

Supporting Information

Fused-Ring Non-Fullerene Acceptor Based on a Benzo[1,2-*b*:4,5-*b'*]dithiophene Central Core with Thieno[3,2-*b*]thiophene Side-Chain for High-Efficient Organic Solar Cells

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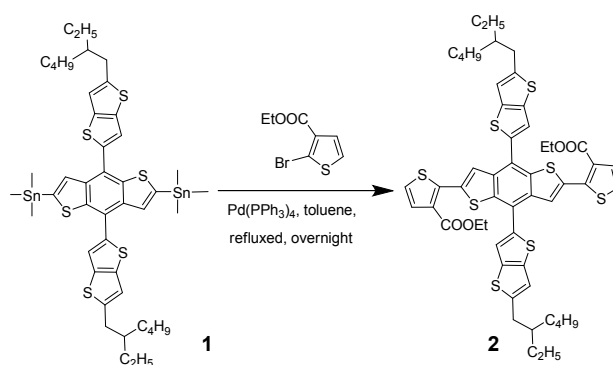
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1. Detailed experimental section

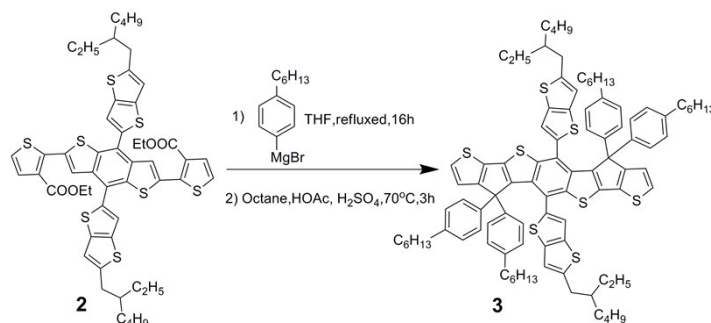
(1) Synthesis

(4,8-bis(5-(2-ethylhexyl)thio[3,4-*b'*]-thiophenyl-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(trimethylstannane) **1** was synthesized according to our previous literature.^[1] Unless stated otherwise, all the chemical reagents and solvents were obtained commercially and were used without further purification. Tetrahydrofuran (THF) was dried by potassium sodium alloy under refluxing condition.

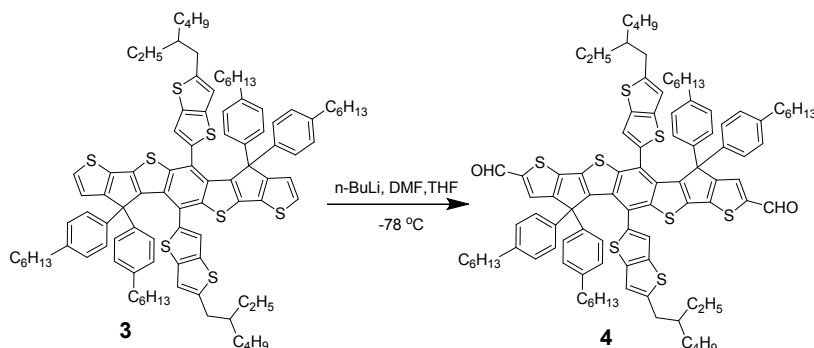


Synthesis of compound 2: Compound **1** (1.02 g, 1 mmol) and Ethyl 2-bromothiophene-3-carboxylate (580 mg, 2.5 mmol) were dissolved in anhydrous toluene (50 mL), then Pd(PPh₃)₄ (58 mg, 0.05 mmol) was added, and the mixture was deoxygenated with argon for 20 min. The solution mixture was stirred at 110 °C for 48 h, and then cooled to room temperature. 100 mL of water was added and the mixture was extracted with dichloromethane (2 × 100 mL). The organic phase was dried over anhydrous Na₂SO₄. After removing the solvent, the residue was purified by column chromatography on silica gel using petroleum ether/dichloromethane (1:2) as an eluent yielding a pale yellow solid (800 mg, 80%). ¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.98 (s, 2H), 7.61 (s, 2H), 7.52 (d, 2H), 7.27 (d, 2H), 7.02 (s, 2H), 4.30 (q, 4H), 2.89 (d, 4H), 1.67-1.69 (m, 2H), 1.33-1.45 (m, 8H), 1.21 (t, 6H), 0.91-0.96 (m, 6H). ¹³C NMR (100

MHz, CDCl₃), δ (ppm): 163.01, 147.96, 142.02, 140.62, 139.58, 138.72, 137.69, 137.02, 135.82, 130.76, 129.55, 125.34, 125.24, 124.07, 120.68, 117.37, 61.03, 41.50, 35.29, 32.42, 28.92, 25.51, 23.08, 14.23, 14.07, 10.87. MS (ESI) m/z: [M] calcd. for C₅₂H₅₄O₄S₈, 998.18; found, 998.01.

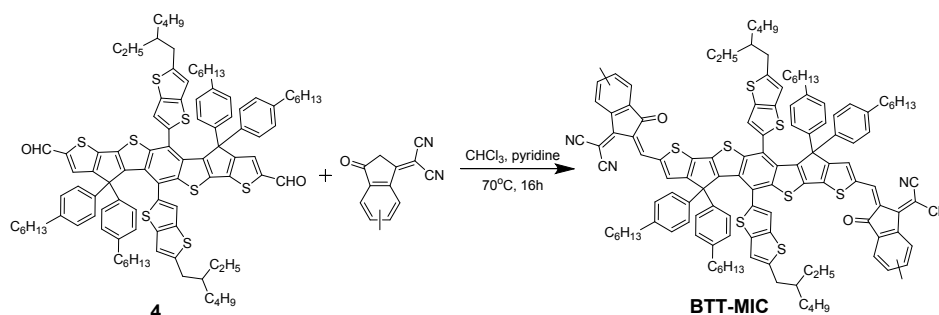


Synthesis of compound 3: A Grignard reagent was prepared by the following procedure: To a suspension of magnesium turnings (188 mg, 7.8 mmol) and 3-4 drops of 1,2-dibromoethane in dry THF (6 mL) was slowly added 1-bromo-4-hexylbenzene (2.07 g, 8.6 mmol) dropwise, and the mixture was stirred for 2 h. To a solution of compound **2** (780 mg, 0.78 mmol) in dry THF (10 mL) under nitrogen was added the prepared Grignard reagent dropwise at room temperature. The resulting mixture was stirred at reflux for 16 h. The reaction solution was extracted with diethylether (3 × 50 mL). The combined organic layer was dried over Na₂SO₄. After removal of the solvent under reduced pressure, a brown solid was obtained and directly used for next step reaction without further purification. To a solution of this brown solid in octane (50 mL) was added acetic acid (10 mL) and sulfuric acid (0.1 mL) slowly. The resulting solution was stirred at 70 °C for 3 h. After removal of the octane under reduced pressure, the residue was extracted by diethyl ether (50 mL × 2). Then, the crude products were purified by column chromatography on silica gel using petroleum ether/dichloromethane (10: 1) to give a yellow solid (510 mg, 2 steps overall yield 43%).

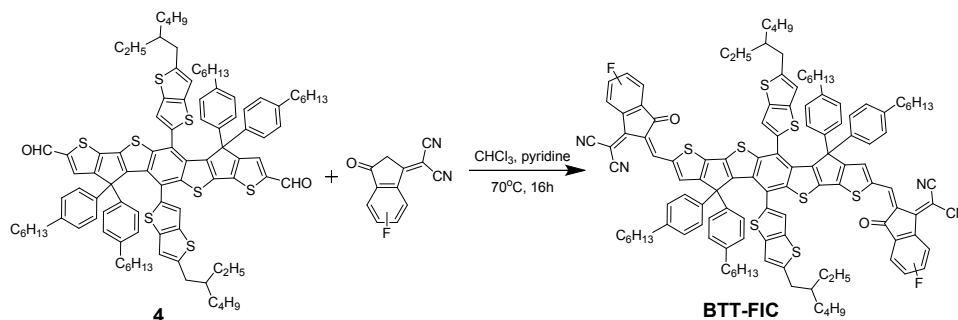


Synthesis of compound 4: In a dry three-necked round-bottomed flask, compound **3** (450 mg, 0.3 mmol) was dissolved in anhydrous THF (20 mL). The mixture was deoxygenated with argon for 20 min. At -78 °C, a solution of *n*-butyllithium (1.6 M in hexane, 1.8 mL, 2.9 mmol) was added dropwise. After 1 h of stirring at -78 °C, anhydrous DMF (0.2 mL) was added to this solution. The mixture was warmed to room temperature and stirred overnight. Brine (25 mL) was added and the mixture was extracted with dichloromethane (2 × 50 mL). The organic phase was dried over anhydrous Na₂SO₄. After the solvent had been removed, the residue was purified by column chromatography on silica gel using petroleum ether/dichloromethane (1: 1) as eluent, yielding a yellow solid (384 mg, 81%). ¹H NMR (400 MHz, CDCl₃), δ (ppm): 9.62 (s, 2H), 7.35 (s, 2H), 6.99-7.05 (m, 8H), 6.80 (s, 2H), 6.71-6.74 (m, 4H), 6.61-6.63 (m, 4H), 6.46 (m, 2H), 2.91 (d, 4H), 2.62 (t, 4H), 2.50 (t, 4H), 1.65-1.72 (m, 10H), 1.33-1.52 (m, 40H), 0.89-1.02 (m, 24). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 182.57, 165.00, 154.41, 150.61, 147.76, 146.01, 143.77, 142.05, 141.35, 140.98, 137.60, 135.54, 134.72, 130.78, 128.40, 128.18, 127.53, 125.64, 122.61, 116.92, 63.43, 41.52, 38.17, 35.56, 35.47, 35.33, 32.56, 32.48, 31.89, 31.52, 31.42, 29.06, 29.01,

25.73, 25.61, 23.14, 22.75, 22.72, 14.26, 14.23, 10.97, 10.86. MS (ESI) m/z: [M] calcd. for C₉₈H₁₁₀O₂S₈, 1574.63; found, 1574.45.



Synthesis of BTT-MIC: To a three-necked round bottom flask were added compound **4** (120 mg, 0.076 mmol), DCI-M (65 mg, 0.3 mmol), pyridine (0.2 mL) and chloroform (20 mL). The mixture was deoxygenated with nitrogen for 20 min and then stirred at reflux for 16 h. After cooling to room temperature, the mixture was poured into methanol (200 mL) and filtered. The crude product was purified by column chromatography on silica gel using petroleum ether/dichloromethane (1: 1) as eluent yielding a purple solid (126 mg, 85%). ¹H NMR (400 MHz, CDCl₃), δ (ppm): 8.62 (s, 2H), 8.49 (d, 1H), 8.40 (s, 1H), 7.74 (d, 1H), 7.63 (s, 1H), 7.47 (m, 2H), 7.33 (s, 2H), 7.03-7.08 (m, 8H), 6.83 (s, 2H), 6.74-6.83 (m, 4H), 6.63-6.65 (m, 4H), 6.47 (d, 2H), 2.94 (d, 4H), 2.63 (t, 4H), 2.48-2.53 (m, 10H), 1.66-1.75 (m, 10H), 1.26-1.42 (m, 40H), 0.88-1.05 (m, 24H). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 187.26, 186.89, 164.65, 159.38, 159.33, 155.38, 155.33, 151.31, 151.19, 150.65, 146.91, 146.81, 145.46, 145.03, 141.35, 141.12, 140.17, 140.08, 139.98, 139.95, 139.89, 139.20, 136.62, 136.44, 136.15, 136.09, 135.68, 135.62, 134.79, 134.30, 134.23, 133.61, 133.46, 133.37, 130.78, 127.43, 127.22, 126.49, 125.17, 124.50, 124.09, 123.01, 122.58, 121.69, 121.23, 121.16, 67.18, 66.64, 62.24, 40.50, 34.52, 34.43, 34.33, 34.20, 31.48, 31.44, 30.83, 30.81, 30.47, 30.38, 28.67, 28.04, 27.99, 27.97, 27.92, 24.69, 24.60, 22.10, 21.70, 21.67, 21.48, 20.97, 13.25, 13.19, 9.95, 9.88. MALDI-TOF-MS m/z: [M] calcd. for C₁₂₄H₁₂₂N₄O₂S₈, 1954.73, found 1954.09.



Synthesis of BTT-FIC: To a three-necked round bottom flask were added compound **4** (120 mg, 0.076 mmol), DCI-F (65 mg, 0.3 mmol), pyridine (0.2 mL) and chloroform (20 mL). The mixture was deoxygenated with nitrogen for 20 min and then stirred at reflux for 16 h. After cooling to room temperature, the mixture was poured into methanol (200 mL) and filtered. The residue was purified by column chromatography on silica gel using petroleum ether/dichloromethane (1:1) as eluent yielding a purple solid (135 mg, 88%). ¹H NMR (400 MHz, CDCl₃), δ (ppm): 8.65 (s, 2H), 8.31 (q, 2H), 7.84 (q, 2H), 7.34 (m, 4H), 7.03-7.06 (m, 8H), 6.83 (s, 2H), 6.72 (br, 4H), 6.63-6.65 (m, 4H), 6.45 (q, 2H), 2.92 (d, 4H), 2.63 (t, 4H), 2.52 (t, 4H), 1.66-1.70 (m, 10H), 1.34-1.42 (m, 40H), 0.91-1.05 (m, 24H). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 186.72, 167.84, 165.88, 165.28, 158.88, 156.91, 153.40, 151.90, 148.06, 147.96, 142.45, 142.25, 142.18, 142.08, 141.22, 141.19, 141.00, 138.12, 137.98, 137.02, 136.94, 136.66, 135.19, 135.11, 134.33, 134.25, 132.97, 131.88, 128.50, 128.41, 128.28, 127.52, 126.40, 122.76, 121.44, 116.96, 116.89, 114.74, 114.51, 114.36, 114.29, 112.82, 112.56, 69.18, 63.30, 41.53, 35.54, 35.45, 35.35, 35.23,

32.51, 32.46, 31.86, 31.84, 31.50, 31.40, 29.70, 29.06, 29.02, 29.00, 28.95, 25.71, 25.63, 23.13, 22.72, 22.70, 14.32, 14.28, 14.22, 10.97, 10.90. MALDI-TOF-MS m/z: [M] calcd. for C₁₂₂H₁₁₆F₂N₄O₂S₈, 1962.68, found 1962.12.

(2) Electrochemical characterization

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of the BTT-MIC and BTT-FIC acceptors were determined by electrochemical cyclic voltammetry (CV). The CV traces of films conducted on a CHI voltammetric analyzer in acetonitrile solution containing 0.1 M tetrabutylammonium hexafluorophosphate (*n*-Bu₄NPF₆) as supporting electrolyte at room temperature by using a scan rate of 100 mV s⁻¹ and conventional three-electrode configuration consisting of a platinum working electrode with 2 mm diameter, a platinum wire counter electrode and a Ag/AgCl wire reference electrode. The potential of ferrocene 0.40 V vs SCE is used as internal standard. On the basis of 4.8 eV below vacuum for the energy level of Fc/Fc⁺, the HOMO and LUMO levels of the both BTT-MIC and BTT-FIC acceptors were calculated from the onset oxidation potentials (E_{onset}^{ox}) and onset reduction potentials (E_{onset}^{red}) respectively according to the following equations:

$$\text{HOMO} = -e(E_{\text{onset}}^{\text{ox}} - E_{\text{Fc/Fc}^+} + 4.8\text{V})$$

$$\text{LUMO} = -e(E_{\text{onset}}^{\text{red}} - E_{\text{Fc/Fc}^+} + 4.8\text{V})$$

(3) Photovoltaic Device Fabrication

The patterned indium tin oxide (ITO) glass coated substrates (sheet resistance 15 Ω/□) were consecutively cleaned in ultrasonic baths containing detergent, de-ionized water and ethanol, respectively. The cleaned ITO substrates were blow-dried by high pure nitrogen gas and then treated by oxygen plasma for 1 min to improve its work function and clearance. Then, poly-(3,4-ethylenedioxythiophene):poly-(styrenesulphonic acid) (PEDOT:PSS) (clevios P VP Al 4083, purchased from H.C. Starck co. Ltd.) thin films were fabricated on the cleaned ITO substrates by spin-coating method at 5000 round per minute (RPM) for 40 s, and then annealed at 150 °C for 10 minutes in ambient conditions. After annealing treatment, the ITO substrates coated PEDOT:PSS films were transferred to a high-purity nitrogen-filled glove box to fabricate active layers. The donor materials PM6 was purchased from Solarmer Materials Inc and used as received. The materials PM6:BTT-MIC and PM6:BTT-FIC were all dissolved in chlorobenzene (with or without 1,8-diiodooctane) to prepare 20 mg/mL blend solutions. The blend solutions were spin-coated on PEDOT:PSS films at 2200 rpm in a high purity nitrogen-filled glove box to fabricate the active layers. Subsequently, the active layers were then annealed for 10 min under different temperatures. The optimized thickness of the active layer is ~100 nm, which was measured by Ambios Technology XP-2 stylus Profiler. After that, PDIN solution (2 mg ml⁻¹ in methanol with 0.25 vol% acetic acid) was spin-coated on the top of active layers at 5000 RPM for 30 s. The cathode of Al was deposited by thermal evaporation with a shadow mask under 10⁻⁴ Pa and the thickness of 100 nm was monitored by a quartz crystal microbalance. Therefore, organic solar cells (OSCs) were fabricated with the architecture of ITO/PEDOT:PSS/active layer/PDIN/Al. The active area of PSCs is about 3.8 mm², which is defined by the vertical overlap of ITO anode and Al cathode.

(3) Space charge-limited current (SCLC) device fabrication

The structure of electron-only devices is ITO/ZnO/active layer/Al and the structure of hole-only devices is ITO/PEDOT:PSS/active layer/MoO₃/Ag. The fabrication conditions of the active layer films are same with those for the solar cells. The charge mobilities are generally described by the Mott-Gurney equation:^[2-4]

$$J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu \frac{V^2}{L^3} \quad (1)$$

where J is the current density, ε_0 is the permittivity of free space (8.85×10^{-14} F/cm), ε_r is the dielectric constant of used materials, μ is the charge mobility, V is the applied voltage and L is the active layer thickness. The ε_r parameter is assumed to be 3, which is a typical value for organic materials. In organic materials, charge mobility is usually field dependent and can be described by the disorder formalism, typically varying with electric field, $E=V/L$, according to the equation:

$$\mu = \mu_0 \exp\left[0.89\gamma\sqrt{\frac{V}{L}}\right] \quad (2)$$

where μ_0 is the charge mobility at zero electric field and γ is a constant. Then, the Mott-Gurney equation can be described by:

$$J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu_0 \frac{V^2}{L^3} \exp\left[0.89\gamma\sqrt{\frac{V}{L}}\right] \quad (3)$$

In this case, The charge mobilities were estimated using the following equation:^[4]

$$\ln\left(\frac{JL^3}{V^2}\right) = 0.89\gamma\sqrt{\frac{V}{L}} + \ln\left(\frac{9}{8} \varepsilon_r \varepsilon_0 \mu_0\right) \quad (4)$$

(4) Solution, Film and Device Characterization

¹H NMR and ¹³C NMR spectra were recorded on a Bruker Advanced II (400 MHz) spectrometer using tetramethylsilane (TMS) as internal standard. The high resolution mass spectra (HRMS) were performed on Thermo Scientific LTQ Orbitrap XI using ESI. The ultraviolet-visible (UV-Vis) absorption spectra of neat and blend films were obtained using a Shimadzu UV-3101 PC spectrometer. The current density-voltage (J - V) curves of all PSCs were measured in a high-purity nitrogen-filled glove box using a Keithley 2400 source meter. AM 1.5G irradiation at 100 mW/cm² provided by An XES-40S2 (SAN-EI Electric Co., Ltd.) solar simulator (AAA grade, 70×70 mm² photobeam size), which was calibrated by standard silicon solar cells (purchased from Zolix INSTRUMENTS CO. LTD). The external quantum efficiency (EQE) spectra of solar cells were measured in air conditions by a Zolix Solar Cell Scan 100. The morphology of the active layers was investigated by atomic force microscopy (AFM) using a Dimension Icon AFM (Bruker) in a tapping mode. Transmission electron microscopy (TEM) images of the active layers were obtained by using a JEOL JEM-1400 transmission electron microscope operated at 80 kV.

2. Additional Experimental Results

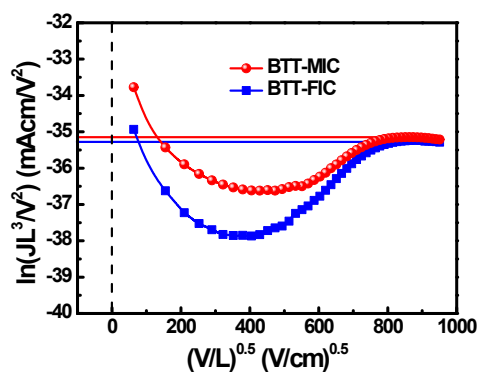


Fig. S1. The $\ln(JL^3/V^2)$ vs $(V/L)^{0.5}$ curves of electron-only ITO/ZnO/BTT-MIC or BTT-FIC/Al device.

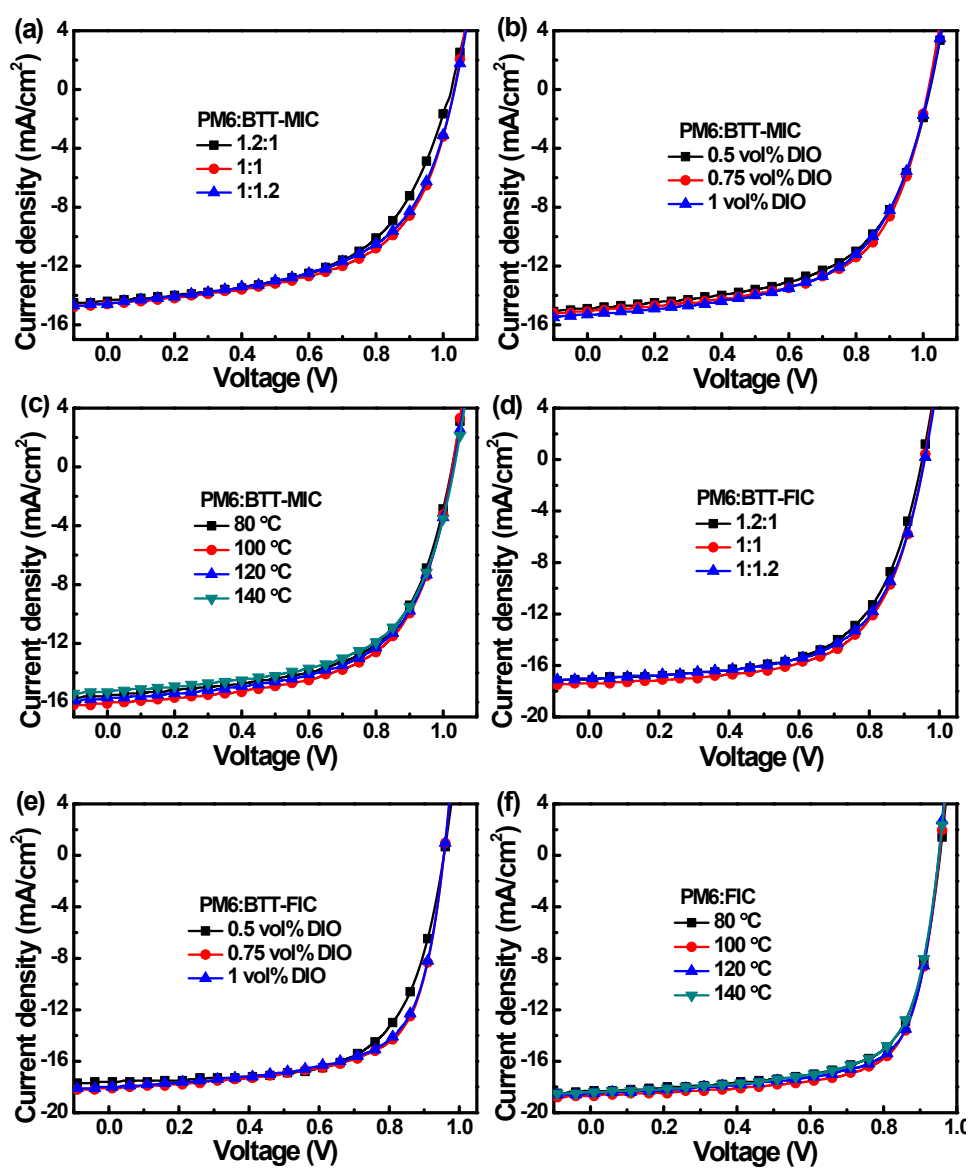


Fig. S2. The J - V curves of BTT-MIC or BTT-FIC based OSCs with (a or d) different ratios of donor to acceptor, (b or e) different contents of DIO as additive and (c or f) different annealing temperature under AM 1.5 G illumination at intensity of 100 mW cm⁻².

Table S1 The photovoltaic parameters of the BTT-MIC or BTT-FIC based OSCs

PM6:BTT-MIC [wt%]:[wt%]	DIO [vol%]	Annealing [°C]	PCE [%]	J_{sc} [mA cm ⁻²]	V_{oc} [V]	FF [%]
1.2:1	w/o	w/o	8.25	14.19	1.031	56.38
1:1	w/o	w/o	8.66	14.37	1.032	58.39
1:1	0.5	w/o	8.85	14.73	1.020	58.89
1:1	0.75	w/o	9.20	14.91	1.015	60.80
1:1	0.75	80	9.64	15.38	1.026	61.11
1:1	0.75	100	10.04	15.90	1.027	61.51
1:1	0.75	120	9.83	15.60	1.031	61.14
1:1	0.75	140	9.51	15.10	1.033	60.97
1:1	1	w/o	9.06	15.15	1.013	59.06
1:1.2	w/o	w/o	8.44	14.30	1.033	57.13

PM6: BTT-FIC [wt%]:[wt%]	DIO [vol%]	Annealing [°C]	PCE [%]	J_{sc} [mA cm ⁻²]	V_{oc} [V]	FF [%]
1.2:1	w/o	w/o	9.98	16.90	0.952	62.07
1:1	w/o	w/o	10.45	17.29	0.957	63.16
1:1	0.5	w/o	11.03	17.54	0.956	65.76
1:1	0.75	w/o	11.64	17.94	0.956	67.90
1:1	0.75	80	12.10	18.26	0.954	69.43
1:1	0.75	100	12.65	18.54	0.953	71.63
1:1	0.75	120	12.47	18.41	0.950	71.37
1:1	0.75	140	12.08	18.27	0.949	69.68
1:1	1	w/o	11.50	17.88	0.956	67.27
1:1.2	w/o	w/o	10.18	16.89	0.959	62.87

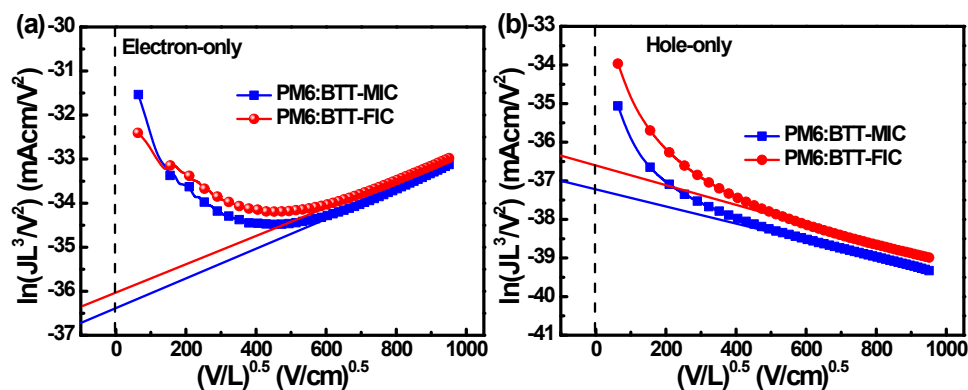
**Fig. S3.** The $\ln(JL^3/V^2)$ vs $(V/L)^{0.5}$ curves of a) electron-only ITO/ZnO/active layer/Al device and b) hole-only ITO/PEDOT:PSS/active layer/MoO₃/Ag devices.

Table S2 Key parameters abstracted from J_{ph} - V_{eff} curves of the optimized OSCs

	J_{sat} [mA cm ⁻²]	J_{ph}^* [mA cm ⁻²]	$J_{ph}^\&$ [mA cm ⁻²]	J_{ph}^*/J_{sat} [%]	$J_{ph}^\&/J_{sat}$ [%]	G_{max} [10 ²⁸ m ⁻³ s ⁻¹]
BTT-MIC	18.65	15.90	12.51	85.25	67.08	1.16
BTT-FIC	19.52	18.54	15.47	94.97	79.25	1.22

J_{sat} is the J_{ph} under condition of $V_{eff}=4$ V;

J_{ph}^* is the J_{ph} at short circuit condition;

$J_{ph}^\&$ is the J_{ph} at maximum power output condition.

Table S3 The μ_e , μ_h and μ_e/μ_h in the BTT-MIC and BTT-FIC based OSCs

	μ_e [cm ² Vs ⁻¹]	μ_h [cm ² Vs ⁻¹]	μ_e/μ_h
PM6:BTT-MIC	5.15×10^{-4}	2.38×10^{-4}	2.16
PM6:BTT-FIC	7.61×10^{-4}	5.70×10^{-4}	1.33

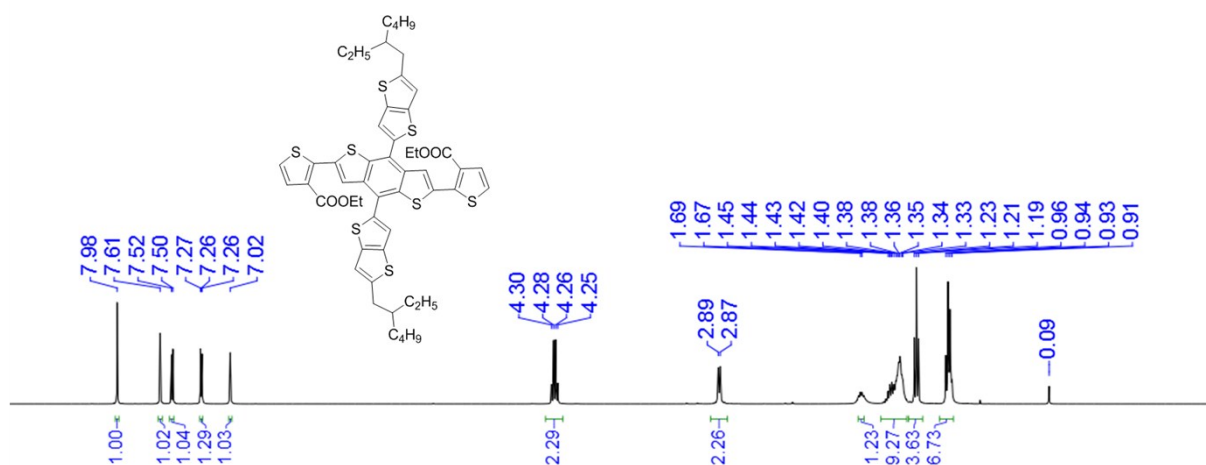
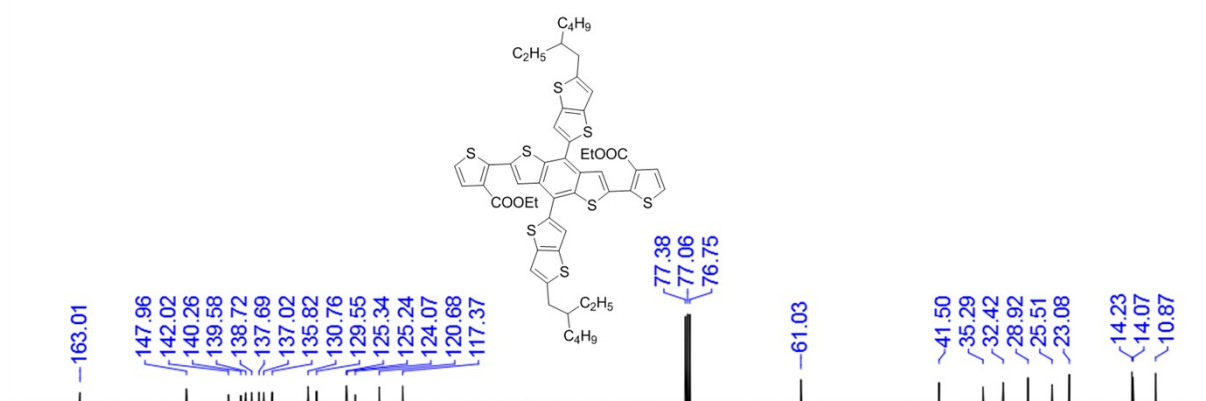
**Fig. S4.** The ¹H NMR spectrum of compound **2** in CDCl₃

Fig. S5. The ^{13}C NMR spectrum of compound **2** in CDCl_3

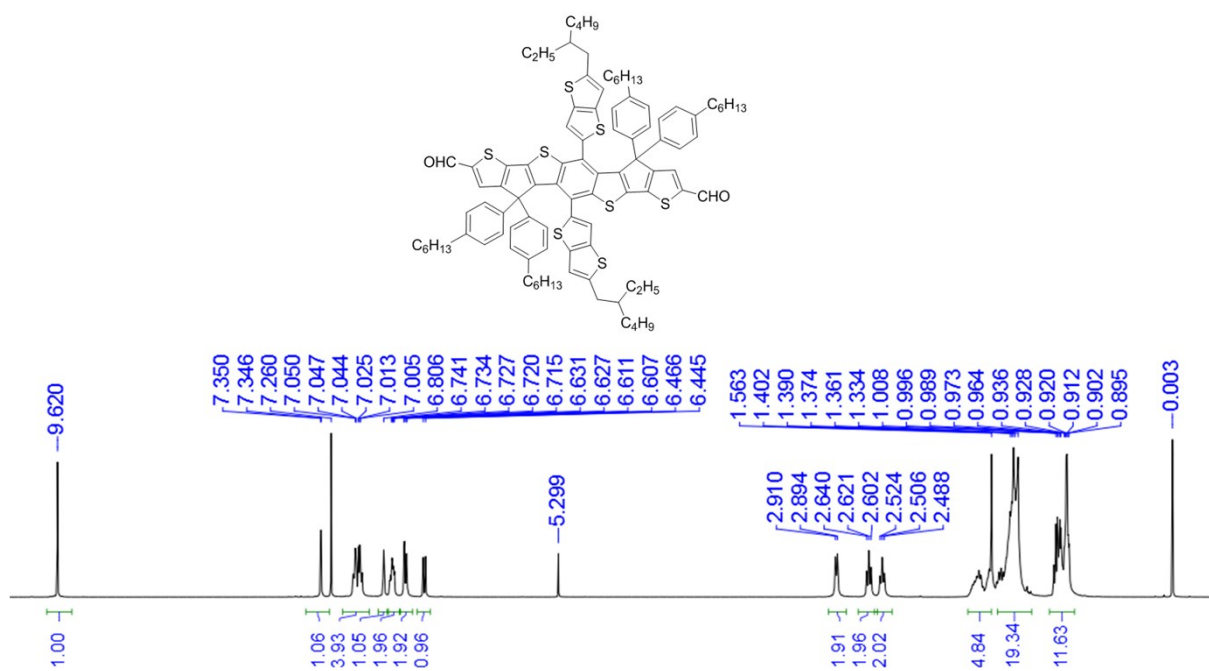


Fig. S6. The ^1H NMR spectrum of compound **4** in CDCl_3

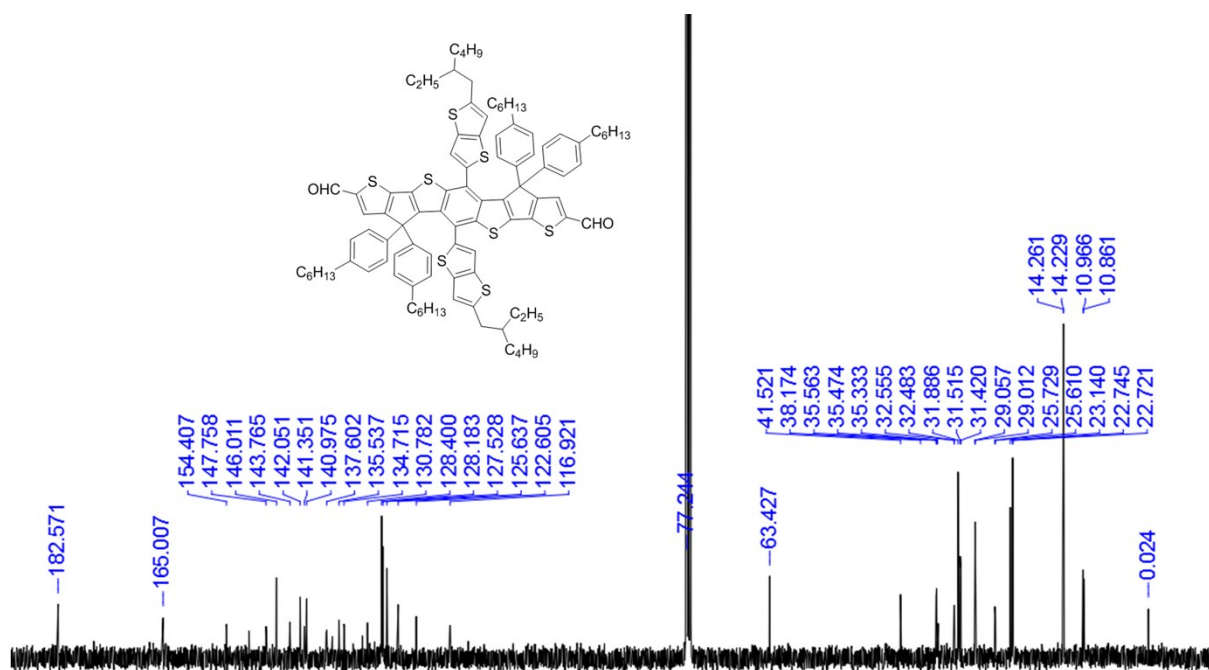


Fig. S7. The ^{13}C NMR spectrum of compound **4** in CDCl_3

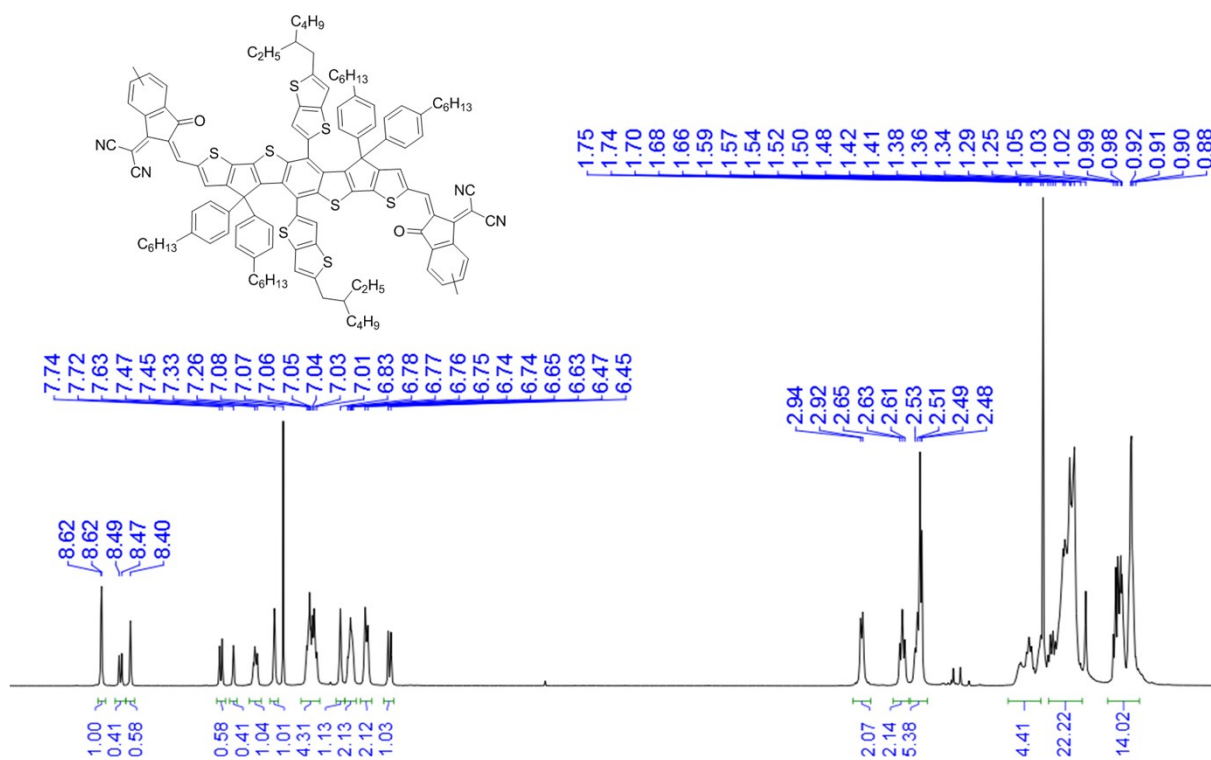


Fig. S8. The ¹H NMR spectrum of compound **BTT-MIC** in CDCl₃

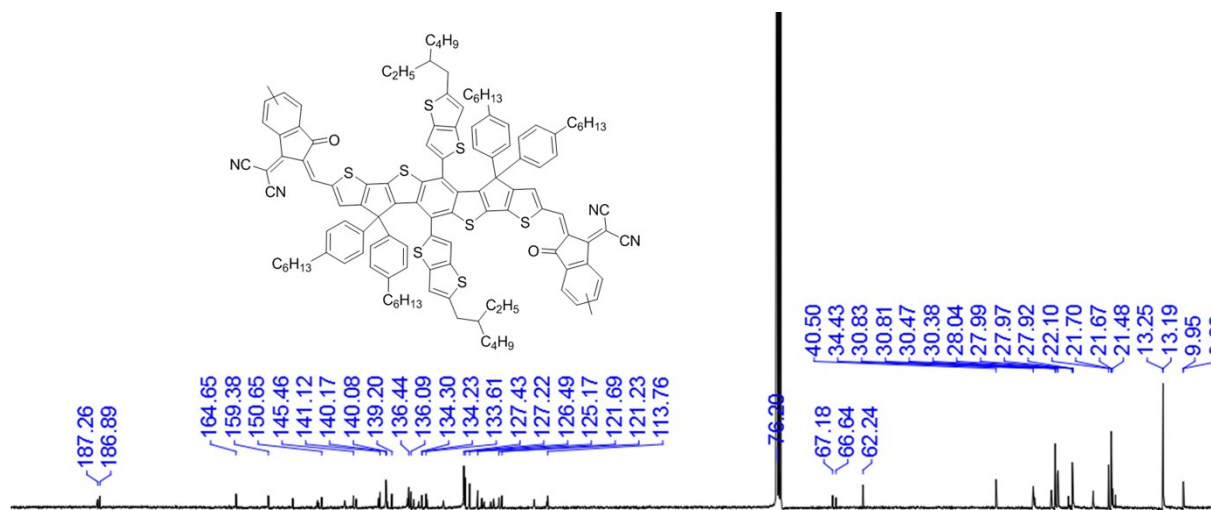


Fig. S9. The ¹³C NMR spectrum of compound **BTT-MIC** in CDCl₃

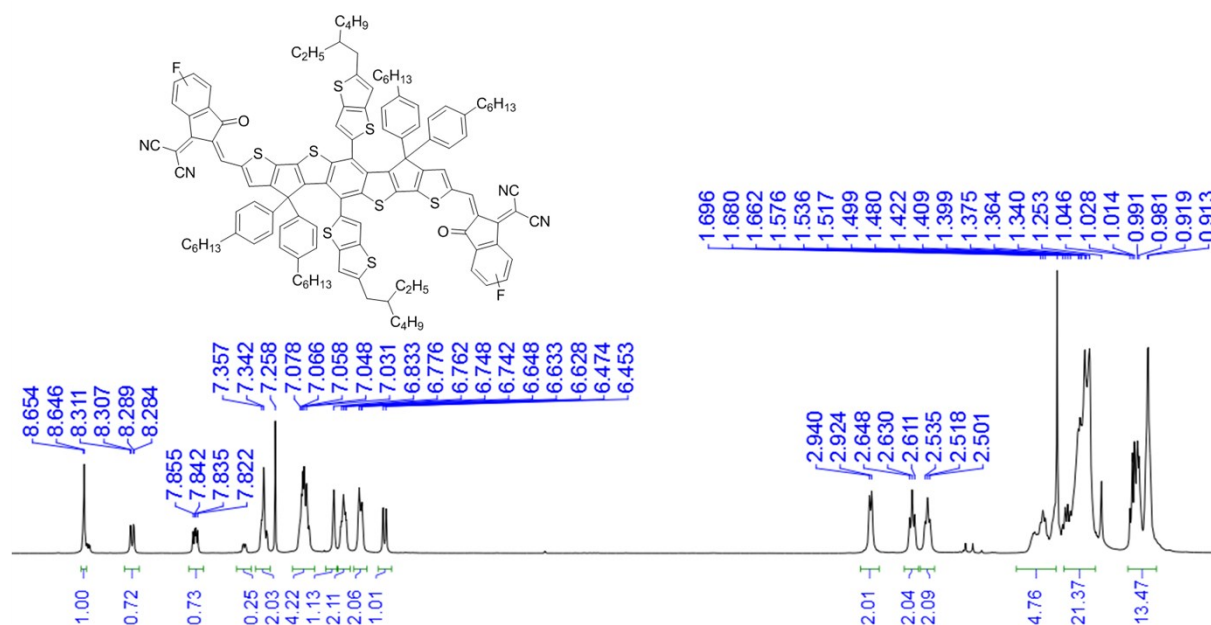


Fig. S10. The ^1H NMR spectrum of compound **BTT-FIC** in CDCl_3

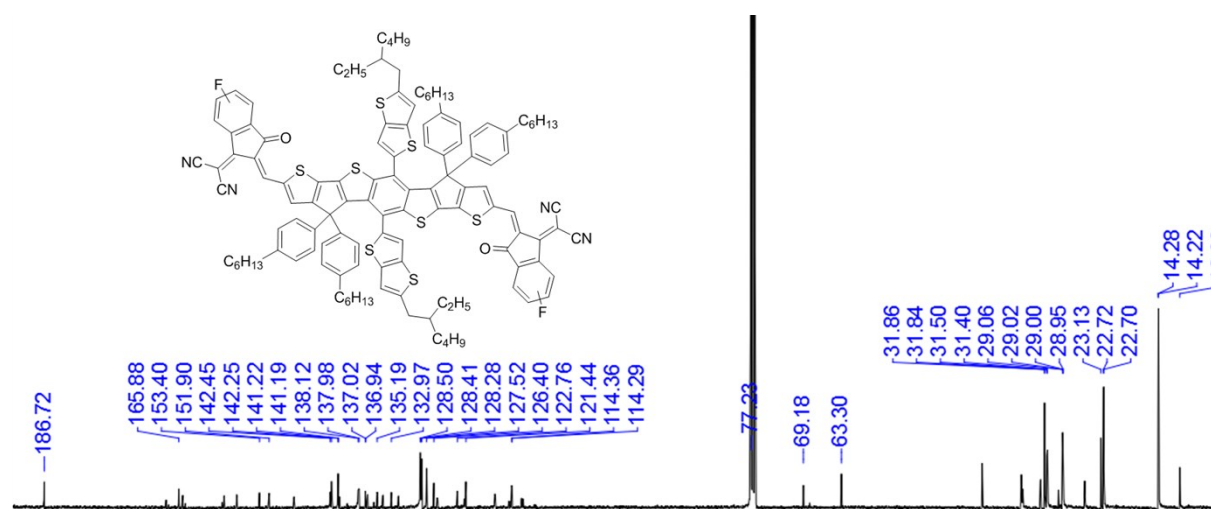


Fig. S11. The ^{13}C NMR spectrum of compound **BTT-FIC** in CDCl_3

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