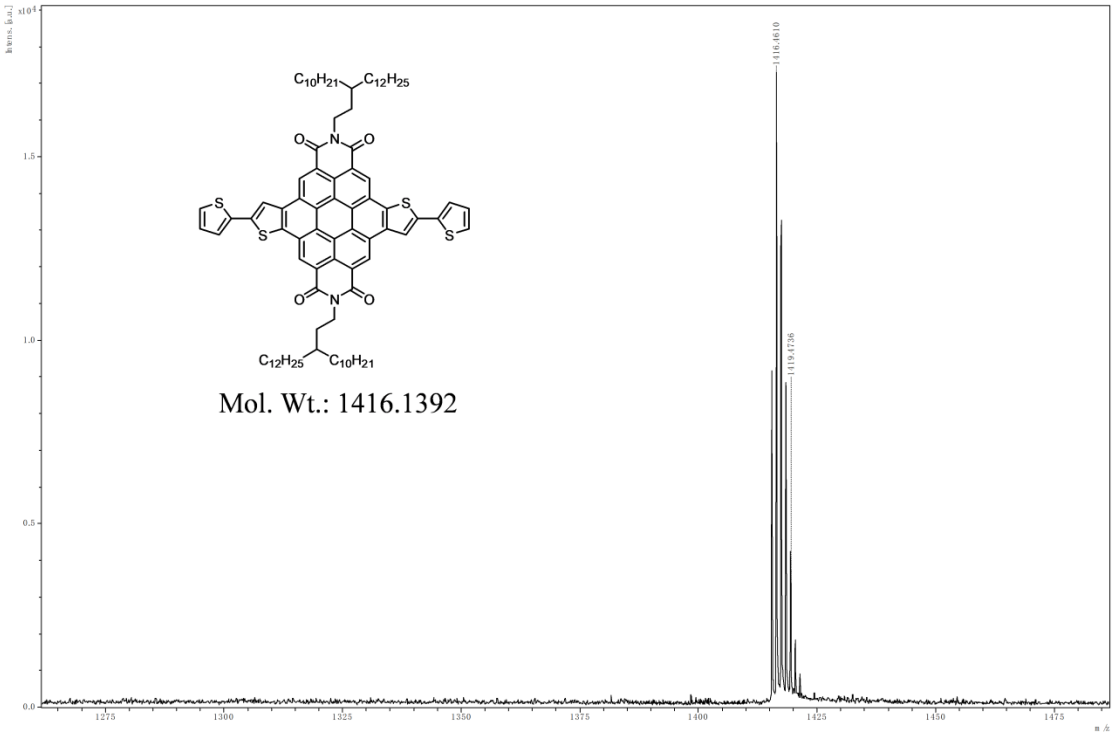

Fig. S11 Mass spectra of **DTCDI-BT**.

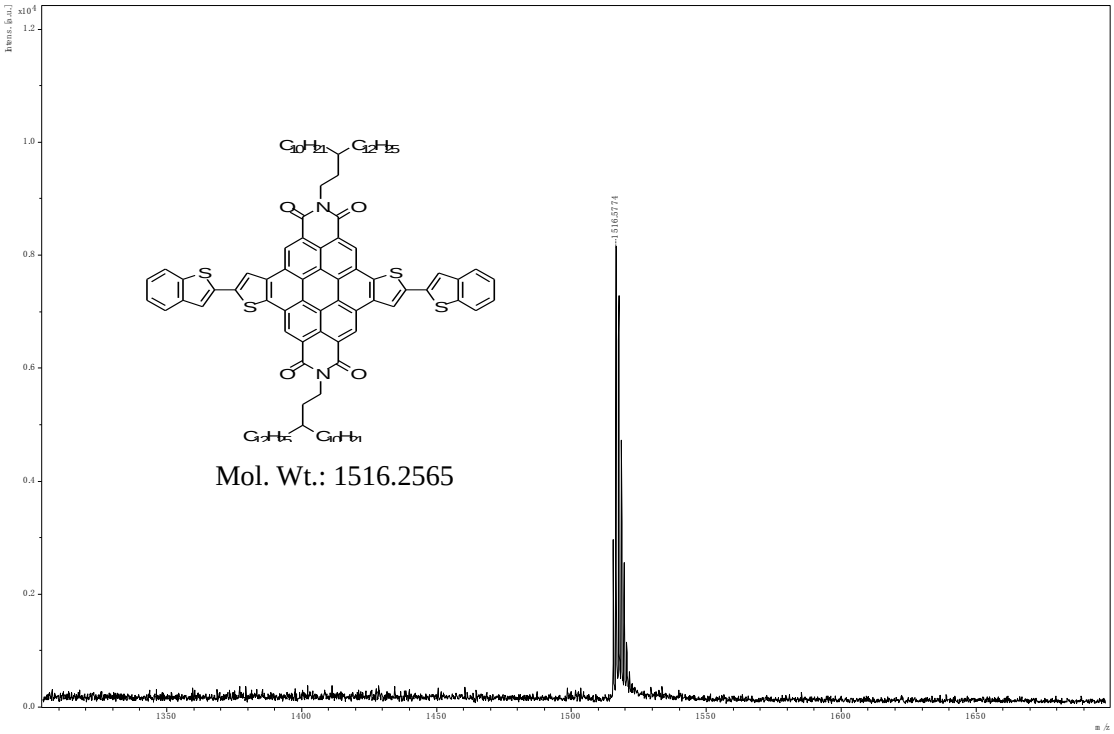

Fig. S12 Mass spectra of **DTCDI-BBT**.

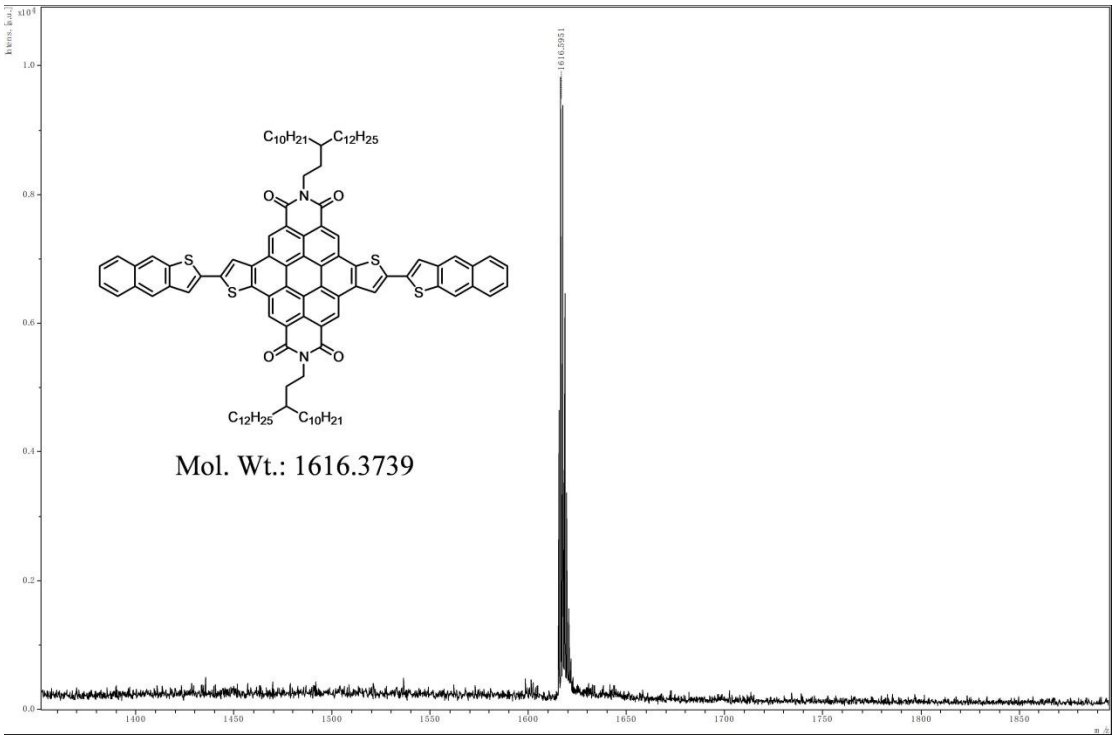

Fig. S13 Mass spectra of **DTCDI-BNT**.

8. FT-TR spectrum

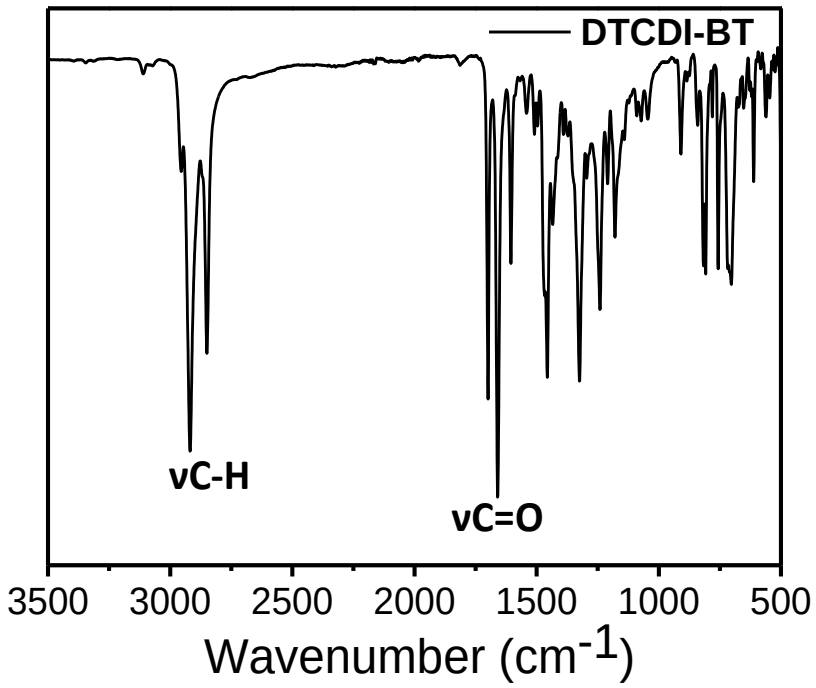

Fig. S14 FT-IR spectra of **DTCDI-BT**.

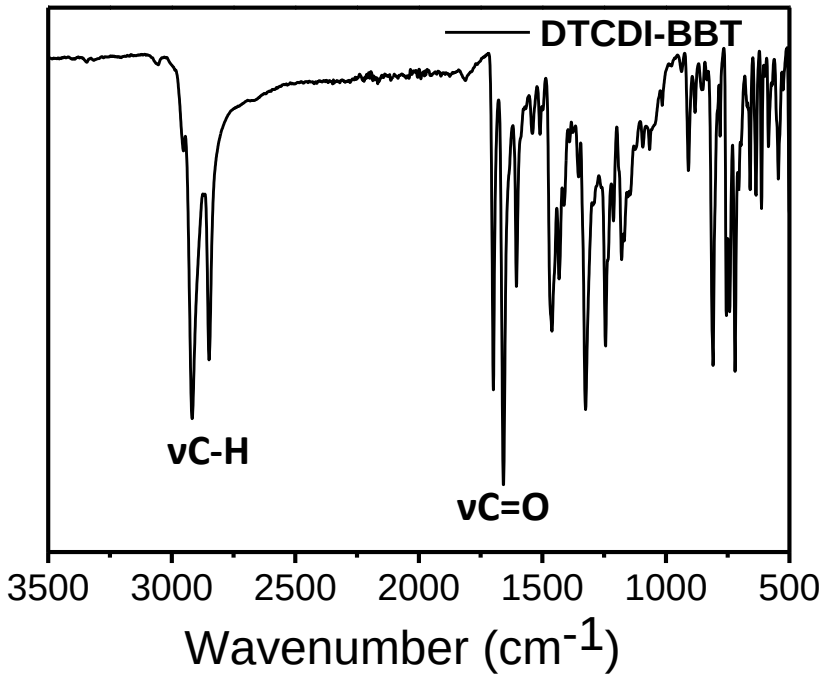

Fig. S15 FT-IR spectra of **DTCDI-BBT**.

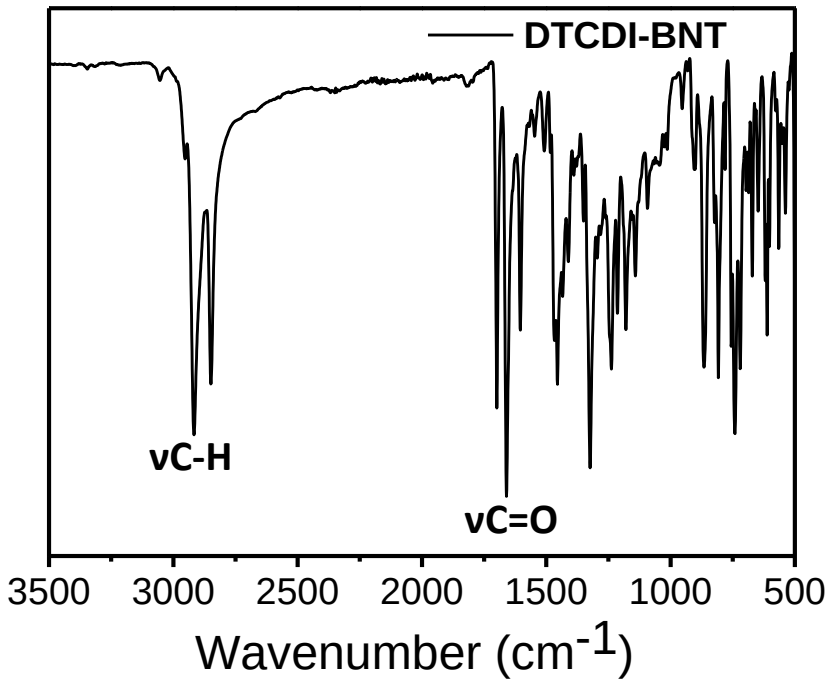

Fig. S16 FT-IR spectra of **DTCDI-BNT**.