

Supporting information

Push-Pull Type Non-Fullerene Acceptors for Polymer Solar Cells: Effect of the Donor Core

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Experimental Section

Materials: All commercially available chemicals were used as received unless otherwise specified. Compound **IT-Sn** was prepared according to the previous reported procedure.¹ **PBDB-T** and MoO₃ (99.9%) were purchased from Solarmer Materials Inc and Alfa Aesar Inc, respectively.

Compound 3: Compound **1** (0.50 g, 0.89 mmol) and compound **2** (0.42 g, 2.67 mmol) were added in 30 mL of tetrahydrofuran (THF). Then, Na₂CO₃ aqueous solution (2 M, 4.24 g) was added. The mixture was deoxygenated by bubbling with nitrogen gas for 30 minutes and then Pd(PPh₃)₄ (0.11 g, 0.09 mmol) was added. The reaction mixture was heated at reflux overnight under nitrogen atmosphere, and then the mixture was cooled to room temperature. The organic layer was extracted by dichloromethane (DCM), and washed with water and brine. The solvent was evaporated and the obtained crude product was purified by column chromatography on silica gel using petroleum ether and DCM as the eluent to give a dark red solid (250 mg, 45% yield). Melting point: 100-102 °C. ¹H NMR (400 MHz, CDCl₃): δ 9.85 (s, 2H), 7.67 (d, *J* = 4.0 Hz, 2H), 7.25–7.23 (m, 4H), 1.97–1.87 (m, 4H), 1.02–0.92 (m, 16H), 0.73–0.61 (m, 14H). HRMS (MALDI) *m/z*: calcd for C₃₅H₄₃O₂S₄ [M+H]⁺, 623.2146; found: 623.2140. Elemental analysis: calcd for C₃₅H₄₂O₂S₄, C: 67.48, H: 6.80; found: C: 67.40, H: 6.79.

CDTDI: Compound **4** (0.39 g, 2 mmol) and compound **3** (0.25 g, 0.40 mmol) were added to a mixture of chloroform (30 mL) with pyridine (1 mL). The reactants were deoxygenated with nitrogen for 30 minutes and refluxed overnight. After the mixture was cooled to room temperature, it was poured into methanol and the precipitate was filtered off. The crude product was purified by column chromatography on silica gel using a mixture of petroleum ether and DCM as the eluent to give a black solid (214 mg, 55% yield). Melting point: 290-292 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.86 (s, 2H), 8.70 (dd, *J* = 6.8, 1.6 Hz, 2H), 7.95–7.93 (m, 2H),

7.81–7.73 (m, 6H), 7.50 (t, $J = 2.4$ Hz, 2H), 7.35 (d, $J = 4.4$ Hz, 2H), 2.03–1.93 (m, 4H), 1.04–0.95 (m, 16H), 0.78–0.64 (m, 14H). ^{13}C NMR (100 MHz, CDCl_3): δ 188.57, 161.28, 160.19, 154.11, 146.59, 140.27, 140.04, 138.24, 137.27, 136.81, 135.79, 135.21, 134.48, 125.31, 124.38, 123.71, 122.17, 121.85, 121.83, 114.64, 114.60, 54.46, 43.31, 35.40, 34.07, 29.71, 27.39, 22.86, 14.11, 10.63. HRMS (MALDI) m/z : calcd for $\text{C}_{59}\text{H}_{51}\text{N}_4\text{O}_2\text{S}_4$ $[\text{M}+\text{H}]^+$, 975.2895; found: 975.2889. Elemental analysis: calcd for $\text{C}_{59}\text{H}_{50}\text{N}_4\text{O}_2\text{S}_4$, C: 72.66, H: 5.17, N: 5.74; found: C: 72.40, H: 5.28, N: 5.46.

Compound 6: IT-Sn (0.84 g, 1.04 mmol) and compound **5** (0.60 g, 3.12 mmol) were dissolved in 30 mL of toluene. The mixture was deoxygenated by bubbling with nitrogen gas for 30 minutes and then $\text{Pd}(\text{PPh}_3)_4$ (0.12 g, 0.10 mmol) was added. The mixture was refluxed overnight under nitrogen atmosphere before it was cooled to room temperature. The solvent was evaporated and the crude product was purified by column chromatography on silica gel using petroleum ether and DCM as the eluent to give an orange solid (230 mg, 32% yield). Melting point: 84–86 °C. ^1H NMR (400 MHz, CDCl_3): δ 9.87 (s, 2H), 7.70 (dd, $J = 4.0, 1.6$ Hz, 2H), 7.58–7.54 (m, 2H), 7.43 (d, $J = 8.0$ Hz, 1H), 7.37 (d, $J = 3.6$ Hz, 1H), 7.30–7.28 (m, 4H), 2.03–1.94 (m, 4H), 1.00–0.81 (m, 16H), 0.73–0.55 (m, 14H). HRMS (MALDI) m/z : calcd for $\text{C}_{41}\text{H}_{47}\text{O}_2\text{S}_4$ $[\text{M}+\text{H}]^+$, 699.2459; found: 699.2453. Elemental analysis: calcd for $\text{C}_{41}\text{H}_{46}\text{O}_2\text{S}_4$, C: 70.44, H: 6.63; found: C: 70.43, H: 6.68.

ITDI: The synthetic route was the same as **CDTDI**. 42% yield. Melting point: 170–172 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.87 (s, 2H), 8.71 (dd, $J = 6.4, 1.2$ Hz, 2H), 7.96 – 7.94 (m, 2H), 7.81 – 7.74 (m, 6H), 7.62 – 7.53 (m, 4H), 7.47 (d, $J = 8.0$ Hz, 1H), 7.40 – 7.38 (m, 3H), 2.08 – 1.97 (m, 4H), 1.02–0.83 (m, 16H), 0.73–0.58 (m, 14H). ^{13}C NMR (100 MHz, CDCl_3): δ 188.27, 160.08, 157.62, 154.82, 154.56, 153.37, 148.13, 146.58, 146.40, 144.82, 139.97, 138.74, 137.97,

137.41, 136.81, 135.82, 135.67, 135.23, 134.48, 131.09, 128.48, 125.27, 124.57, 124.45, 123.77, 123.70, 122.46, 121.96, 121.76, 120.84, 120.00, 54.62, 43.73, 35.17, 34.31, 28.60, 27.54, 22.85, 14.09, 10.75. HRMS (MALDI): calcd for $C_{65}H_{55}N_4O_2S_4$ $[M+H]^+$, 1051.3208; found: 1051.3205. Elemental analysis: calcd for $C_{65}H_{54}N_4O_2S_4$, C: 74.25, H: 5.18, N: 5.33; found: C: 73.99, H: 5.43, N: 4.95.

Measurements: 1H NMR and ^{13}C NMR spectra were measured in $CDCl_3$ on Bruker AVANCE-400 spectrometer with tetramethylsilane (TMS) as the internal reference. Elemental analysis was performed on an Elementar Vario MICRO analyzer. The melting points of the compounds were measured on WRX-4 Melting Point apparatus. Mass spectra were conducted on a Thermo Fisher Scientific LTQ FT Ultra spectrometer. UV-vis absorption spectra were taken on Perkin-Elmer Lambda 350 UV-vis spectrophotometer. Atomic force microscopy (AFM) was conducted in the tapping mode with a Bruker Nanoscope V station. Mobility measurements were conducted on an Agilent 4155C semiconductor parameter analyzer. The thickness of the film was measured by a Bruker Dektak XT surface profilometer. Solar cell characterization was performed under AM 1.5 G irradiation (100 mW cm^{-2}) from an Oriel Sol3A simulator (Newport) with a NREL certified silicon reference cell. After a simple encapsulation by epoxy kits (general purpose, Sigma Aldrich) in the glove-box, the PSCs were illuminated through their ITO sides. Current density–voltage ($J-V$) curves were tested in air by a Keithley 2440 source measurement unit. External quantum efficiency (EQE) spectra were measured on a Newport EQE measuring system.

Electron mobility was measured using the space charge limited current model (SCLC), using a diode configuration of ITO/ZnO/active layer/Ca/Al, and taking current–voltage measurements

in the range of 0–10 V in the dark. The SCLC mobilities were estimated by fitting the results to the Mott–Gurney relationship,²

$$J = \frac{9}{8} \epsilon_0 \epsilon_r \mu \frac{V^2}{L^3}$$

where ϵ_0 is the permittivity of free space ($8.85 \times 10^{-12} \text{ F m}^{-1}$), ϵ_r is the dielectric constant of the active layer material (assumed to be 3, which is a typical value for organic semiconductors), μ is the electron mobility, V is the voltage drop across the device ($V = V_{\text{APPL}} - V_{\text{BI}}$, where V_{APPL} is the applied voltage to the device, and V_{BI} is the built-in voltage due to the difference in work function of the two electrodes), and L is the active layer thickness.

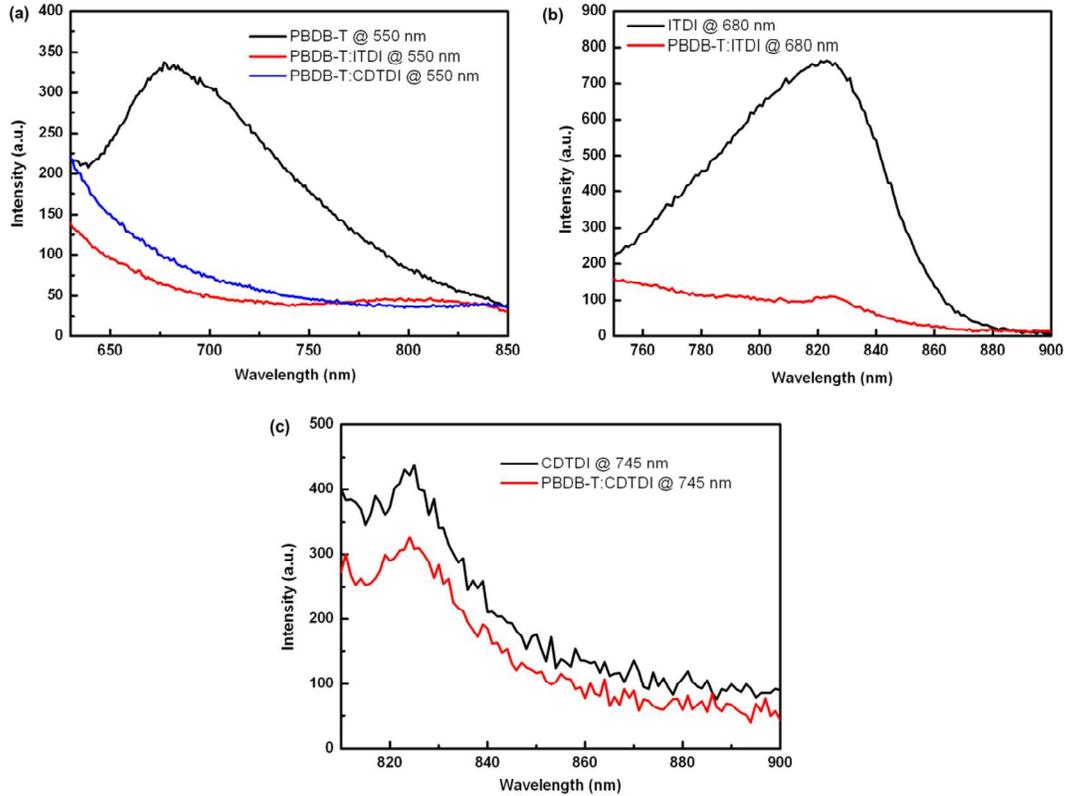


Figure S1. Photoluminescence spectra of (a) **PBDB-T**, **PBDB-T:ITDI**, and **PBDB-T:CTDI**, excited at 550 nm, (b) **ITDI** and **PBDB-T:ITDI** excited at 680 nm, and (c) **CTDI** and **PBDB-T:CTDI** excited at 745 nm.

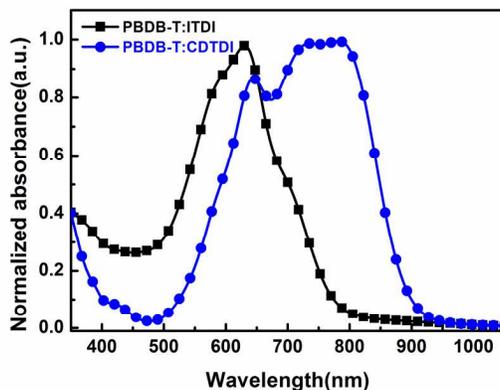


Figure S2. The normalized absorption spectra of **PBDB-T:ITDI** and **PBDB-T:CDTDI** blend films.

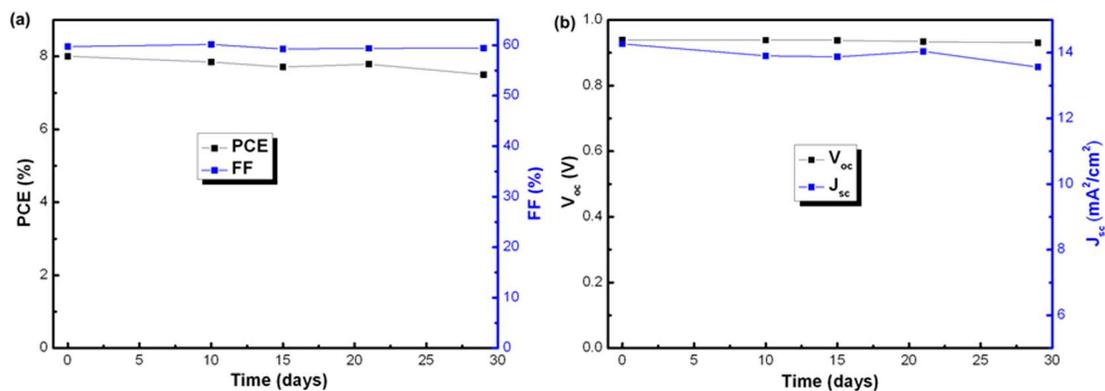


Figure S3. Device stability of **PBDB-T:ITDI**-based PSCs: (a) PCE and FF *versus* storage time, (b) V_{oc} and J_{sc} *versus* storage time. The samples were encapsulated with epoxy and stored in air.

Table S1. Device performances of PSCs based on **PBDB-T:ITDI** (D/A; 1:1) with different annealing temperatures (T).

Active layer	T [°C]	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE (best) [%] ^a
PBDB-T:ITDI	100	0.92 ± 0.00	13.80 ± 0.11	55.03 ± 0.79	7.00 ± 0.15 (7.20)
PBDB-T:ITDI	120	0.93 ± 0.01	13.55 ± 0.37	58.04 ± 0.68	7.28 ± 0.08 (7.36)
PBDB-T:ITDI	140	0.93 ± 0.00	13.02 ± 0.25	58.42 ± 0.87	7.05 ± 0.13 (7.25)

^a Average PCEs and standard deviations were obtained from 8 devices.

Table S2. Device performances of PSCs based on **PBDB-T:ITDI** (D/A; 1:1) with different additive.

Additive	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE (best) [%] ^a
1% DPE	0.93 ± 0.00	13.77 ± 0.16	59.43 ± 0.39	7.61 ± 0.06 (7.67)
2% DPE	0.94 ± 0.00	13.94 ± 0.29	59.78 ± 0.56	7.82 ± 0.11 (8.00)
3% DPE	0.94 ± 0.00	12.49 ± 0.19	59.05 ± 0.35	6.90 ± 0.10 (7.04)
1% DIO	0.93 ± 0.00	13.46 ± 0.11	58.00 ± 0.59	7.28 ± 0.12 (7.44)

^a Average PCEs and standard deviations were obtained from 8 devices.

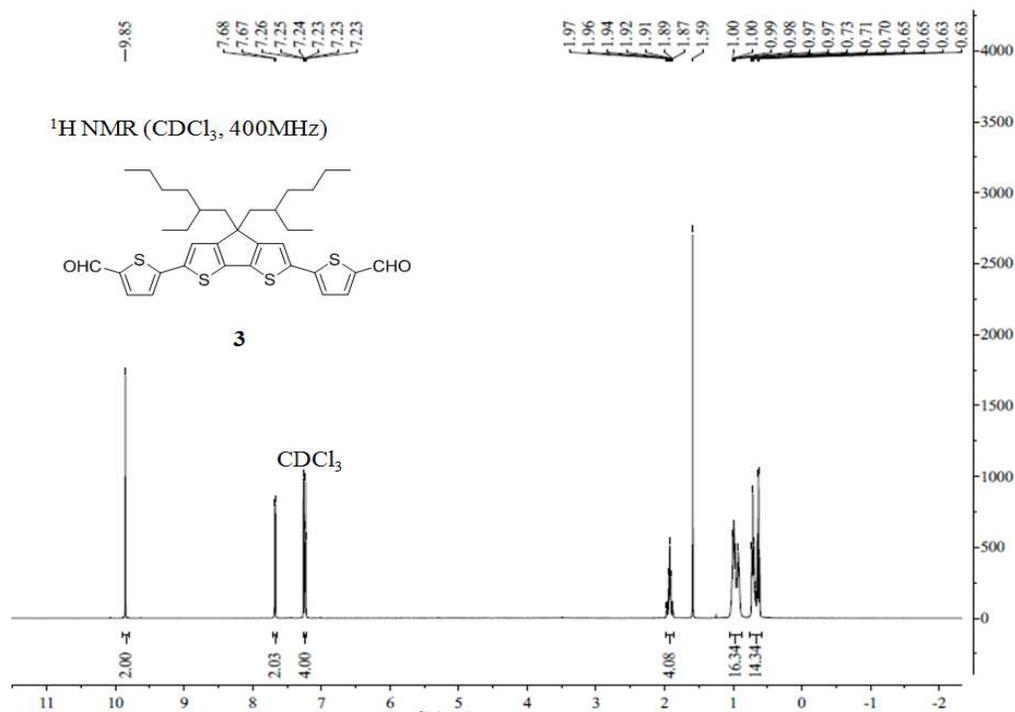


Figure S4. ¹H NMR spectrum of compound **3**.

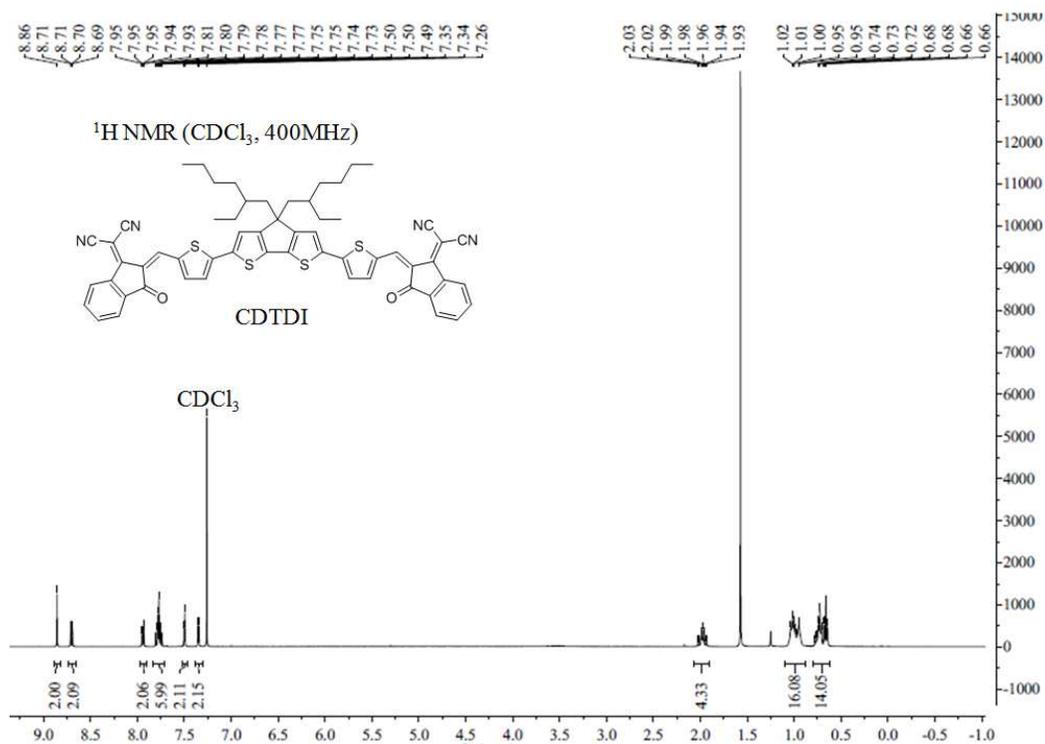


Figure S5. ¹H NMR spectrum of CDTDI.

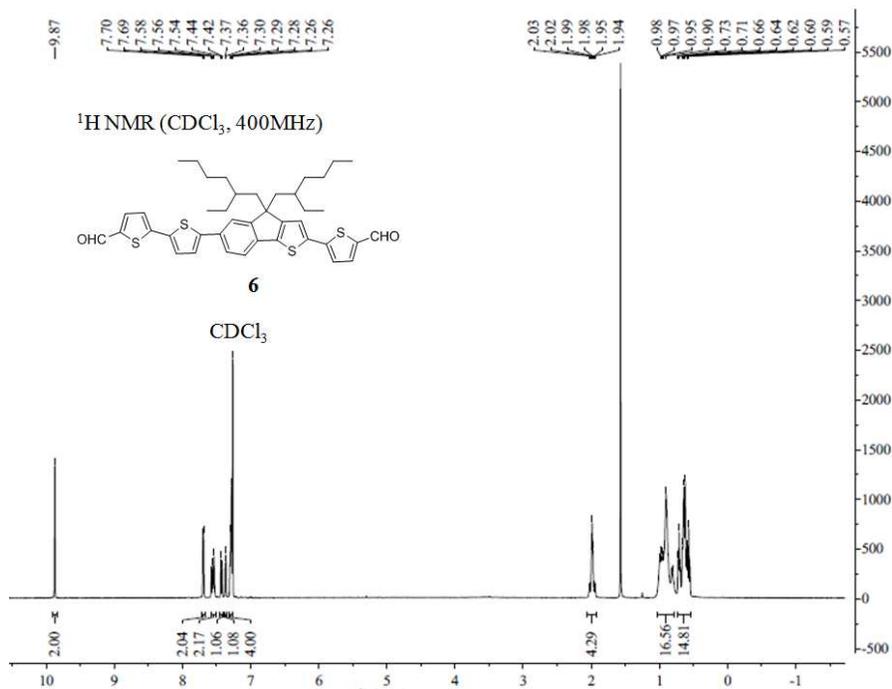


Figure S6. ¹H NMR spectrum of compound 6.

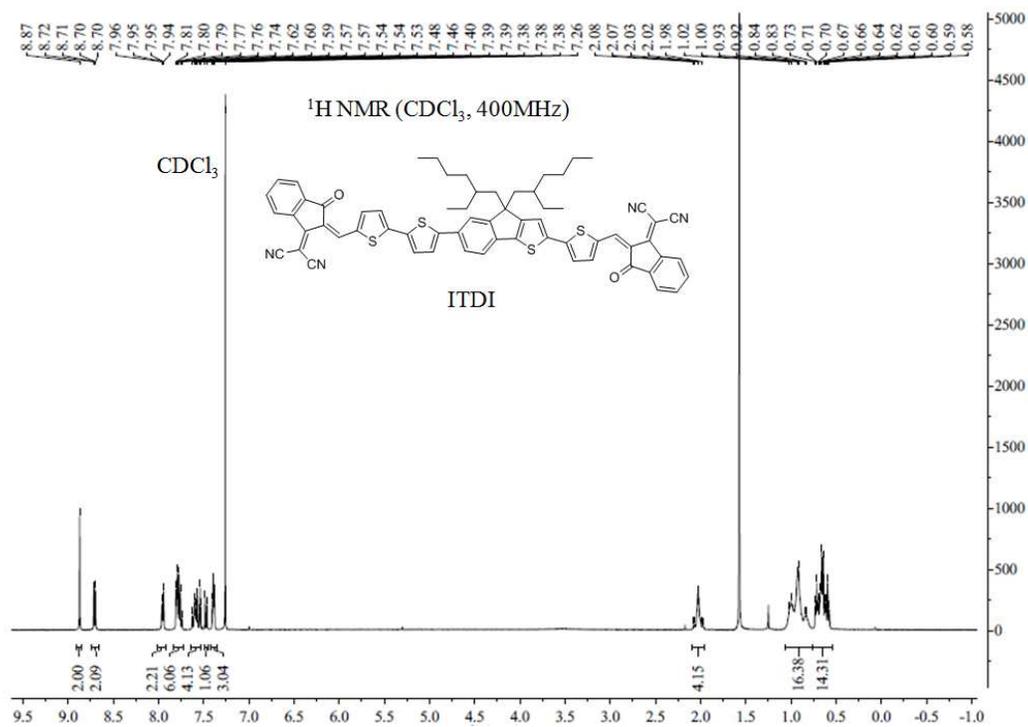


Figure S7. ¹H NMR spectrum of ITDI.

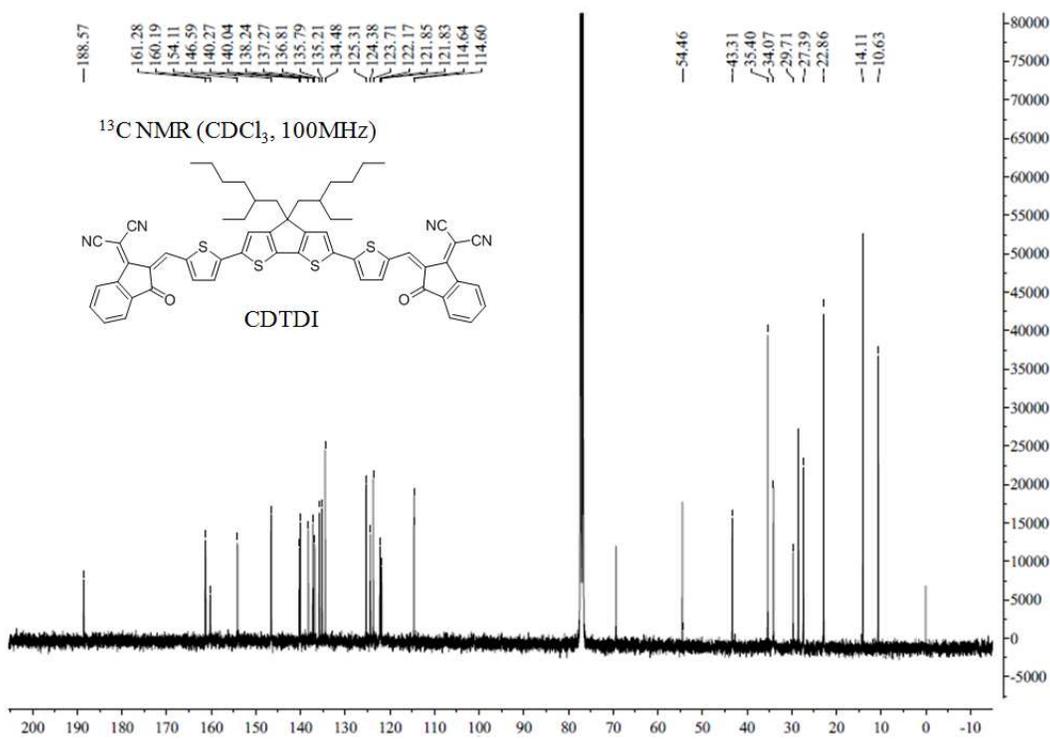


Figure S8. ¹³C NMR spectrum of CDTDI.

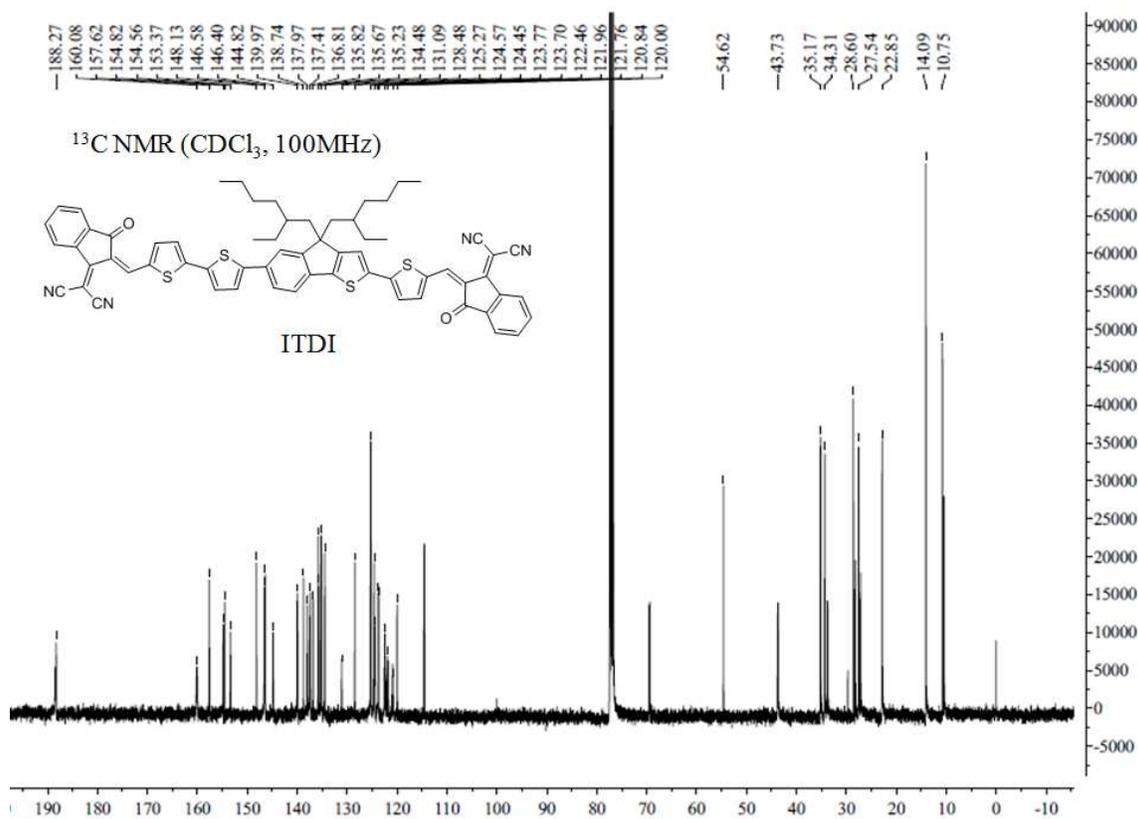


Figure S9. ¹³C NMR spectrum of ITDI.

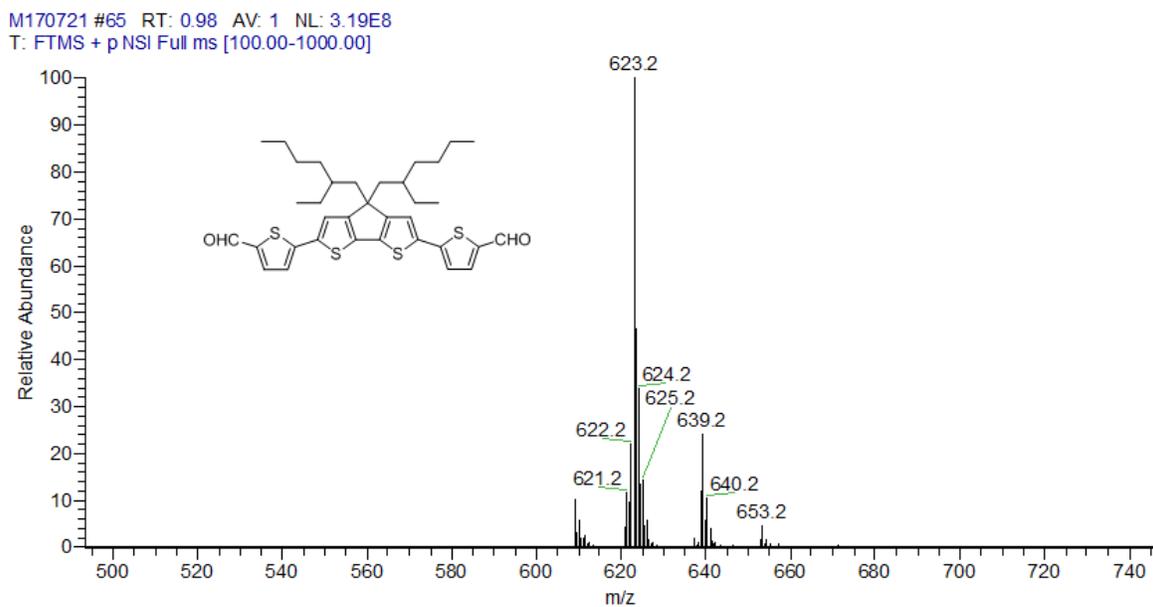


Figure S10. Mass spectrum of compound 3.

M170723 #17 RT: 0.25 AV: 1 NL: 8.11E7
T: FTMS + p NSI Full ms [100.00-1000.00]

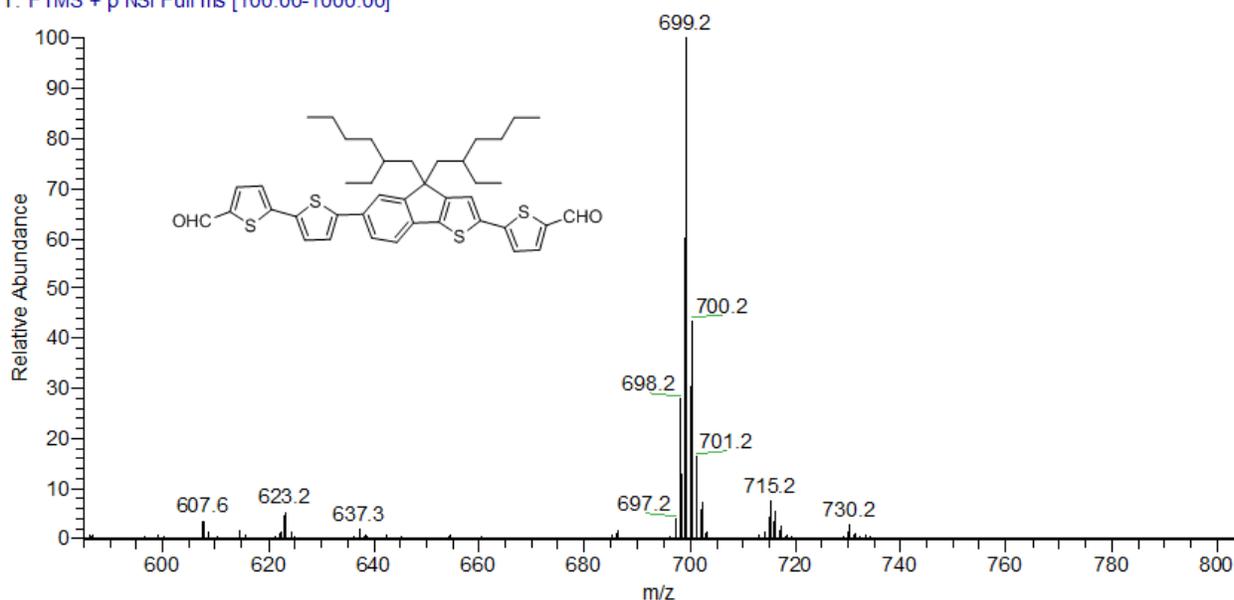


Figure S11. Mass spectrum of compound 6.

M170385 #178 RT: 2.66 AV: 1 NL: 3.02E6
T: FTMS + p NSI Full ms [100.00-1500.00]

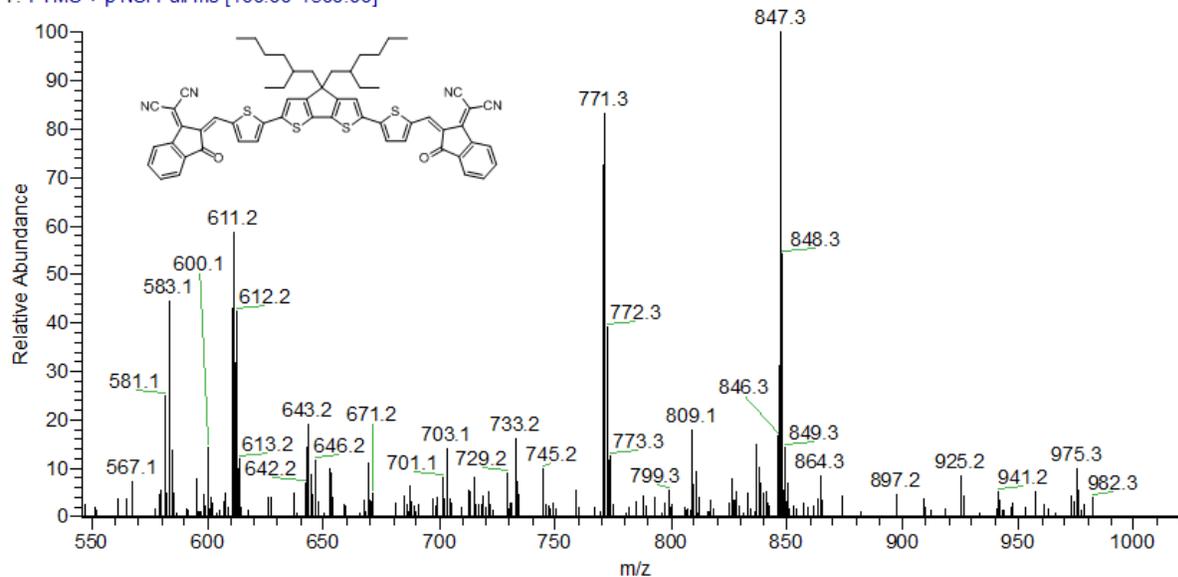


Figure S12. Mass spectrum of CDTDI.

M170387 #63 RT: 0.93 AV: 1 NL: 1.86E6
T: FTMS + p NSI Full ms [100.00-1500.00]

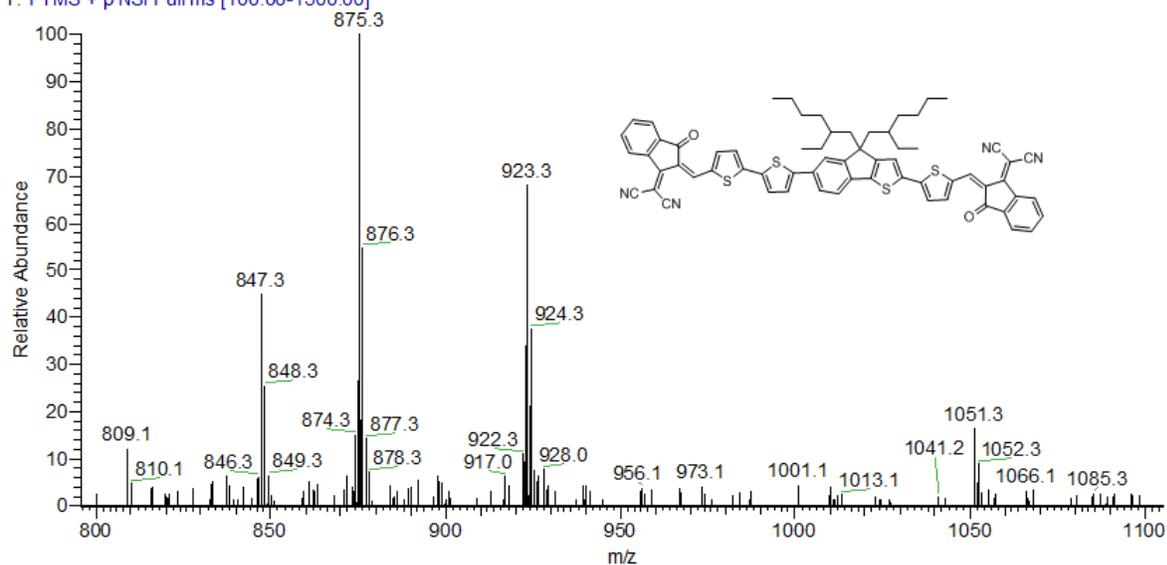


Figure S13. Mass spectrum of ITDI.

REFERENCES

- (1) Wang, M.; Cai, D.; Yin, Z.; Chen, S.-C.; Du, C.-F.; Zheng, Q., Asymmetric-Indenothiophene-Based Copolymers for Bulk Heterojunction Solar Cells with 9.14% Efficiency. *Adv. Mater.* **2016**, 28 (17), 3359-3365.
- (2) Shen, Y. L., Hosseini, A. R., Wong, M. H. and Malliaras, G. G., How to Make Ohmic Contacts to Organic Semiconductors. *ChemPhysChem*, **2004**, 5 (1), 16-25.