

Electronic Supplementary Information

Regulating Exciton Bonding Energy and Bulk-Heterojunction Morphology in Organic Solar Cells via Methyl Functionalized Non-Fullerene Acceptors

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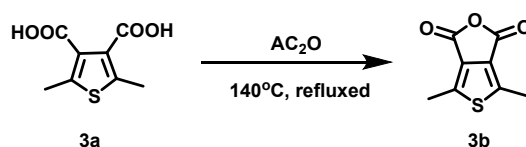
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General information

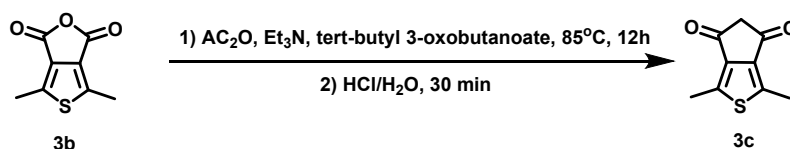
2-methylthiophene, 2,5-dimethylthiophene and thiophene-3,4-dicarboxylic acid (compound **1a**) were purchased from commercial sources. Compound **2a**, **3a**, CPTCN, CPTCN-M and BTTDC-CHO were synthesized according to previous literatures. ¹H NMR and ¹³C NMR spectra of all compounds were recorded on a Bruker Advanced II (400 MHz) spectrometer. Mass spectra were measured on a Thermo Trace DSQ II GC/MS and the matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF-MS) were performed on 5800 MALDI-TOF/TOF mass spectrometry (AB SCIEX, USA) in positive mode. Cyclic voltammetry (CV) measurements of SMAs thin films were conducted on a CHI voltammetric analyzer in acetonitrile solution with 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. UV-vis spectra were measured using a Shimadzu UV-2700 recording spectrophotometer. Atomic force microscopy (AFM) images were obtained by using a NanoMan VS microscope in the tapping-model.

Synthesis

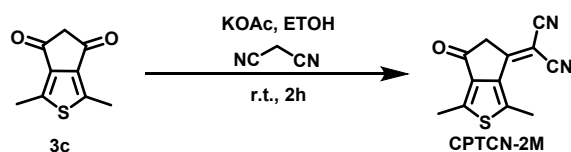


Synthesis of *4,6-dimethyl-1H,3H-thieno[3,4-c]furan-1,3-dione* (compound **3b**): To a 100 ml round-bottom flask, compound **3a** (3.0 g, 15 mmol) and acetic anhydride (50 ml) were added, and then the mixture was refluxed overnight. After cooling to room temperature, the acetic anhydride was evaporated under vacuum, and the residue was purified by silicon chromatography with CH₂Cl₂ as eluent to get pure compound **3b** (2.60g, 95%). ¹H NMR (400MHz, CDCl₃), δ (ppm): 2.66 (s, 6H); ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 157.22, 145.30, 129.89, 13.66. MS (EI) m/z : [M] calcd. for C₈H₆O₃S, 182.00; found, 182.79.

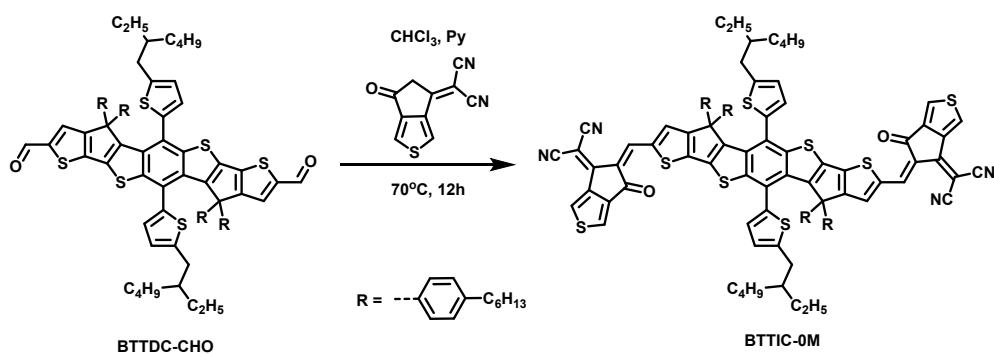


Synthesis of *1,3-dimethyl-4H-cyclopenta[c]thiophene-4,6(5H)-dione* (compound **3c**): To a 150 ml round-bottom flask, compound **3b** (2.50 g, 13.7 mmol), acetic anhydride (80 ml), triethylamine (7 ml) and *tert*-butyl 3-oxobutanoate (2.60g, 16.4

mmol) were added and stirred at 85°C for 12h. The reaction mixture was poured over ice with HCl, the oily product was extracted, dried with Na₂SO₄, and the solvent was evaporated *in vacuo*. The resulting carboxylic acid was treated with conc. HCl at reflux for 10 min, cooled to room temperature, and extracted with CH₂Cl₂ (3 × 50 mL). The combined organic extracts were dried (Na₂SO₄) and the solvent was evaporated *in vacuo*. The crude product was suspended in a minimum amount of diethyl ether, stirred at room temperature for 1 h and was filtered off. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 3.40 (s, 2H), 2.67 (s, 6H); ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 190.94, 143.13, 141.59, 54.03, 13.73. MS (EI) *m/z*: [M] calcd. for C₉H₈O₂S, 180.02; found, 180.49.

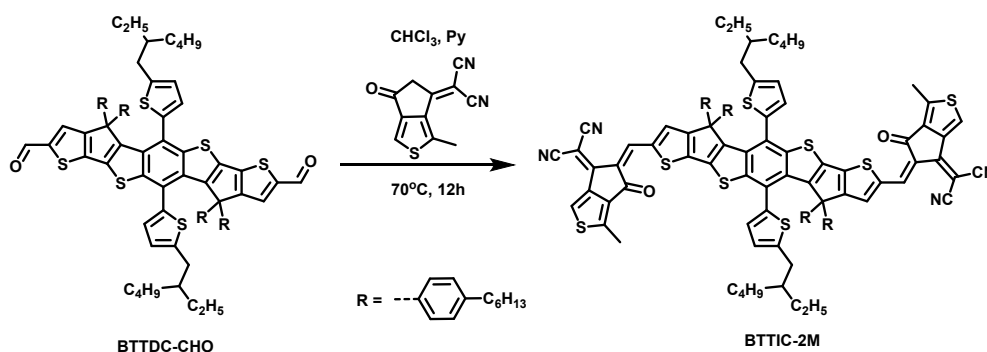


Synthesis of **2-(1,3-dimethyl-6-oxo-5,6-dihydro-4H-cyclopenta[c]thiophen-4-ylidene)malononitrile (CPTCN-2M)**: Compound **3c** (1.7 g, 10 mmol), malononitrile (1.32 g, 20 mmol) were dissolved in 30 ml absolute ethanol, and then anhydrous sodium acetate (1.64 g, 20 mmol) was added while stirring. After 40 min, the mixture was poured into water, and acidified to pH 1–2 by addition of the hydrochloric acid. The crude product was purified by silicon chromatography with CH₂Cl₂ to get pure product (35%). ¹H NMR (400 MHz, CDCl₃), δ (ppm): 3.89 (s, 2H), 2.88 (s, 3H), 2.66 (s, 3H); ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 188.13, 162.08, 144.07, 142.76, 141.65, 139.55, 113.78, 113.03, 52.03, 17.73, 13.17. MS (EI) *m/z*: [M] calcd. for C₁₂H₈N₂OS, 228.04; found, 228.59.



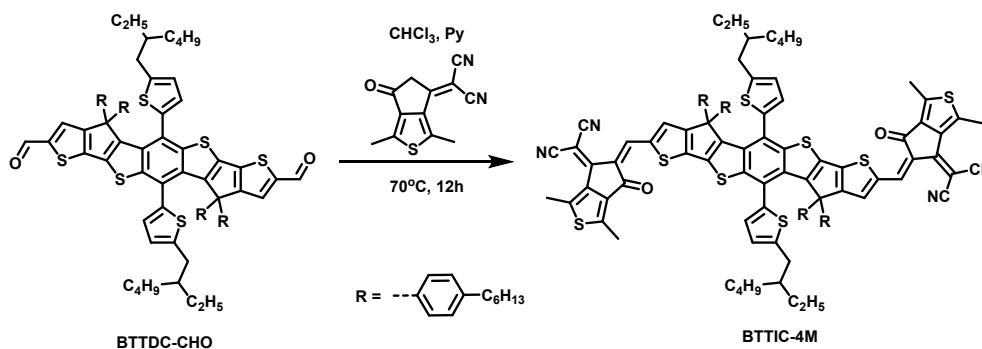
Synthesis of **BTIC-0M**: To a 100 ml round bottom flask, compound **4** (250 mg, 0.17 mmol) and CPTCN (136 mg, 0.68 mmol) were added under argon protection. Then, deoxidized chloroform (30 ml) was added and stirred for a while when pyridine (1 ml) was added. The mixture was kept stirring at 70°C for 16 h. After removal of chloroform of reaction mixture under reduced pressure, 100 ml methanol was added and the precipitate was collected by filtration. The residue was purified by column chromatography on silica gel using a mixture solvent as eluent (petroleum ether/dichloromethane, v/v = 1/1) to give a dark solid (264 mg, 85%). ¹H NMR (400 MHz, CDCl₃), δ (ppm): 8.60 (s, 2H), 8.25 (d, *J* = 2.4 Hz, 2H), 7.82 (d, *J* = 2.0 Hz, 2H), 7.34 (s, 2H), 6.92-7.00 (m, 16H), 6.42 (d, *J* = 3.6 Hz, 2H), 6.11 (d, *J* = 3.2 Hz, 2H), 2.55-2.79 (m, 12H), 2.25 (s, 1H), 2.20 (s, 1H), 1.62 (m, 8H), 1.26-1.36 (m, 40H), 0.87-1.02 (m, 24H). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 181.40, 165.78, 157.09, 156.06, 153.94, 152.22, 146.89, 146.74, 142.38, 142.19, 142.07, 141.85, 141.51, 141.07, 139.33, 137.89, 135.34, 135.25, 134.90, 134.69, 131.66, 130.35, 128.36, 128.19, 127.58, 127.45, 126.83, 125.23, 124.58, 115.12, 114.42, 66.62, 62.32, 41.38, 41.14, 35.60, 35.47, 33.82, 32.46, 32.37, 31.76, 31.74, 31.52, 31.46, 29.68, 29.21, 29.06, 28.94, 28.87, 25.61, 25.34, 23.20, 23.14, 22.65, 22.63, 14.34, 14.30, 14.13, 10.88,

10.71. MALDI-TOF-MS m/z: [M] calcd. for C₁₁₄H₁₁₄N₄O₂S₈, 1826.67; found, 1826.19.



Synthesis of **BTTIC-2M**: To a 100 ml round bottom flask, compound **4** (250 mg, 0.17 mmol) and CPTCN-M (146 mg, 0.68 mmol) were added under argon protection. Then, deoxidized chloroform (30 ml) was added and stirred for a while when pyridine (1 ml) was added. The mixture was kept stirring at 70°C for 16 h. After removal of chloroform of reaction mixture under reduced pressure, 100 ml methanol was added and the precipitate was collected by filtration. The residue was purified by column chromatography on silica gel using a mixture solvent as eluent (petroleum ether/dichloromethane, v/v = 1/1) to give a dark solid (252 mg, 80%). ¹H NMR (400 MHz, CDCl₃), δ (ppm): 8.56 (s, 2H), 7.98 (s, 2H), 7.29 (s, 2H), 6.88-7.02 (m, 16H), 6.40 (d, *J* = 3.2 Hz, 2H), 6.12 (s, 2H), 2.74-2.81 (m, 2H), 2.70 (s, 6H), 2.58 (q, *J*₁ = 8.4 Hz, *J*₂ = 16 Hz, 8H), 1.53-1.62 (m, 12H), 1.32-1.36 (m, 40H), 0.87-1.00 (m, 24H). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 182.57, 182.54, 165.59, 156.86, 155.75, 153.50, 152.11, 146.80, 146.60, 144.43, 142.15, 141.97, 141.81, 140.88, 138.84, 137.66, 136.88, 135.38, 135.28, 134.91, 134.80, 131.61, 130.28, 128.44, 128.33, 128.16, 128.03, 127.97, 126.71, 124.94, 124.54, 115.10, 114.59, 66.09, 63.28, 41.27, 41.08, 35.60, 35.46, 33.72, 33.64, 32.46, 32.32, 31.76, 31.74, 31.54, 31.47, 29.21, 28.99,

28.93, 25.54, 25.20, 23.20, 23.15, 22.66, 22.63, 14.33, 14.30, 14.14, 13.37, 10.89, 10.60. MALDI-TOF-MS m/z: [M] calcd. for C₁₁₆H₁₁₈N₄O₂S₈, 1854.70; found, 1854.63.



Synthesis of **BTTIC-4M**: To a 100 ml round bottom flask, compound **4** (250 mg, 0.17 mmol) and CPTCN-2M (155 mg, 0.68 mmol) were added under argon protection. Then, deoxidized chloroform (30 ml) was added and stirred for a while when pyridine (1 ml) was added. The mixture was kept stirring at 70°C for 16 h. After removal of chloroform of reaction mixture under reduced pressure, 100 ml methanol was added and the precipitate was collected by filtration. The residue was purified by column chromatography on silica gel using a mixture solvent as eluent (petroleum ether/dichloromethane, v/v = 1/1) to give a dark solid (262 mg, 82%). ¹H NMR (400 MHz, CDCl₃), δ (ppm): 8.53 (s, 2H), 7.29 (s, 2H), 6.88-7.00 (m, 16H), 6.40 (d, *J* = 3.6 Hz, 2H), 6.10 (s, 2H), 2.54-2.73 (m, 26H), 1.62 (m, 8H), 1.32-1.36 (m, 40H), 0.87-1.00 (m, 24H). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 182.23, 158.78, 157.10, 152.01, 151.01, 146.74, 146.59, 141.96, 141.77, 141.62, 138.34, 137.18, 135.57, 135.01, 131.60, 130.32, 128.49, 128.35, 128.17, 124.56, 116.05, 115.53, 67.13, 63.36, 41.34, 41.14, 35.65, 35.52, 33.80, 32.54, 32.39, 31.81, 31.80, 31.58, 31.50, 29.27, 29.06, 28.99, 25.62, 25.28, 23.25, 23.21, 22.71, 22.68, 18.57, 14.37, 14.34, 14.18, 13.05,

10.94, 10.58. MALDI-TOF-MS m/z: [M] calcd. for C₁₁₈H₁₂₂N₄O₂S₈, 1882.73; found, 1882.35.

Devices fabrication and characterization

Organic solar cells (OSCs) devices using BTTIC-0M, BTTIC-2M and BTTIC-4M as electron acceptors and PBDB-T as electron donor were fabricated with a structure of ITO/PEDOT:PSS/active layer/ZrAcac/Al. The patterned ITO-coated glass was scrubbed by detergent and then cleaned inside an ultrasonic bath by using deionized water, acetone, and isopropyl alcohol sequentially and dried overnight in an oven. Before use, the glass substrates were treated in a UV-Ozone Cleaner for 20 min to improve its work function and clearance. The SMA (BTTIC-0M, BTTIC-2M or BTTIC-4M) and PBDB-T (weight ratio of 1:1) were dissolved in chloroform with 0.5 % DIO addition, then the mixture was stirred overnight at room temperature to obtain a blend solution with a total concentration of 16 mg/mL. A thin PEDOT: PSS (Heraeus Clevios P VP A 4083) layer (40 nm) was spin-coated onto the ITO substrates and then dried at 150 °C for 10 min in air. The PEDOT:PSS coated ITO substrates were fast transferred to a N₂ filled glove-box for further processing. The blend solution was spin-cast on the top of PEDOT: PSS layer at 2000 rpm for 40 s. Then it was annealed at 100 °C for 5 min. Subsequently, the active layer coated substrates were quickly transferred to a glove-box integrated thermal evaporator for electrode deposition. A thin ZrAcac layer and Al layer (100 nm) were sequentially evaporated under vacuum of 5×10⁻⁵ Pa through a shadow mask. The active area of each device was 5.9 mm² controlled by a

shadow mask. The optimal blend thickness measured on a Bruker Dektak XT stylus profilometer was about 100 nm. The current-voltage (J - V) characteristic curves of all packaged devices were measured by using a Keithley 2400 Source Meter in air. Photocurrent was measured under AM 1.5G (100 mW cm⁻²) using a Newport solar simulator in an Air. The light intensity was calibrated using a standard Si diode (with KG5 filter, purchased from PV Measurement) to bring spectral mismatch to unity. EQEs were measured using an Enlitech QE-S EQE system equipped with a standard Si diode. Monochromatic light was generated from a Newport 300W lamp source.

SCLC measurements

The electron-only SCLC devices were a stack of ITO/ZnO/active layer/ZrAcac/Al, and the hole-only devices were a stack of ITO/V₂O₅/active layer/V₂O₅/Al. The electron-only and hole-only SCLC devices fabrication processing methods are same with those for solar cell. The charge carrier mobility was determined by fitting the dark current to the model of a single carrier SCLC according to the equation:

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

where J is the current density, L is the film thickness of the active layer, μ is the charge carrier mobility, ε_r is the relative dielectric constant of the transport medium, and ε_0 is the permittivity of free space. $V = V_{\text{app}} - V_{\text{bi}}$, where V_{app} is the applied voltage, V_{bi} is the offset voltage. The carrier mobility can be calculated from the slope of the $J^{1/2} \sim V$ curves.

GIWAXS and RSoXS measurements

All the tested samples were fabricated under the same condition of best-performance devices on the cleaned Si substrates. GIWAXS measurement was performed at beamline 7.3.3 at the Advanced Light Source of Lawrence Berkeley National Lab (LBNL). The 10 K eV X-ray beam was incident at a grazing angle of $0.12^\circ - 0.16^\circ$ to obtain optimal signal-to-background ratio. The scattered X-ray signals were detected by using a Dectris Pilatus 2M photon counting detector. The whole experiments were carried out in helium atmosphere. RSoXS measurement was carried out at beamline 11.0.1.2 at the Advanced Light Source of LBNL. Samples for RSoXS measurement were transferred by floating in water to a 1.5 mm x 1.5mm, 100 nm thick Si_3N_4 membrane supported by a 5 mm x 5 mm, 200 μm thick Si frame (Norcada Inc.). 2D scattering patterns were collected on an in-vacuum CCD camera (Princeton Instrument PI-MET). The sample detector distance was calibrated from diffraction peaks of a triblock copolymer poly(isoprene-*b*-styrene-*b*-2-vinyl pyridine), which has a known spacing of 391 Å. The beam size at the sample is approximately 100 μm by 200 μm .

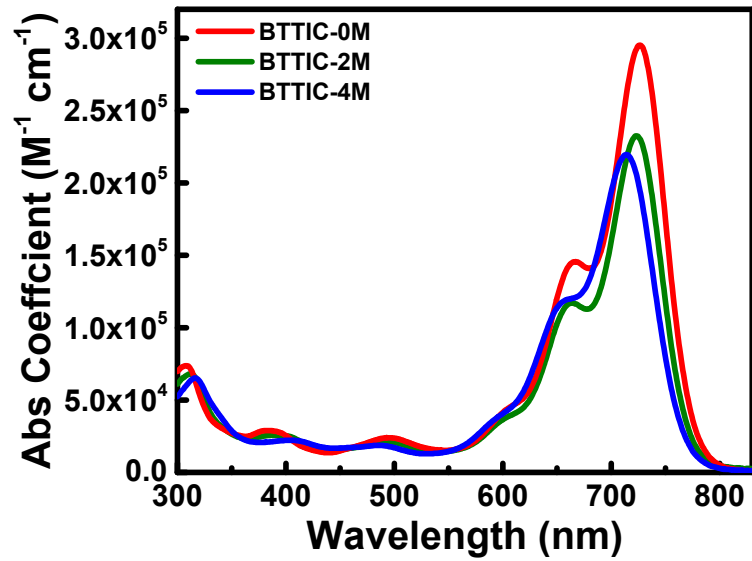


Fig. S1. The molar absorption coefficient spectra of BTTIC-0M, BTTIC-2M and BTTIC-4M in chloroform solution.

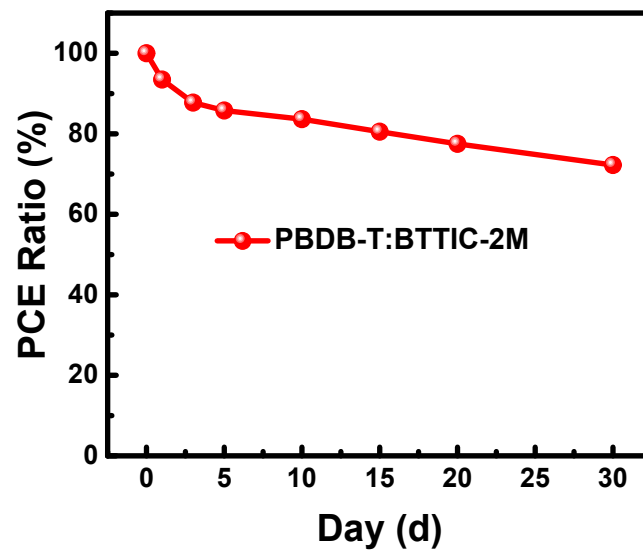


Fig. S2. The long-term stability curve of best-performing OSCs based on PBDB-T:BTTIC-2M.

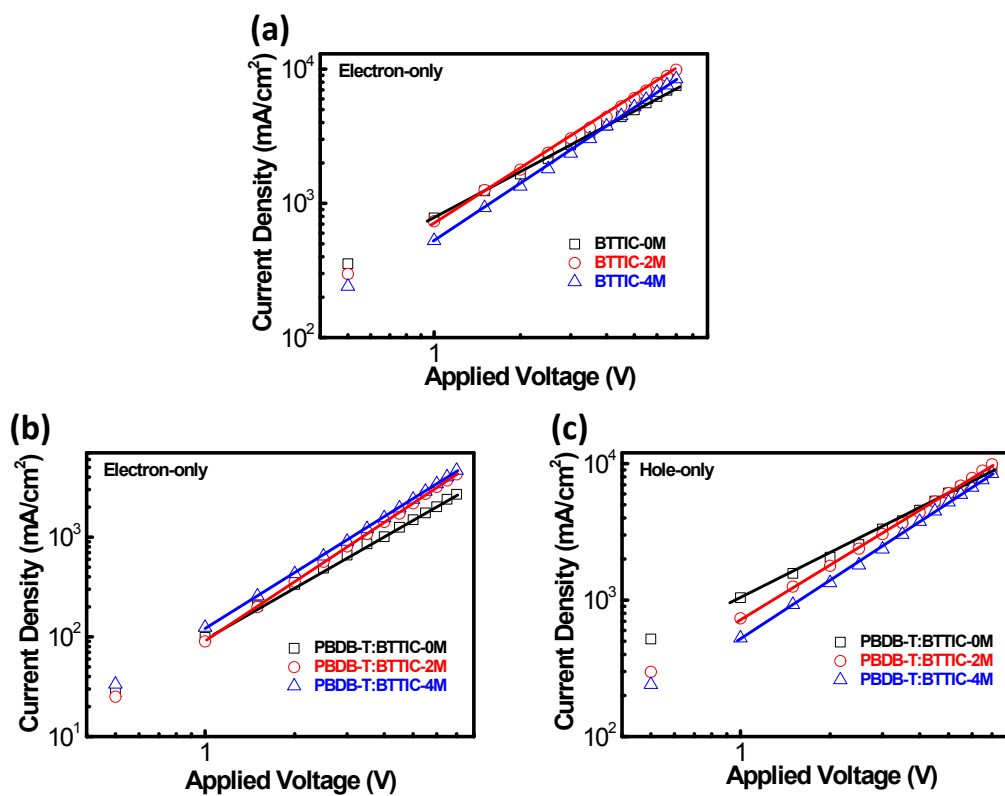


Fig. S3. a) The J - V curves of BTTIC-0M-, BTTIC-2M- and BTTIC-4M-based electron-only devices. b) The J - V curves of PBDB-T:BTTIC-0M-, PBDB-T:BTTIC-2M- and PBDB-T:BTTIC-4M-based electron-only devices. c) The J - V curves of PBDB-T:BTTIC-0M-, PBDB-T:BTTIC-2M- and PBDB-T:BTTIC-4M-based hole-only devices.

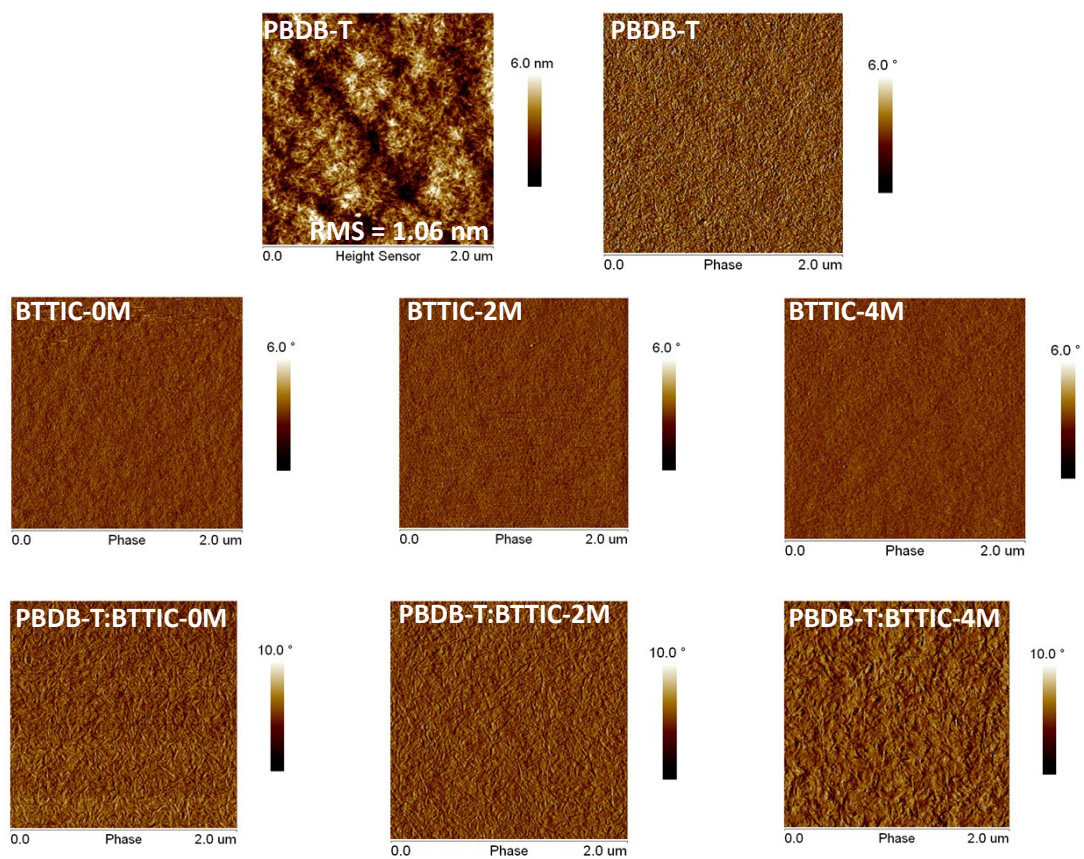


Fig. S4. The AFM height and phase images of PBDB-T, and phase images of BTTIC-0M-, BTTIC-2M- and BTTIC-4M-based neat and blend films.

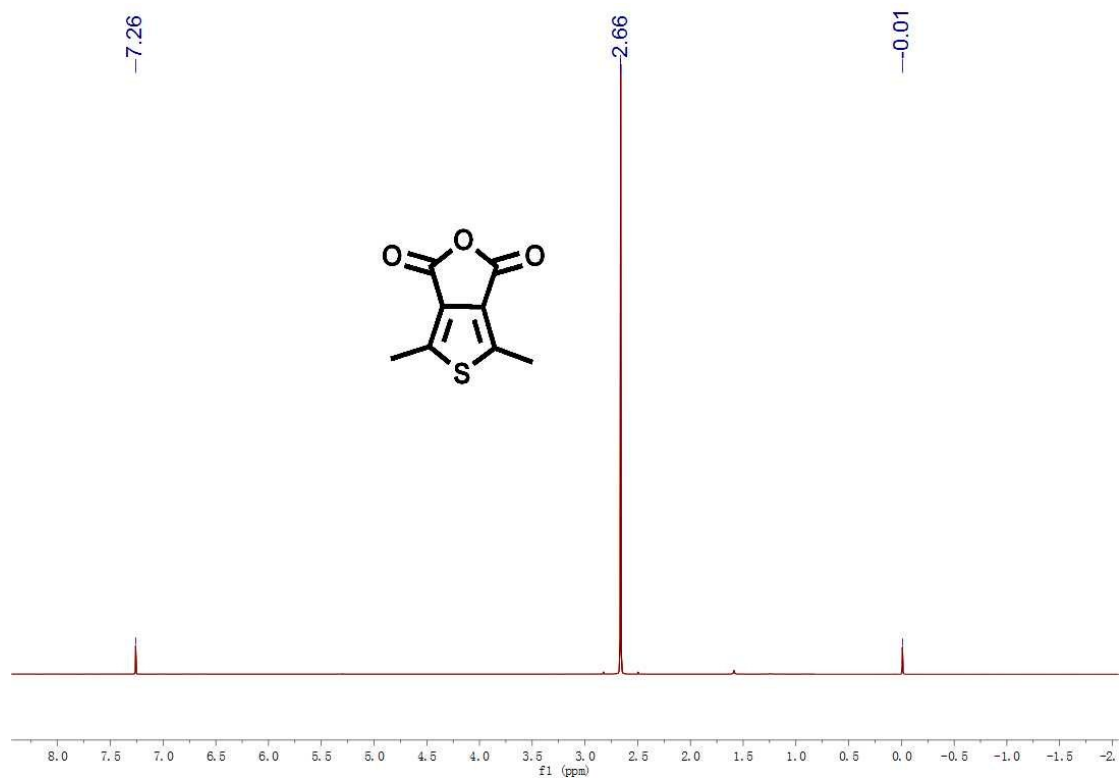


Fig. S5. The ¹H NMR spectrum of compound **3b**.

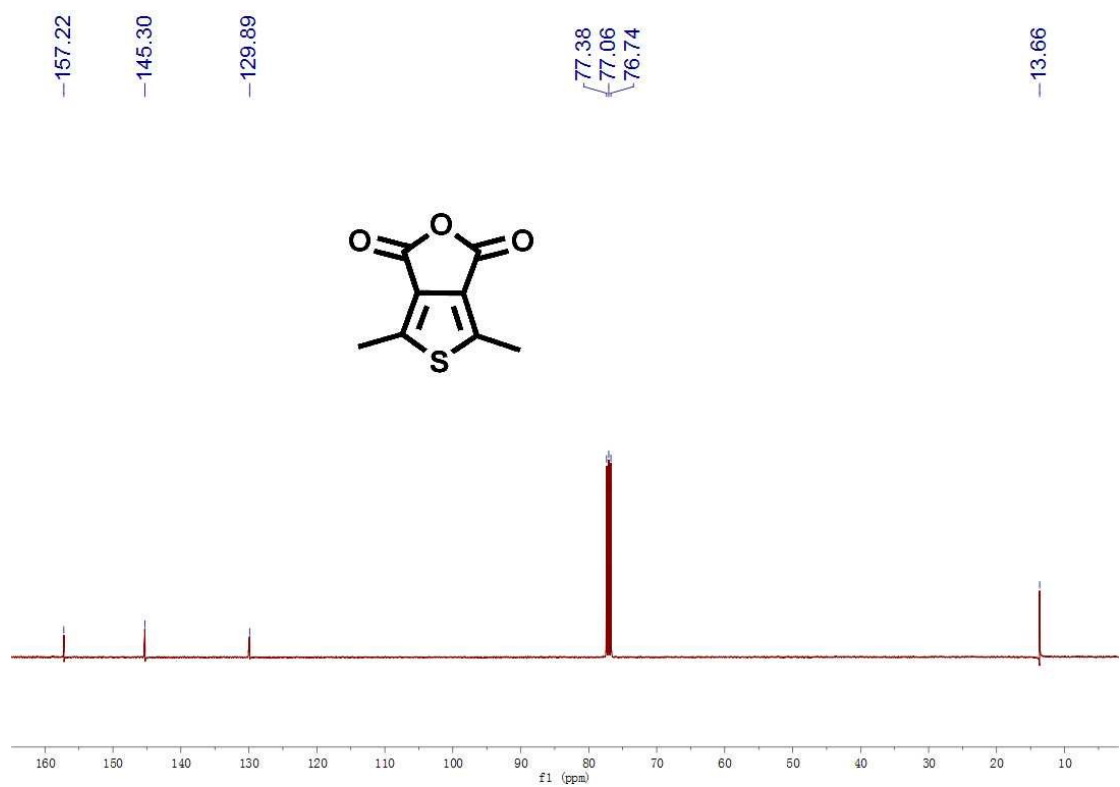


Fig. S6. The ¹³C NMR spectrum of compound **3b**.

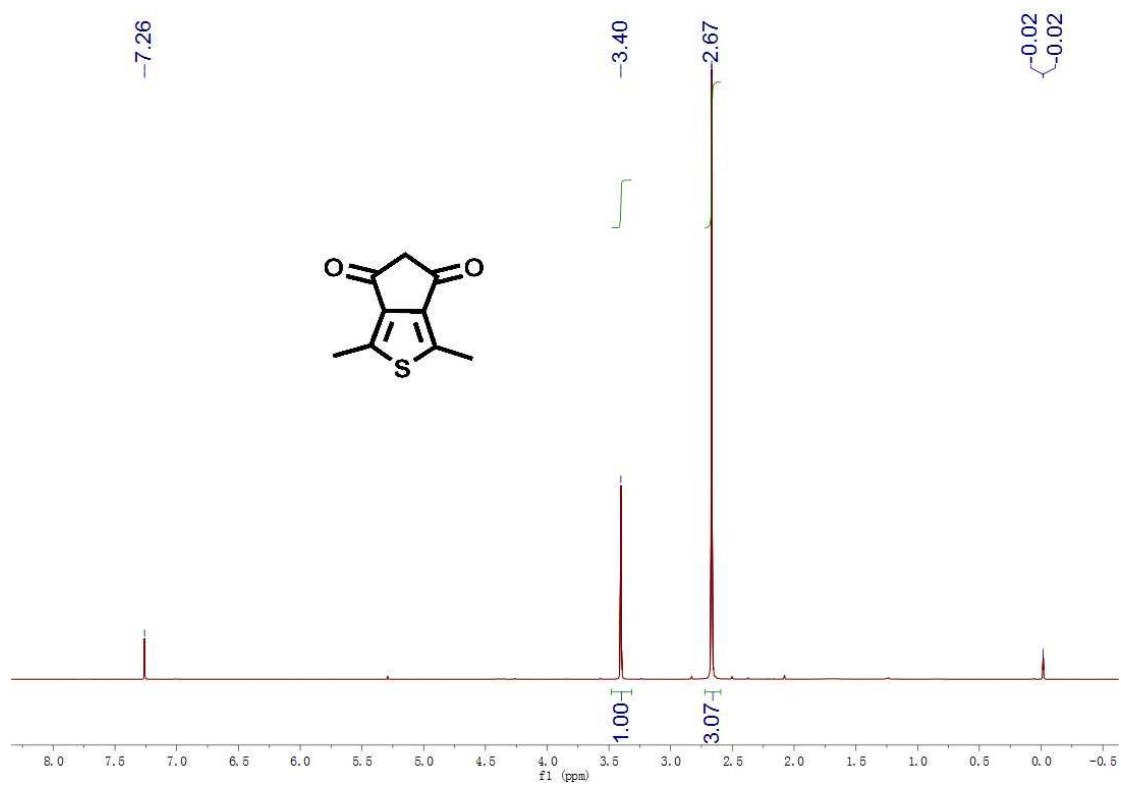


Fig. S7. The ^1H NMR spectrum of compound **3c**.

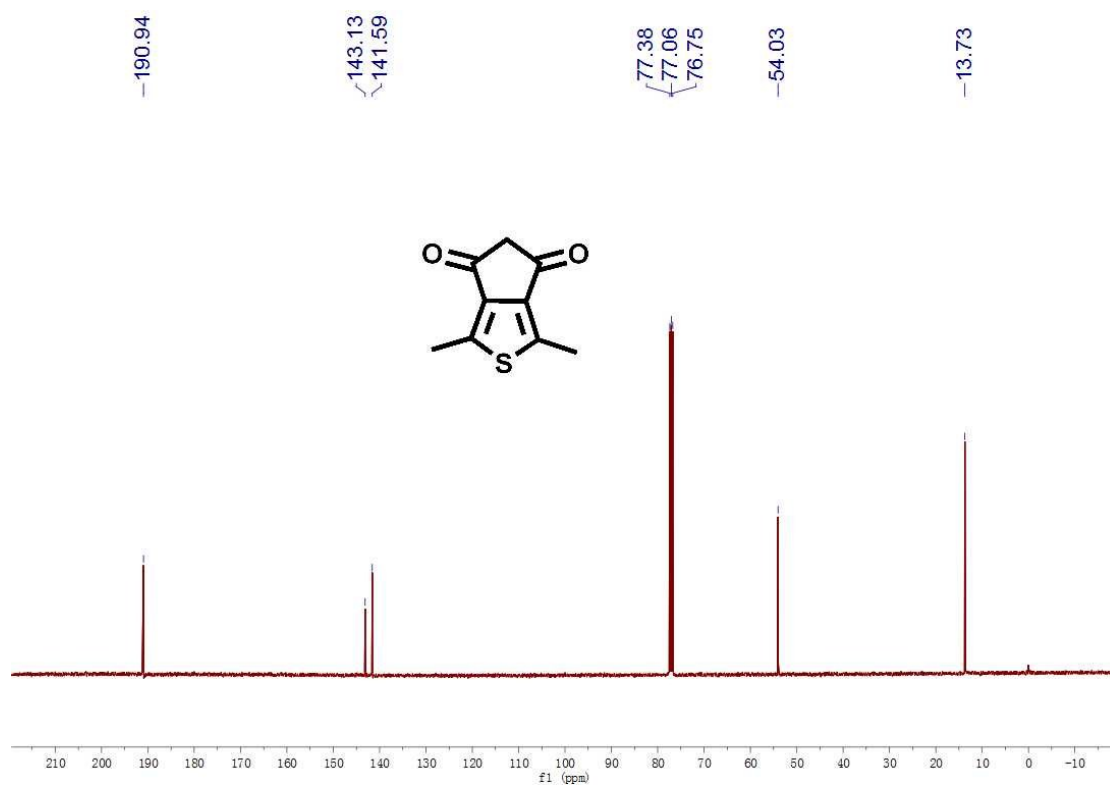


Fig. S8. The ^{13}C NMR spectrum of compound **3c**.

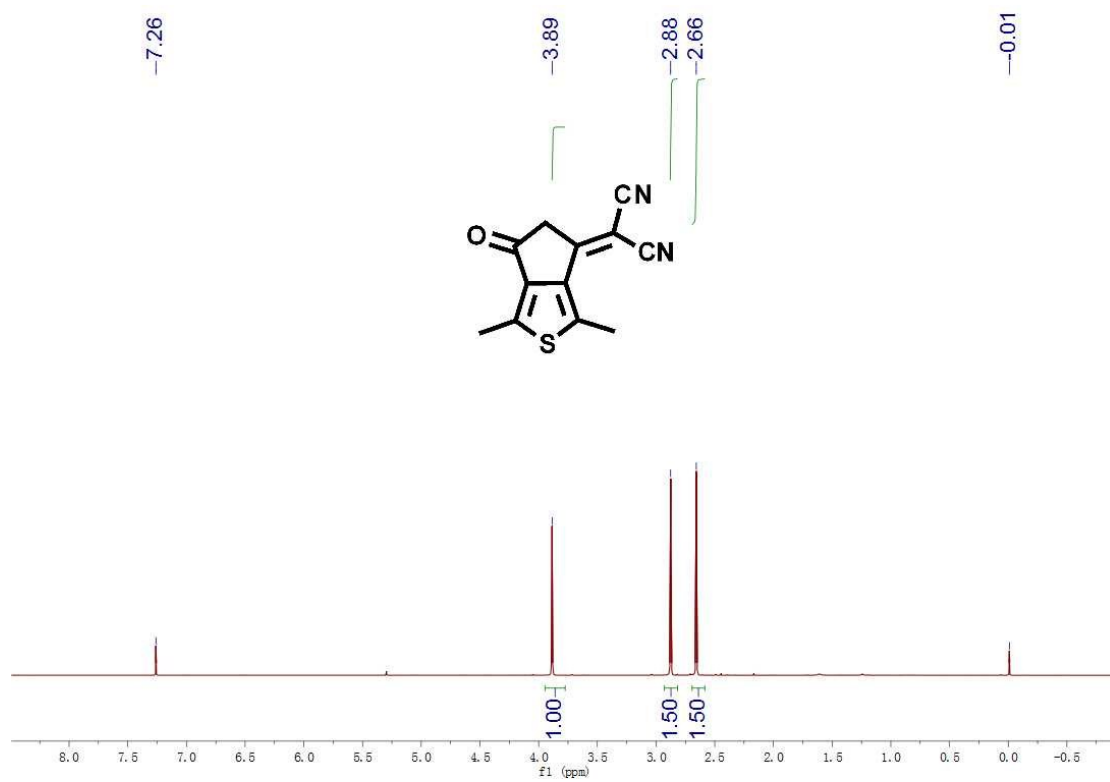


Fig. S9. The ¹H NMR spectrum of CPTCN-2M.

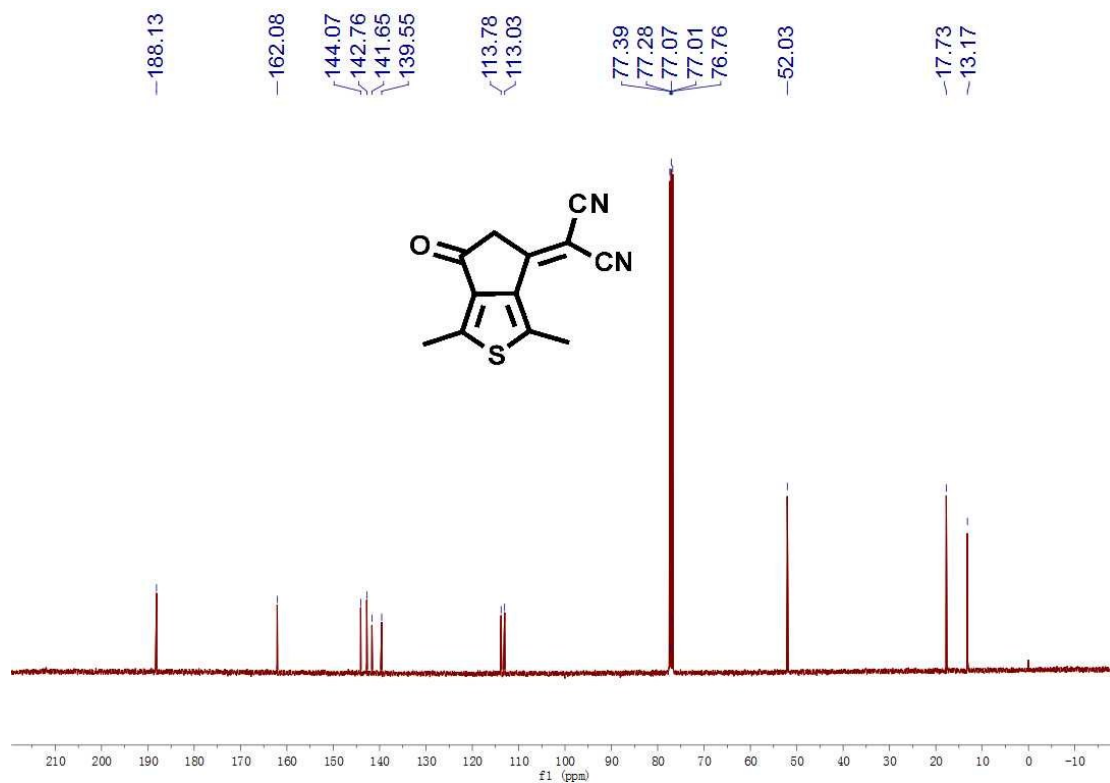


Fig. S10. The ¹³C NMR spectrum of CPTCN-2M.

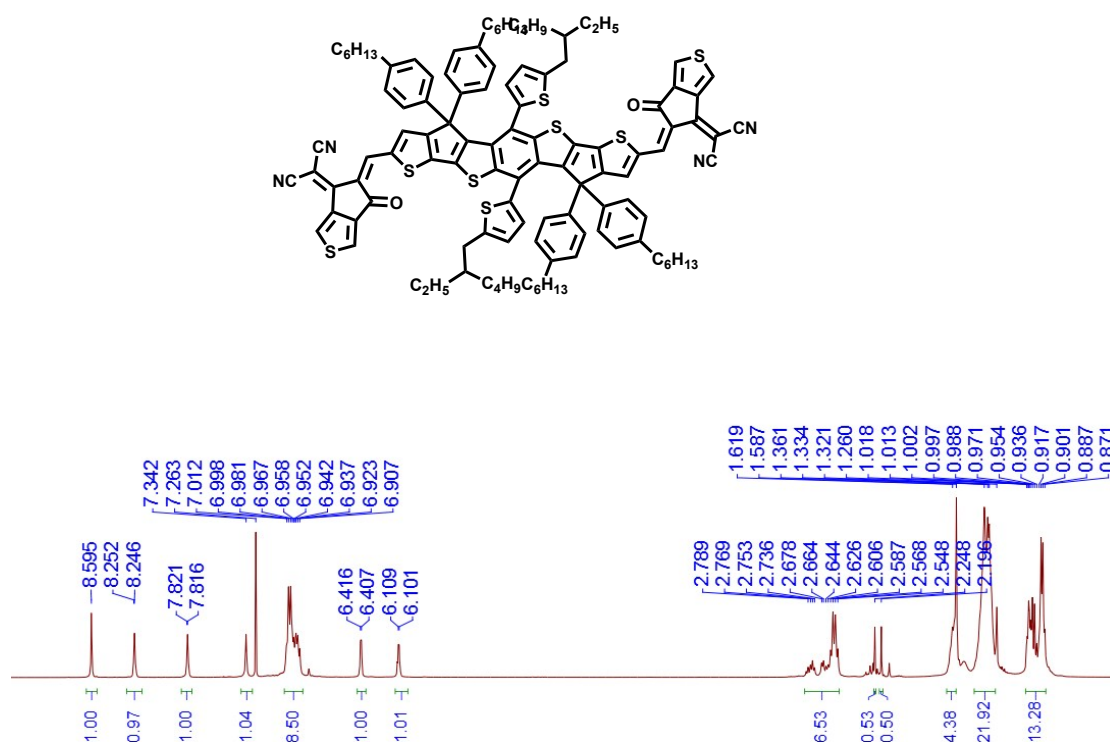


Fig. S11. The ¹H NMR spectrum of BTTIC-0M.

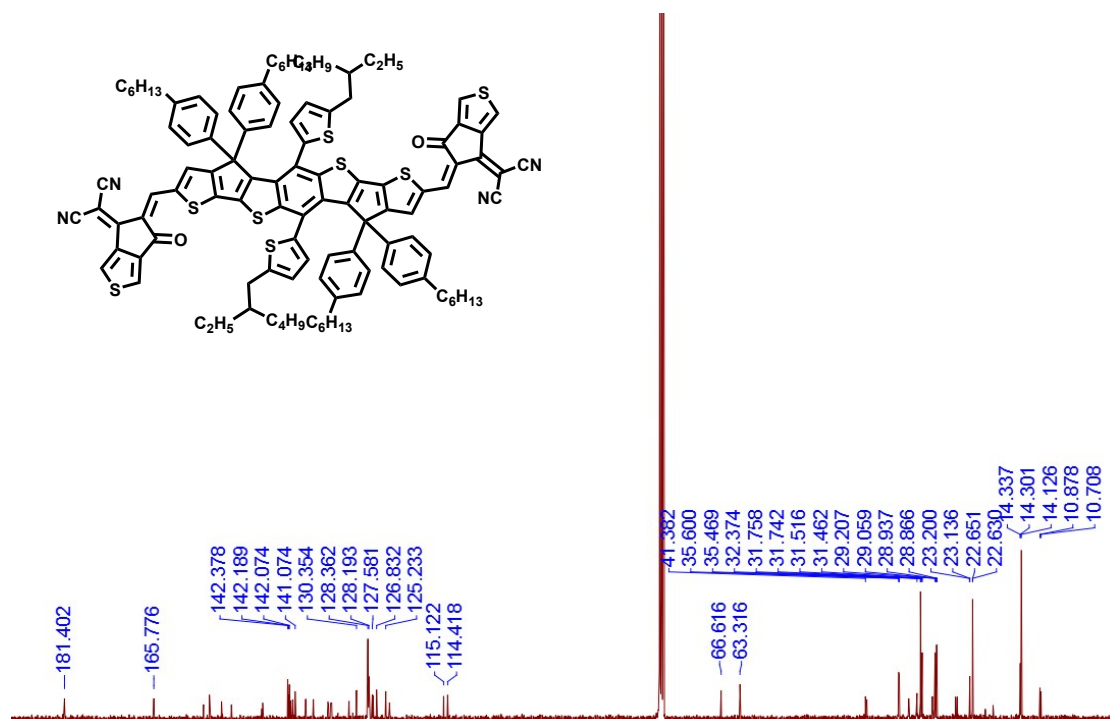


Fig. S12. The ^{13}C NMR spectrum of BTTIC-0M.

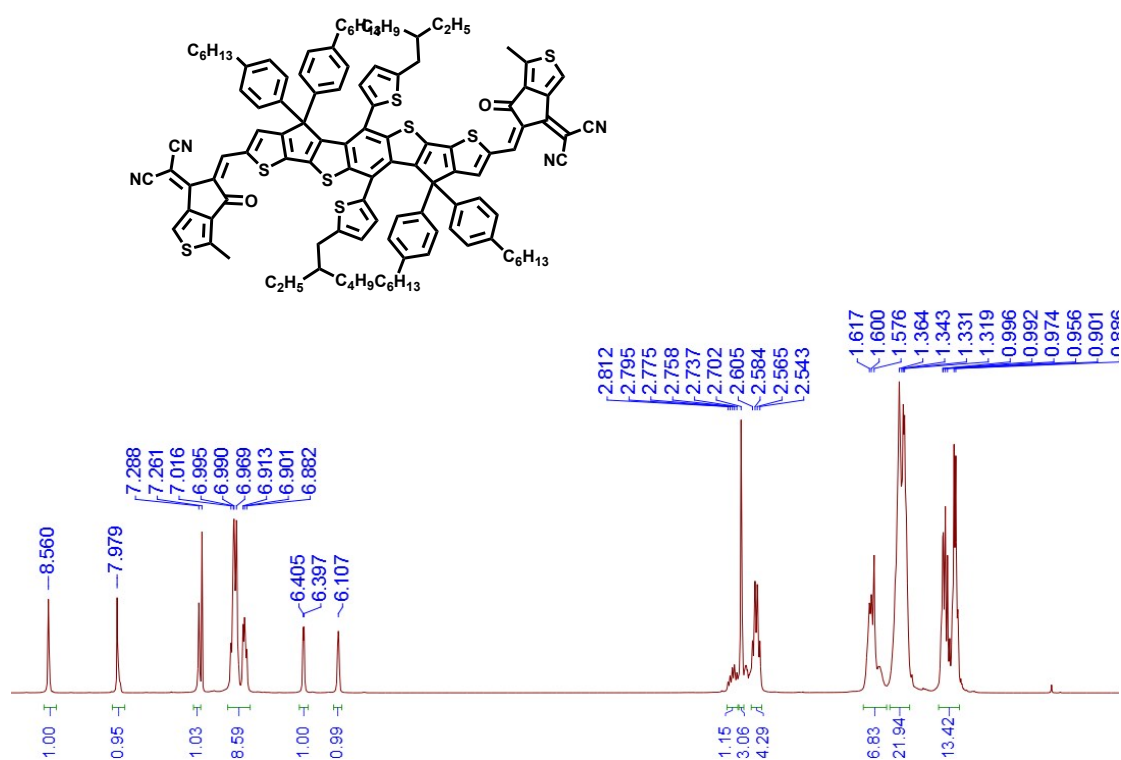


Fig. S13. The ^1H NMR spectrum of BTTIC-2M.

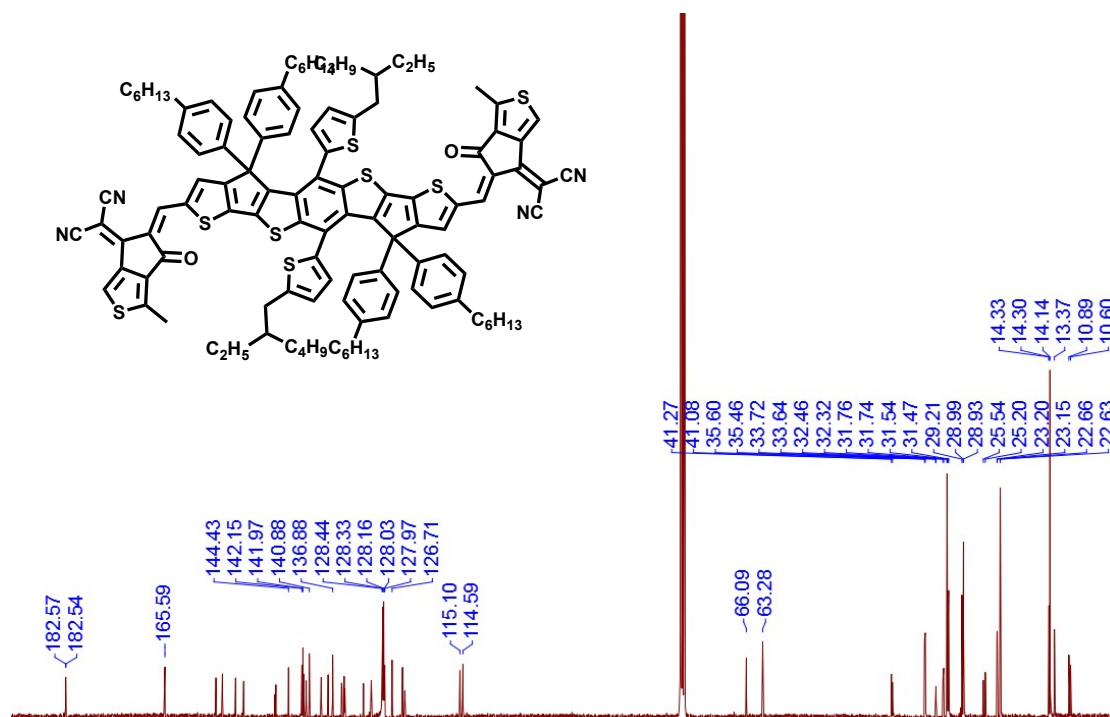


Fig. S14. The ^{13}C NMR spectrum of BTTIC-2M.

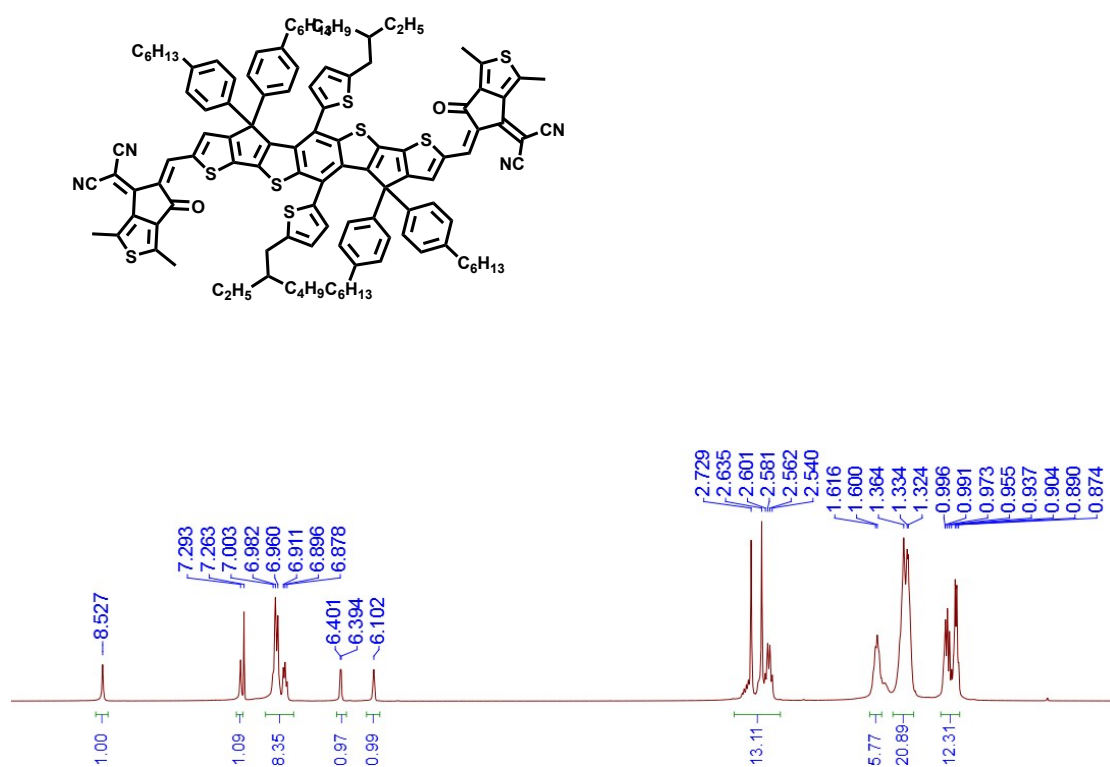


Fig. S15. The ^1H NMR spectrum of BTTIC-4M.

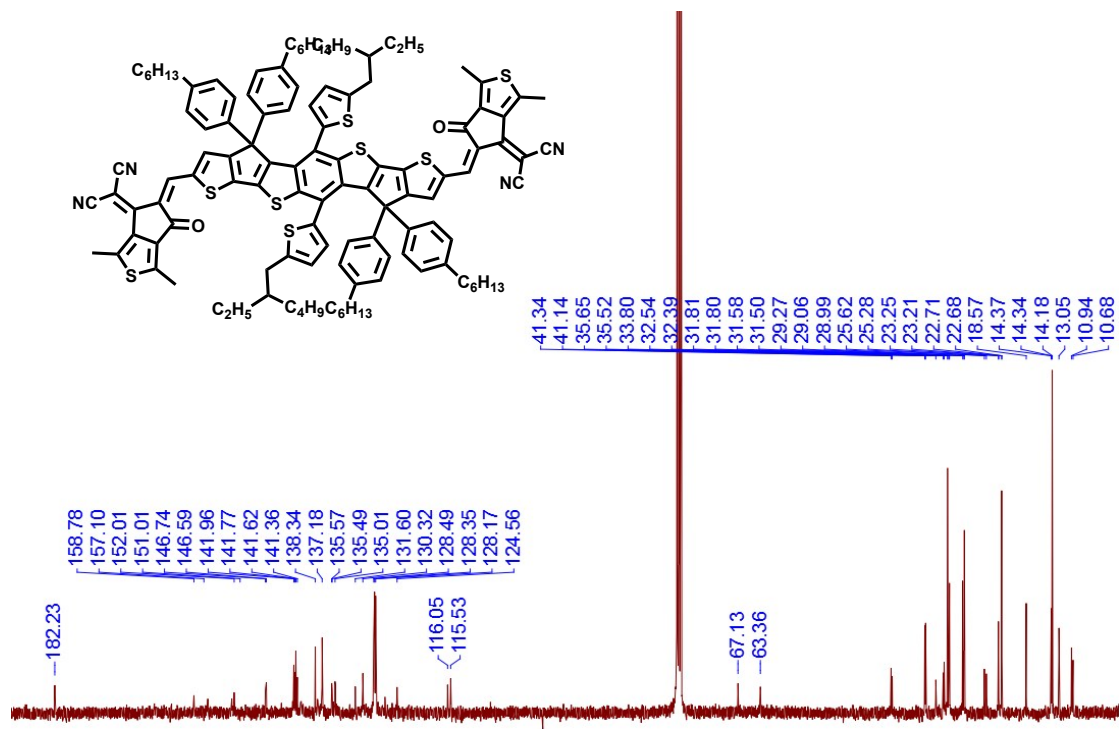


Fig. S16. The ¹³C NMR spectrum of BTTIC-4M.