

Highly Efficient Organic Solar Cells Based on S,N-heteroacene Non-fullerene Acceptors

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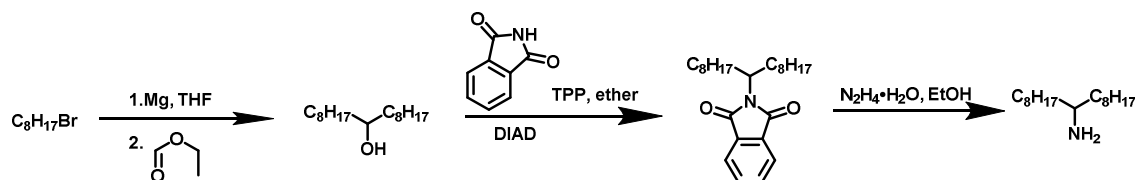
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1. EXPERIMENTAL SECTION

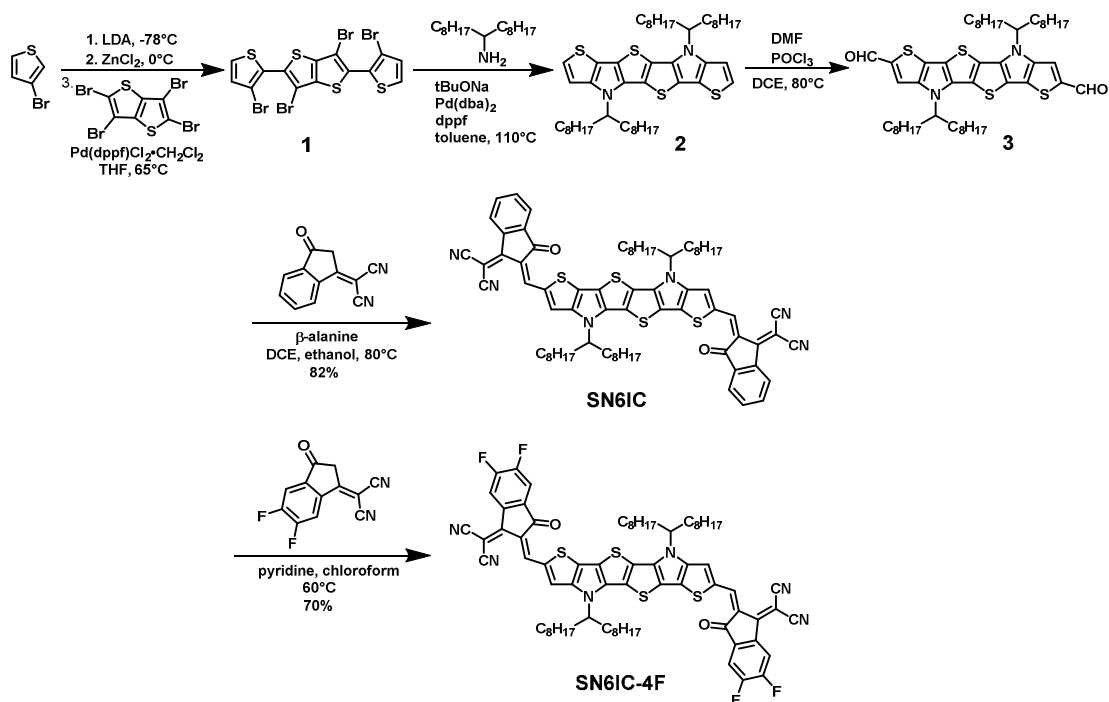
1.1. Materials and Synthesis.

Tetrabutylammonium hexafluorophosphate (Bu₄NPF₆), ferrocene (FC), magnesium, triphenylphosphine, diisopropyl azodicarboxylate (DIAD), phthalimide, hydrazine monohydrate, n-butyllithium (n-BuLi, 2.5M in THF), [1,1'-bis(diphenylphosphino)ferrocene] dichloropalladium(II), complex with dichloromethane (Pd(dppf)Cl₂·CH₂Cl₂), bis(dibenzylideneacetone)palladium(0) (Pd(dba)₂), 1,1'-ferrocenediyl-bis(diphenylphosphine) (dppf), sodium tert-butoxide and β-alanine were purchased from Sigma-Aldrich.

2-(3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (IC) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (DFIC) were purchased from Sunatech. THF, diethyl ether, ethyl formate, diisopropylamine, phosphorus oxychloride (POCl₃), N,N-dimethylformide (DMF), 1,2-dichloroethane (DCE), acetonitrile(ACN), toluene were dried and distilled before use.

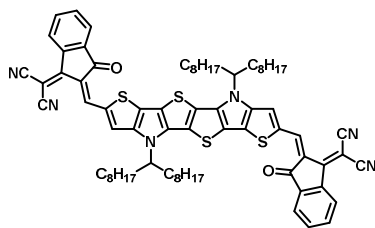


1-octylnonylamine was synthesized following the procedure reported in Lin's paper¹.



The intermediate aldehyde **3** was synthesized following the procedure reported in Wong's paper².

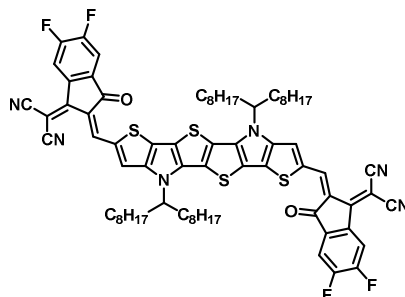
2,2'-((2Z,2'Z)-((thieno[3,2-b]thieno[2''',3''':4'',5'']pyrrolo[2'',3'':4',5']thieno[2',3':4,5]thieno[2,3-d]pyrrole,4,9-dihydro-4,9-di-1-octylnonyl-2,7-diyl)bis(methanylylidene))bis(3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile (**SN6IC**)



Compound **3** (60 mg, 0.07 mmol), 2-(3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (40 mg, 0.21 mmol) and β-alanine (2 mg) were dissolved in the mixture of dichloroethane and absolute ethanol (20 mL, v/v, 3/1) in a degassed two-neck round-bottom flask. The resultant mixture was stirred at reflux overnight in nitrogen atmosphere. After removal of solvent under vacuum, the product was purified by flash chromatography with the eluent of dichloromethane/hexanes=2/1. And the final material was further purified by recrystallization via chloroform and methanol before device application, to obtain a black solid (69 mg, 82% yield). ¹H NMR (300 MHz, CDCl₃) δ 8.89 (s, 2H), 8.63 (t, 2H), 7.93 (t, 2H), 7.91 (t, 2H), 7.84 (s, 2H), 7.73 (t, 4H), 4.37 (m, 2H), 2.18 (m, 4H), 2.07 (m, 4H), 1.33 (m, 12H), 1.20 (m, 36H), 0.80 (t, 12H). ¹³C NMR (75 MHz, CDCl₃) δ 188.01, 160.36, 139.95, 138.35, 137.03, 136.85, 134.82, 134.11, 126.58, 125.05, 123.50, 121.29, 115.09, 114.94, 77.43, 77.01, 76.91, 76.58,

67.66, 61.92, 60.29, 35.49, 31.69, 29.25, 29.17, 29.06, 26.83, 22.53, 20.94, 14.16, 13.97. HR-MS (ESI) *m/z* calcd. For (Chemical Formula: C₇₄H₈₂N₆O₂S₄): 1214.5376. Found: 1214.5388.

2,2'-((2*Z*,2'*Z*)-((thieno[3,2-*b*]thieno[2''',3'''':4'',5'']pyrrolo[2'',3'':4',5']thieno[2',3':4,5]thieno[2,3-*d*]pyrrole,4,9-dihydro-4,9-di-1-octylnonyl-2,7-diyl)bis(methanylylidene))bis((5,6-difluoro-3-oxo-2,3-dihydro-1*H*-indene-2,1-diylidene))dimalononitrile (SN6IC-4F)



Compound 3 (250 mg, 0.29 mmol), 2-(5,6-difluoro-3-oxo-2,3-dihydro-1*H*-inden-1-ylidene) malononitrile (200 mg, 0.87 mmol) were dissolved in 30 ml chloroform in a degassed two-neck round-bottom flask. 0.1 ml pyridine was charged, before the resultant mixture was stirred at reflux overnight in nitrogen atmosphere. After removal of solvent under vacuum, the product was purified by flash chromatography with the eluent of dichloromethane/hexanes=2/1. And the final material was further purified by recrystallization via chloroform and methanol before device application, to obtain a black solid (260 mg, 70% yield). ¹H NMR (500 MHz, CDCl₃) δ 8.90 (s, 2H), 8.52 (dd, 2H), 7.87 (br, 2H), 7.68 (t, 2H), 4.37 (m, 2H), 2.15 (m, 4H), 2.05 (m, 4H), 1.32 (m, 12H), 1.18 (m, 36H), 0.80 (t, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 185.79, 158.43, 153.27, 138.45, 136.82, 136.53, 136.49, 134.44, 127.03, 120.40, 114.72, 114.62, 77.25, 77.00, 76.74, 68.08, 31.69, 29.22, 29.10, 29.06, 26.74, 22.55, 14.02. HR-MS (ESI) *m/z* calcd. For (Chemical Formula: C₇₄H₇₈F₄N₆O₂S₄): 1286.4976. Found: 1286.5005.

1.2. Theoretical Calculations.

The CAM-B3LYP long range corrected hybrid functional along with 6-31g(d) basis set has been used to optimize the geometries and calculate the orbital energies. The optimized structures are confirmed to be the true minima via the frequency calculations. All the calculations are performed in the gas phase using Gaussian 16 program.

1.3. Instrumentation.

The ¹H NMR and ¹³C NMR spectra were recorded in a solution of CDCl₃ using Bruker DRX 300 NMR and Bruker DRX 500 NMR spectrometers. AutoFlex II mass spectrometer was conducted to obtain high resolution (HR) ESI mass spectra. UV-vis-NIR absorption spectra were recorded by a Varian Cary 5000. Photoluminescence emission spectra were acquired using a modified Horiba LabRAM HR-800, a 795 nm laser diode excitation source, and a 10× objective (NA = 0.25). The adjustable confocal hole before the monochromator was set at 800 μm. A 150 gr/mm Czerny-Turner monochromator blazed at 1200 nm was used, and the emitted light was collected with a silicon CCD array detector. The electrochemical

measurements were conducted on a CHI660C electrochemical workstation with 0.1 M Bu₄NPF₆ as the supporting electrolyte. A three-electrode electrolytic cell with a glassy carbon working electrode, a platinum gauze counter electrode, and a silver wire quasi-reference electrode was used in our nonaqueous electrochemical measurements and an *iR* drop was compensated.

1.4. Device Fabrication.

Polymer solar cells (PSCs) were fabricated in the configuration of the traditional sandwich structure of ITO/PEDOT:PSS/active layer/C60-bissalt/Ag. ITO-coated glass was cleaned by ultrasonic agitation in acetone, detergent, deionized water and isopropanol sequentially followed by plasma treatment for 3 min. Then the PEDOT:PSS (Baytron PVP 4083) was spin-cast on the ITO glass at 4000 rpm for 30 s and annealed at 150 °C for 10 min in air. The devices were transferred into a glovebox filled with N₂. Active layer solutions (PBDB-T:Acceptor weight ratio is 1:1) were prepared in chlorobenzene (CB) with or without 0.3% 1,8-diiodooctane (DIO). The total active layer solution concentration is 20 mg ml⁻¹. Then the active layers were spin coated from the PBDB-T:Acceptor solution on the substrates with 3000 rpm spin-coating speed to form about 100 nm film thickness. Finally, the C60-bissalt dissolved in methanol with a concentration of 2 mg/ml was spin-coated on top of active layer. The device fabrication was finished by depositing 150 nm Ag in vacuum chamber of 10⁻⁷ Torr. Typical cells have devices area of ~3.14 mm², which is defined by a metal mask with an aperture aligned with the device area.

1.5. Characterization of OSCs

The I-V characteristic curves were recorded in a Keithley 2400 source unit under a simulated solar irradiance (solar simulator from Newport Inc.) A certified silicon diode, which can be traced back to NREL, is used to calibrate the illumination intensity to 1 sun (100 mW/cm²). A neutral filter is used to study the light intensity dependent device performance. EQE spectra were measured in an assembled setup including a stable light source, light chopper, monochromator, and lock-in amplifier.

1.6. SCLC measurements

The electron-only device with structure of ITO/ZnO/PBDB-T:Acceptor/C60-bissalt/Ag were fabricated. The carrier mobilities were measured using the space-charge-limited-current (SCLC) model, which is described by:

$$J = 9\epsilon_0\epsilon_r u V^2 / 8L^3$$

where *J* is the current density, *L* is the film thickness of active layer, ϵ_0 is the permittivity of free space (8.85×10^{-12} F m⁻¹), ϵ_r is the relative dielectric constant of the transport medium, *u* is the hole or electron mobility, *V* is the internal voltage in the device and $V = V_{\text{appl}} - V_r - V_{\text{bi}}$, where *V_{appl}* is the applied voltage to the device, *V_r* is the voltage drop due to contact resistance and series resistance across the electrodes, and *V_{bi}* is the built-in voltage due to the relative work function difference of the two electrodes. The thickness of the BHJ blend for

SCLC measurement was about 100 nm. The electron mobility can be calculated from the slope of the $J^{1/2} \sim V$ curves.

1.7. Morphology Characterization

Grazing incidence x-ray diffraction (GIXD) characterization of active layer was performed at beamline 7.3.3, Advanced Light Source (ALS), Lawrence Berkeley National Lab (LBNL). X-ray energy was 10 keV and operated in top off mode. The scattering intensity was recorded on a 2D image plate (Pilatus 1M) with a pixel size of 172 μ m (981 \times 1043 pixels). The samples were \sim 10 mm long in the direction of the beam path, and the detector was located at a distance of 300 mm from the sample center (distance calibrated by AgB reference). The incidence θ angle was chosen to be 0.16° (above critical angle) for GIXD measurement. OPV samples were prepared on PEDOT:PSS covered Si wafers in a similar manner to the OPV devices. RSoXS was performed at beamline 11.0.1.2 Lawrence Berkeley National Lab. Thin films were flowed and transferred onto Si₃N₄ substrate and experiment was done in transition mode.

2. ADDITIONAL FIGURES AND TABLES

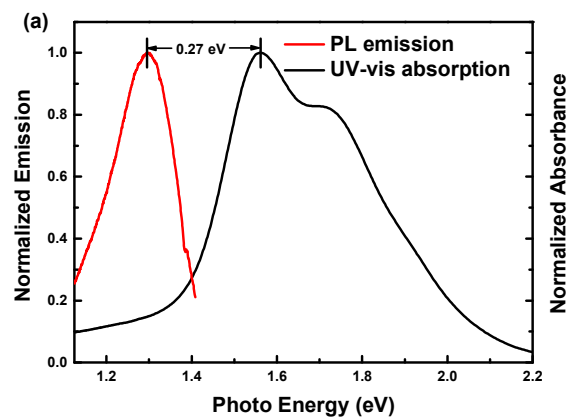


Figure S1. PL emission and UV-vis absorption spectra of F6IC.

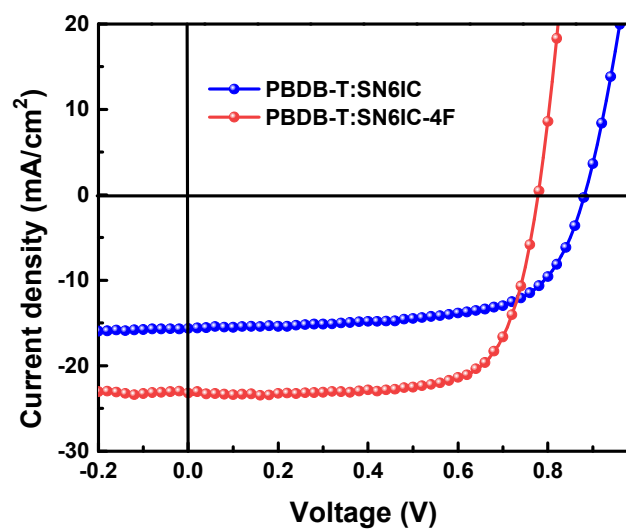


Figure S2. *J-V* curves of the optimized device of PBDB-T:SN6IC and PBDB-T:SN6IC-4F based devices with 0.3% DIO.

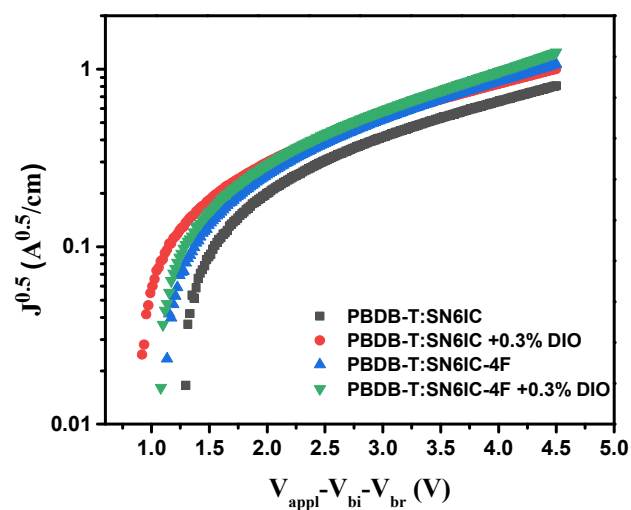


Figure S3. Electron mobilities of blend film based on **PBDB-T:SN6IC**, **PBDB-T:SN6IC-4F** and with **DIO** additive.

Table S1. Electron mobilities of blend film based on **PBDB-T:SN6IC**, **PBDB-T:SN6IC-4F** and with **DIO** additive.

Active layer	PBDB-T:SN6IC	PBDB-T:SN6IC (DIO)	PBDB-T:SN6IC-4F	PBDB-T:SN6IC-4F (DIO)
Electron mobility ($10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	2.42	2.95	3.94	5.00

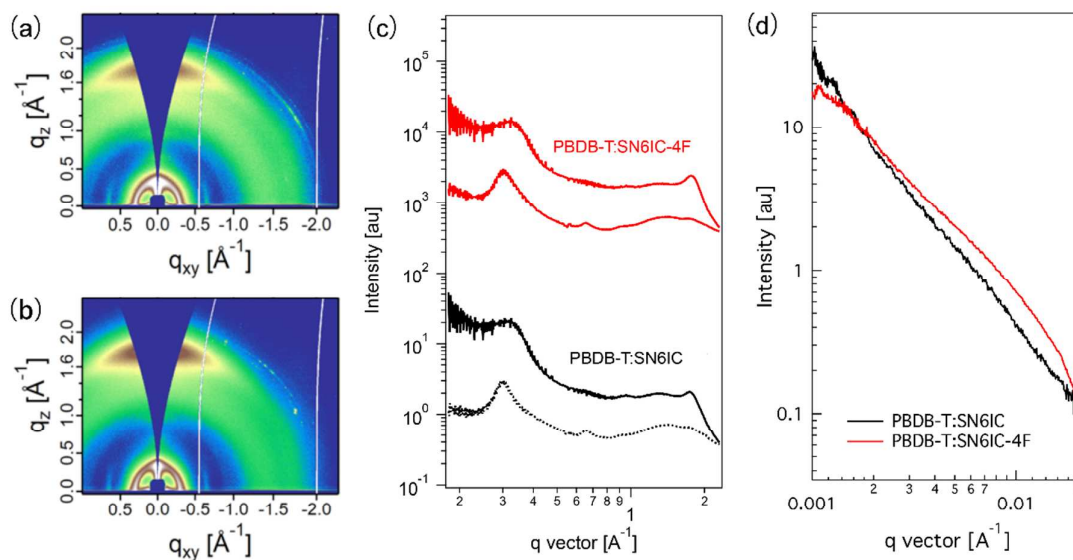


Figure S4 (a) GIWAXS of PBDB-T:SN6IC blend film with DIO; (b) GIWAXS of PBDB-T:SN6IC-4F blend film with DIO; (c) in-plane (dotted line) and out-of-plane (solid line) line-cut profiles of GIWAXS patterns; (d) RSOXS of BHJ thin films.

3. SPECTRAL CHARTS OF NMR AND MS

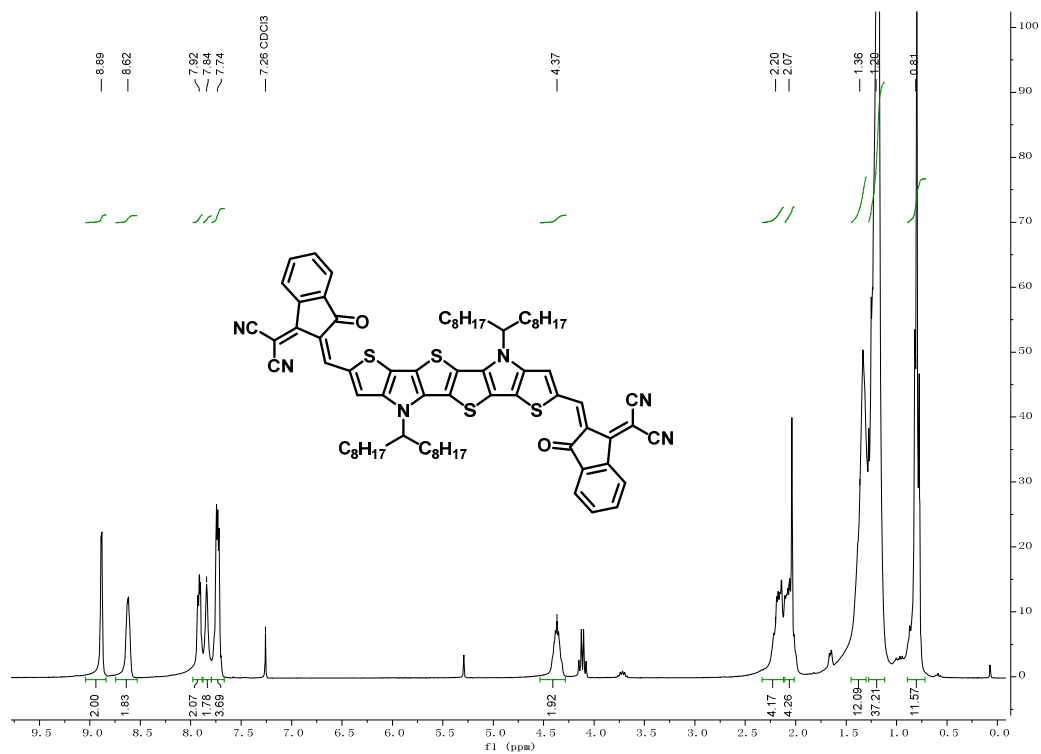


Figure S5. The ¹H NMR spectrum (300 MHz) of SN6IC in CDCl₃.

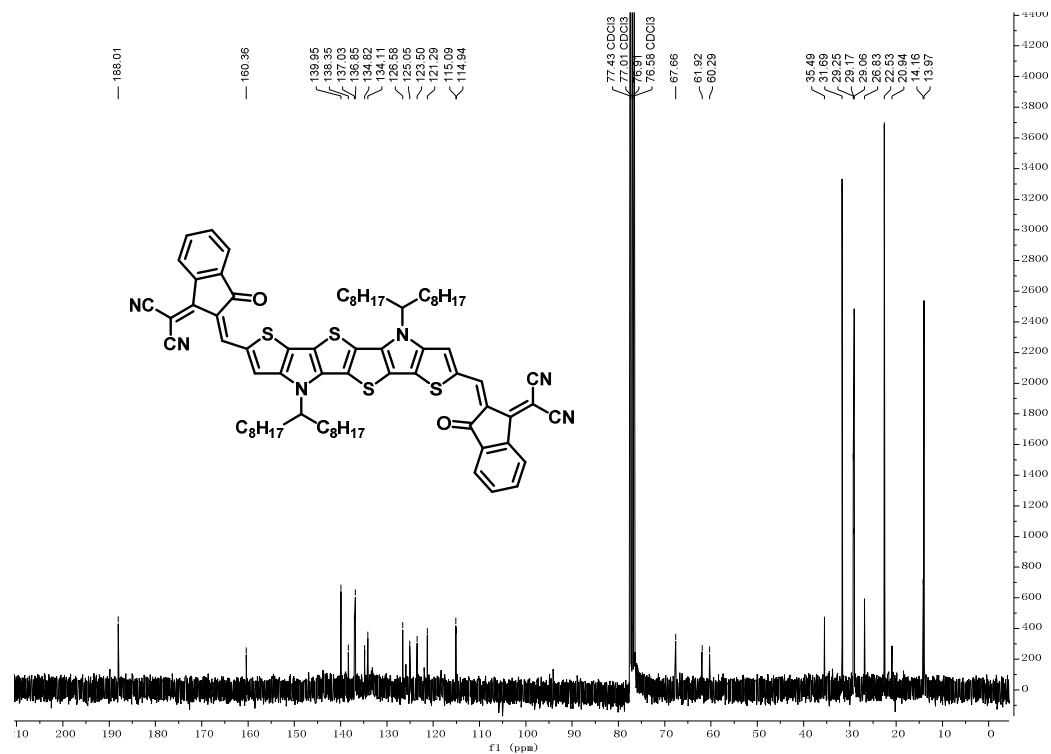


Figure S6. The ¹³C NMR spectrum (75 MHz) of SN6IC in CDCl₃.

20180220_004 #8-15 RT: 0.34-0.51 AV: 8 NL: 4.48E3
T: FTMS + p ESI SIM ms [1214.00-1222.00]

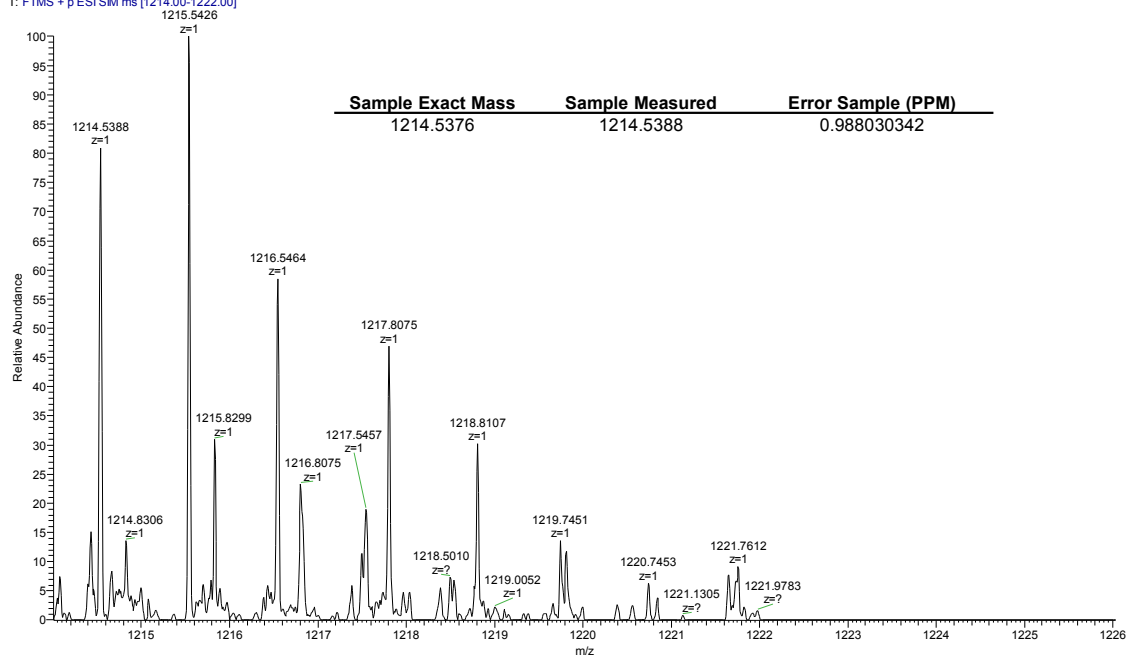


Figure S7. The high resolution mass spectrum (ESI) of SN61C.

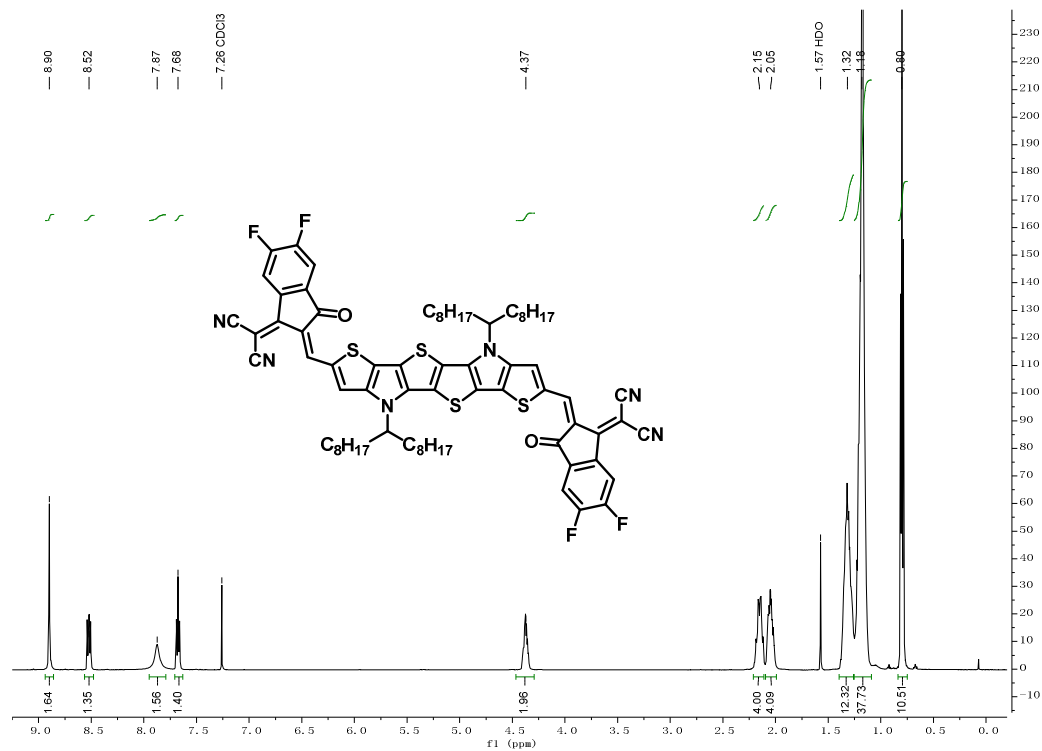


Figure S8. The ¹H NMR spectrum (500 MHz) of SN6IC-4F in CDCl₃.

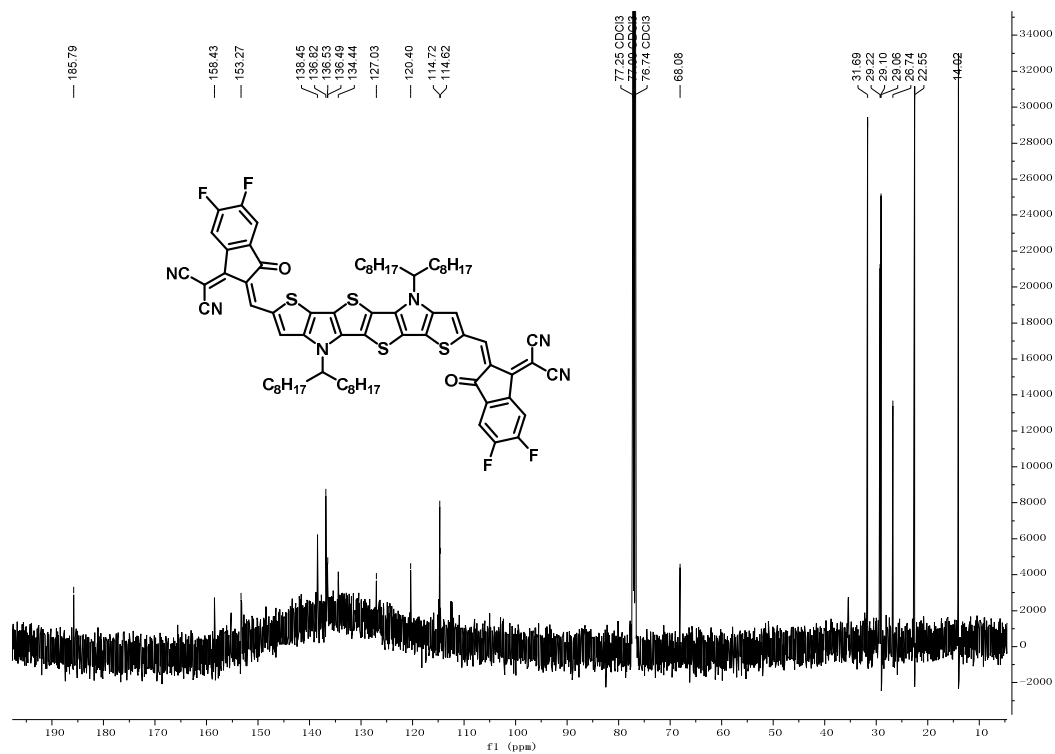
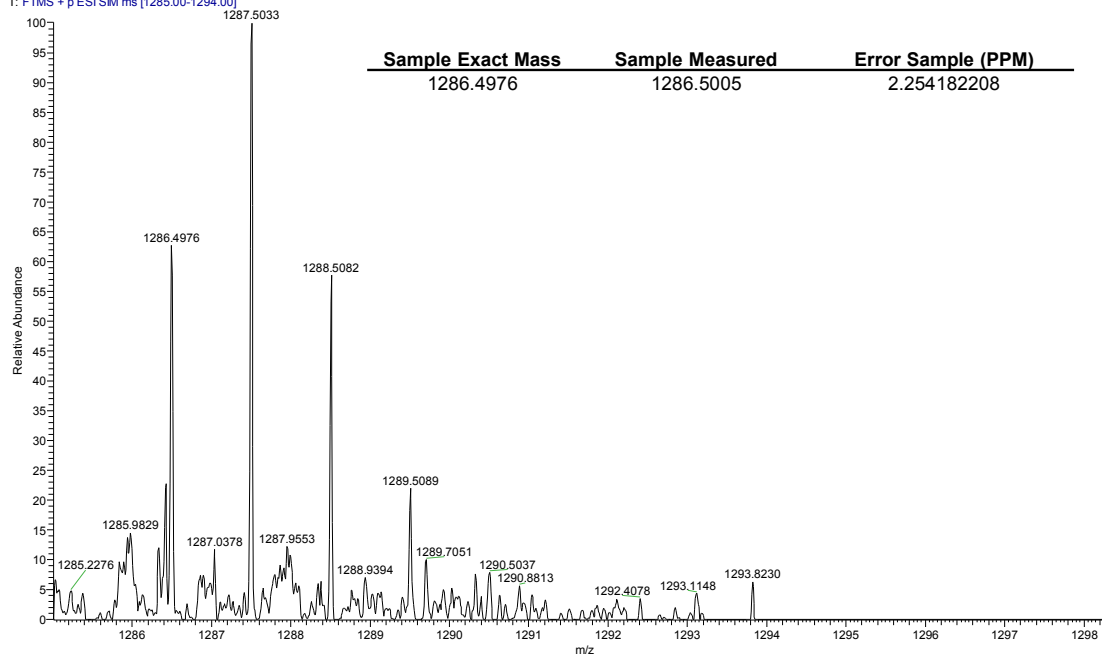


Figure S9. The ^{13}C NMR spectrum (126 MHz) of SN6IC-4F in CDCl_3 .

20180220_003 #4-11 RT: 0.12-0.36 AV: 8 NL: 2.99E3
T: FTMS + p ESI SIM ms [1285.00-1294.00]



Sample Exact Mass	Sample Measured	Error Sample (PPM)
1286.4976	1286.5005	2.254182208

Figure S10. The high resolution mass spectrum (ESI) of SN6IC-4F.

4. REFERENCE

- (1) Sahu, D.; Padhy, H.; Patra, D.; Yin, J.-F.; Hsu, Y.-C.; Lin, J.-T.; Lu, K.-L.; Wei, K.-H.; Lin, H.-C. Synthesis and applications of novel acceptor–donor–acceptor organic dyes with dithienopyrrole- and fluorene-cores for dye-sensitized solar cells. *Tetrahedron* **2011**, *67*, 303–311.
- (2) Chung, C.-L.; Chen, C.-H.; Tsai, C.-H.; Wong, K.-T. Novel organic dyes containing N-bridged oligothiophene coplanar cores for dye-sensitized solar cells. *Org. Electron.* **2015**, *18*, 8–16.