Supporting Information

Simultaneously Increasing Open-Circuit Voltage and Short-Circuit Current to Minimize Energy Loss of Organic Solar Cells via Designing Asymmetrical Non-Fullerene Acceptor

Wei Gao,[ab] Tao Liu,*[c] Jiewei Li,[e] Yiqun Xiao,[d] Guangye, Zhang,[c] Yuzhong Chen,[c] Cheng Zhong,[a] Xinhui Lu,*[d] He Yan*[c] and Chuluo Yang*[ab]

[a]Department of Chemistry and Hubei Key Lab on Organic and Polymeric Optoelectronic Materials, Wuhan University, Wuhan, 430072, People's Republic of China
E-mail: clyang@whu.edu.cn

[b]Shenzhen Key Laboratory of Polymer Science and Technology, College of Materials Science and Engineering, Shenzhen University, Shenzhen 518060, China

[c]Department of Chemistry and Hong Kong Branch of Chinese National Engineering Research Center for Tissue Restoration & Reconstruction, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong
E-mail: liutaozhx@ust.hk, hyan@ust.hk

[d]Department of Physics, Chinese University of Hong Kong, New Territories, Hong Kong
E-mail: xhlu@phy.cuhk.edu.hk

[e]Key Laboratory of Flexible Electronics (KLOFE) & Institute of Advanced Materials (IAM), Nanjing Tech University (NanjingTech), Nanjing 211800, China

Synthesis

Toluene and tetrahydrofuran (THF) were dried by potassium sodium alloy under refluxing condition, (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(trimethylstannane) (compound **1**, purity 98%) and 1-bromo-4-hexylbenzene (purity 98%) were purchased from Derthon and Energy Chemical, respectively, and other solvents

and reagents were received from commercial sources and used without further purification unless otherwise stated. Ethyl 2-bromothiophene-3-carboxylate, ethyl 2-bromothieno[3,2-*b*]thiophene-3-carboxylate,2-(1-methyl-6-oxo-5,6-dihydro-4*H*-cyclopenta[*c*]thiophen-4-ylidene)malononitrile (CPTCN-M) and BTTIC were prepared according to the reported methods.[1-4]

Synthesis of ***compound 2***: To a dry three-neck flask was added compound **1** (1.0 g, 1.1 mmol), Pd_2dba_3 (50.4 mg, 0.055 mmol), tri-o-tolylphosphine (26.8 mg, 0.088 mmol) and dry toluene (100 ml) under argon protection. The mixture kept stirring at 60ºC, and ethyl 2-bromothiophene-3-carboxylate (283 mg, 1.2 mmol) in 30 ml toluene was dropwise added within 1 hour, which was then heated to 90ºC for 3 hours. Ethyl 2-bromothieno[3,2-*b*]thiophene-3-carboxylate (348 mg, 1.2 mmol) in 10 ml toluene was added and then heated at 110ºC overnight. After cooling to room temperature, KF aqueous solution was added and stirring for a while. The mixture was extracted with chloroform and washed with water for three times. The collected organic phase was evaporated and the residue was purified by automatic column machine using petroleum ether/dichloromethane (from 30:1 to 15:1, v/v) as eluent to get the product as a yellow oil (550 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.04 (s, 1H), 7.94 (s, 1H), 7.53 (d, *J* = 5.2 Hz, 1H), 7.49 (d, *J* = 5.2 Hz, 1H), 7.35 (q, *J* = 3.2 Hz, 2H), 7.28 (d, *J* = 5.6 Hz, 1H), 7.24 (d, *J* = 5.6 Hz, 1H), 6.90 (d, *J* = 3.2 Hz, 2H), 4.38 (q, *J* = 6.8 Hz, 2H), 4.28 (q, *J* = 7.2 Hz, 2H), 2.87 (d, *J* = 6.8 Hz 4H), 1.66-1.69 (m, 2H), 1.32-1.47 (m, 16 H), 1.28 (t, *J* = 6.8 Hz, 3H), 1.22 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR

(100 MHz, $CDCl_3$), δ (ppm): 163.04, 161.98, 146.04, 146.02, 144.31, 142.07, 141.33, 139.92, 139.84, 136.91, 136.58, 135.62, 135.45, 130.75, 129.57, 129.52, 127.97, 126.04, 125.51, 125.33, 125.21, 124.06, 123.90, 121.58, 118.70, 61.33, 60.92, 41.42, 34.20, 32.43, 28.87, 25.63, 23.00, 14.15, 14.01, 10.87. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{50}H_{55}O_4S_7^+$, 943.21398; found, 943.21350.

Synthesis of compound 3: To a stirring solution of compound **2** (500 mg, 0.53 mmol) in dry THF (30 ml) under argon condition was added (4-hexylphenyl)magnesium bromide which was prepared from 1-bromo-4-hexylbenzene (1.28 g, 5.3 mmol) and magnesium (140 mg, 5.9 mmol) in THF (10 ml). Then the mixed solution was heated to reflux for 16 h. After cooling to room temperature, the solution was poured into water and extracted with ethyl acetate, then washed with saturated salt water several times and dried with anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the crude product was obtained and then used in the next step without further purification. The crude product was dissolved in chloroform/glacial acetic acid (5:1 v/v), and 1 ml concentrated sulfuric acid in 5 ml glacial acetic acid was dropwise added into the solution, then the mixture was refluxed for 3 h. After cooling to room temperature, the mixture was extracted with dichloromethane and washed with water. The collected organic layer was dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel using a mixture solvent as eluent (petroleum ether/dichloromethane, v/v = 15/1) to give a yellow solid (350 mg, 45%). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.15 (q, J = 5.2 Hz, 2H), 7.06 (d, J

= 4.8 Hz, 1H), 6.91-7.02 (m, 16H), 6.78 (dd, J_1 = 1.2 Hz, J_2 = 4.8 Hz, 1H), 6.46 (s, 1H), 6.41 (d, J = 2.8 Hz, 1H), 6.12-6.15 (m, 1H), 6.07-6.10 (m, 1H), 2.63-2.78 (m, 4H), 2.56-2.57 (m, 8H), 2.24-2.35 (m, 10 H), 1.12-1.29 (m, 40H), 0.79-1.04 (m, 24H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 164.85, 154.55, 150.37, 150.14, 149.47, 146.11, 145.93, 141.88, 141.60, 141.35, 140.96, 136.63, 136.24, 135.13, 134.18, 132.98, 131.07, 130.68, 130.16, 128.47, 128.23, 128.00, 127.86, 127.45, 125.85, 124.60, 124.45, 124.30, 122.53, 120.07, 63.42, 63.22, 53.36, 39.51, 39.46, 39.16, 38.93, 37.59, 37.53, 37.48, 37.20, 35.71, 35.58, 34.48, 33.77, 33.55, 33.29, 33.18, 33.13, 32.84, 32.57, 32.36, 32.03, 31.88, 31.61, 31.56, 30.48, 30.26, 30.14, 30.06, 29.81, 29.77, 29.65, 29.58, 29.47, 29.31, 29.03, 28.97, 28.88, 28.05, 27.53, 27.19, 27.01, 26.85, 26.79, 26.55, 26.49, 24.90, 24.56, 23.32, 23.23, 23.14, 22.78, 22.73, 22.69, 20.22, 19.90, 19.86, 19.78, 19.28, 14.62, 14.48, 14.36, 14.24, 14.19, 11.47, 10. 94. HRMS (ESI) m/z: $[M]^+$ calcd. for $C_{94}H_{110}S_7^+$, 1462.66470, found 1462.66455.

Synthesis of ***compound 4***: To a dry 100 mL two-necked round bottom flask, 10 ml anhydrous *N*, *N*-dimethylformamide (DMF) was added, and the solution was cooled to 0ºC and stirred when 2 ml phosphorous oxychloride ($POCl_3$) was added by syringe under argon protection. The mixture was stirred at 0ºC for 1 hour, and then compound **3** (330 mg, 0.226 mmol) in dry 1, 2-dichloroethane (20 ml) was added. Then, the mixture solution was allowed to reflux overnight. After cooling to room temperature, 100 ml water was added and the mixture was extracted with dichloromethane (DCM), and the organic layer was collected, washed with water and dried with anhydrous

Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using a mixture solvent as eluent (petroleum ether/dichloromethane, v/v = 2/1) to give an orange solid (302 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 9.78 (s, 1H), 9.64 (s, 1H), 7.80 (s, 1H), 7.39 (d, 1H), 6.88-6.98 (m, 16H), 6.45 (s, 1H), 6.39 (d, 1H), 6.10-6.13 (m, 1H), 6.05-6.08 (m, 1H), 2.65-2.75 (m, 4H), 2.52-2.59 (m, 8H), 1.51-1.57 (m, 10H), 1.25-1.36 (m, 40H), 0.86-0.99 (m, 24H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 182.77, 182.56, 164.74, 154.60, 154.53, 152.93, 150.94, 150.43, 145.64, 144.23, 143.60, 142.79, 141.85, 141.75, 141.68, 141.57, 140.66, 139.09, 135.74, 134.32, 133.95, 131.32, 130.99, 130.49, 130.35, 129.59, 128.46, 128.25, 128.11, 127.90, 125.94, 125.62, 124.40, 63.48, 41.58, 41.31, 35.63, 35.50, 33.99, 32. 47, 31.80, 31.54, 29.22, 28.96, 28.92, 28.84, 28.76, 25.75, 25.66, 23.26, 23.17, 22.68, 14.36, 14.33, 14.16, 10.95, 10.91, 10.83. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{96}H_{111}O_2S_7^+$, 1519.66235; found, 1519.66205.

Synthesis of ***a-BTTIC***: To a 100 ml round bottom flask, compound **4** (152 mg, 0.1 mmol) and CPTCN-M (85.6 mg, 0.4 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 (175 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.57 (s, 1H), 8.56 (s, 1H), 8.18 (s, 1H), 8.04 (s, 1H), 8.01 (s, 1H), 7.30 (s, 1H), 6.89-7.01 (m, 16H), 6.49 (d, *J* = 2.4 Hz, 1H), 6.39 (d, *J* = 2.8 Hz, 1H), 6.17 (s, 1H), 6.04-6.07 (m, 1H), 2.68-2.80 (m, 10H), 2.56 (m, 8H), 1.57 (m, 10H), 1.32-1.40 (m, 40H), 0.87-1.01 (m, 24H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 182.64, 182.08, 165.52, 157.03, 155.96, 155.89, 155.19,154.86, 153.86, 152.16, 146.84, 146.24, 144.44, 144.39, 144.09, 142.41, 142.12, 142.07, 141.65, 140.79, 138.87, 138.48, 137.04, 136.96, 135.42, 131.06, 129.47, 128.66, 128.43, 128.36, 128.08, 127.82, 126.68, 126.06, 124.87, 124.67, 115.22, 115.15, 114.69, 114.52, 66.66, 65.96, 63.74, 63.32, 41.60, 41.25, 41.12, 36.98, 35.66, 35.52, 33.76, 32.56, 32.45, 31.80, 31.55, 31.44, 29.73, 29.23, 28.99, 28.96, 28.81, 26.88, 25.77, 25.56, 25.24, 23.28, 23.23, 23.19, 22.71, 22.69, 14.37, 14.19, 13.56, 13.43, 10.90, 10.67. MALDI-TOF-MS m/z: [M] calcd. for $C_{118}H_{118}N_4O_2S_9$, 1910.67, found 1910.34.

Measurements

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Advanced II (400 MHz) spectrometers. The high resolution mass spectra (HRMS) and matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF-MS) were performed on Thermo Scientific LTQ Orbitrap Xl using ESI and 5800 MALDI-TOF/TOF mass spectrometry (AB SCIEX, USA) in positive mode, respectively. UV-Vis absorption spectra were measured by a Shimadzu UV-2700 recording spectrophotometer. Cyclic voltammetry (CV) measurements of thin films

were conducted on a CHI voltammetric analyzer in acetonitrile solution with 0.1 M tetrabutylammonium hexafluorophosphate (*n*-Bu_4NPF_6) 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. DFT calculations were performed by using Gaussian at the B3LYP/6-31G* level. Atomic force microscopy (AFM) images were obtained by using a NanoMan VS microscope in the tapping-model.

Devices fabrication and characterization

Organic solar cells (OSCs) were fabricated with a device structure of ITO/PEDOT: PSS/active layer/ZrAcac/Al. The ITO-coated glass was washed 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. A thin PEDOT: PSS (Heraeus Clevios P VP A 4083) layer with a thickness of about 40 nm was spin-cast onto the ITO substrates at 4000 rmp for 40 s, and then dried at 150 °C for 10 min in air. The PEDOT:PSS coated ITO substrates were fast transferred to a N_2 filled glove-box for further processing. The donor:acceptor blends with weight ratio of 1:1 and total concentration of 16 mg/mL were dissolved in chloroform and 0.25% DIO was added. Then the solution was stirred overnight for intensive mixing in a nitrogen-filled glove box. The blend solution was spin-cast on

the top of PEDOT: PSS layer at 2700 rmp for 40 s. Then it was annealed at 100 °C for 5 min to remove the residual solvent. 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 5.90 mm^2 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 in an Air Mass 1.5 Global (AM 1.5 G) solar simulator (Class AAA solar simulator, Model 94063A, Oriel) with an irradiation intensity of 100 mW cm^{-2}, which was measured by a calibrated silicon solar cell and a readout meter (Model 91150V, Newport). IPCE spectra were measured by using a QEX10 Solar Cell IPCE measurement system (PV measurements, Inc.).

SCLC

The electron and hole mobility of BTTIC and BTOIC neat and blend films were measured by using the method of space-charge limited current (SCLC). The electron-only SCLC device was a stack of ITO/ZnO/active layer/ZrAcac/Al, and the hole-only device was a stack of ITO/MoO_x/active layer/ MoO_x /Al. The electron-only and hole-only SCLC devices fabricating methods were same with those for solar cells. The charge carrier mobility was determined by fitting the dark current to the model of

a single carrier SCLC according to the equation: $J = 9\varepsilon_0\varepsilon_r\mu V^2/8d^3$, where J is the current density, d 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. $V = V_{app} - V_{bi}$, 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.

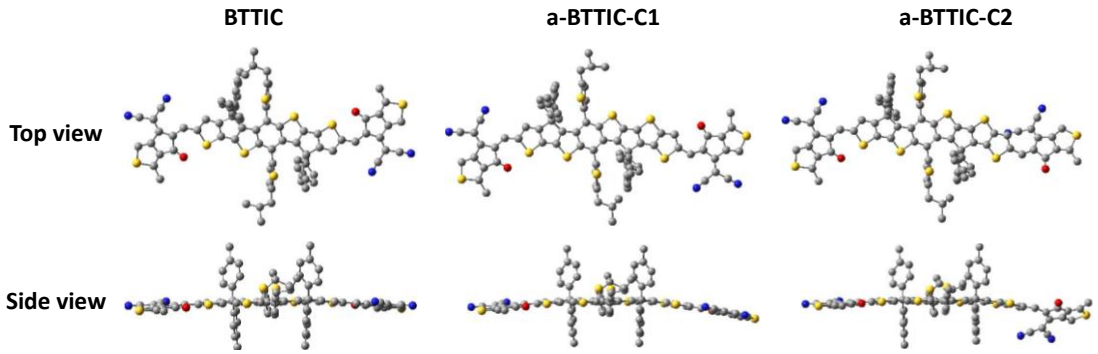

Figure S1. The top and side view of BTTIC, a-BTTIC-C1 and a-BTTIC-C2.

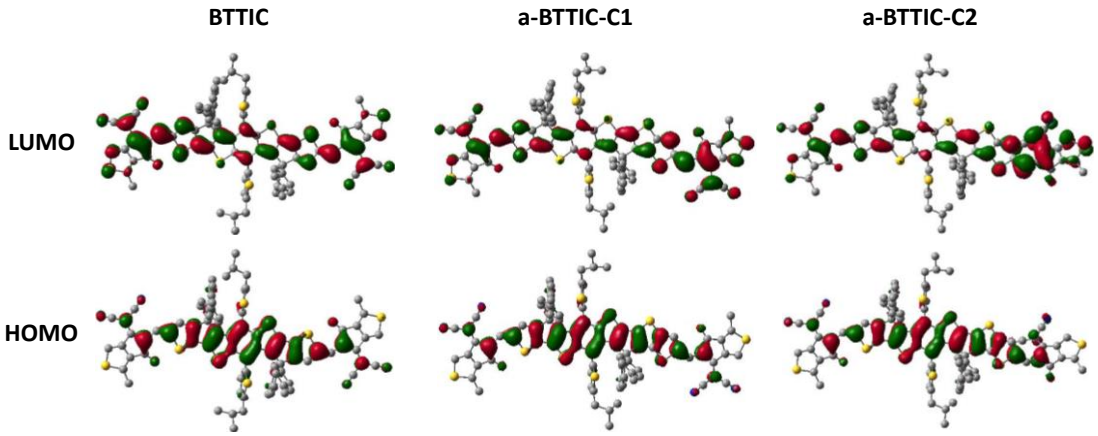

Figure S2. The LUMO and HOMO distribution of BTTIC, a-BTTIC-C1 and a-BTTIC-C2.

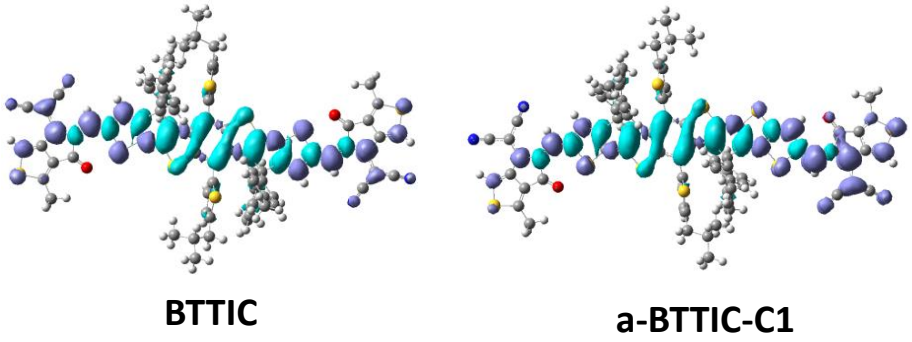

Figure S3. The charge density difference (CDD) for electronic exciton of BTTIC, a-BTTIC-C1 and a-BTTIC-C2.

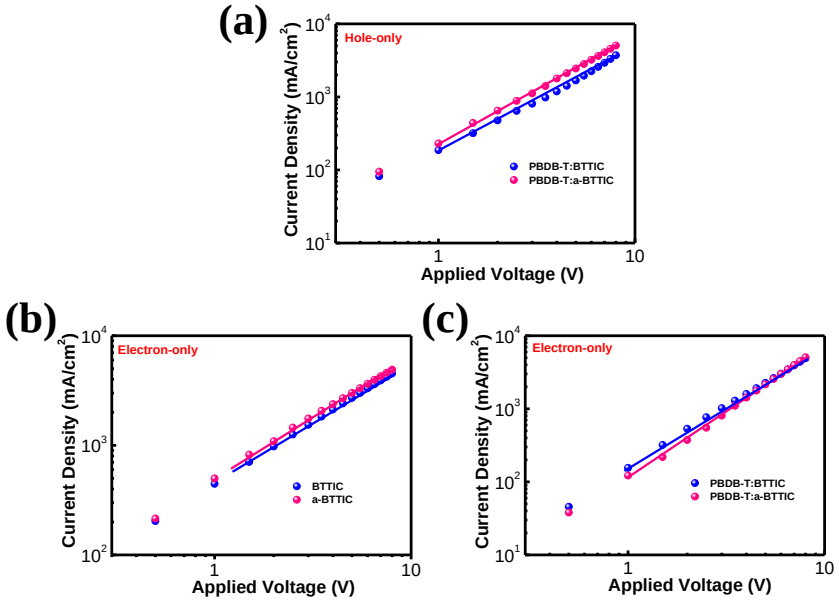

Figure S4. a) The *J-V* curves of PBDB-T:BTTIC- and PBDB-T:a-BTTIC-based hole-only devices. b) The *J-V* curves of BTTIC- and a-BTTIC-based electron-only devices. c) The *J-V* curves of PBDB-T:BTTIC- and PBDB-T:a-BTTIC-based electron-only devices.

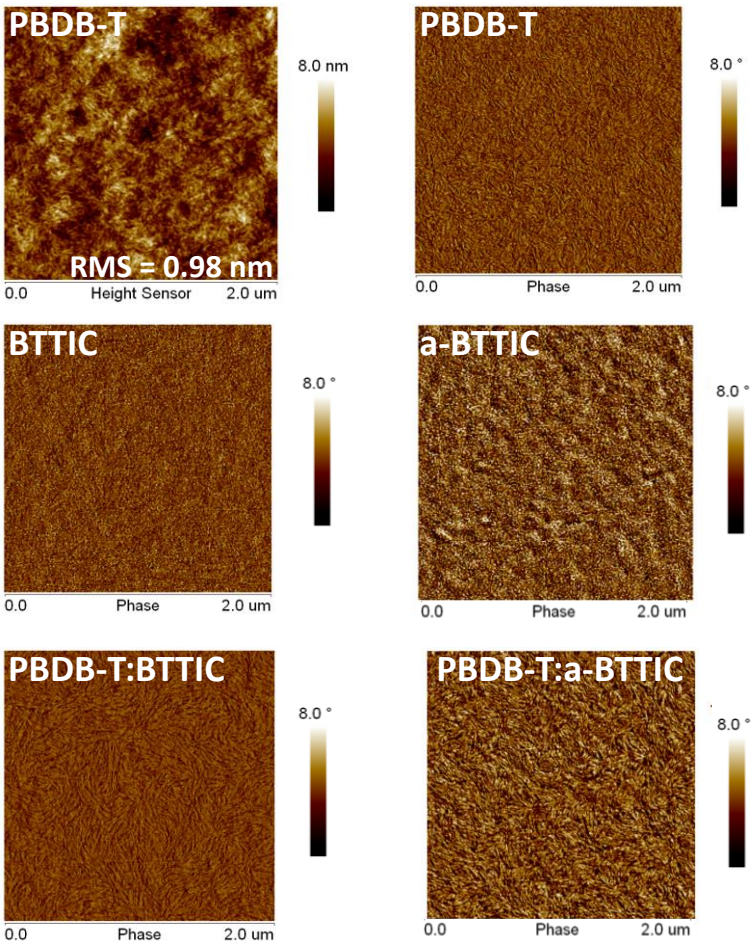

Figure S5. The AFM height and phase images of PBDB-T neat film, and phase images of BTTIC- and a-BTTIC-based neat and blend films.

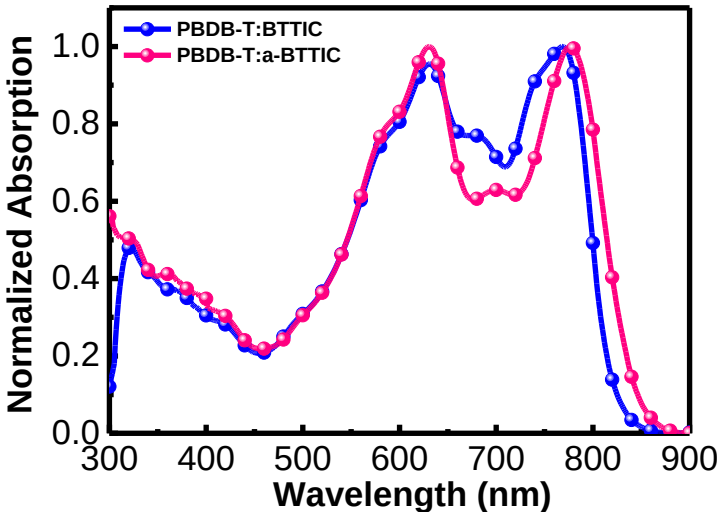

Figure S6. The normalized UV-vis absorption of PBDB-T:BTTIC and

PBDB-T:a-BTTIC blend films.

Table S1. The average and mean square error values of V_{OC}, J_{SC}, FF and PCE of PBDB-T:BTTIC- and PBDB-T:a-BTTIC-based OSCs (30 devices).

Active layer	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
PBDB-T:BTTIC	0.895 (0.898 ± 0.004)	19.45 (19.13 ± 0.25)	73.8 (73.4 ± 0.5)	12.86 (12.61 ± 0.17)
PBDB-T:a-BTTIC	0.904 (0.899 ± 0.004)	20.31 (20.10 ± 0.40)	74.0 (73.4 ± 0.5)	13.60 (13.26 ± 0.25)

Table S2. Key photovoltaic parameters calculated from the J_{ph}-V_{eff} curves of PBDB-T:BTTIC- and PBDB-T:a-BTOIC-based devices.

Active layer	J_{sat}[a] (mA cm^{-2})	J_{ph}*[b] (mA cm^{-2})	J_{ph}&[c] (mA cm^{-2})	J_{ph}*/J_{sat} (%)	J_{ph}&/J_{sat} (%)
PBDB-T:BTTIC	20.125	19.449	16.768	96.6	83.3
PBDB-T:a-BTTIC	20.961	20.312	17.874	96.9	85.3

[a]The J_{ph} under condition of V_{eff} = 2.0 V, [b]The J_{ph} under short circuit condition. [c]The J_{ph} under maximum power output condition.

Table S3. Morphological parameters obtained from GIWAXS.

Samples	**100**			**010**		
	location (Å^{-1})	*d*-spacing[c)] (Å)	CL[d)] (Å)	location (Å^{-1})	*d*-spacing[c)] (Å)	CL[d)] (Å)
PBDB-T	0.290	21.7	58.8	1.72	3.29	18.9
BTTIC	0.296	21.2	57.3	1.79	3.16	25.4
a-BTTIC	0.306	18.5	58.5	1.83	3.09	28.7
PBDB-T:BTTIC	0.302	18.7	88.0	1.71	3.31	18.1
PBDB-T:a-BTTIC	0.293	19.3	72	1.78	3.18	22.5

[a)]Calculated from $d = \pi/q$, where q is the location of maximum peak of RSoXS profile. [b)]Integrated area of RSoXS profile. [c)]Calculated from $d = 2\pi/q$, where q is the location of the (100) or (010) diffraction peak. [d)]Obtained from Scherrer equation: CL =

$2\pi K/\Delta q$, where Δq is the full-width at the half-maximum of the peak and K is the Scherrer factor.

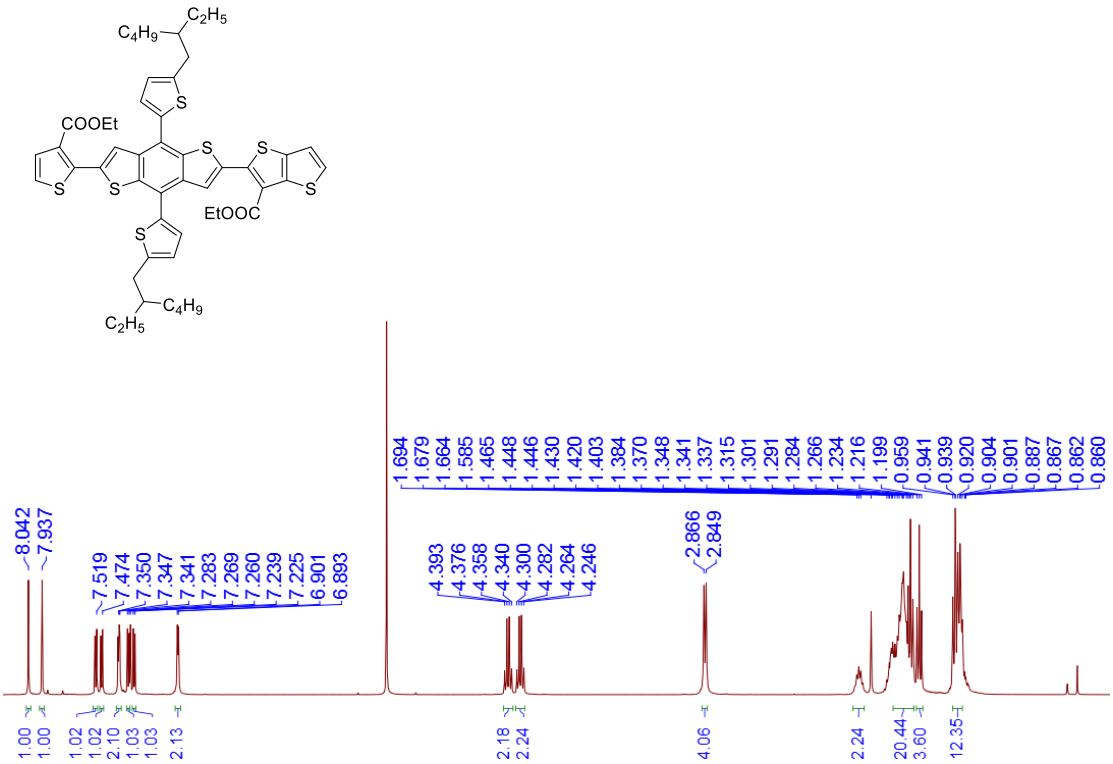

Figure S7. The ^{1}H NMR spectrum of compound **2**.

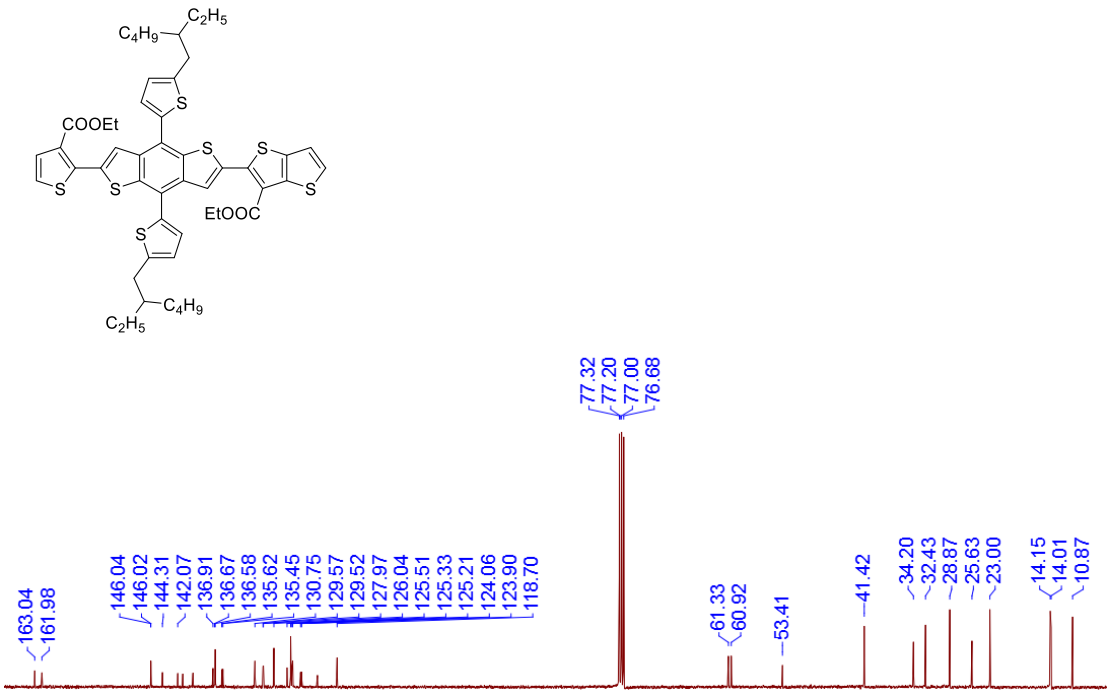

Figure S8. The ^{13}C NMR spectrum of compound **2**.

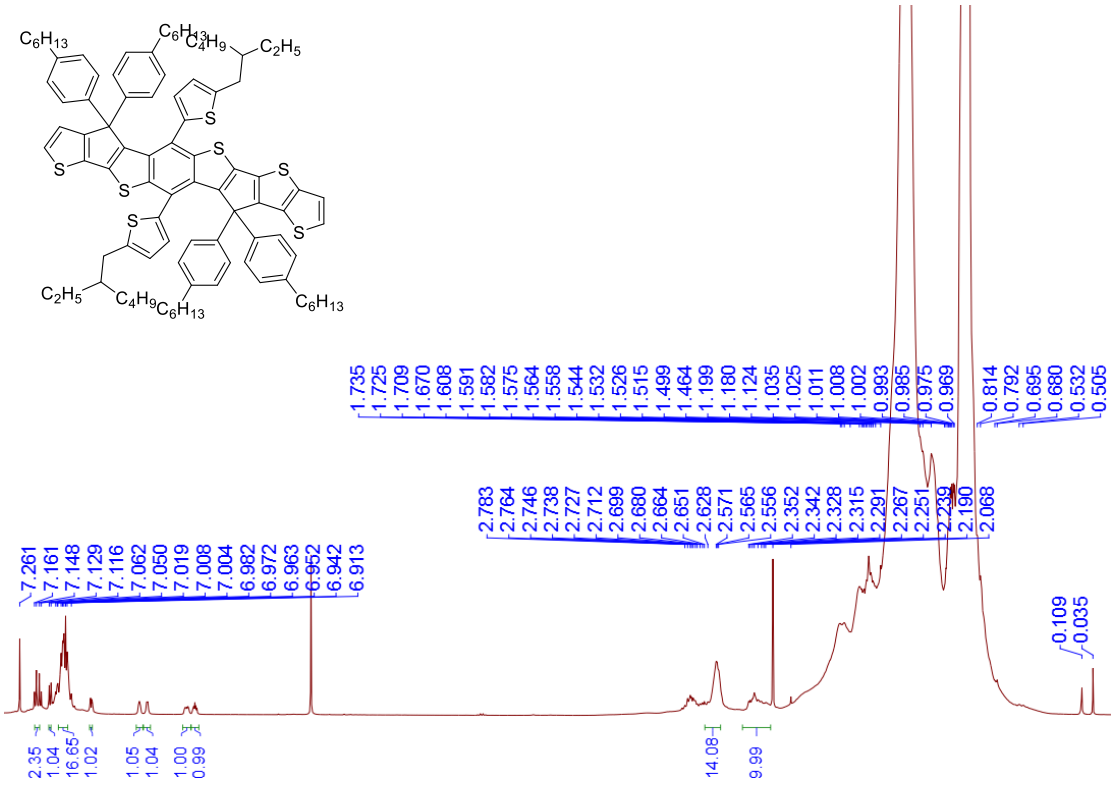

Figure S9. The ^{1}H NMR spectrum of compound **3**.

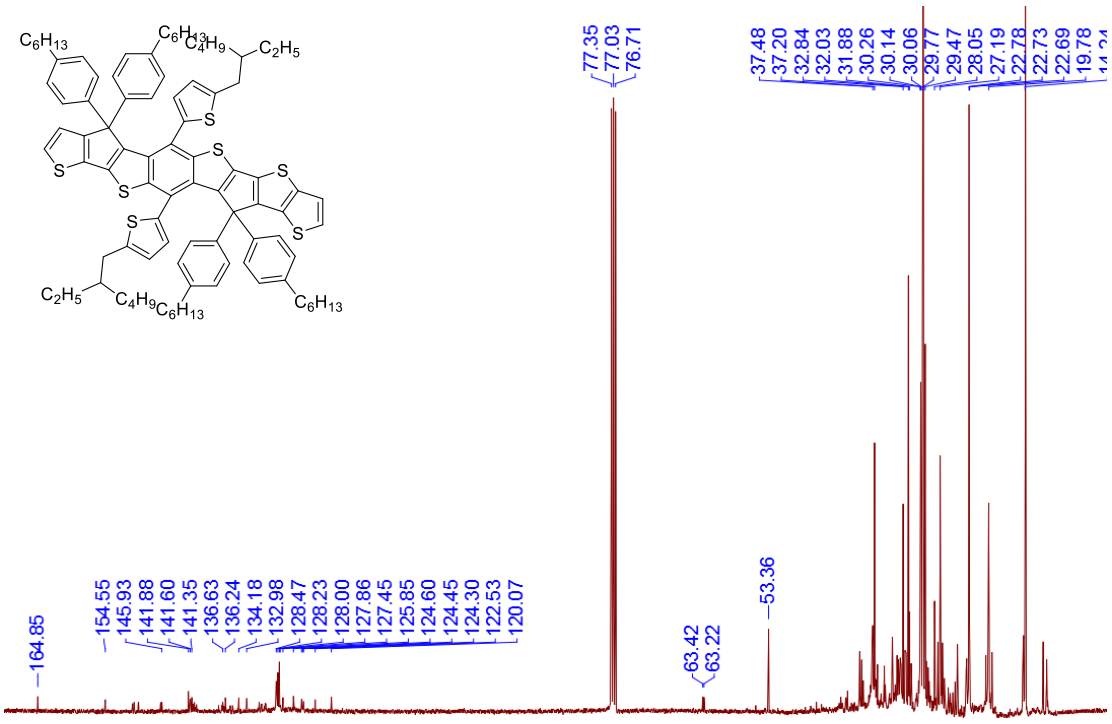

Figure S10. The ^{13}C NMR spectrum of compound **3**.

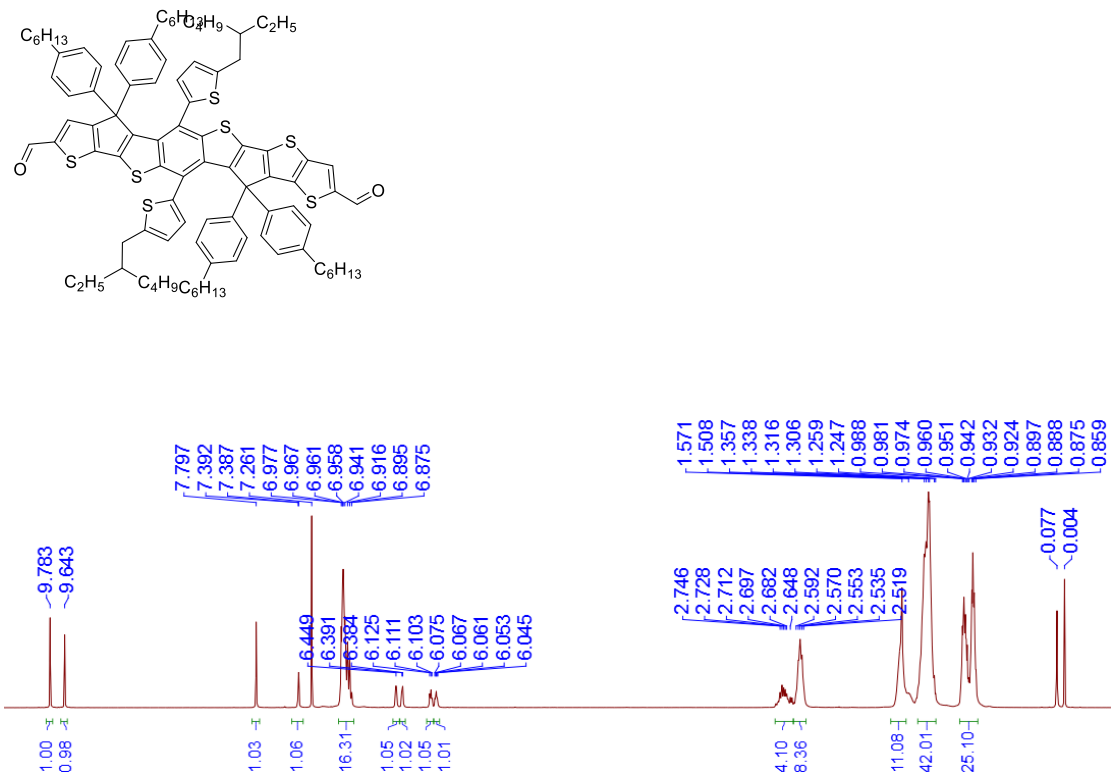

Figure S11. The ^{1}H NMR spectrum of compound **4**.

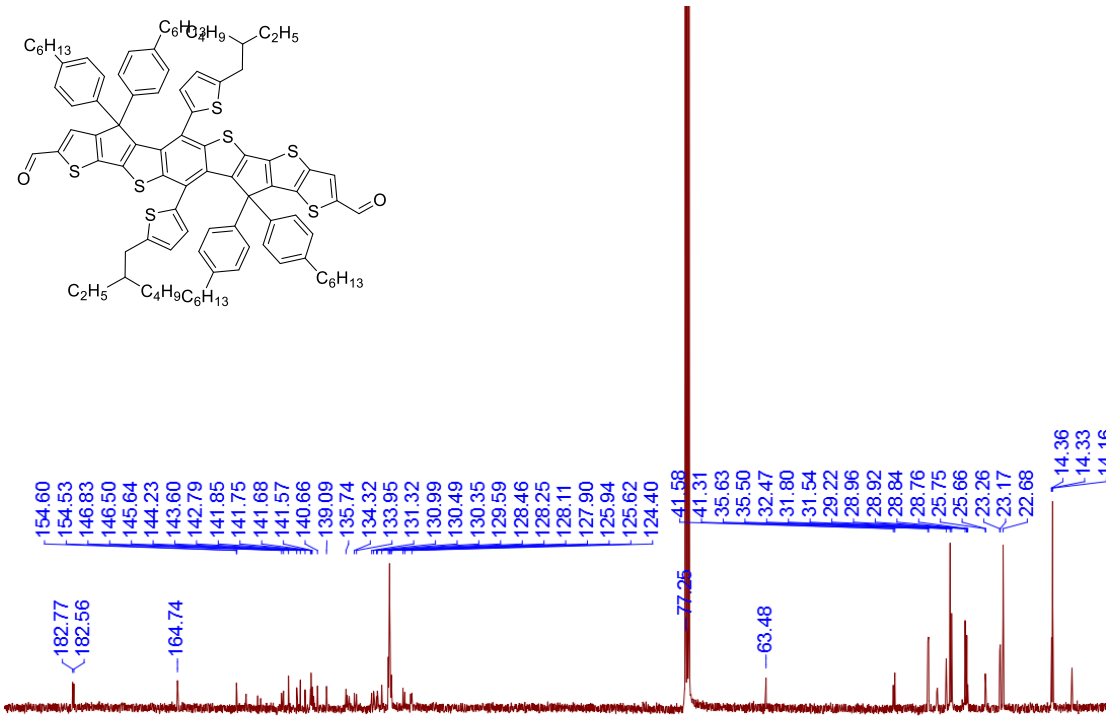

Figure S12. The ^{13}C NMR spectrum of compound **4**.

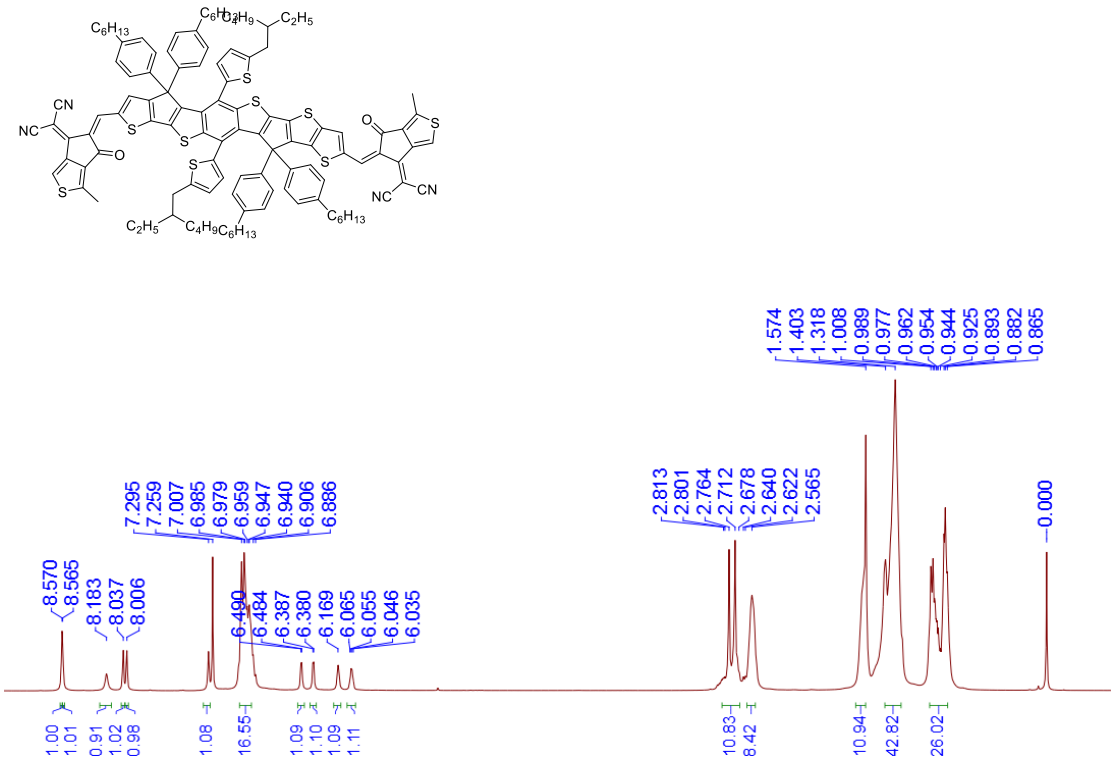

Figure S13. The ^{1}H NMR spectrum of a-BTTIC.

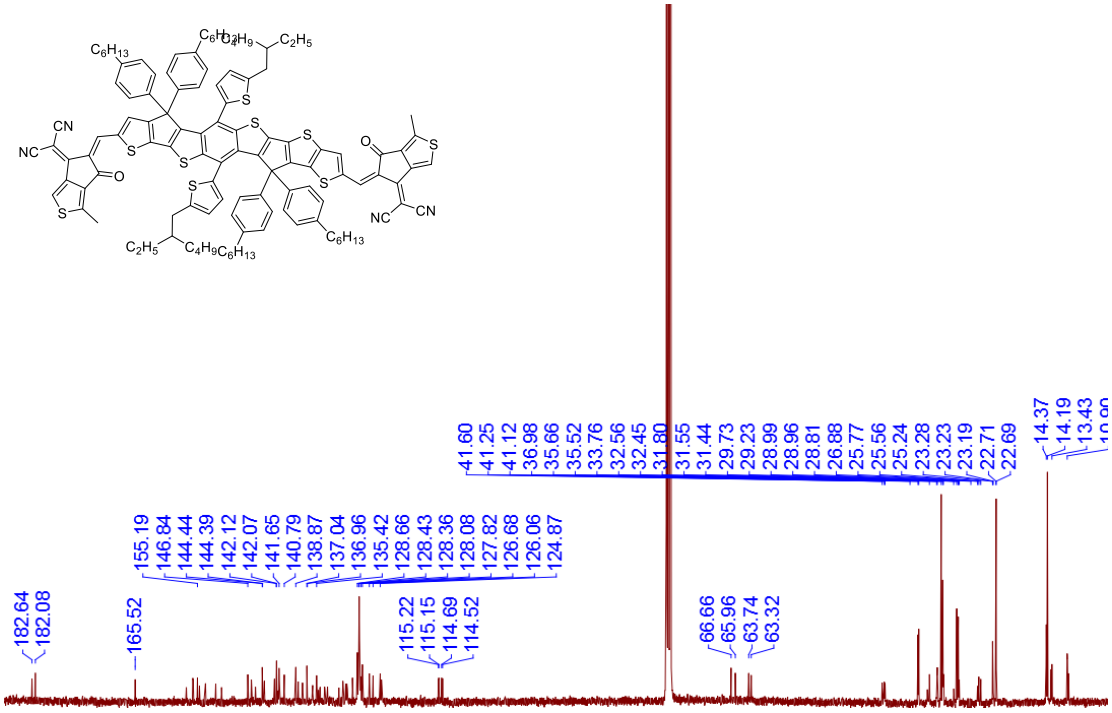

Figure S14. The ^{13}C NMR spectrum of a-BTTIC.

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