

Electronic Supplementary Information

Side Chain Engineering on Dithieno[3,2-b:2,3-d]pyrrol Fused Electron Acceptors for Efficient Organic Solar Cells

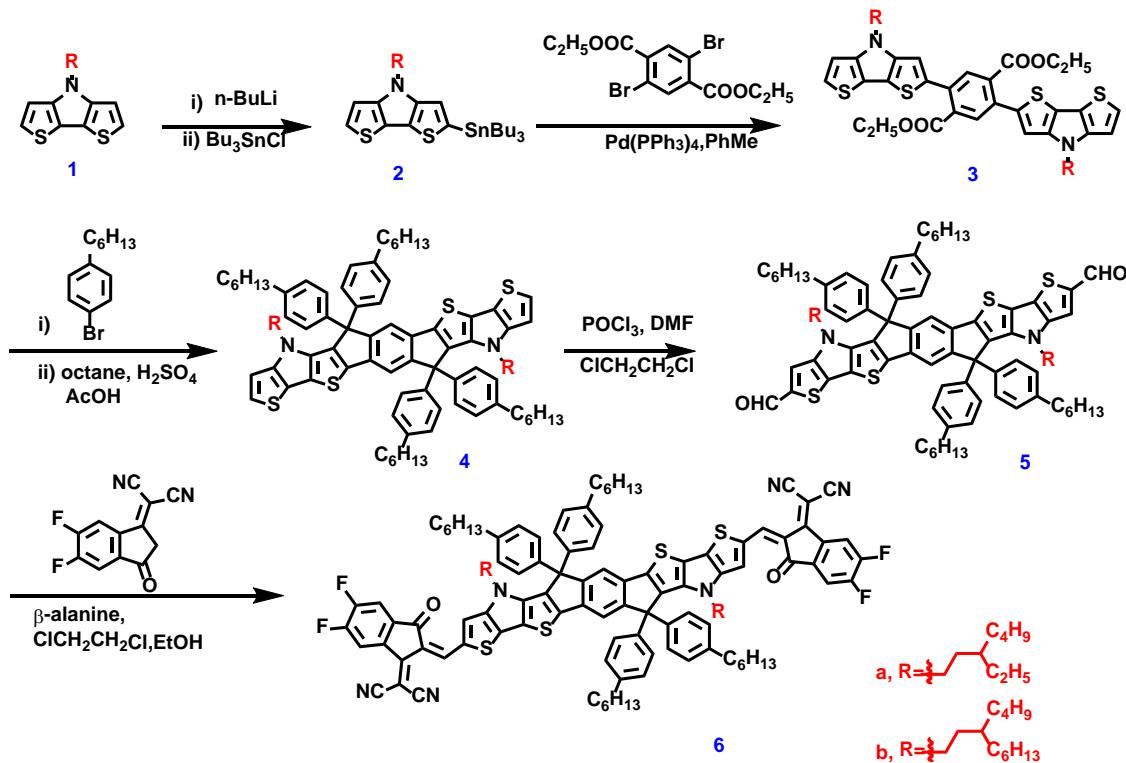
Haohao Feng^{a**}, Xin Song^{b**}, Ming Zhang^c, Jiangsheng Yu^d, Zhuohan Zhang^a, Renyong Geng^b, Linqiang Yang^a, Feng Liu^{c*}, Derya Baran^{b*}, Weihua Tang^{a*}

Table of content

1. Materials and Synthesis.....	2
2. Material Characterization.....	6
3. NMR and Mass Spectra.....	6
4. TG Analysis, UV-vis Absorption and CV measurement.....	9
5. Devices Fabrication and Measurements.....	9
6. SCLC Mobility Measurements.....	10

1. Materials and Synthesis

Unless stated otherwise, all commercially available chemicals and solvents were purchased from Aladdin, Sigma-Aldrich, or J&K Chemical Co., and used without further purification. Tetrahydrofuran (THF) and toluene were distilled from sodium before use, and 1,2-dichloroethane was dried with calcium hydride. 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene) malononitrile (2F-IC) were purchased from Derthon Optoelectronic Materials Science Technology Co. LTD. 4-(2-ethylhexyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole (**1a**) and 4-(2-butyloctyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole (**1b**) was synthesized with similar methods referring to the previous literature procedures¹.



Scheme S1. Synthetic route to different alkyl side-chain INP-based acceptors.

Synthesis of compound 2 and 3

Compound **1a** (1.50 g, 5.15 mmol) was dissolved in freshly distilled THF (20 mL) at -78 °C. *n*-BuLi (2.06 mL, 5.15 mmol, 2.5 M in hexane) was added into the above solution dropwise over 10 min under nitrogen. After stirring at -78 °C for 1.5 h, tributyltin chloride (2.01 g, 6.18 mmol) was added dropwise over 10 min. The solution was then warmed to room temperature. After stirring for another 3 h, water was added to quench the reaction. The reaction mixture was extracted with diethyl ether twice, then the organic layers dried over anhydrous MgSO₄. After solvent removal, compound **2a** was obtained and used directly without further purification. Compound **2a**, diethyl 2,5-dibromoterephthalate (0.77 g, 2.02

mmol), Pd(PPh₃)₄ (232.90 mg, 201.54 μ mol) were added in anhydrous toluene (30 mL), refluxed for one day under nitrogen. After general work-up, the crude product was purified by silica gel column chromatography (petroleum ether/dichloromethane =3:2 v/v) to afford a brown solid **3a** (2.40 g, 58%). ¹H NMR (500 MHz, CDCl₃, δ): 7.84 (s, 2H), 7.17 (d, J = 5.3 Hz, 2H), 7.04 (s, 2H), 6.99 (d, J = 5.3 Hz, 2H), 4.25 (q, J = 7.1 Hz, 4H), 4.06 (t, J = 7.1 Hz, 4H), 2.00 – 1.91 (m, 2H), 1.41 – 1.23 (m, 16H), 1.14 (t, J = 7.1 Hz, 6H), 0.94 – 0.84 (m, 12H). ¹³C NMR (125 MHz, CDCl₃, δ): 168.72, 145.22, 145.11, 137.76, 134.29, 134.05, 131.85, 124.02, 116.25, 115.19, 111.30, 62.12, 47.89, 32.18, 30.80, 29.65, 29.53, 27.42, 23.00, 14.46, 14.35, 14.00. MALDI-TOF MS (*m/z*): [M + H]⁺ calcd. for C₄₄H₅₂N₂O₄S₄, 800.2810; found, 800.2809.

By adopting the same procedure as for **3a**, we can obtain compound **3b** with **2b** to afford the *title* compound as a brown solid (2.45 g, 52%). ¹H NMR (500 MHz, CDCl₃, δ): 7.84 (s, 2H), 7.16 (d, J = 5.3 Hz, 2H), 7.04 (s, 2H), 6.98 (d, J = 5.3 Hz, 2H), 4.25 (d, J = 7.1 Hz, 4H), 4.05 (d, J = 7.4 Hz, 4H), 1.36-1.19 (m, 34H), 1.14 (m, 6H), 0.91-0.81 (m, 12H). ¹³C NMR (125 MHz, CDCl₃, δ): 168.45, 145.37, 145.27, 137.55, 134.10, 133.92, 131.69, 123.75, 115.99, 114.92, 111.23, 61.90, 52.04, 39.30, 31.98, 31.83, 31.51, 29.79, 28.90, 26.68, 23.19, 22.81, 14.23, 14.17. MALDI-TOF MS (*m/z*): [M + H]⁺ calcd. for C₅₂H₆₈N₂O₄S₄, 912.4062; found, 912.4059.

Synthesis of compound 4

The solution of 4-hexyl-1-bromobenzene (1.44 g, 5.59 mmol) in anhydrous THF (15 mL) was cooled to -78 °C and added *n*-BuLi (2.20 mL, 5.49 mmol, 2.5 M in hexane). The solution of compound **3a** (0.8 g, 1.00 mmol) in THF (15 mL) was added slowly and kept at -78 °C for 30 min, after the reaction mixture was stirring for 1 h at -78 °C. The reaction mixture was stirred at room temperature for 3-4 hours and extracted twice with ethyl acetate. The combined organic layers were dried over anhydrous MgSO₄. After removal of the solvent under reduced pressure, the yellow residue was dissolved in hexane (100 mL) and acetic acid (50 mL), then concentrated H₂SO₄ (0.5 mL) was added dropwise slowly. The solution was stirring at room temperature for 20 min before quenching it with water. The resulting mixture was extracted with ethyl acetate (3×100 mL), washed with water for three times, and dried over anhydrous MgSO₄. After removal of the solvent under reduced pressure, the residue was purified using column chromatography on silica gel employing petroleum ether/dichloromethane (10:1, v/v) as the eluent, affording a yellow solid **4a** (0.72 g, 55%). ¹H NMR (500 MHz, CDCl₃, δ): 7.30 (t, J = 7.3 Hz, 8H), 7.27 (s, 2H), 7.08 – 7.01 (m, 10H), 6.89 (d, J = 4.9 Hz, 2H), 3.59 (d, J = 8.1 Hz, 4H), 2.60 – 2.49 (m, 8H), 1.56 (s, 8H), 1.37 – 1.23 (m,

32H), 0.86 (t, J = 6.5 Hz, 14H), 0.74 (t, J = 7.3 Hz, 6H), 0.66 – 0.57 (m, 7H), 0.52 (t, J = 7.3 Hz, 7H). ^{13}C NMR (125 MHz, CDCl_3 , δ): 156.47, 144.68, 142.05, 140.95, 140.11, 139.17, 136.06, 129.22, 128.65, 122.83, 117.73, 116.48, 115.04, 111.90, 62.80, 48.65, 35.96, 32.31, 32.12, 31.68, 30.75, 29.70, 29.59, 27.26, 23.01, 14.50. MALDI-TOF MS (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{88}\text{H}_{108}\text{N}_2\text{S}_4$, 1320.7395; found, 1320.7380.

By adopting the same procedure as for **4a**, we can obtain compound **4b** with **3b** to afford the *title* compound as a pale yellow solid (0.82 g, 58%). ^1H NMR (500 MHz, CDCl_3 , δ): 7.30 (dd, J = 8.3, 2.7 Hz, 8H), 7.27 (s, 2H), 7.07-7.02 (m, 10H), 6.88 (d, J = 5.2 Hz, 2H), 3.58 (d, J = 8.2 Hz, 4H), 2.58-2.51 (m, 8H), 1.59-1.54 (m, 8H), 1.35-1.24 (m, 28H), 1.18 (m, 5H), 1.11-0.96 (m, 13H), 0.95-0.89 (m, 4H), 0.89-0.78 (m, 24H), 0.73 (t, 6H), 0.64-0.53 (m, 8H). ^{13}C NMR (125 MHz, CDCl_3 , δ): 156.59, 144.40, 141.86, 141.21, 141.05, 139.86, 139.04, 135.69, 129.32, 128.51, 122.30, 117.58, 116.58, 114.71, 112.57, 62.85, 53.00, 37.63, 35.78, 31.95, 31.60, 30.95, 30.69, 29.71, 29.39, 29.22, 26.93, 23.08, 22.81, 14.31, 14.19. MALDI-TOF MS (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{96}\text{H}_{124}\text{N}_2\text{S}_4$, 1432.8647; found, 1432.8656.

Synthesis of compound 5

Extra dry DMF (5 mL) and Phosphorus oxychloride (POCl_3 , 0.3 mL) was added in a solution of compound **4a** (500 mg, 0.38 mmol) in dry 1,2-dichloroethane ($\text{ClCH}_2\text{CH}_2\text{Cl}$, 20 mL) at 0 °C under nitrogen. The mixture was stirred at 0 °C for 1 h and then heated to 85 °C for 3 h. The mixture was poured into ice water (100 mL), neutralized with Na_2CO_3 (aq), and extracted with dichloromethane. The organic layer was washed with water and brine, dried over anhydrous MgSO_4 . After removal of the solvent under reduced pressure, the residue was purified using column chromatography on silica gel employing petroleum ether/dichloromethane (3:2, v/v) as the eluent, affording a yellow solid **5a** (450 mg, 85%). ^1H NMR (500 MHz, CDCl_3 , δ): 9.82 (s, 2H), 7.50 (s, 2H), 7.34 (s, 2H), 7.29 (d, J = 8.3 Hz, 8H), 7.08 (d, J = 8.3 Hz, 8H), 3.64 - 3.62 (m, 4H), 2.57 - 2.54 (m, 8H), 1.57 (m, 12H), 1.37 – 0.94 (m, 38H), 0.87 (m, 12H), 0.75 (t, J = 7.3 Hz, 6H), 0.57 (t, J = 7.4 Hz, 6H). ^{13}C NMR (125 MHz, CDCl_3 , δ): 182.99, 157.26, 146.25, 144.25, 142.57, 140.06, 139.80, 138.33, 136.40, 129.03, 128.88, 125.06, 120.05, 118.31, 115.86, 62.92, 48.74, 35.92, 32.26, 32.09, 31.64, 30.80, 29.67, 29.56, 27.22, 22.98, 14.47. MALDI-TOF MS (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{90}\text{H}_{108}\text{N}_2\text{O}_2\text{S}_4$, 1376.7294; found, 1376.7345.

By using the same procedure as for **5a**, we can obtain compound **5b** with **4b** to afford the *title* compound as a pale yellow solid (435 mg, 76%). ^1H NMR (500 MHz, CDCl_3 , δ): 9.82 (s, 2H), 7.49 (s, 2H), 7.35 (s, 2H), 7.28 (d, J = 6.0 Hz, 8H), 7.08 (d, J = 7.9 Hz, 9H), 3.63 (d, J = 8.2 Hz, 4H), 2.58-2.54 (m, 9H), 1.58 (d, J = 7.6 Hz, 10H), 1.37-0.90 (m, 59H), 0.89-0.80 (m,

26H), 0.74 (t, 6H), 0.64-0.55 (m, 8H). ^{13}C NMR (125 MHz, CDCl_3 , δ): 182.82, 157.37, 146.42, 145.32, 143.88, 142.40, 139.73, 139.52, 138.18, 136.03, 129.12, 128.73, 125.13, 120.72, 118.14, 115.54, 62.97, 53.11, 37.91, 35.74, 31.91, 31.56, 30.95, 30.72, 29.71, 29.36, 29.20, 26.92, 23.08, 22.78, 14.28, 14.15. MALDI-TOF MS (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{98}\text{H}_{124}\text{N}_2\text{O}_2\text{S}_4$, 1488.8579; found, 1488.8547.

Synthesis of INPIC- EH

Under the protection of argon, Compound **5a** (150.0 mg, 108.85 μmol), 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene) malononitrile (200.43 mg, 807.76 μmol) and β -alanine (1.80mg, 20.20 μmol) was dissolved in a mixture of $\text{ClCH}_2\text{CH}_2\text{Cl}$ and EtOH (8 mL/4 mL). After stirring at 80 °C for 4 h, the mixture was poured into water and then extracted with CHCl_3 (3×30 mL), the organic layer was dried over anhydrous MgSO_4 . After removal of the solvent under reduced pressure, the residue was purified using column chromatography on silica gel employing petroleum ether/dichloromethane (2:1, v/v) as the eluent, affording a yellow solid black solid (156 mg, 80%). ^1H NMR (500 MHz, CDCl_3 , δ): 8.82 (s, 2H), 8.49 (m, 2H), 7.63 (t, $J = 7.6$ Hz, 4H), 7.40 (s, 2H), 7.28 (m, 8H), 7.11 (d, $J = 8.4$ Hz, 8H), 3.64 (d, $J = 8.3$ Hz, 4H), 2.61 – 2.54 (m, 8H), 1.57 (m, 12H), 1.37 – 0.94 (m, 38H), 0.87 (m, 12H), 0.75 (t, $J = 7.3$ Hz, 6H), 0.57 (t, $J = 7.4$ Hz, 6H). ^{13}C NMR (125 MHz, CDCl_3 , δ): 185.90, 158.71, 158.25, 152.98, 151.87, 148.84, 142.73, 139.43, 138.30, 137.27, 136.49, 135.94, 134.42, 128.79, 128.54, 119.62, 116.14, 115.12, 114.76, 77.32, 77.07, 76.82, 66.82, 62.89, 52.97, 38.97, 35.56, 31.73, 31.73, 31.44, 31.22, 29.98, 29.74, 29.15, 28.82, 23.44, 22.96, 22.62, 14.05, 11.05. MALDI-TOF MS (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{114}\text{H}_{112}\text{F}_4\text{N}_6\text{O}_2\text{S}_4$, 1800.7699; found, 1800.7650.

Synthesis of INPIC- OB

By using the same procedure as for INPIC-EH, we can obtain INPIC-OB with **5b** to afford the *title* compound as a black-green solid (154 mg, 80%). ^1H NMR (500 MHz, CDCl_3 , δ): 8.82 (s, 2H), 8.49 (m, 2H), 7.62 (t, $J = 7.5$ Hz, 4H), 7.41 (s, 2H), 7.33-7.26 (m, 8H), 7.11 (d, $J = 8.0$ Hz, 8H), 3.63 (d, $J = 8.2$ Hz, 4H), 2.62-2.53 (m, 8H), 1.61-1.56 (m, 8H), 1.40-0.91 (m, 42H), 0.90-0.71 (m, 24H), 0.67-0.55 (m, 8H). ^{13}C NMR (125 MHz, CDCl_3 , δ): 186.04, 158.96, 158.46, 155.29, 153.22, 152.17, 149.17, 146.75, 142.87, 139.59, 138.45, 137.50, 136.71, 136.13, 135.67, 134.59, 128.98, 126.93, 119.75, 119.27, 116.35, 115.26, 114.72, 112.47, 112.30, 67.05, 63.10, 53.36, 37.83, 35.76, 31.91, 31.57, 31.03, 30.77, 29.78, 29.37, 29.10, 26.86, 23.14, 22.80, 14.29, 14.15. MALDI-TOF MS (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{122}\text{H}_{128}\text{F}_4\text{N}_6\text{O}_2\text{S}_4$, 1912.8951; found, 1912.8916.

2. Material Characterization

¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE III 500 MHz instrument with sample solutions in CDCl₃ using tetramethylsilane (TMS) as internal standard. The matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a Bruker Autoflex TOF/TOF spectrometer. Ultraviolet-visible (UV-Vis) absorption spectra of diluted solutions (dissolved in chloroform) and films were taken on a UV-Vis instrument Evolution 220 (Thermo Fisher). The thermogravimetric analyses (TGA) was performed on a TA instrument (TGA/SDTA851e) with heating rate of 20 °C·min⁻¹ under nitrogen gas flow, with the temperature corresponding to 5% weight loss defined as decomposition temperature (*T_d*). The electrochemical cyclic voltammetry was conducted on a CHI 600D electrochemical workstation, using glassy-carbon, platinum-wire and Ag/Ag⁺ electrode as working electrode, counter electrode, and reference electrode, respectively. All initial potentials were determined in tetrabutylammonium hexafluorophosphate (0.1 M anhydrous acetonitrile solution) under N₂ atmosphere at a scan rate of 50 mV·s⁻¹. After completing the measurement, ferrocene was further measured as an internal standard (absolute energy level of 4.8 eV below vacuum). HOMO=−[4.8−E_{ox}−E_(Fc/Fc+)]eV, LUMO=−[4.8−E_{red}−E_(Fc/Fc+)]eV.

3. NMR and Mass Spectra

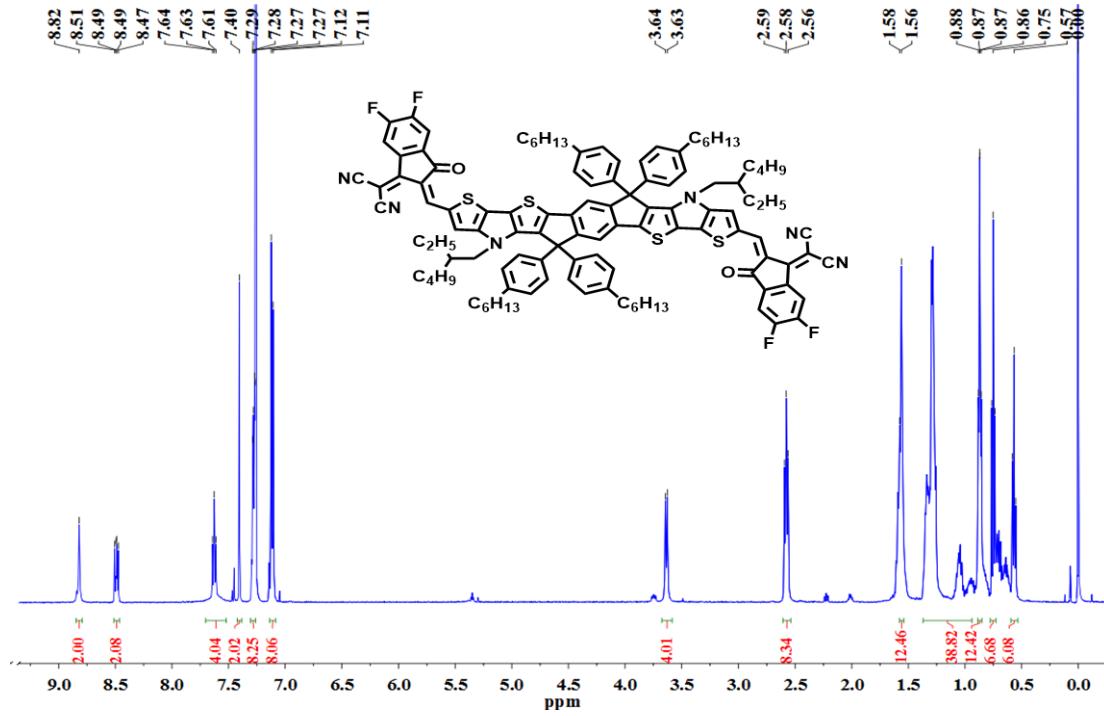


Figure S1. ¹H NMR spectrum of INPIC-EH.

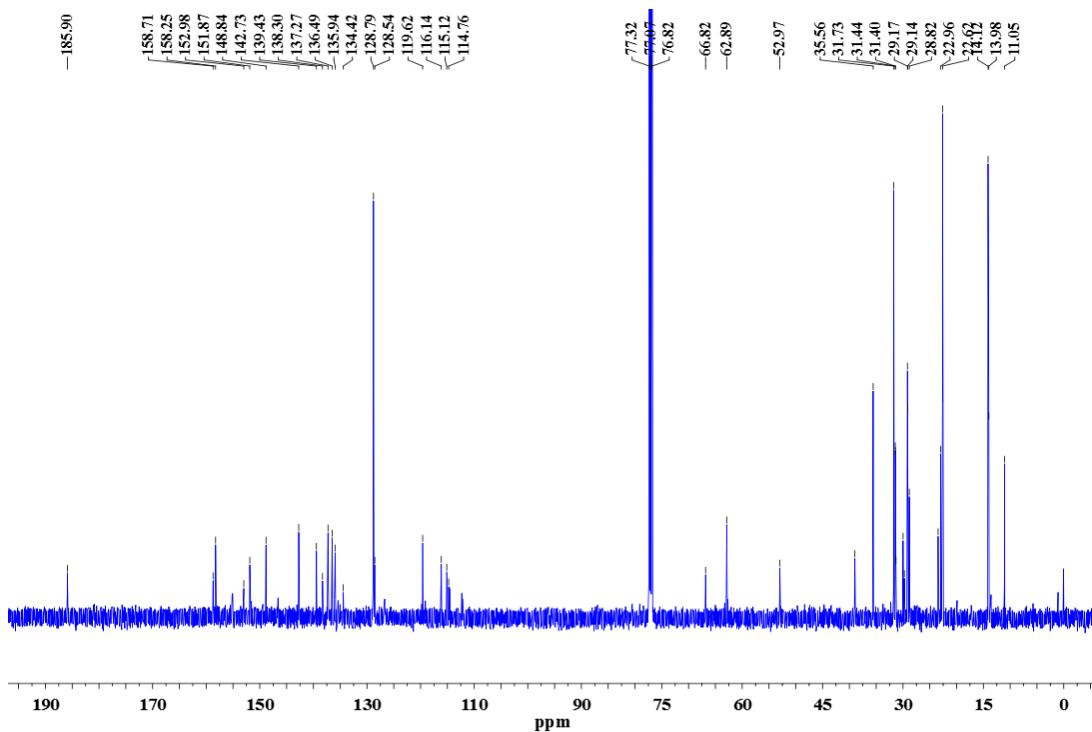


Figure S2. ^{13}C NMR spectrum of INPIC-EH.

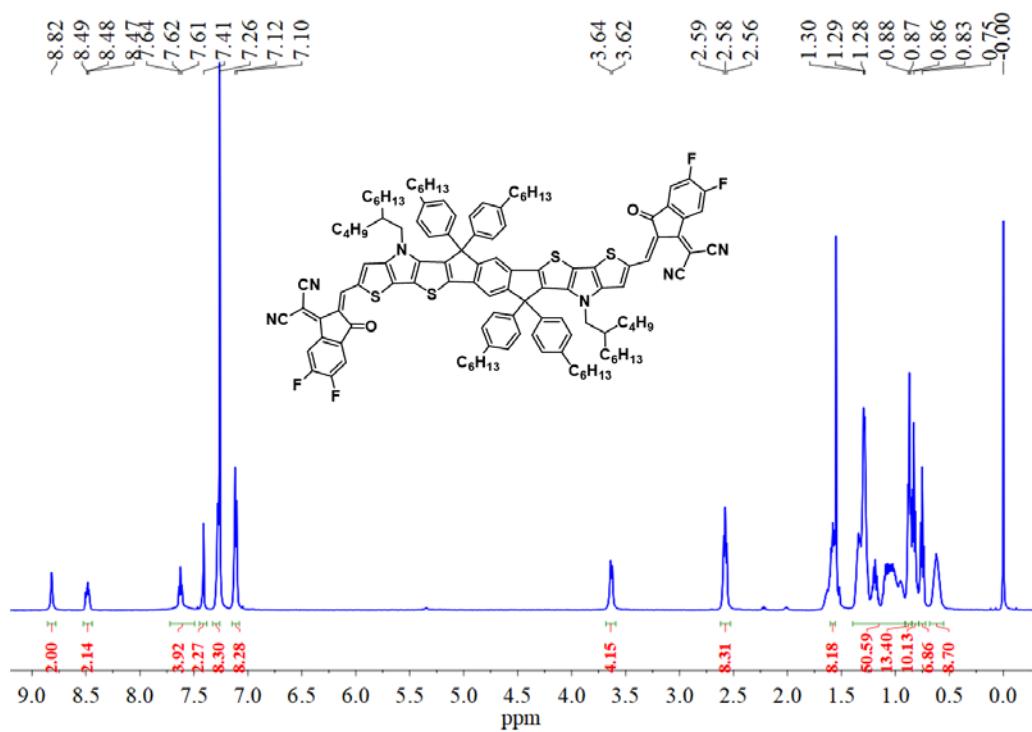


Figure S3. ^1H NMR spectrum of INPIC-BO.

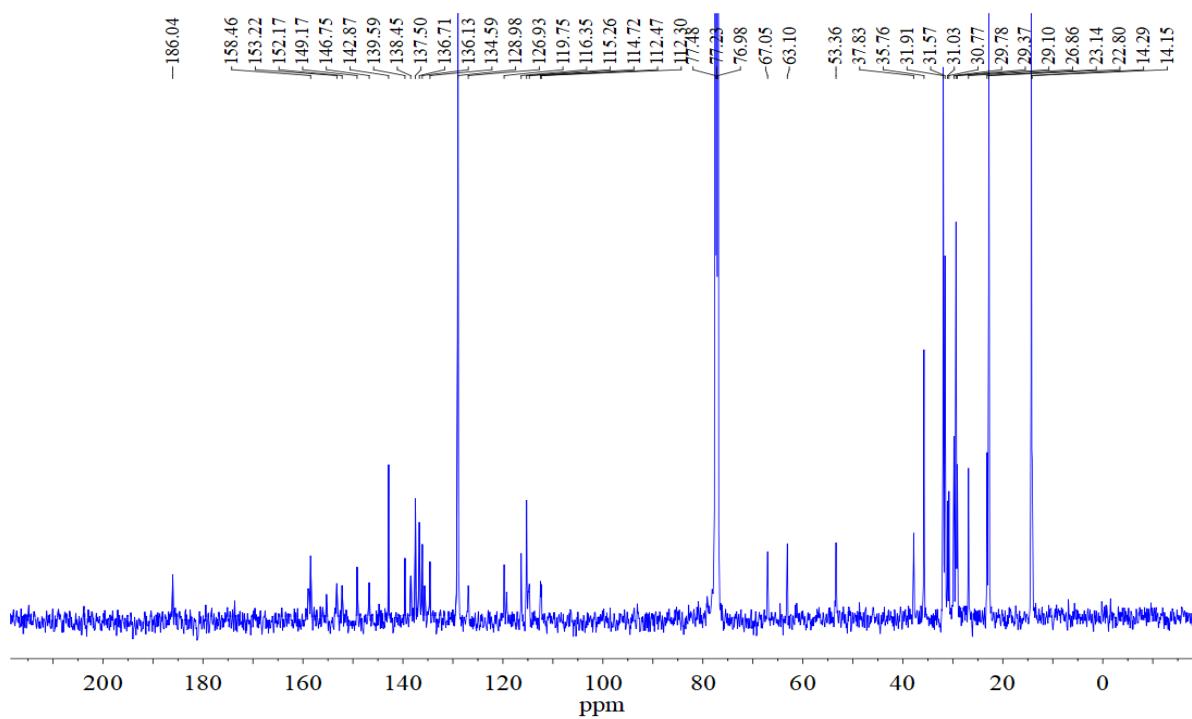


Figure S4. ^{13}C NMR spectrum of INPIC-BO.

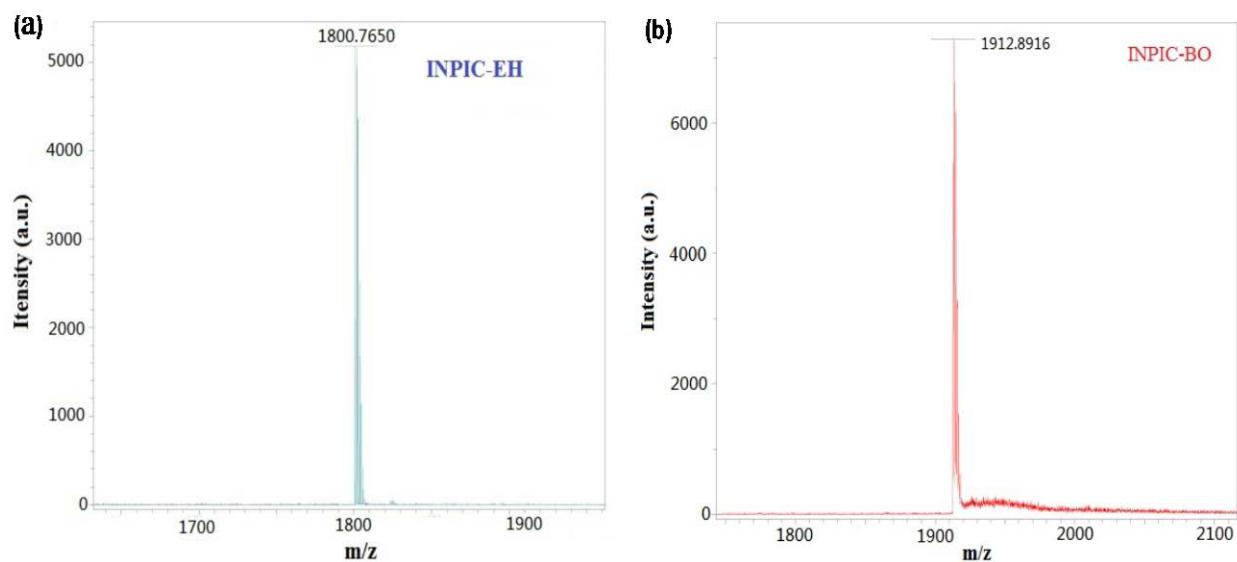


Figure S5. The MALDI-TOF MS plot of INPIC-EH and INPIC-BO.

4. TG Analysis, UV-vis Absorption and CV measurement

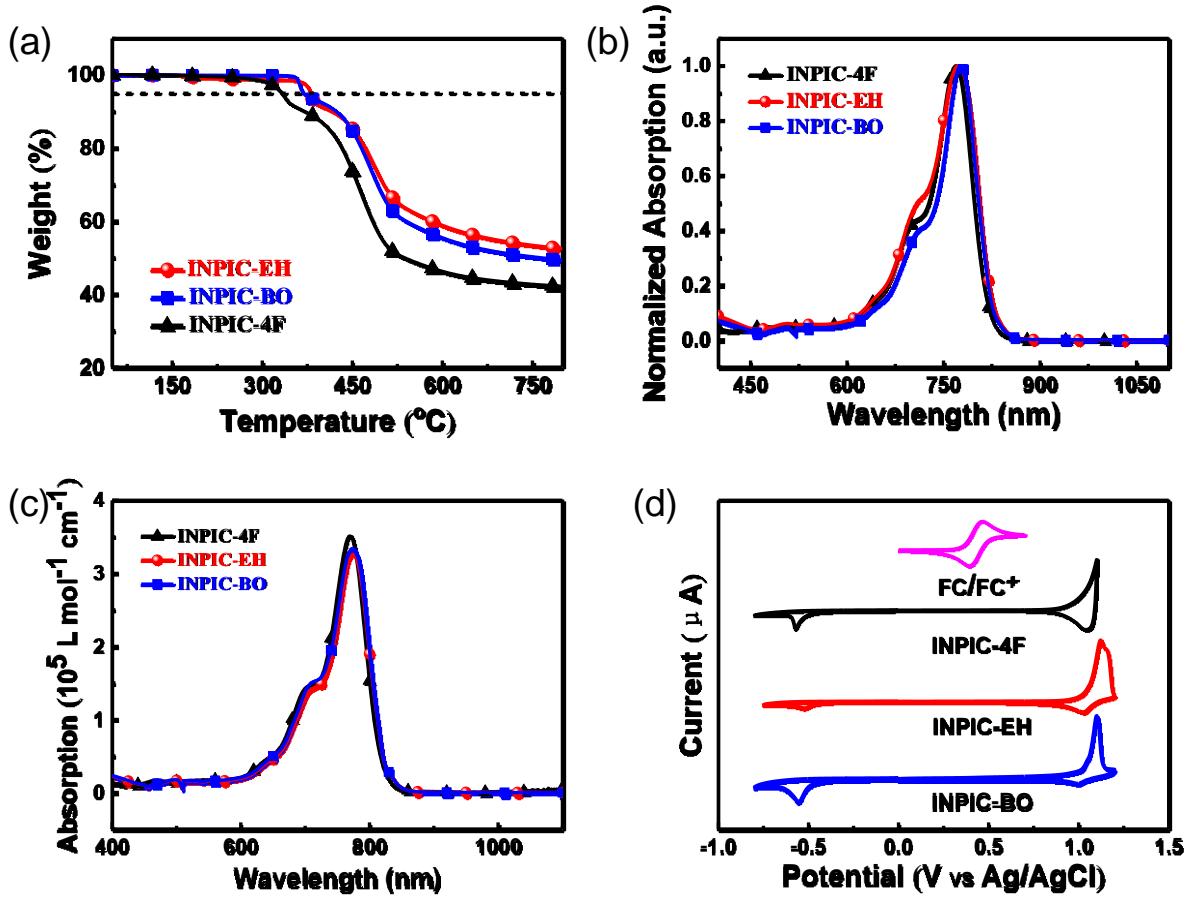


Figure S6. (a) Normalized UV-vis absorption spectra of three acceptors in a chloroform solution; (b) UV-vis absorption spectra of three acceptors in a chloroform solution with a concentration of 1×10^{-5} mol/L. (c) TG curves of three acceptors; (d) CV measurement of the three acceptors.

5. Devices Fabrication and Measurements

PBDB-T was purchased from Solarmer Inc. Zinc oxide precursor solution was prepared by dissolving 2.4 g of zinc acetate dehydrate (sigma) and 0.647 ml of ethanolamine (sigma) in 30 ml of 2-methoxyethanol (sigma). Then ZnO precursor solution was stirred overnight to get the transparent solution. D:A blend (1:1 weight ratio, 20 mg/ml) was dissolved in chlorobenzene:1,8-diiodooctane (DIO) mixed solvent with volume ratio of 99.5:0.5, then stirring the solution in 100 °C. The fabrication and measurement methods of devices are as follows: after a thorough cleaning of the indium-tin oxide (ITO)-coated glass substrate with detergent, deionized water, acetone, and isopropyl alcohol under ultrasonication for 15 minutes. The ITO glass substrates were treated with UV-ozone for 15 minutes and then the sol-gel-derived ZnO films were spin-coated onto the ITO substrates followed by thermal treatment at 200 °C for 30 min. After ZnO film preparation, the substrates were transferred

into nitrogen-filled glove-box. The blend solution was spin-coated with speed of 2500 rpm and annealed at 100 °C for 10 min. A 7 nm MoO₃ layer and a 100 nm Ag layer were subsequently evaporated at a pressure of less than 2x10⁻⁶ Tor through a shadow mask.

6. SCLC Mobility Measurements

Electron-only devices were fabricated with the device structure ITO/ZnO/PBDB-T:Acceptor/Ca/Al. The mobilities were determined by fitting the dark current to the model of a single carrier SCLC³ which is described by the equation:

$$J = \frac{9}{8} \epsilon_0 \epsilon_r \mu_h \frac{V^2}{d^3}$$

where J is the current, μ_h is the zero-field mobility, ϵ_0 is the permittivity of free space, ϵ_r is the relative permittivity of the material, d is the thickness of the active layer, and V is the effective voltage. Hole mobilities were measured in a device configuration of ITO/PEDOT:PSS/Acceptor/MoO_x/Ag. The other processes are same with hole mobilities.

Table S1. Hole and electron mobilities of the films.

Blend film	μ_h [cm ² V ⁻¹ s ⁻¹]	μ_e [cm ² V ⁻¹ s ⁻¹]	μ_h/μ_e
PBDB-T:INPIC-4F	2.64x10 ⁻⁴	2.64x10 ⁻⁴	1.00
PBDB-T:INPIC-EH	2.21x10 ⁻⁴	1.92x10 ⁻⁴	1.15
PBDB-T:INPIC-BO	2.06x10 ⁻⁴	8.60x10 ⁻⁵	2.40

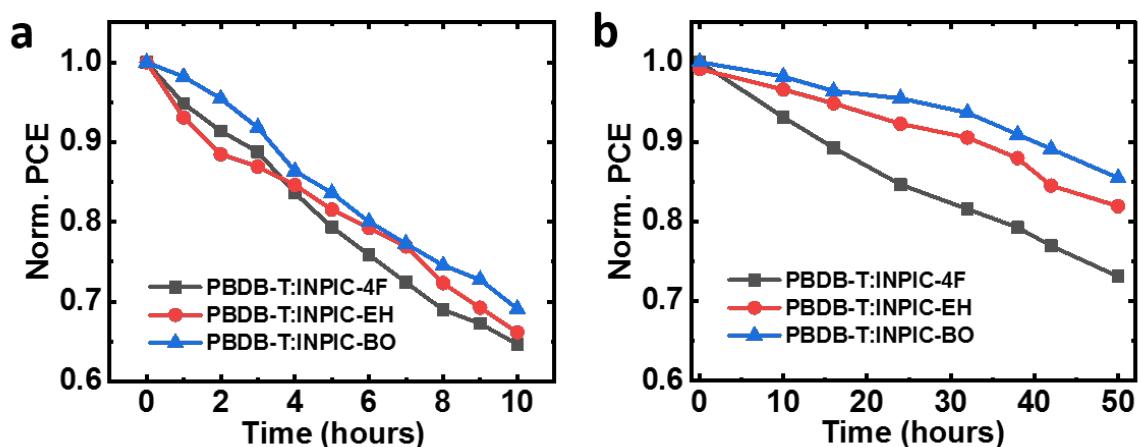


Fig. S7 (a) Photo-stability of NFA-based solar cells (nitrogen atmosphere, under constant AM1.5G illumination at 1 sun, room temperature) for 10 hours. (b) Shelf storage lifetime (dark, nitrogen atmosphere, room temperature) comparison of different sidechain based NFA system for 50 hours.

Reference

1. Hendel, S. J.; Poe, A. M.; Khomein, P.; Bae, Y.; Thayumanavan, S.; Young, E. R. Photophysical and electrochemical characterization of BODIPY-containing dyads comparing the influence of an A–D–A versus D–A motif on excited-state photophysics. *The Journal of Physical Chemistry A* **2016**, *120* (44), 8794-8803.
2. Mihailescu, V. D.; Wildeman, J.; Blom, P. W. M. Space-charge limited photocurrent. *Phys. Rev. Lett.* **2005**, *94* (12), 126602.
3. Davids, P. S.; Campbell, I. H.; Smith, D. L. Device model for single carrier organic diodes. *J. Appl. Phys.* **1997**, *82* (12), 6319-6325.