Supporting Information

A narrow band gap non-fullerene electron acceptor based on dithieno 3,2-b:2',3'-dlpyrrole unit for high performance organic solar cells with minimal highest occupied molecular orbital offset

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1. Materials

Dichloromethane (DCM)，acetone and petroleum ether used for silica gel column chromatography were analytical grade. Terahydrofuran (THF) and N,N'-dimethylformamide (DMF) were purified through a standard solvent system. Chloroform and acetonitrile used for optical and electrochemical measurements were purchased from Sigma-Aldrich. All the other reagents and chemicals were purchased from commercial sources (Aldrich, J&K, Energy) and used without further purification.

2. Synthesis

Synthesis of compound 3:

2, 3-dibromothiophene (4.24 g, 17.50 mmol) dissolved in 40 ml dry ethyl ether under argon. N-butyl lithium (1.6 M in hexane, 11.08 ml, 17.70 mmol) was added

dropwise to the system at -78 °C and the mixture was stirred at -78 °C for 1 hour. After that, a solution of $ZnCl_2$ in dry THF (125 mg/ml, 19.60 ml, 18.00 mmol) was added dropwise and the mixed solution was warmed slowly to 0 °C. After stirring at 0 °C for 1 hour, Pd(dppf)Cl$_2$ (250 mg, 0.34 mmol) and 2,3,5,6-tetrabro-mothieno[3,2-b]thiophene (2 g, 4.39 mmol) were added to the solution and the mixture was stirred at 50 °C for 24 hours. Then 100 ml water was added and the solid was filtered off. The insoluble yellow solid was washed with ethyl ether and acetone in sequence, and compound 3 was obtained as an insoluble yellow solid. (2 g, 73.4%). ^{1}H NMR (CDCl$_3$, 400 MHz): 7.48 (d, 2H), 7.12 (d, 2H). There was no ^{13}C NMR spectroscopy because of the poor solubility of compound 3.

Synthesis of compound 4:

3,6-Dibromo-2,5-bis(3-bromothien-2-yl)thieno[3,2-b]thiophene (586 mg, 0.94 mmol), sodium-tert-butoxide (1.45 g, 15.12 mmol), dppf (210 mg, 0.38 mmol) and Pd(dba)$_2$ (54 mg, 0.09 mmol) were added to 40 ml dry toluene and the mixture was stirred at room temperature for 15 min. Then 1-hexylheptylamine (0.45 g, 2.26 mmol) was added to the mixed solution and the system was stirred at 110 °C for 24 hours. After cooling down to room temperature, the solution was extracted with ethyl ether and dichloromethane. After removing the solvent under vacuum, the crude product was purified by silica gel chromatography (eluent: hexane/ dichloromethane 8:1). Finally, compound 4 was obtained as a yellow solid (130 mg, 20%). ^{1}H NMR (CDCl$_3$, 400 MHz): 7.09 (d, 2H), 7.06 (d, 2H), 4.36 (m, 2H), 2.14 (m, 4H), 1.96 (m, 4H), 1.26 (m, 32H), 0.80 (t, 12H). ^{13}C NMR (TCE-d2, 100 MHz): δ (ppm): 144.17, 138.82, 123.60, 123.33, 117.88, 115.87, 113.64, 62.29, 37.02, 32.81, 30.16, 28.02, 23.69, 15.08. HRMS (MALDI-TOF): m/z calcd. for C$_{40}$H$_{58}$N$_2$S$_4$ (M+) 694.35; found 694.30.

Synthesis of compound 5:

Compound 4 (480 mg, 0.69 mmol) was dissolved in 40 ml dry THF at -78 °C. Then n-butyl lithium (1.6 M in hexane, 1 mL, 1.60 mmol) was added dropwise to the solution and the reaction was warmed slowly to -30 °C. After that, dry DMF (0.2 ml, 2.58 mmol) was added dropwise to the mixture at -78 °C. After stirred at room temperature overnight, the reaction was quenched with 40 ml water. The solution was extracted by dichloromethane for three times. The redundant solvent was removed under vacuum, and the crude product was purified by silica gel chromatography (eluent: petroleum ether/dichloromethane 1:1) and compound 5 was obtained as an orange solid (440 mg, 85%). ^{1}H NMR (CDCl$_3$, 400 MHz): 9.91 (s, 2H), 7.72 (s, 2H), 4.40 (m, 2H), 2.16 (m, 4H), 2.02 (m, 4H), 1.27 (m, 32H), 0.81 (t, 12H). ^{13}C NMR (TCE-d2, 100 MHz): δ (ppm): 183.23, 143.80, 142.32, 141.84, 125.91, 125.67, 120.69, 117.65, 62.68, 36.70, 32.44, 29.75, 27.70, 23.32, 14.71. HRMS (MALDI-TOF): m/z calcd. for C42H58N2O2S4 (M+) 750.34; found 750.30.

Synthesis of SNIC-F:

Compound 5 (225 mg, 0.30 mmol) and INCN-F (582 mg, 3 mmol) were dissolved in 40 ml chloroform. Then 0.90 ml pyridine was added to the solution, and the mixture was stirred at 65 °C for 16 hours. After that, the redundant chloroform was removed under vacuum. Then, the brown solid was purified by silica gel chromatography (eluent: dichloromethane) to obtain SNIC-F as a dark red solid (199 mg, 76%). ^{1}H NMR (CDCl$_3$, 400 MHz): 8.91 (s, 2H), 8.71 (q, 0.6H), 8.37 (q, 1.4H), 7.93 (m, .3.4H), 7.57 (q, 0.6H), 7.43 (m, 2H), 4.40 (m, 2H), 2.20 (m, 4H), 2.08 (m, 4H), 1.36 (m, 32H), 0.82 (t, 12H). ^{13}C NMR (CDCl3, 100 MHz): δ (ppm): 186.76, 168.08, 167.52, 165.34, 164.93, 159.46, 159.05, 142.25, 138.45, 136.96, 135.81, 133.00, 126.89,126.29, 125.67, 121.52, 121.29, 121.02, 114.62, 112.78, 112.52, 110.51, 68.26, 62.02, 35.49, 31.53, 28.85, 26.81, 22.50, 13.98. HRMS (MALDI-TOF): m/z calcd. for C66H64F2N6O2S4 (M+) 1138.39; found 1138.40.
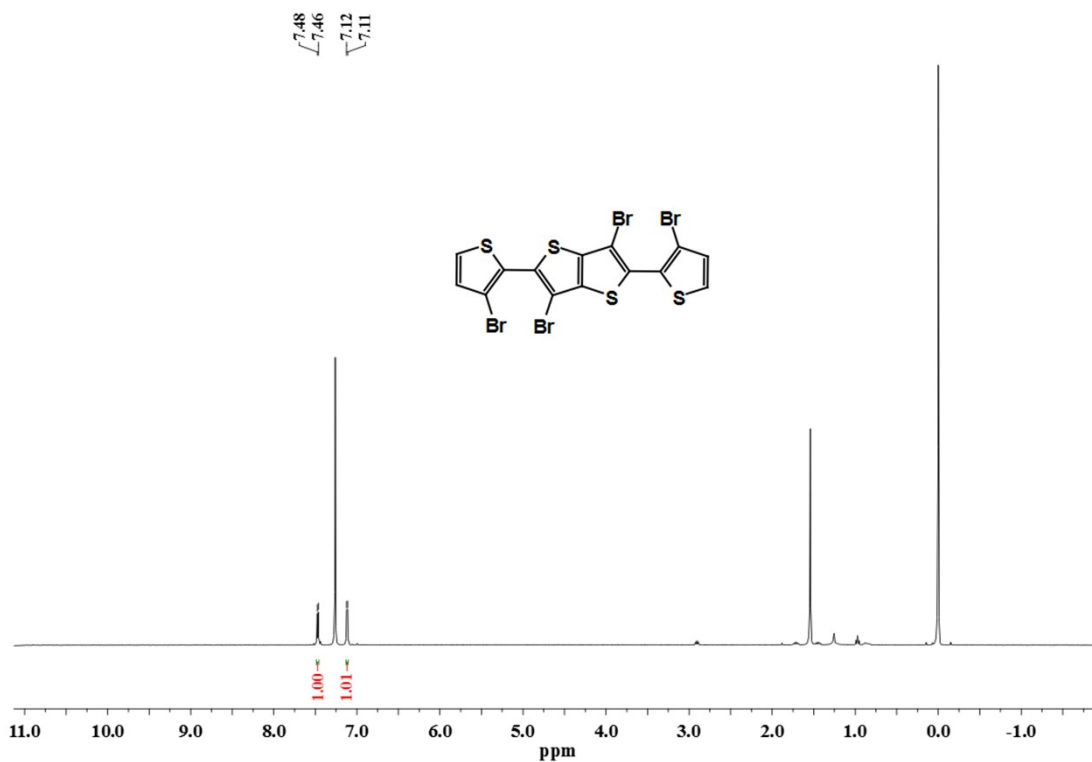
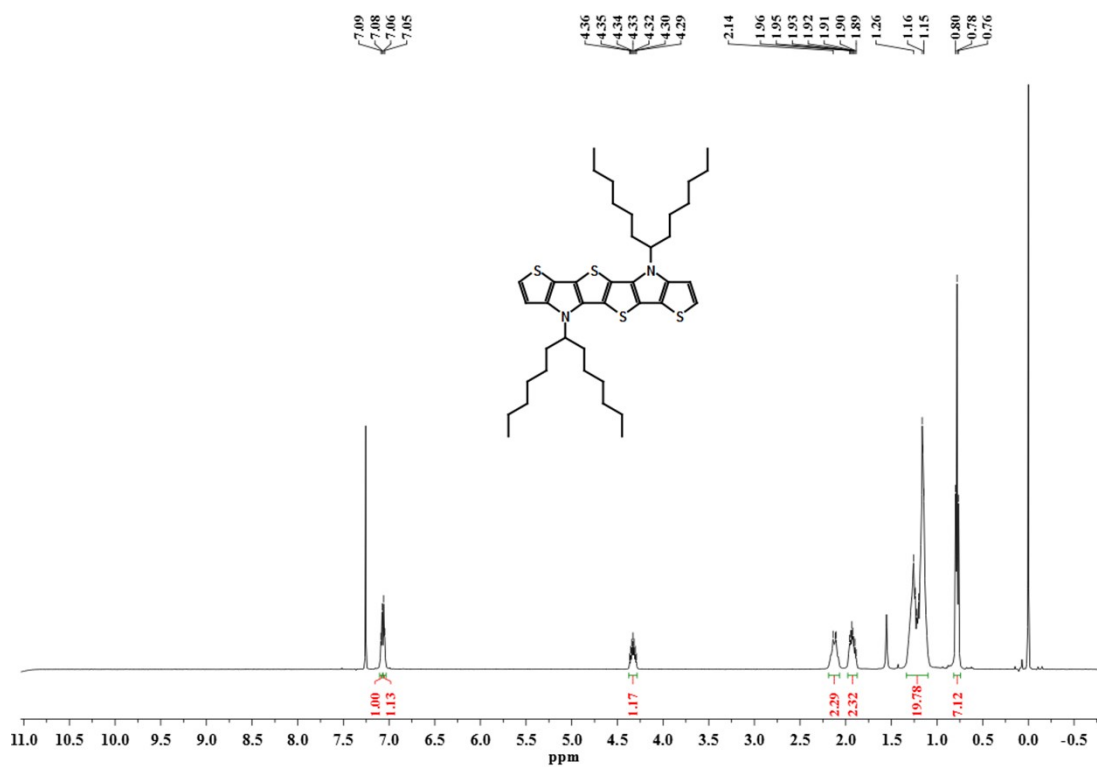**Figure S1**. ^{1}H NMR spectrum of compound 3.

Figure S2. ^{1}H NMR spectrum of compound 4.

144.17
138.82
123.60
123.33
117.88
115.87
113.64
62.29
37.02
32.81
30.16
28.02
23.69
15.08

230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
ppm
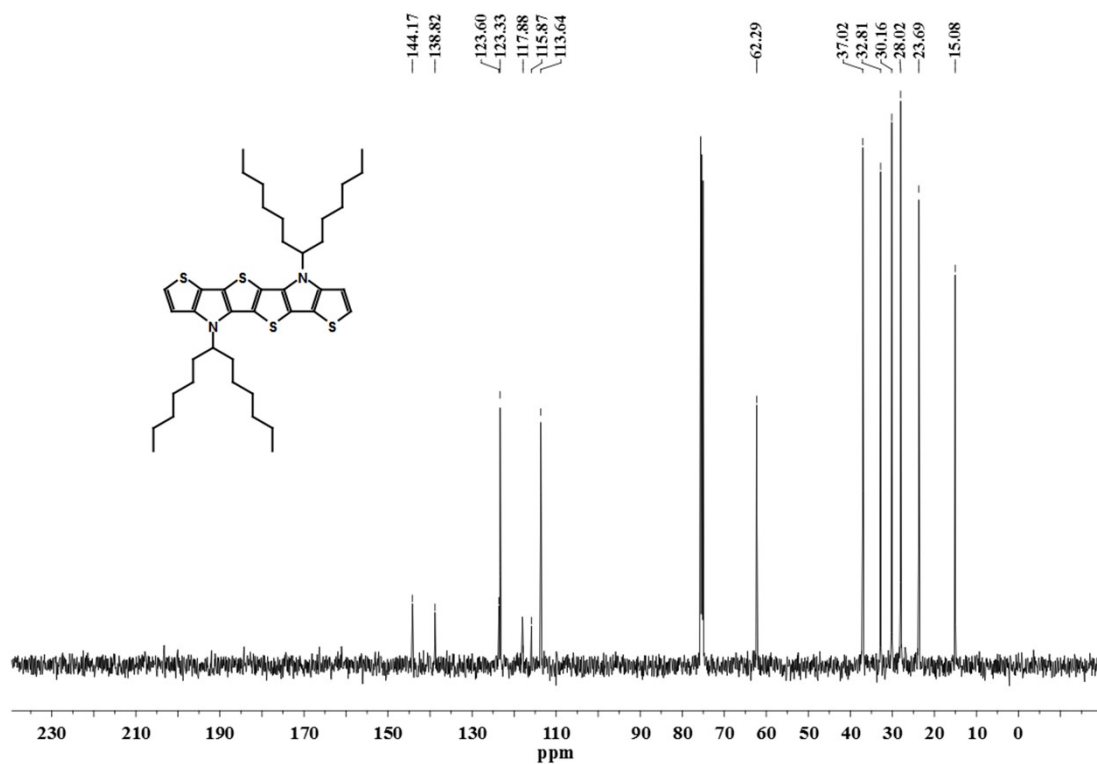
Figure S3. ^{13}C NMR spectrum of compound 4.

9.91
7.72
4.39
4.38
4.37
2.16
2.13
2.04
2.03
2.02
2.00
1.99
1.18
1.17
0.81
0.80
0.78

1.00
0.99
1.16
1.99
2.05
16.60
5.77

10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
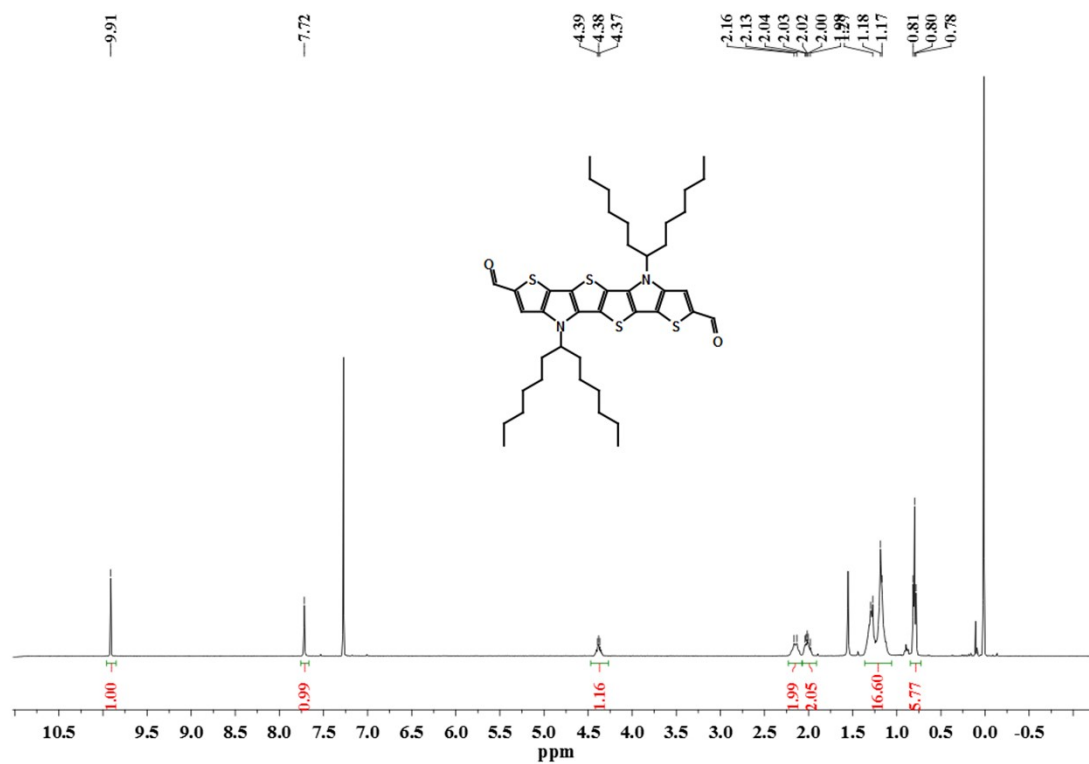ppm

Figure S4. ^{1}H NMR spectrum of compound 5.
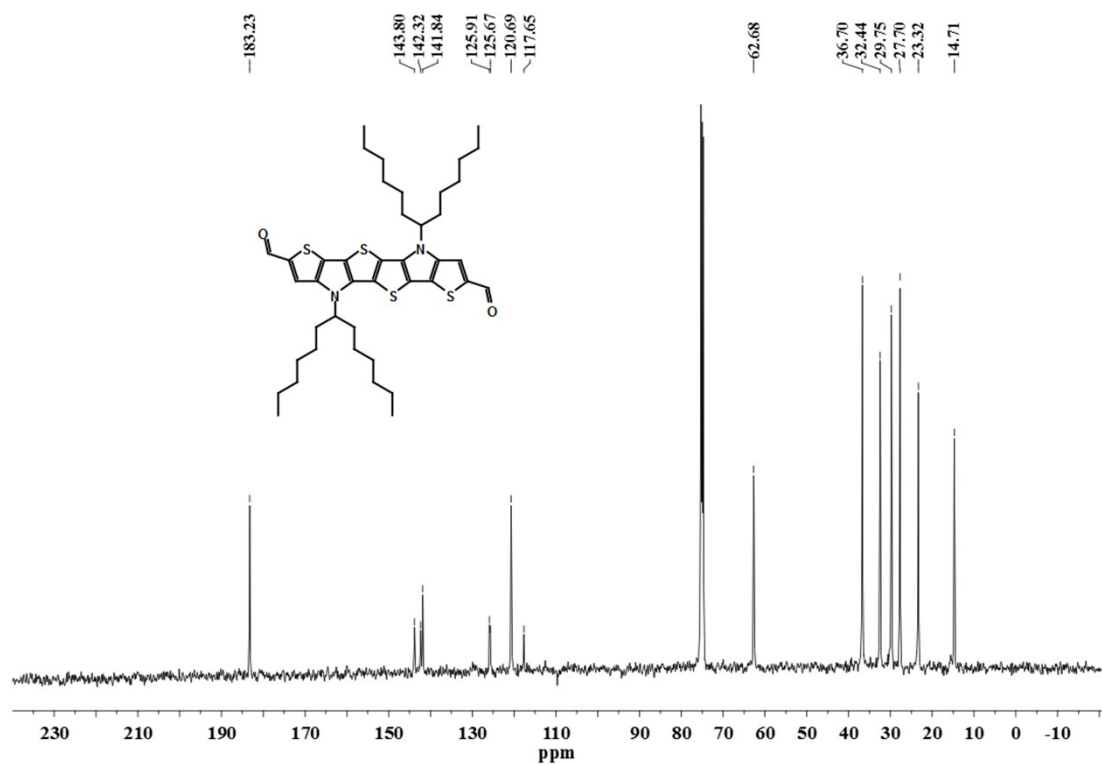
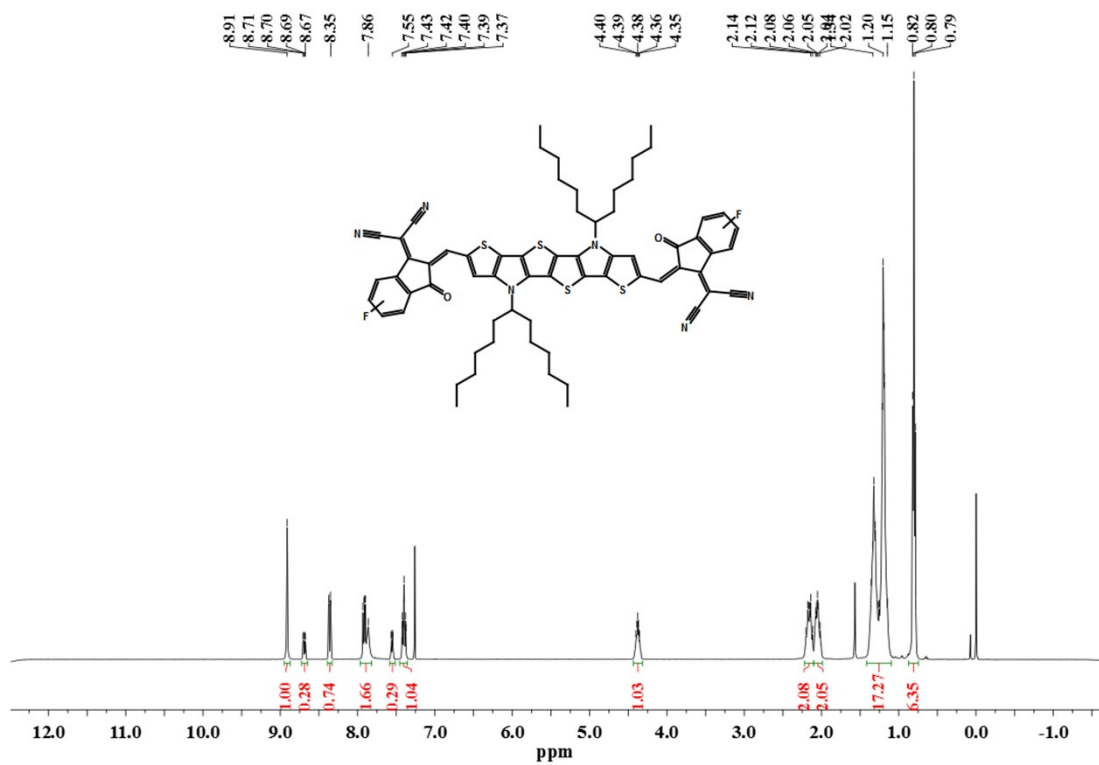**Figure S5**. ^{13}C NMR spectrum of compound 5.

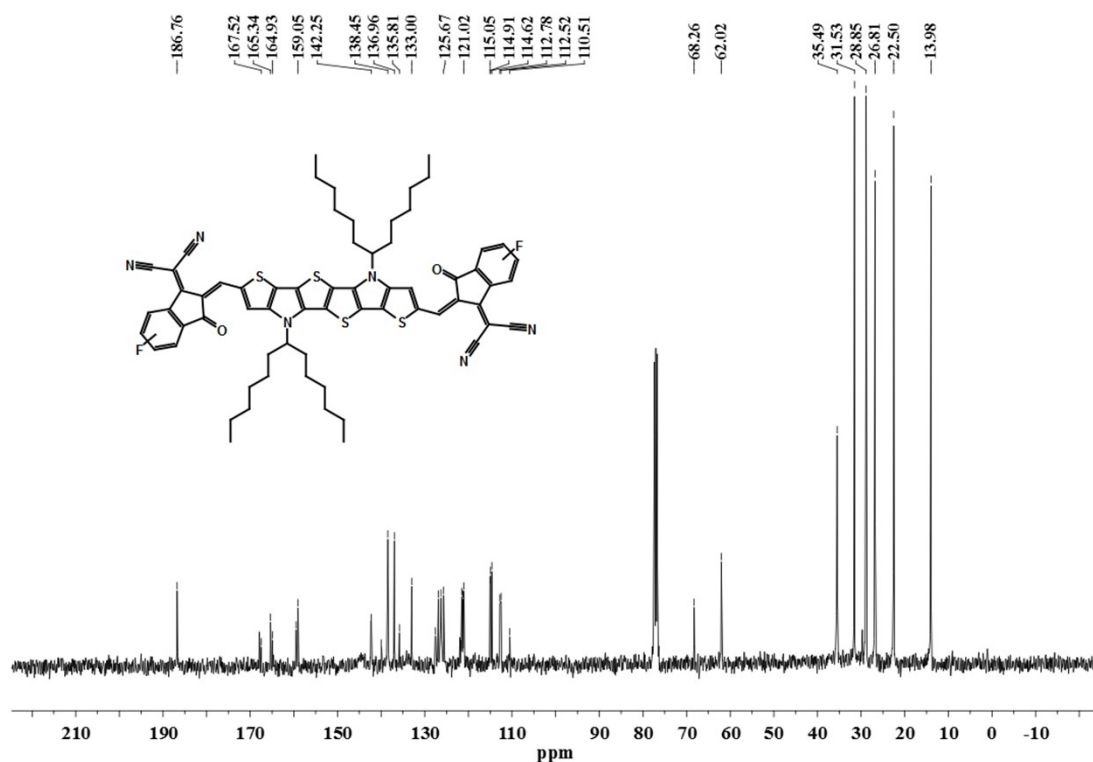**Figure S6**. ^{1}H NMR spectrum of SNIC-F.

Figure S7. ^{13}C NMR spectrum of SNIC-F.

2. Cyclic voltammetry (CV)

PBTIBDTT and SNIC-F electrochemical property were performed on a CHI600D electrochemical instrument, with a glassy carbon as the working electrode, an Ag/AgNO$_3$ as the reference electrode, and a Pt wire as the respectively electrode in the solution of Tetrakis-(n-butyl) ammonium hexafluorophosphate (Bu$_4$NPF$_6$) (0.1 M) in anhydrous acetonitrile. The ferrocene/ferrocenium redox couple (Fc/Fc$^+$) was used to calibrate potential of Ag/AgNO$_3$ reference electrode. The PBTIBDTT and SNIC-F were drop-coated on the working electrode in a CB solution. The HOMO energy values were calculated from E$_{HOMO}$=-(E$_{OX}$ - E$_{Ferrocene}$ + 4.80) (eV), and the LUMO energy values were calculated by E$_{LUMO}$= E$_{HOMO}$ + E$_g$ (where E$_g$ was determined from the UV–vis-NIR spectra).

3. UV-vis absorption

UV-vis absorption spectra were collected on a Perkin-Elmer UV-vis Lambda 750, and testing over the range of 300-1000 nm.

4. Atomic force microscopy (AFM)

AFM images were obtained from a SPA300HV instrument with an SPI 3800 controller (Seiko Instruments).

5. Grazing incidence wide angle X-ray scattering (GIWAXS)

GIWAXS measurements were conducted on BL14B1 (λ = 0.69 Å) at Shanghai Synchrotron Radiation Facility. Samples were spin-coated on the cleaned Si substrates.

6. Fabrication of devices

All the OSCs were fabricated with a architecture of glass/ITO/PEDOT:PSS/active layer/PDIN/Al. The ITO substrates were cleaned by detergent solution, deionized water, isopropanol and acetone in sequence under ultrasonication, and then dried by nitrogen and treated with UV-ozone for 20 min. A thickness of 30 nm PEDOT:PSS layer was spin-coated on the cleaned ITO surface, then annealed at 150 °C for 20 min. The active layers were spin-coated from chlorobenzene solution (with polymer concentration of 7 mg mL^{-1}), added with or without 1-CN at 1000-2000 rpm for 2 min to obtain conceivable films in a nitrogen glovebox, and then 30 nm PDIN was spin-coating on the active layer. Finally, 100 nm Al was deposited on the PDIN layer. The active area of 9 mm^2 was defined by the overlapping of patterned anode and cathode. The *J-V* curves were measured in a nitrogen glovebox using Keithley-2400 source meter at AM 1.5 G illumination of 100 mW cm^{-2} using a solar simulator (SAN-EI, XES-70S1, San-Ei. Electric Co. Ltd., Osaka, Japan) with a standard silicon solar cell as a reference to adjust the light intensity. The thicknesses of the films were obtained on a KLA-Tencor D-100 surface profiler. The EQE spectra of devices were tested using chopped monochromatic light from a xenon lamp under ambient conditions. A standard silicon solar cell was used as a reference to determine the light intensity at each wavelength.

7. SCLC Measurements

The carrier mobilities were measured by the space charge limited current (SCLC) method with hole-only device (ITO/PEDOT:PSS/active layer/Au) and electron-only device (ITO/ZnO/active layer/PDIN/Al). The measurements of the *I-V* curves were carried out in dark on a computer-controlled Keithley 2400 source-measure unit. The hole and electron mobility was estimated by fitting the *I-V* curves with SCLC model and the Mott-Gurney law: $\ln{(I/V^2)} = 0.89\beta(V/L)^{1/2} + \ln{(9\mu\varepsilon_0\varepsilon S/(8L^3))}$ Where *I* is the current, *V* is the applied voltage, β is the field activation factor, *L* is the thickness of films, μ is the mobility, ε_0 is the permittivity of free space, ε is the relative permittivity, and *S* is the area of films.
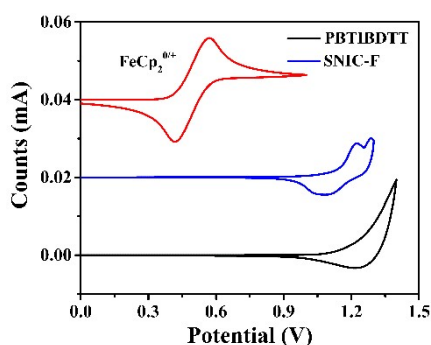

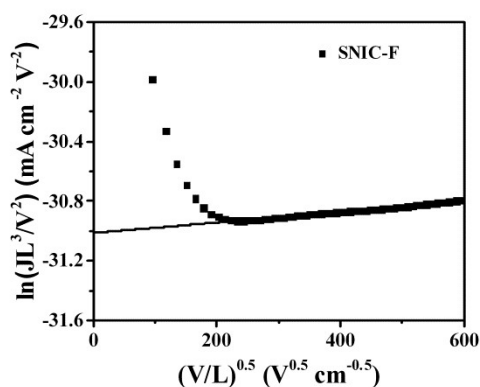**Figure S8.** Cyclic voltammetry of SNIC-F, PBTIBDTT and Fc/Fc$^+$.

Figure S9. *J-V* characteristic in dark of electron-only device based on SNIC-F.
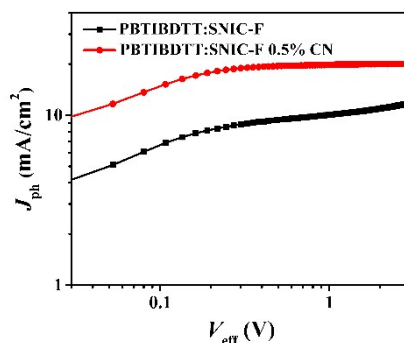
Figure S10. Curves of J_{ph} with respect to V_{eff} of devices processed with/without 1-CN as solvent additive.

Table S1. Device data of the OSCs based on PBTIBDTT:SNIC-F with different D/A weight ratios directly spin-coated from CB solution.

D/A ratio	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)
1:0.5	0.74	6.05	0.36	1.61
1:0.8	0.81	9.95	0.63	5.08
1:1	0.78	9.30	0.65	4.72
1:1.2	0.78	8.95	0.65	4.54

Table S2. Device data of the OSCs based on PBTIBDTT:SNIC-F (D/A = 1:0.8) with different 1-CN content in CB solution.

1-CN content (%)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)
0.3	0.80	9.50	0.67	5.09
0.5	0.83	19.64	0.69	11.25
0.8	0.81	13.39	0.67	7.27

Table S3. Device data of the OSCs based on PBTIBDTT:SNIC-F (D/A = 1:0.8, 0.5% 1-CN) with different active layer thickness.

Thickness [nm]	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)
110	0.83	17.07	0.72	10.20
130	0.82	18.39	0.70	10.56
150	0.83	19.64	0.69	11.25
180	0.82	18.96	0.67	10.42
250	0.81	19.01	0.60	9.24

Table S4. Hole and electron mobility of the PBTIBDTT/SNIC-F film.

Additive	μ_e (cm^2 V^{-1} s^{-1})	μ_h (cm^2 V^{-1} s^{-1})	μ_h/μ_e
None	1.78×10^{-5}	2.16×10^{-4}	12.1
0.5% 1-CN	1.18×10^{-4}	1.02×10^{-3}	8.6