Supporting Information for

2-Dimensional Cross-Shaped Tetrathienonaphthalene-Based Ladder-Type Acceptor for High-Efficiency Organic Solar Cells

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CONTENT

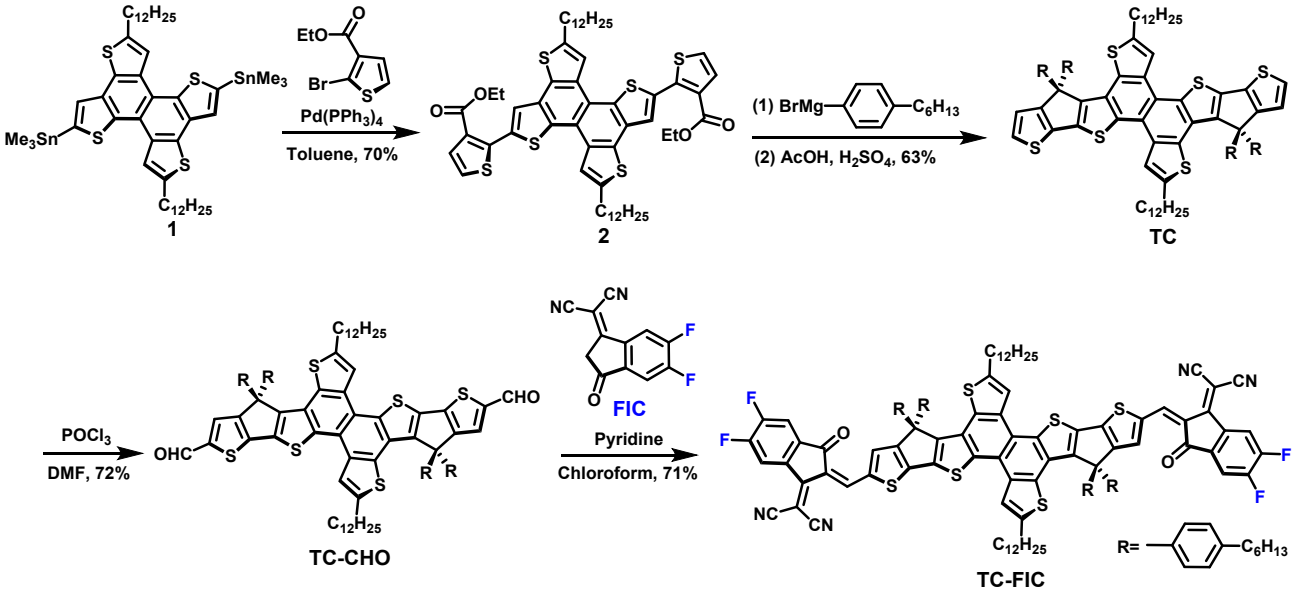
1. General Measurement and Characterization.

^{1}H and ^{13}C NMR spectra were measured using Varian 400 MHz instrument spectrometer and obtained in deuterated chloroform ($CDCl_3$) with TMS as internal reference unless otherwise stated, and chemical shifts (δ) are reported in parts per million. Absorption spectra were taken on a HP8453 UV-vis spectrophotometer. Differential scanning calorimetery (DSC) was conducted on a TA Q200 Instrument under nitrogen atmosphere at a heating/cooling rate of 10 °C/min. Thermogravimetric analysis (TGA) was recorded on a Perkin-Elmer Pyris under nitrogen atmosphere at a heating rate of 10 °C/min. Electrochemical cyclic voltammetry was conducted on a CH instruments electrochemical analyzer. A carbon glass was used as the working electrode and a Ag/AgCl electrode as the reference electrode, while 0.1 M tetrabutylammonium hexafluorophosphate in dichloromethane was the electrolyte. All CV measurements were calibrated against an internal standard of ferrocene (F_c), the ionization potential (IP) value of which is −4.8 eV for the Fc/Fc^+ redox system (−4.8 eV with respect to zero vacuum level). The ionization potential values were obtained from the equation: IP = $-(E_{ox}^{onset} - E_{(Fc)}^{onset} + 4.8)$ eV. The electron affinity (EA) values were obtained from the equation EA = $-(E_{red}^{onset} - E_{(Fc)}^{onset} + 4.8)$ eV, where the $E_{(Fc)}$ value was for Fc/Fc^+ versus Ag/Ag^+. Quantum−chemical calculations were performed with the Gaussian09 suite[S1] employing the wB97xD density functional in combination with the 6-311G(d,p) basis set. The wB97xD functional we used was built-in basis set in Gaussian 09 with no further range-separation parameter changes. Considering an insignificant effect on electronic properties, all the side-chain substituents were replaced with methyl groups. Geometry optimizations were performed with tight SCF and convergence criteria and an ultrafine integration grid by applying the GEDIIS optimization algorithm. The minimum nature of each stationary point was confirmed by a frequency analysis.

GIWAXS experiments were conducted at National Synchrotron Radiation Research Center (NSRRC) on beamline BL23A in Taiwan. The samples were irradiated with an X-ray energy of 10.09 keV (λ = 1.23 Å) at a fixed incident angle of 0.08° through a coupled double crystal Si(111)/multilayer (Mo/B4C) monochromator, and the GIWAXS patterns were recorded on a 2D image detector (Pilatus 1M-F area detector). The thin films for GIWAXS measurement were prepared under identical conditions used for the OPV devices.

2. Experimental Procedures

The synthetic procedures of compound (**1**) was described in a previous report.



Scheme 1. Synthetic route of TC-FIC.

Synthesis of Compound 2.

Compound **1** (500 mg, 0.493 mmol), ethyl 2-bromothiophene-3-carboxylate (244 mg, 1.035 mmol), and $Pd(PPh_3)_4$ (28 mg, 0.025 mmol) were dissolved in anhydrous toluene (30 mL), and the mixture was deoxygenated with N_2 for 20 min. The solution mixture was heated to reflux for 16 h under N_2 atmosphere and then cooled to room temperature. After cooling to room temperature and removing the solvent under reduced pressure, the residue was purified by column chromatography in silica gel (hexane/dichloromethane, v/v, 3:1) and then recrystallized from ethyl acetate to give orange solid **2** (344 mg, 70 %). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.21 (s, 1H), 8.03 (s, 1H), 7.61 (d, J = 5.6 Hz, 1H), 7.34 (d, J = 5.6 Hz, 1H), 4.35 (q, J = 7.2 Hz, 2H), 3.11 (t, J = 7.6 Hz, 2H), 1.90-1.86 (m, 2H), 1.51-1.25 (m, 18H), 0.87 (t, J = 7.2 Hz, 3H).^{13}C NMR ($CDCl_3$, 100 MHz): δ 163.10, 145.34, 141.74, 134.50, 133.37, 133.00, 132.95, 132.63, 130.92, 129.42, 125.08, 123.71, 122.28, 121.23, 60.96, 31.91, 31.71, 31.09, 29.73, 29.68, 29.64, 29.61, 29.54, 29.45, 29.35, 29.25, 22.68, 14.24, 14.11. HRMS (FD, $C_{56}H_{68}O_4S_6$): calcd, 996.3436; found, 996.3440.

Synthesis of Compound TC.

A Grignard reagent was prepared by the following procedure: To a suspension of magnesium turnings (360 mg, 15.0 mmol) and 3-4 drops of 1,2-dibromoethane in dry THF (10 mL) was slowly added 1-bromo-4-hexylbenzene (3.62 g, 15.0 mmol) dropwise, and the mixture was stirred for 45 min. To a solution of compound **2** (1 g, 1 mmol) in dry THF (40 mL) under nitrogen was added 4-hexylbenzene 1-magnesium bromide (5 mL, 5 mmol) dropwise at room temperature. The resulting mixture was refluxed for 16 h. The mixture was extracted with CH_2Cl_2 (50 mL × 3). The combined organic layer was dried over $MgSO_4$. After removing the solvent under reduced pressure, the orange residue was resolved by octane (70 mL) and acetic acid (7 mL), then sulfuric acid (0.7 mL, 14 mmol) was added dropwise slowly. The resulting solution was stirred for 3 h at 65 °C and then quenched with water. The residue was extracted by CH_2Cl_2 (50 mL × 3). The combined organic layer was dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/dichloromethane, v/v, 19:1) to give an orange solid **TC** (950 mg, 63%). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.37 (s, 1H), 7.43 (d, *J* = 8.4 Hz, 4H), 7.26 (d, *J* = 4.8 Hz, 1H), 7.08 (d, *J* = 5.2 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 4H), 2.94 (t, *J* = 8.0 Hz, 2H), 2.54 (t, *J* = 7.6 Hz, 4H), 1.68-1.64 (m, 2H), 1.56-1.51(m, 2H), 1.35-1.26 (m, 32H), 0.88-0.83 (m, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 163.38, 151.73, 145.96, 141.66, 138.58, 135.55, 134.85, 134.72, 133.05, 132.12, 129.37, 129.00, 127.90, 126.83, 123.03, 121.63, 120.99, 63.24, 37.09, 35.54, 33.19, 31.92, 31.69, 31.60, 31.43, 31.27, 30.72, 30.16, 30.03, 29.75, 29.73, 29.70, 29.66, 29.47, 29.38, 29.36, 29.09, 26.73, 22.69, 22.58, 14.12, 14.07, 1.01.; HRMS (FD, $C_{100}H_{124}S_6$): calcd, 1516.8022; found, 1516.7999.

Synthesis of Compound TC-CHO.

To a two-neck flask $POCl_3$ (151 mg, 0.97 mmol) was added dropwise into anhydrous DMF (3.7 mL) at 0 ºC to form the Vilsmeier reagent. Then the solution of **TC** (700 mg, 0.46 mmol) in anhydrous 1,2-dichloroethane (35 mL) was added, followed by heating to reflux for 16 h. After cooling to room temperature, the mixture was poured into ice water and stirred for another 30 min. Then the mixture

was neutralized with aqueous $NaHCO_3$ and extracted with CH_2Cl_2 (50 mL × 3). The combined organic layer was dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/ dichloromethane, v/v, 2/1) to give an orange solid **TC-CHO** (515 mg, yield 72%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.78 (s, 1H), 8.34 (s, 1H), 7.70 (s, 1H), 7.41 (d, *J* = 8.4 Hz, 4H), 7.05 (d, *J* = 8.4 Hz, 5H), 2.94 (t, *J* = 7.6 Hz, 4H), 2.54 (t, *J* = 7.6 Hz, 4H), 1.68-1.64 (m, 2H), 1.56-1.52 (m, 2H), 1.29-1.26 (m, 32H), 0.92-0.83 (m, 9H).^{13}C NMR ($CDCl_3$, 100 MHz):δ 182.53, 163.40, 155.58, 147.10, 145.18, 145.03, 142.35, 137.72, 137.07, 134.15, 133.47, 132.36, 131.38, 129.25, 129.10, 128.20, 124.45, 123.97, 122.25, 120.89, 63.51, 35.52, 31.92, 31.67, 31.60, 31.43, 31.25, 30.71, 30.18, 29.72, 29.69, 29.63, 29.43, 29.37, 29.05, 22.68, 22.57, 14.10, 14.06, 1.01.; HRMS (FD, $C_{102}H_{124}O_2S_6$): calcd, 1572.7920.; found, 1572.7929.

Synthesis of TC-FIC. FIC (117 mg, 0.508 mmol) was added into the solution of **TC-CHO** (200 mg, 0.127 mmol) in chloroform (18 mL) with pyridine (0.1 mL), the mixture was deoxygenated with nitrogen for 20 min and then refluxed for 10 h. After cooling to room temperature and removal of the solvent under reduced pressure, the residue was then washed with methanol and hexane. The crude product was purified by silica gel column (hexane/dichloromethane, v/v, 1/1) to give a deep blue solid **TC-FIC** (180 mg, 71%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.79 (s, 1H), 8.38 (dd, *J* = 6.4, 4.8 Hz, 1H), 8.25 (s, 1H), 7.71 (s, 1H), 7.44 (d, *J* = 8.0 Hz, 4H), 7.11 (d, *J* = 8.0 Hz, 4H), 2.98 (t, *J* = 8.0 Hz, 2H), 2.57 (t, *J* = 8.0 Hz, 4H), 1.77-1.70 (m, 2H), 1.61-1.54 (m, 2H), 1.41-1.24 (m, 32H), 0.88-0.83 (m, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz):δ 185.92, 164.61, 158.21, 158.00, 155.49, 148.10, 142.71, 140.35, 139.16, 138.75, 138.13, 136.36, 134.23, 134.23, 134.04, 133.73, 133.61, 132.52, 129.30, 129.25, 128.42, 122.66, 120.69, 120.20, 114.81, 114.59, 114.34, 112.23, 68.47, 63.55, 35.54, 31.93, 31.66, 31.36, 31.26, 30.73, 29.75, 29.70, 29.48, 29.38, 29.17, 29.06, 22.68, 22.56, 14.10, 14.05.; HRMS (FD, $C_{126}H_{128}N_4O_2F_4S_6$): calcd, 1996.8292; found, 1996.8276.

3. Two-dimensional Conjugated Strategy in Materials for OPV

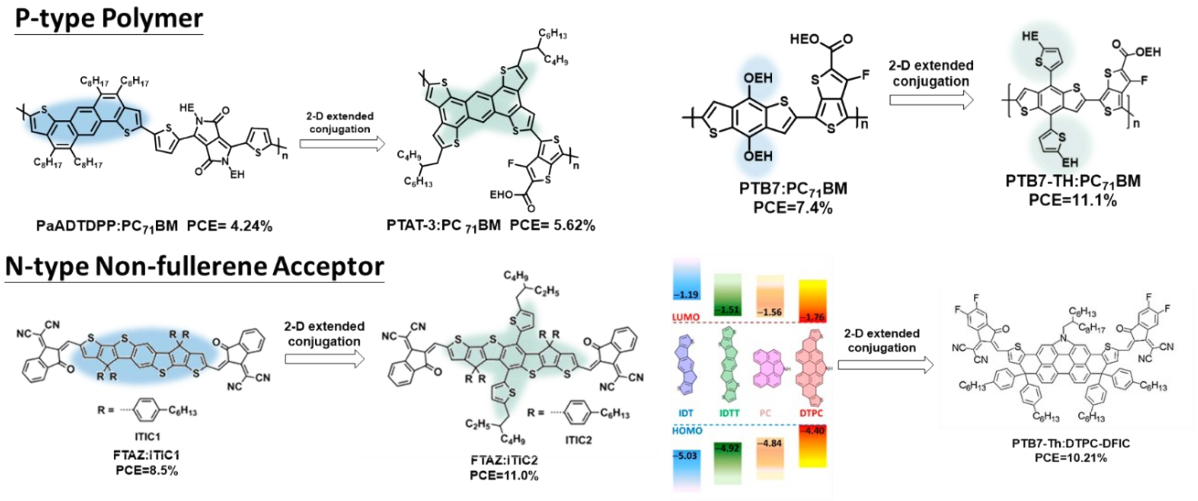


Figure S1. Representative examples of vertically extended p-type and n-type materials in the literature.

4. TGA and DSC Analysis

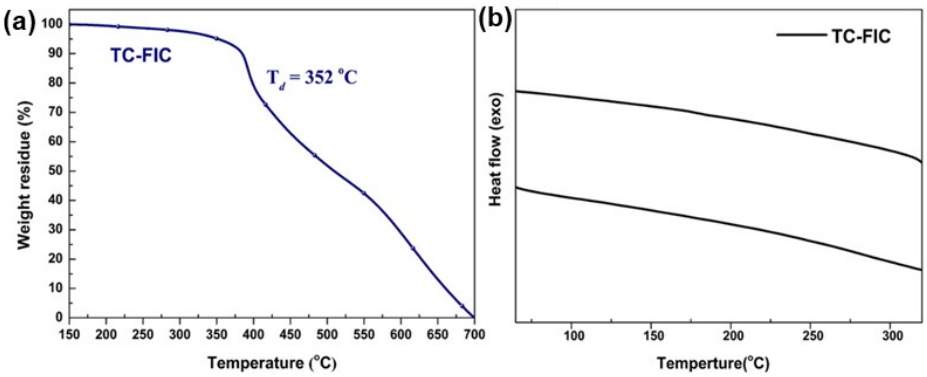


Figure S2. (a) Thermogravimetric analysis and (b) differential scanning calorimetry of **TC-FIC**.

5. Molar Extinction Coefficient Spectrum

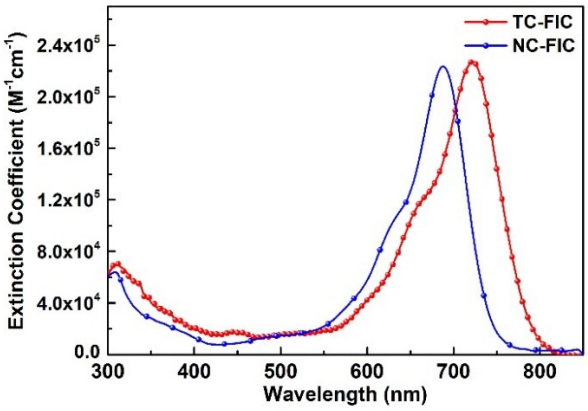


Figure S3. Molar extinction coefficient (ε) of NC-FIC and TC-FIC. (3.71×10^{-6} M for NC-FIC and 2.90×10^{-6} M for TC-FIC, respectively)

6. Cyclic Voltammogram

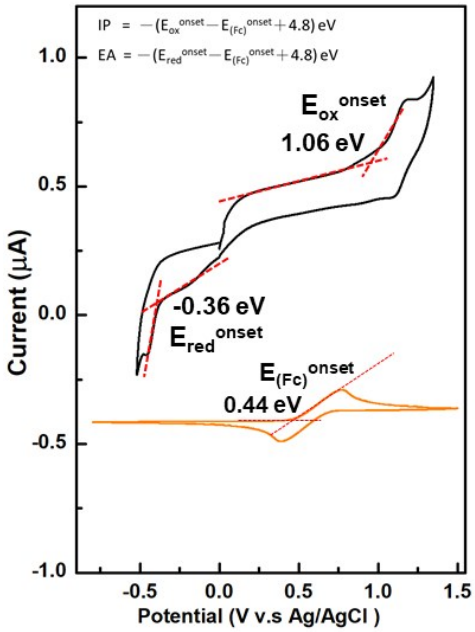


Figure S4. Cyclic voltammogram of TC-FIC in dichloromethane at a scanning rate of 100 mV/S.

7. Charge Densities of the Cations and Anions

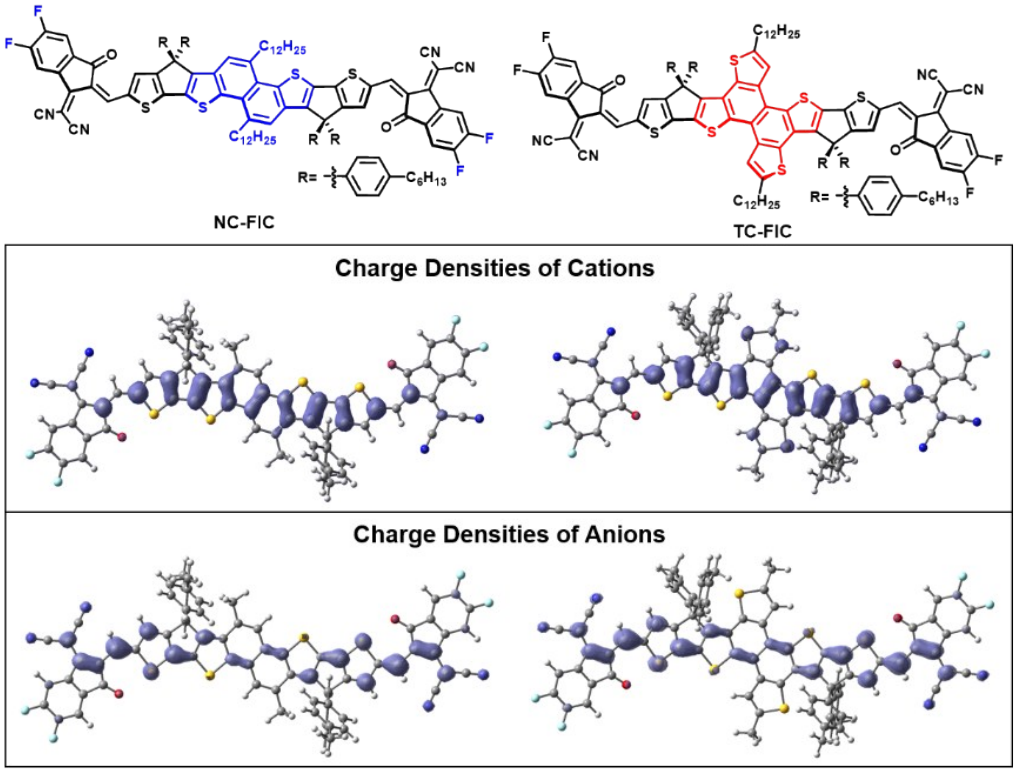


Figure S5. The cationic/anionic molecular orbitals of TC-FIC and NC-FIC with optimized geometries calculated at the level of WB97XD /6-311G(d,p).

8. SCLC Measurements

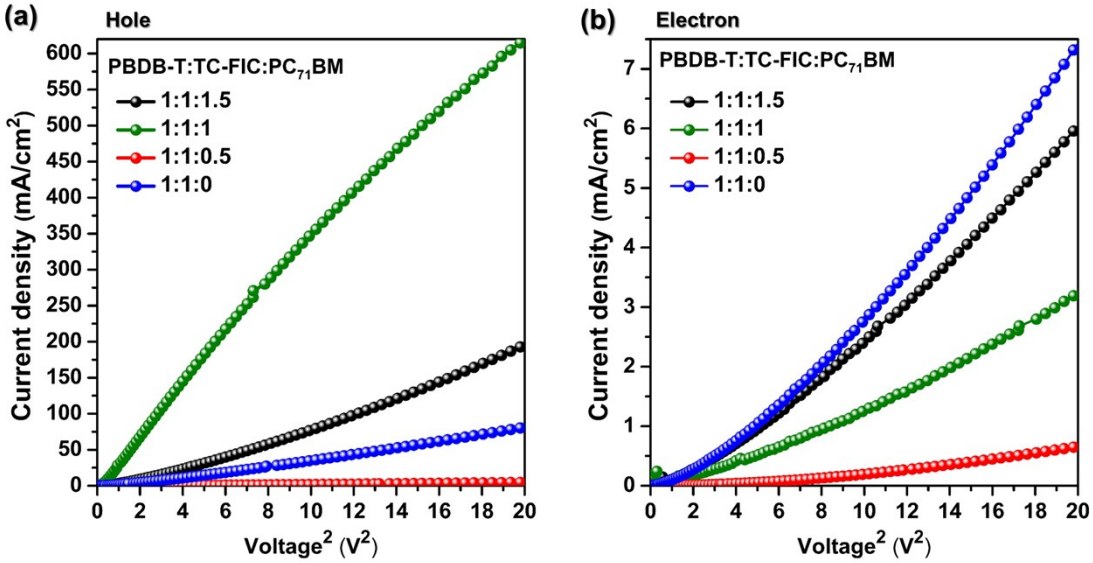


Figure S6. *J-V* curves of the (a) hole-only and (b) electron-only device characteristics of PBDB-T:TC-FIC:$PC_{71}BM$-based device.

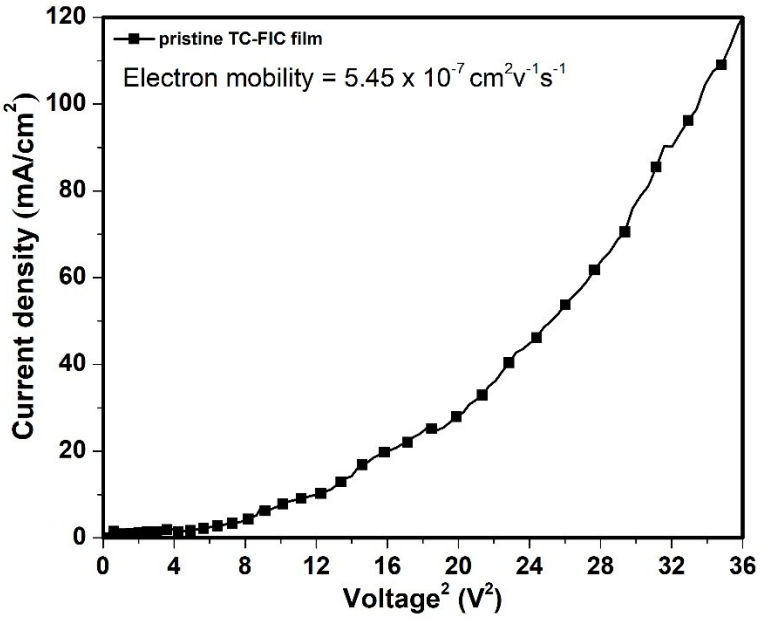


Figure S7. *J-V* curves of the electron-only device characteristics of TC-FIC pristine device.

Table S1. Hole and electron mobility of PBDB-T:TC-FIC:$PC_{71}BM$ and PBDB-T:NC-FIC:$PC_{71}BM$ blends measured by the SCLC Model.

Device	Blend ratio (wt%)	μ_h ($cm^2V^{-1}s^{-1}$)	μ_e ($cm^2V^{-1}s^{-1}$)
PBDB-T:TC-FIC:$PC_{71}BM$	1:1:0	1.83×10^{-5}	7.00×10^{-7}

	1:1:0.5	2.10×10^{-4}	4.16×10^{-5}
	1:1:1	1.54×10^{-4}	3.31×10^{-5}
	1:1:1.5	5.27×10^{-5}	5.43×10^{-6}
PBDB-T:NC-FIC:$PC_{71}BM$	1:1:0	1.00×10^{-6}	6.97×10^{-7}
	1:1:0.5	1.98×10^{-5}	7.18×10^{-6}
	1:1:1	2.49×10^{-5}	8.14×10^{-6}
	1:1:1.5	2.60×10^{-5}	1.73×10^{-5}

9. Fabrication and Characterization of OPV devices

The fabrication of the inverted device follows the procedures: The ITO-coated glass substrates were cleaned by ultrasonic cleaner in detergent, DI-water, acetone and isopropyl alcohol for 10 min, respectively, and subsequently treated with UV-ozone for 45 min. The ZnO precursor solution (diethyl zinc) in THF was spin coated onto pre-treated ITO-coated glass and followed by thermal annealing at 170 °C in air for 15 min to crystallize the film (thickness = ca. 50 nm). The detailed processing parameters are as follows: The chlorobenzene (CB) solution of PBDB-T/TC-FIC (8 mg mL^{-1}; 3000 rpm) and PBDB-T/TC-FIC/$PC_{71}BM$ (7 mg mL^{-1}; 3000 rpm) in a different weight ratio with 0.5 vol% DIO as additive were prepared and stirred 12 h at 80 °C. Active layers were formed by spin-coating on top of the ZnO/ITO substrate with the thickness of ca 100 nm and the substrates were thermally annealed at 150 °C for 15 min in the glove box. Finally, an MoO_3 layer (thickness = ca. 7 nm) and silver top anode (thickness = ca. 150 nm) were then thermally evaporated through a shadow mask under high vacuum ($<1 \times 10^{-6}$ Torr) to complete the inverted devices. The devices without encapsulation were characterized in ambient condition. Each device was constituted of 4 pixels defined by an active area of 0.04 cm^2. Current-voltage characteristics were measured by a Keithley 2400 SMU under the irradiation of AM 1.5G San-Yi solar simulator with JIS AAA spectrum. The characteristics of the solar cells were optimized by testing approximately 25 cells. Finally, the $J - V$ curves were measured in air under an AM 1.5 G spectrum from a solar simulator. IPCE spectra were measured using a lock-in amplifier with a current preamplifier under short-circuit conditions with illumination by monochromatic light from a 250 W quartz-halogen lamp (Osram) passing through a monochromator (Spectral Products CM110).

10. Computational Details

Cartesian coordinates (Å) of the Gaussian WB97XD/6−311G(d,p) optimized structures

NC-FIC

C	1.83876100	-0.13077500	-0.06681800
C	2.26600400	1.20015200	0.06404100
C	0.47363500	-0.51555800	-0.07025900
C	1.27622300	2.22580800	0.22779800
C	-0.04115200	1.86046100	0.21881500
C	-0.47360200	0.51572000	0.07027500
S	-3.15668300	1.26457400	0.23185300
S	3.15670900	-1.26442500	-0.23180100
C	-4.27468100	-0.03825600	0.14565800
C	-3.70194600	-1.27397200	0.00428600
C	3.70198600	1.27411900	-0.00423200
C	4.27471400	0.03839500	-0.14556300
C	5.70631900	0.15365500	-0.15798200
C	6.03766000	1.48745600	-0.02781900
C	-5.70628500	-0.15353100	0.15812600
C	-6.03761600	-1.48733200	0.02793800
C	7.41227200	1.67919600	0.02232500
C	8.13454100	0.48633000	-0.07749700
S	7.04787100	-0.89284000	-0.23400900
C	4.78560800	2.36476400	0.03457900
C	4.75494800	3.12494200	1.37173000
C	4.65410000	4.50531700	1.47751700
C	4.80956600	2.37805300	2.55237200
C	4.60764000	5.12306700	2.72493500
H	4.58060800	5.11871800	0.58886400
C	4.76009900	2.99390600	3.79031300
H	4.88453900	1.29629700	2.50024000
C	4.65914800	4.38394400	3.90095900
H	4.51972000	6.20361800	2.77524300
H	4.79831300	2.38712900	4.68965100
C	4.77578600	3.24158200	-1.22537500
C	3.84444800	3.06492900	-2.24286900
C	5.77175400	4.20542700	-1.41593400
C	3.89137700	3.83696300	-3.40055300
H	3.06642600	2.31725400	-2.14946300

C	5.81529300	4.97252100	-2.56748300
H	6.52268800	4.36904200	-0.65151600
C	4.87116500	4.80526600	-3.58400100
H	3.14621700	3.67401900	-4.17241500
H	6.59940000	5.71439600	-2.68127100
C	4.61653200	5.04595800	5.25243800
H	4.41532000	6.11490600	5.16386600
H	3.84143300	4.60255200	5.88285500
H	5.57047500	4.92426900	5.77385100
C	4.92394500	5.65026400	-4.82884200
H	4.75602000	6.70480500	-4.59236400
H	5.90285000	5.57587800	-5.30987000
H	4.16613100	5.34098900	-5.55055200
C	-4.78555700	-2.36462600	-0.03452500
C	-4.75492800	-3.12476600	-1.37169800
C	-4.65405900	-4.50513600	-1.47752300
C	-4.80959400	-2.37784600	-2.55231800
C	-4.60762200	-5.12285300	-2.72495800
H	-4.58052600	-5.11855900	-0.58888800
C	-4.76015100	-2.99366700	-3.79027600
H	-4.88458500	-1.29609300	-2.50015500
C	-4.65917700	-4.38370000	-3.90096200
H	-4.51968000	-6.20340100	-2.77529800
H	-4.79840300	-2.38686700	-4.68959700
C	-4.77567400	-3.24148200	1.22540100
C	-5.77157800	-4.20539700	1.41593400
C	-3.84433300	-3.06480900	2.24289100
C	-5.81505400	-4.97253900	2.56745200
H	-6.52250500	-4.36903400	0.65151400
C	-3.89120100	-3.83688800	3.40054700
H	-3.06636000	-2.31708100	2.14950200
C	-4.87092500	-4.80526100	3.58396700
H	-6.59910900	-5.71447100	2.68122000
H	-3.14604400	-3.67392600	4.17240800
C	-4.92363700	-5.65030900	4.82877800
H	-5.90254900	-5.57602500	5.30980600
H	-4.75561900	-6.70482600	4.59226100
H	-4.16585000	-5.34099400	5.55050000

C	-4.61658400	-5.04567700	-5.25246000
H	-3.84153700	-4.60221200	-5.88289800
H	-4.41531100	-6.11461700	-5.16392300
H	-5.57055700	-4.92402600	-5.77382700
C	9.55195200	0.51658600	-0.04731700
C	10.53239100	-0.43645100	-0.10331600
C	-8.13451000	-0.48623200	0.07769700
C	-9.55192400	-0.51652800	0.04754300
C	11.65869900	-2.52039000	-0.06802000
C	12.63378200	-1.52821200	0.02023300
C	13.97384000	-1.89231600	0.13105900
C	14.27266200	-3.24065000	0.14796400
C	13.28416000	-4.22034600	0.05359400
C	11.95434900	-3.87107700	-0.05630200
H	11.18260800	-4.62699800	-0.12805600
H	9.89225600	1.53976300	0.05592100
C	-10.53242800	0.43644500	0.10354900
C	-11.65896000	2.52025600	0.06778700
C	-12.63392300	1.52795800	-0.02045300
C	-13.97400300	1.89189300	-0.13156400
C	-11.95475900	3.87090800	0.05579400
C	-13.28459000	4.22001100	-0.05439000
C	-14.27297000	3.24019200	-0.14876300
H	-11.18311500	4.62692900	0.12754800
H	-14.78950600	1.18857700	-0.20868000
H	-9.89218700	-1.53972100	-0.05571000
H	7.91157100	2.63259100	0.13549600
C	-11.97472800	0.19831500	0.03992300
C	-10.32059300	1.89513300	0.16432100
O	-9.26927000	2.49118500	0.26216600
C	11.97472400	-0.19848000	-0.03975300
C	10.32039000	-1.89510500	-0.16426100
O	9.26897700	-2.49102100	-0.26198400
C	12.64168900	0.99703600	-0.06660000
C	-12.64153500	-0.99727900	0.06710400
C	-12.00787400	-2.26898100	0.19663500
N	-11.53998500	-3.31707000	0.30558300
C	-14.06204700	-1.10667300	-0.00997700

N	-15.20456700	-1.24590600	-0.07193100
C	12.00821800	2.26889300	-0.19553900
N	11.54051600	3.31711800	-0.30398800
C	14.06222900	1.10619900	0.01029500
N	15.20478200	1.24523600	0.07210100
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C	0.04118800	-1.86029800	-0.21880600
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C	-2.26596700	-1.19999400	-0.06402000
C	-1.83872800	0.13093400	0.06684300
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C	-1.64002500	-3.66534700	-0.45104200
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H	-2.36120800	-4.02472200	0.28435300
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H	2.36123300	4.02488100	-0.28436500
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F	13.65324000	-5.49863100	0.07458100
F	15.54044800	-3.63417800	0.25689600
F	-15.54077800	3.63356500	-0.25799300
F	-13.65380600	5.49825200	-0.07566500

TC-FIC

C	1.84153100	-0.16850900	0.69534100
C	-1.87112800	0.17189400	0.77788200
C	-2.32798100	-1.15519800	0.73433800
S	-3.19149100	1.30725300	0.55588500
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C	-3.74476400	-1.22671400	0.54804000
C	3.71034600	1.23447800	0.45491700

C	4.25805300	-0.00033000	0.24223200
C	5.67401900	0.11913200	0.03124300
C	6.01770600	1.45277200	0.12978300
C	-5.71620300	-0.10787400	0.17887400
C	-6.03365100	-1.45063800	0.11848300
C	7.38201800	1.65162100	-0.03882100
C	8.08199800	0.46477700	-0.27398400
S	6.98891000	-0.91838200	-0.27650200
C	4.79035000	2.32387200	0.40560900
C	4.92831200	2.98510500	1.79225300
C	4.77954700	4.34661200	2.01654500
C	5.20433500	2.16628300	2.89250300
C	4.90909200	4.87801700	3.29791200
H	4.54687700	5.01465700	1.19803900
C	5.33004400	2.69618200	4.16394100
H	5.32357000	1.09684500	2.75114700
C	5.18653700	4.06828300	4.39194700
H	4.78388400	5.94660100	3.43979800
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C	4.62953600	3.28991300	-0.77208800
C	3.61599900	3.14898900	-1.71309300
C	5.57743100	4.29711800	-0.97879000
C	3.53850000	3.99901200	-2.81282400
H	2.87411700	2.36689000	-1.60634500
C	5.49698700	5.14186100	-2.07241300
H	6.38835800	4.43214200	-0.27208100
C	4.47046000	5.01141600	-3.01115500
H	2.73456100	3.86297200	-3.52892400
H	6.24834600	5.91417800	-2.20308500
C	5.33066800	4.63531600	5.77904200
H	5.17230100	5.71510400	5.78499900
H	4.60789300	4.18238800	6.46334900
H	6.32807800	4.43658000	6.18107700
C	4.37992600	5.94812400	-4.18629700
H	4.05052400	6.94087000	-3.86491000
H	5.35249400	6.06791500	-4.66990900
H	3.66895700	5.58456000	-4.93030500
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C	-3.98785200	-5.24341000	-2.01073900
H	-4.37598300	-5.08877000	0.08392200
C	-4.03558200	-3.20784800	-3.25282000
H	-4.48279500	-1.43486400	-2.15270800
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H	-6.58974600	-4.35327100	0.78132000
C	-4.70303800	-3.51531300	4.02286600
H	-3.64810700	-2.04866000	2.88472100
C	-5.67020400	-4.51376200	4.04505900
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C	-8.09504600	-0.46197600	-0.29803600
C	-9.48896200	-0.50424000	-0.55769300
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H	-9.81641800	-1.53470300	-0.61881000
H	7.88818200	2.60722800	0.00282500
C	-11.88120000	0.19450400	-0.98270100

C	-10.25303200	1.90378800	-0.73453700
O	-9.21643500	2.50802300	-0.55918400
C	11.87477900	-0.19105700	-0.92361100
C	10.22171800	-1.89214000	-0.83235700
O	9.17141500	-2.49156700	-0.74396300
C	12.53713700	1.00691000	-0.95437000
C	-12.53917700	-1.00480700	-1.04339000
C	-11.91828500	-2.27605300	-0.85919300
N	-11.46185400	-3.32494600	-0.71504500
C	-13.93935800	-1.12201100	-1.29187500
N	-15.06535100	-1.26895200	-1.48964100
C	11.91077700	2.27929600	-0.79843000
N	11.44905400	3.32902900	-0.67952000
C	13.94483700	1.12219800	-1.15720000
N	15.07704200	1.26737400	-1.31709400
C	-7.37991100	-1.65469900	-0.15423100
S	-7.03746700	0.93257800	-0.08743400
H	-7.86184700	-2.61841300	-0.25524200
C	2.30322800	1.15701900	0.70539300
C	-0.02509100	1.88571700	1.00048000
C	0.46385900	-0.52406600	0.84085800
C	0.00736200	-1.88762400	0.93217600
C	-0.48864600	0.52621200	0.88244500
C	1.33591600	2.17297000	0.91685900
C	-0.78792100	3.08057300	1.24554200
S	1.64506800	3.86959200	1.09831400
C	-1.35398900	-2.17711400	0.87533500
C	0.78003600	-3.08291100	1.13817700
S	-1.65394300	-3.87694200	1.04253500
C	0.03848900	-4.21379000	1.21566300
C	-0.04171500	4.20858800	1.31694800
C	0.51831600	-5.61241300	1.43590900
H	0.26177300	-6.25749600	0.59167000
H	1.60315700	-5.61466800	1.55015800
H	0.07744400	-6.04892000	2.33557200
C	-0.51048900	5.60466600	1.57379500
H	-1.59404500	5.61118300	1.69943200
H	-0.05767000	6.01701500	2.47897400

H	-0.25807600	6.26799400	0.74261600
H	-1.85196400	3.12189400	1.41474400
H	1.84844300	-3.12121500	1.27945800
C	-11.57268200	2.51834200	-0.99919800
C	-11.86470100	3.86633500	-1.09644600
C	-13.17609800	4.20592100	-1.35544300
C	-14.15028200	3.21942000	-1.50957500
C	-13.85459400	1.87387800	-1.41093100
H	-14.65882000	1.16562200	-1.54180400
C	12.52318100	-1.51441400	-1.11191400
C	13.85408600	-1.87167800	-1.31726100
C	14.14242200	-3.21424700	-1.46535500
C	13.15211300	-4.19536400	-1.41423800
C	11.54723700	-2.50824300	-1.06215000
C	11.83167500	-3.85317500	-1.21060300
H	11.05854600	-4.60992300	-1.17002600
H	-11.10377400	4.62710700	-0.97640500
H	14.67118500	-1.16780100	-1.36651700
F	13.51057200	-5.46775300	-1.56613600
F	15.40152300	-3.60072200	-1.66335100
F	-15.40082700	3.60361500	-1.75929800
F	-13.54102500	5.48085700	-1.46465900

Table S2. The calculated IP and EA value of TC-FIC and NC-FIC.

Equation[a]	**IP (eV)**[b]	**EA (eV)**[c]
ΔE **[NC-FIC]**$^{+}$ $-\Delta E$ **[NC-FIC]**	6.480	-
ΔE **[NC-FIC]** $-\Delta E$ **[NC-FIC]**$^{-}$	-	2.979
ΔE **[TC-FIC]**$^{+}$ $-\Delta E$ **[TC-FIC]**	6.320	-
ΔE **[TC-FIC]** $-\Delta E$ **[TC-FIC]**$^{-}$	-	2.984

[a] ΔE = Sum of electronic and thermal Free Energies = $\varepsilon_0 + G_{corr.,}$

[b] IP value was calculated from the difference between the total energies of cation and neutral states.

[c] EA value was calculated from the difference between total energies of neutral states and anion.

11. ^{1}H and ^{13}C NMR Spectra

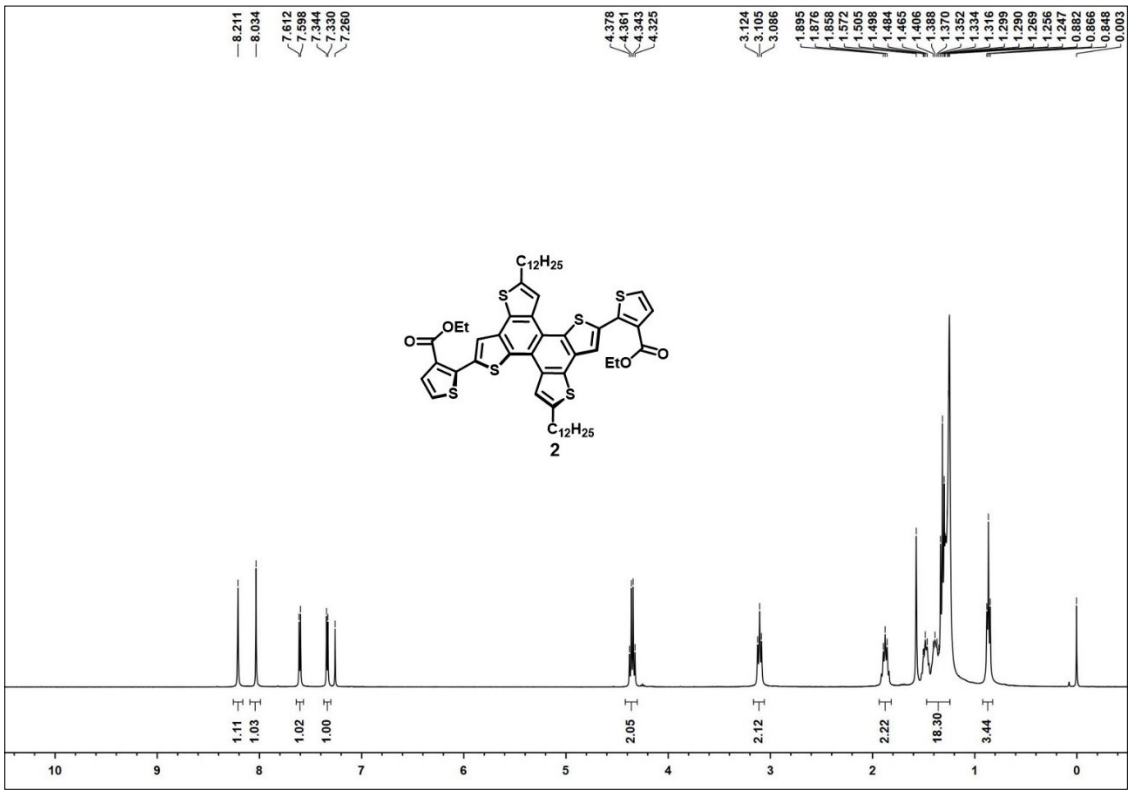

Figure S5. ^{1}H NMR spectrum of compound **2** at 300 K in $CDCl_3$.

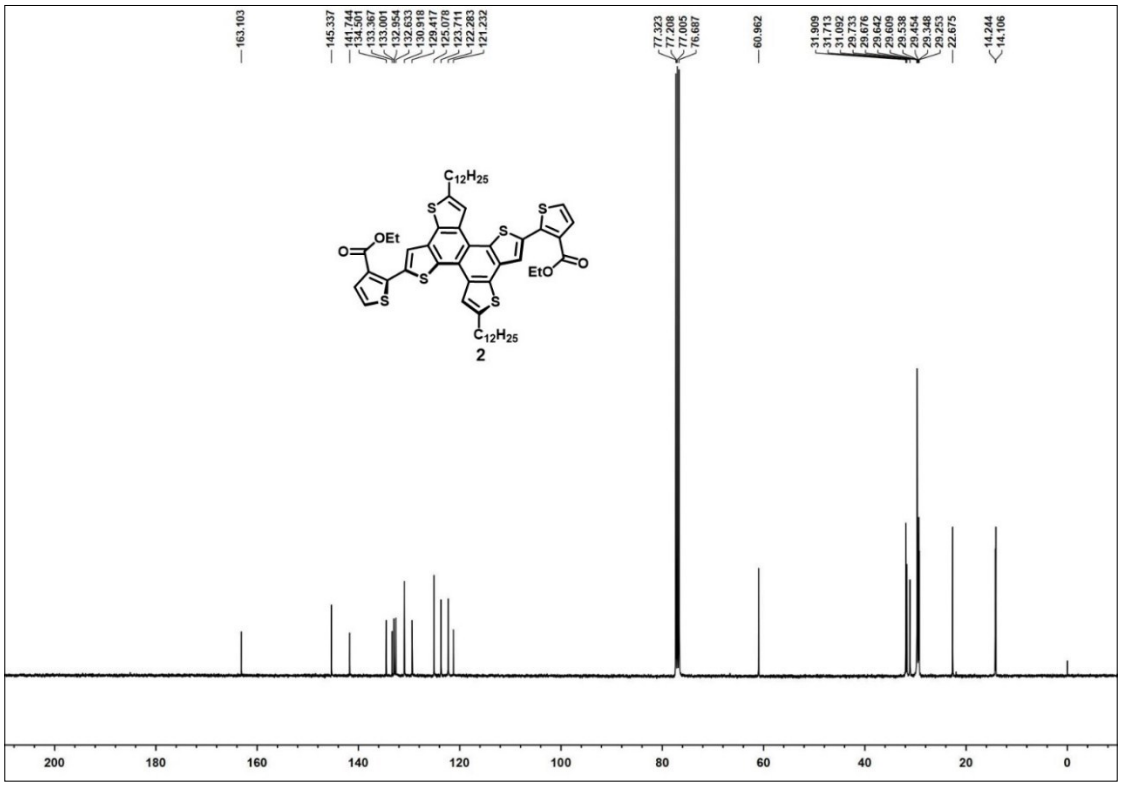

Figure S6. ^{13}C NMR spectrum of compound **2** at 300 K in $CDCl_3$.

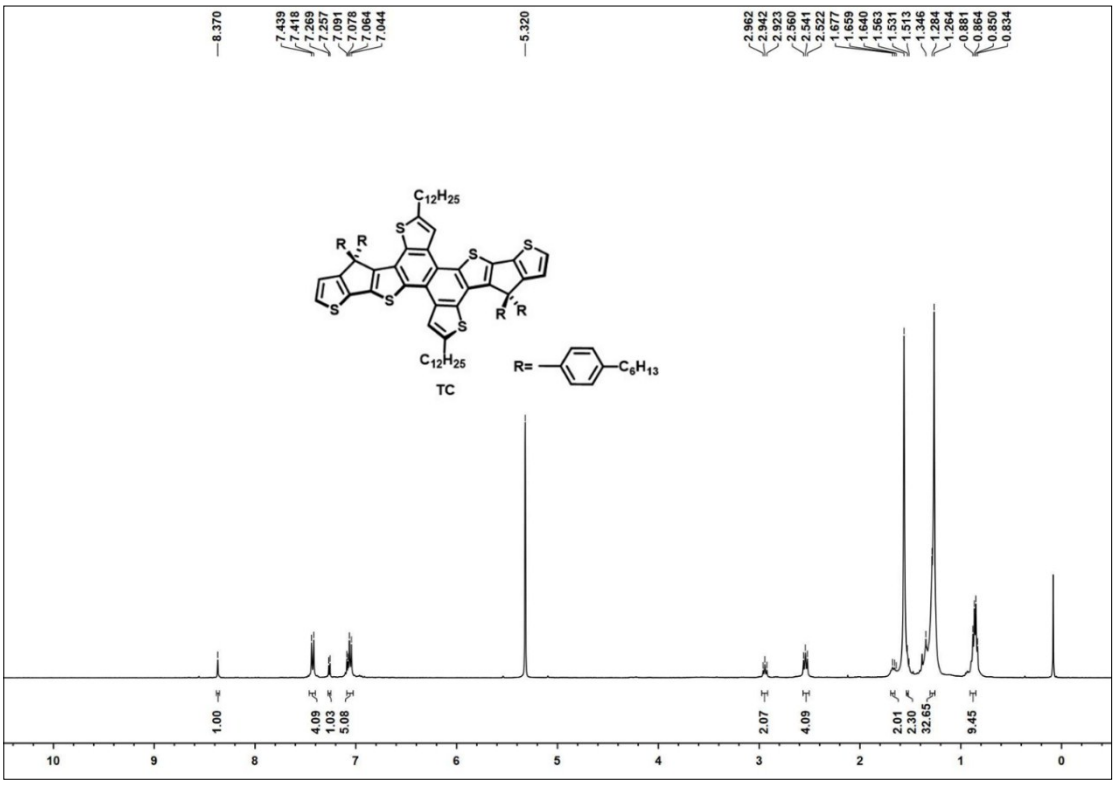

Figure S7. ^{1}H NMR spectrum of **TC** at 300 K in $CDCl_3$.

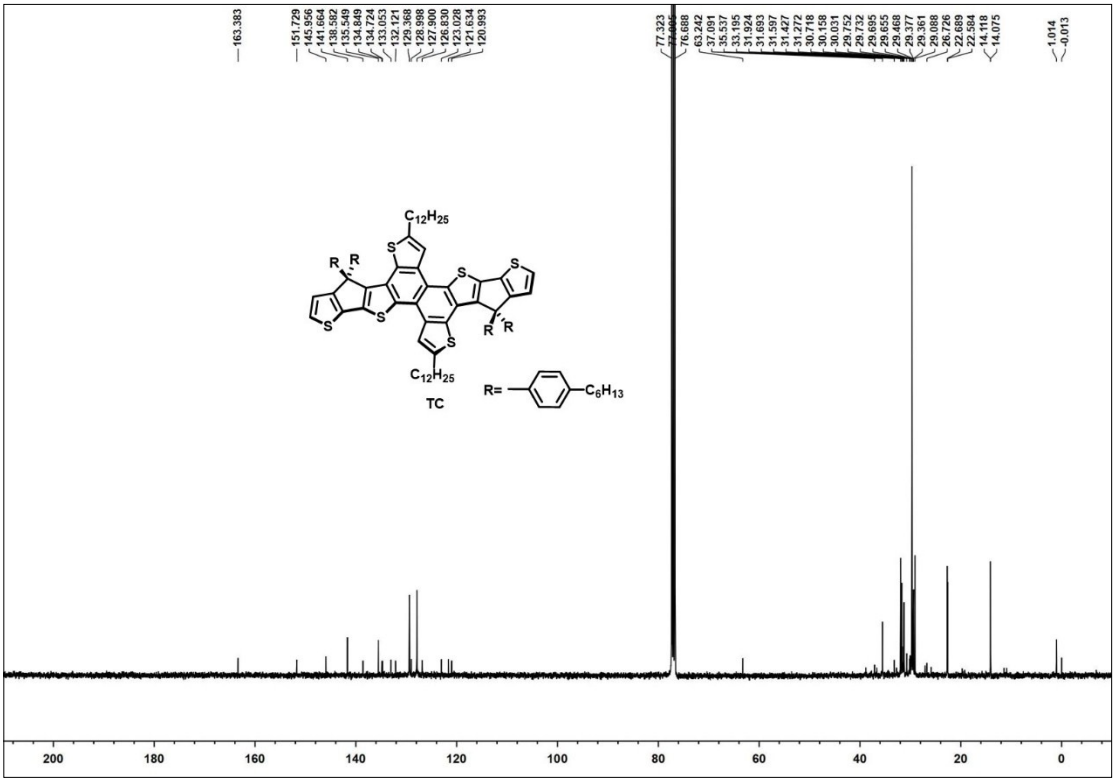

Figure S8. ^{13}C NMR spectrum of **TC** at 300 K in $CDCl_3$.

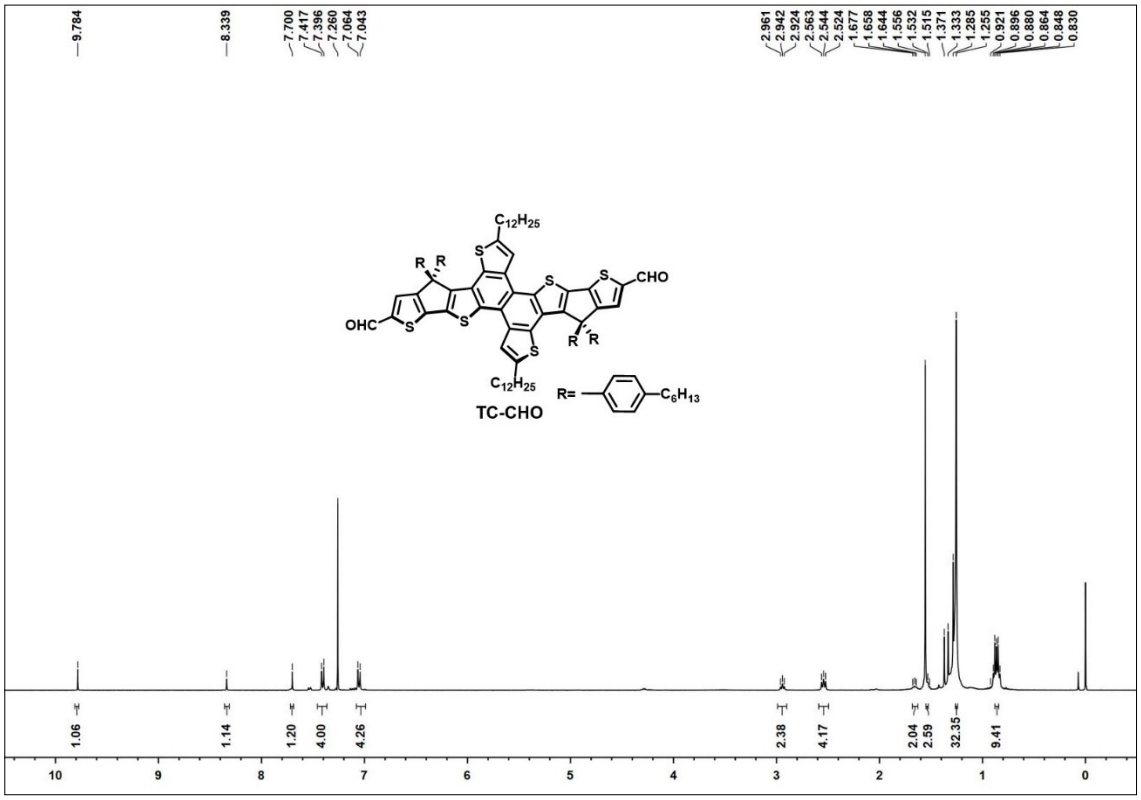

Figure S9. ^{1}H NMR spectrum of **TC-CHO** at 300 K in $CDCl_3$.

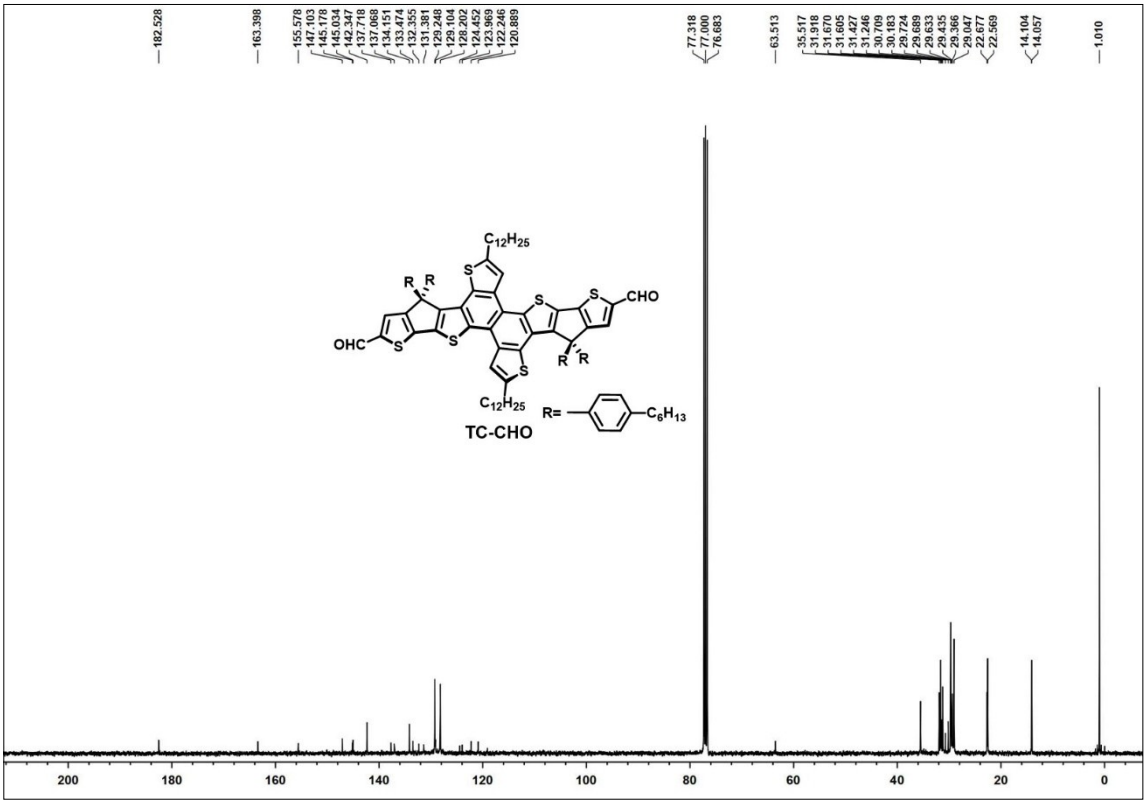

Figure S10. ^{13}C NMR spectrum of **TC-CHO** at 300 K in $CDCl_3$.

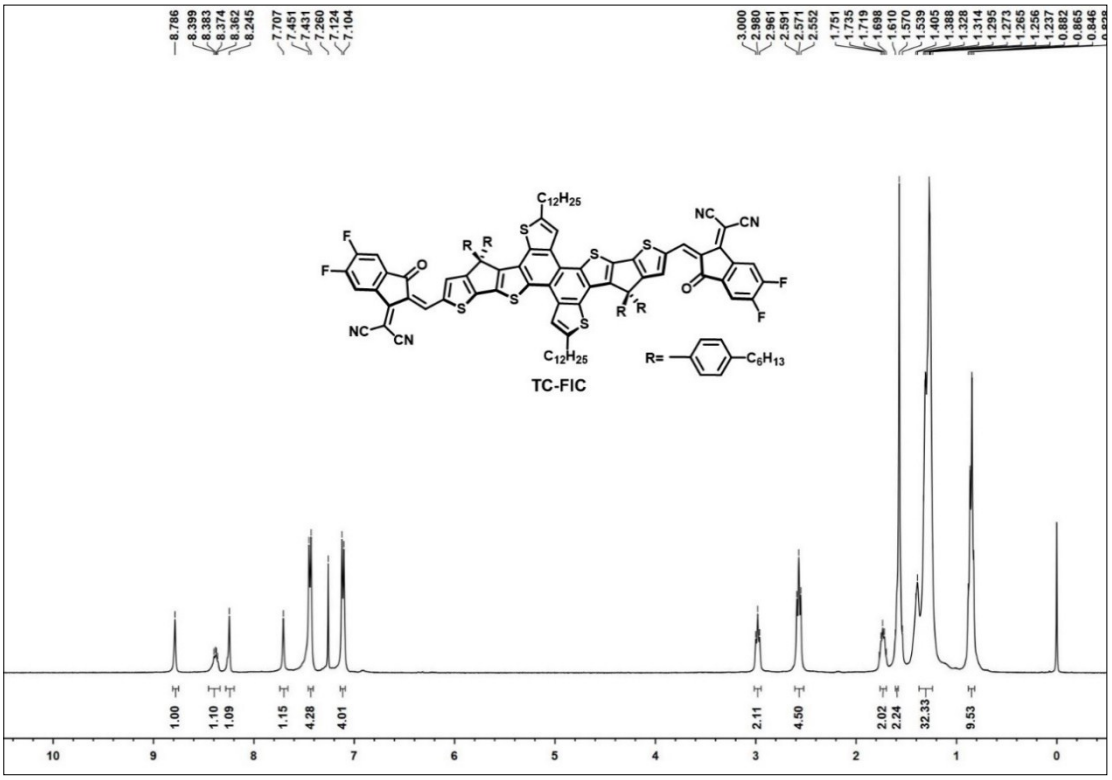

Figure S11. ^{1}H NMR spectrum of **TC-FIC** at 300 K in $CDCl_3$.

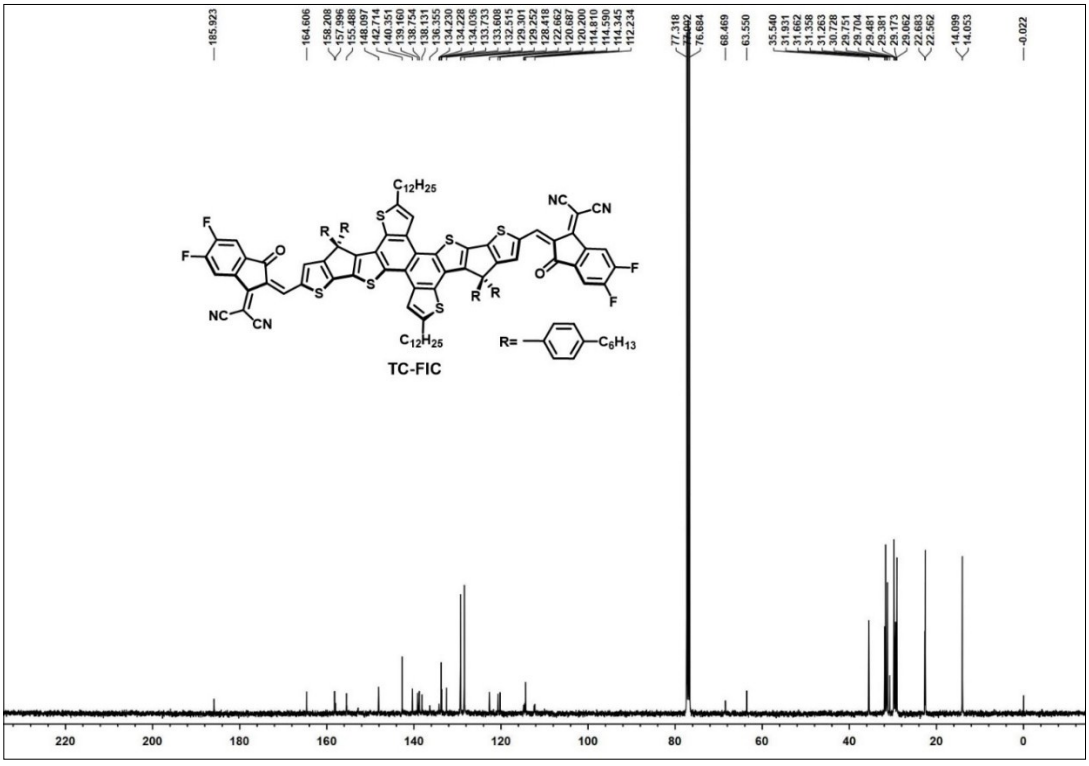

Figure S12. ^{13}C NMR spectrum of **TC-FIC** at 300 K in $CDCl_3$.

12. References

(S1) Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. Gaussian, Inc., Wallingford CT, **2009**.