

Supporting Information

Title: Simultaneously Enhance the Molecular Planarity and the Solubility for Non-Fullerene Acceptors: Effect of Aliphatic Side-Chain Substitution on Photovoltaic Performance

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Experimental Part

1. Materials and Instruments.

The catalyst precursor Pd(PPh₃)₄ was prepared according to the literature procedure and stored in a Schlenk tube under nitrogen atmosphere. Unless otherwise noted, all chemicals were purchased from Aldrich or Acros and used without further purification. Tetrahydrofuran (THF) and toluene were distilled over sodium and benzophenone under nitrogen atmosphere. All reactions were performed under an atmosphere of nitrogen and monitored by thin layer chromatography (TLC) with silica gel 60 F254 (Merck, 0.2 mm). Column chromatography was carried out on silica gel (200-300 mesh). ¹H and ¹³C NMR spectra were recorded on a Bruker DM300 or AV 400 spectrometer in CDCl₃. The gel permeation chromatography (GPC) measurements were performed at 80 °C on a PL-220 (Polymer Laboratories) chromatography connected to a differential refractometer with chlorobenzene as an eluent. The electrochemical behavior of the compounds was investigated using cyclic voltammetry (CHI 630A Electrochemical Analyzer) with a standard three-electrode electrochemical cell in a 0.1 M tetrabutylammonium tetrafluoroborate solution in acetonitrile at room temperature under an atmosphere of nitrogen with a scanning rate of 30 mV/s. A Pt plate working electrode, a Pt wire counter electrode, and an Ag/AgNO₃ (0.01 M in CH₃CN) reference electrode were used. The experiments were calibrated with the standard ferrocene/ferrocenium (*F*_c) redox system and assumption

that the energy level of F_c is 4.8 eV below vacuum. UV-visible absorption spectra were obtained on a PerkinElmer UV-vis spectrometer model Lambda 750. The thickness of the blend films was determined by a Dektak 6 M surface profilometer. Elemental analyses were performed on a Flash EA 1112 analyzer. Thermal gravimetric analysis (TGA) measurements were performed on a Pyris 1 TGA instrument under a nitrogen atmosphere at a heating rate of 10 °C/min to record the TGA curves. DSC measurements were carried out on a DSC8000 (Perkin Elmer) instrument with indium and zinc employed for the temperature calibration. Samples of ca. 2.0 mg were sealed in aluminum pans, and a nitrogen gas purge with a flux of ca. 20 mL/min was used to prevent oxidative degradation of samples during the temperature scan. The samples were heated at a rate of 10 °C/min. Atomic force microscopy (AFM) measurements were performed under ambient conditions using a Digital Instrument Multimode Nanoscope IIIA operating in the tapping mode and the bright-field transmission electron microscope (TEM) images were obtained from a TEM, Tecnai F20, FEI instrument with an accelerating voltage of 200 kV. The X-ray diffraction (XRD) patterns were collected using a PANalytical X'Pert PRO MPD diffractometer with Cu KR radiation.

2. Charge mobilities of blend films measured by SCLC

Hole mobilities were measured in a device configuration of ITO/PEDOT: PSS /polymer:PC₇₁BM/Au. The conductivity of ITO was 20 C/square. PEDOT:PSS is Baytron Al 4083 from H. C. Starck and was filtered with a 0.45 µm polyvinylidene difluoride (PVDF) film before use. A thin layer of PEDOT:PSS was spin-coated on top of cleaned ITO substrate at 3000 rpm/s for 60 s and dried subsequently at 130 °C for 15 min on a hotplate before transferred into a glove box. The thickness of the PEDOT:PSS layer was about 40 nm. The blend of polymers and small molecules was dissolved in DCB containing DIO in a concentration of 4 mg/mL (polymer) with the corresponding additives, heated at 100 °C overnight to ensure the sufficient dissolution, and then spin-coated onto PEDOT:PSS layer. The top electrode was thermally evaporated with a 100 nm of gold at a pressure of 10⁻⁴ Pa through a shadow mask. Dark Current-voltage characteristics were recorded using an Agilent B2902A

Source in a dark circumstance in a range of 0 V to 10.0 V. The temperature while measuring the dark J - V curves was approximately 25 °C. The hole mobilities was calculated according to the Mott-Gurney equation: $J = 9\varepsilon_0\varepsilon_r\mu V^2/8L^3$, in which d is the thickness of active layer, ε_0 is the vacuum dielectric constant, ε_r is the relative dielectric constant of polymer. Electron mobilities were measured in a device configuration of FTO/active layer /Al. The other processes are same with hole mobilities.

3. Polymer Solar Cell Fabrication and Characterization

PSCs were fabricated with the device configuration of (ITO) /ZnO/active layer/MoO₃/Ag. The conductivity of ITO was 20 Ω/. The ITO-coated glass substrates were thoroughly cleaned by deionized water, acetone, and isopropanol twice successively at first. After the substrates were dried at 150 °C for 15 minutes, thin layers of sol-gel ZnO (30 nm) were spin-coated on them and then annealed at 200 °C for 1 hour in the air. The blend of polymers and small molecule was dissolved in DCB with DIO with the polymer concentration of 4 mg ml⁻¹, and heated at 110 °C at least 5 h to ensure a sufficient dissolution, and then spin-coated onto ZnO modified glass substrates. Followed 10 nm thick MoO₃ film and 100 nm thick Al layer were deposited sequentially to complete the inverted device. Six cells were fabricated on one substrate with an effective area of 0.04 cm². Current-voltage characteristics were recorded using an Enli Technology Ltd., Taiwan (SS-F53A) AAA class solar simulator under AM 1.5G with an intensity of 100 mW cm⁻² as the white light source and the intensity was calibrated with a standard single crystal Si photovoltaic cell. The temperature while measuring the J - V curves was approximately 25 °C. The EQE measurements of PSCs were performed by the solar cell spectral response measurement system QE-R3011 (Enli Technology Ltd., Taiwan), which was calibrated by monocrystalline silicon solar cell in advance.

4. Synthesis of polymer and small molecules

Synthesis of polymer

The donor polymer **PBDB-T** was synthesized according to the reported procedure.^[S 2]

Synthesis of compound 1

Compound 1 was synthesized according to the reported procedure.^[S 3]

Synthesis of compound 2

In a dry three-necked round-bottomed flask, compound 1 (521 mg, 0.57 mmol) was dissolved in anhydrous THF (25 mL). The mixture was deoxygenated with argon for 30 min. At -78 °C, a solution of n -butyllithium (2.4 M in hexane, 0.59 mL, 1.42 mmol) was added dropwise. After 1 h of stirring at -78 °C, anhydrous DMF (0.18 mL) was added to this solution. The mixture was warmed to room temperature and stirred overnight. Water (10 mL) was added and the mixture was extracted with dichloromethane (3 × 50 mL). The organic phase was dried over anhydrous MgSO₄ and filtered. After the solvent had been removed from the filtrate, the residue was purified by column chromatography on silica gel using petroleum ether/dichloromethane (1:1) as eluent, yielding a yellow solid (422 mg, 76%). ¹H NMR (500 MHz, CDCl₃): δ 9.94 (s, 2H), 7.68 (s, 4H), 7.49 (s, 2H), 2.07-2.11 (m, 8H), 1.95-1.98 (m, 4H), 1.05-1.45(m,56H), 0.80-0.95 (m, 18H).

Synthesis of FTIC-C8C6

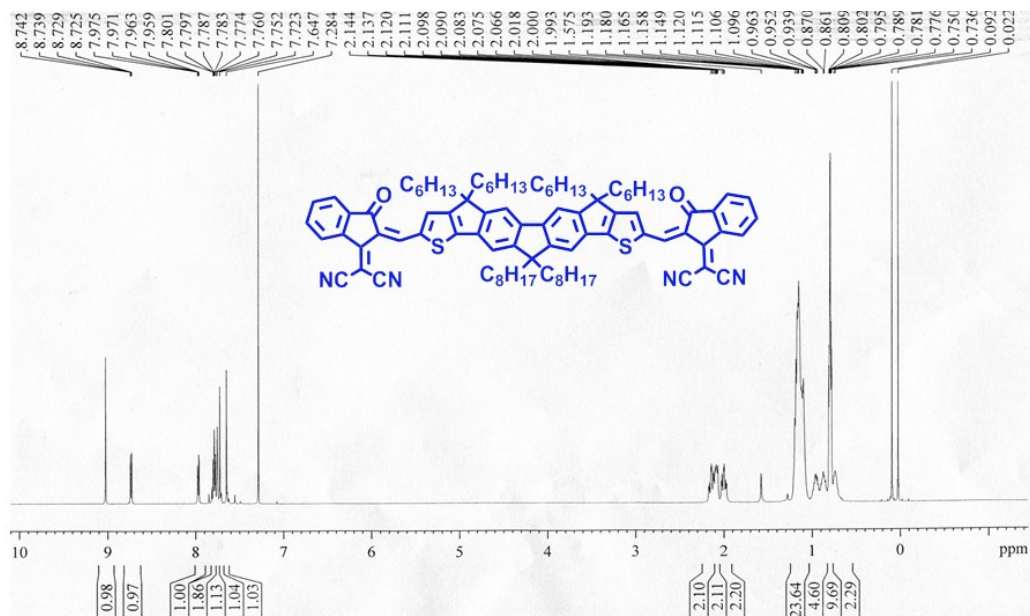
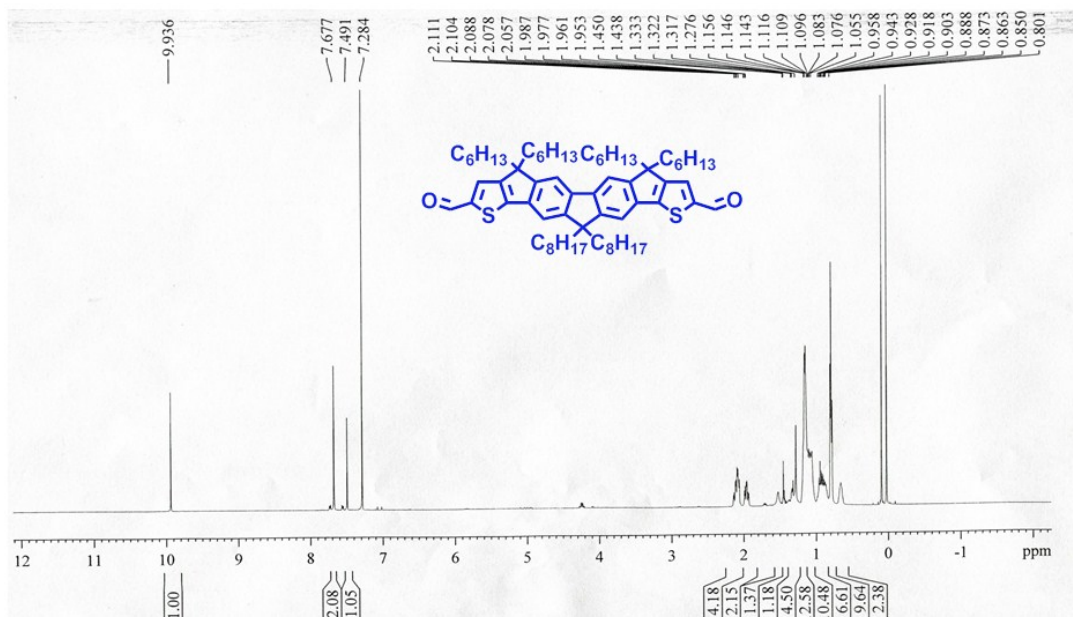
Compound 2 (340 mg, 0.35 mmol) and INCN (1.02 g, 3.50 mmol) were dissolved in dry CHCl₃ (50 mL). The mixture was deoxygenated with argon gas for 30 min, and then 1 ml pyridine were added. The mixture stirred at room temperature for 24h under argon gas. Then, the mixture was poured into water (20 mL) and extracted with dichloromethane (3 × 100 mL). The organic layer was washed with water, and then dried over anhydrous MgSO₄. After removing the solvent, the residue was purified using column chromatography on silica gel employing petroleum ether/CH₂Cl₂ (1:1) as an eluent, yielding a dark blue solid (370 mg, 78%). ¹H NMR (500 MHz, CDCl₃): δ 9.05 (s, 2H), 8.72-8.74 (m, 2H), 7.95-7.97 (m, 2H), 7.78-7.80 (m, 4H), 7.76 (s, 2H), 7.72 (s, 2H), 7.65 (s, 2H), 2.10-2.14 (m, 8H), 1.98-2.08 (m, 4H), 1.07-1.22 (m, 56H), 0.75-0.96 (m, 18H). ¹³C NMR (100 MHz, CDCl₃): δ 188.40, 161.97, 160.92, 156.71, 156.34, 152.31, 142.47, 140.38, 139.98, 138.70, 138.20, 136.96, 136.71, 134.96, 134.34, 125.25, 123.64, 121.23, 116.15, 115.05, 114.96, 114.49, 68.22, 54.71, 54.23, 40.45, 39.17, 31.77, 31.49, 29.93, 29.92, 29.59, 29.22, 24.36, 23.88, 22.59, 22.55,

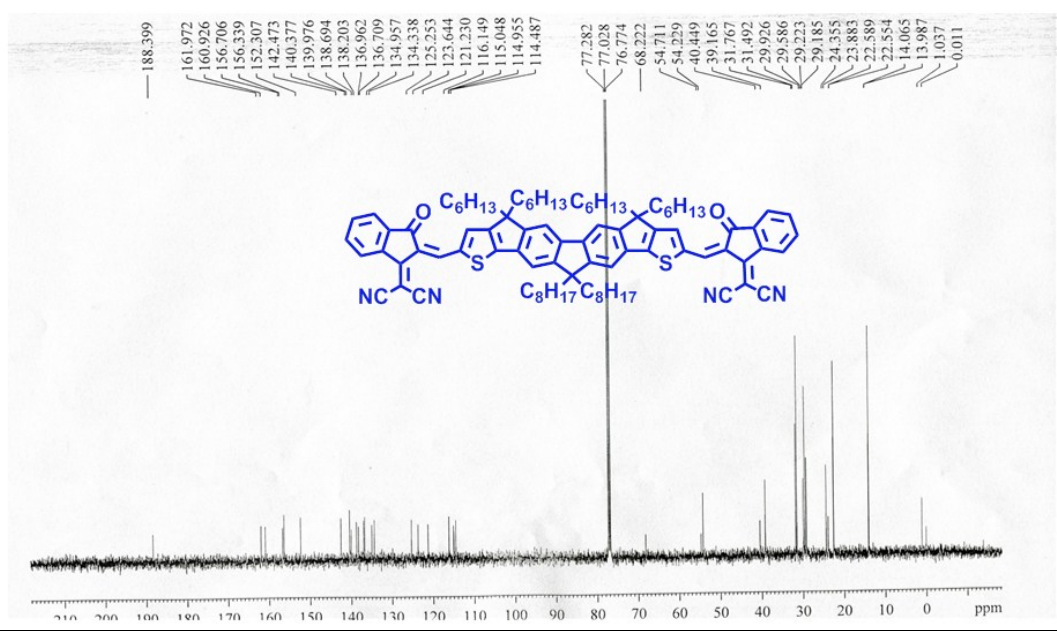
14.07, 13.99. Anal. Calcd for: C₈₉H₁₀₂N₄O₂S₂: N 4.23, C 80.74, H 7.77. Found: N 4.03, C 80.70, H 7.74.

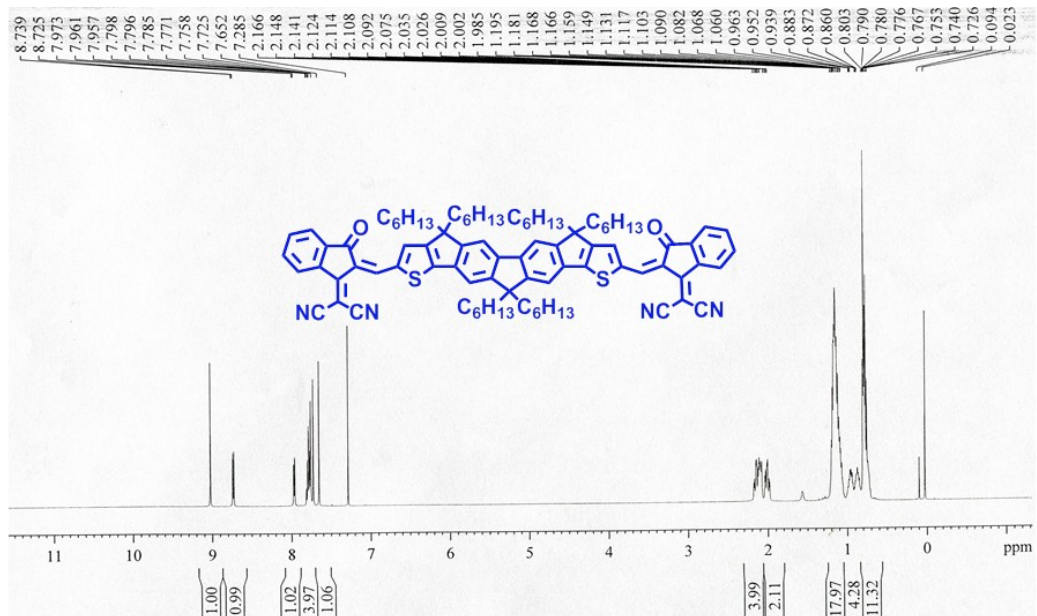
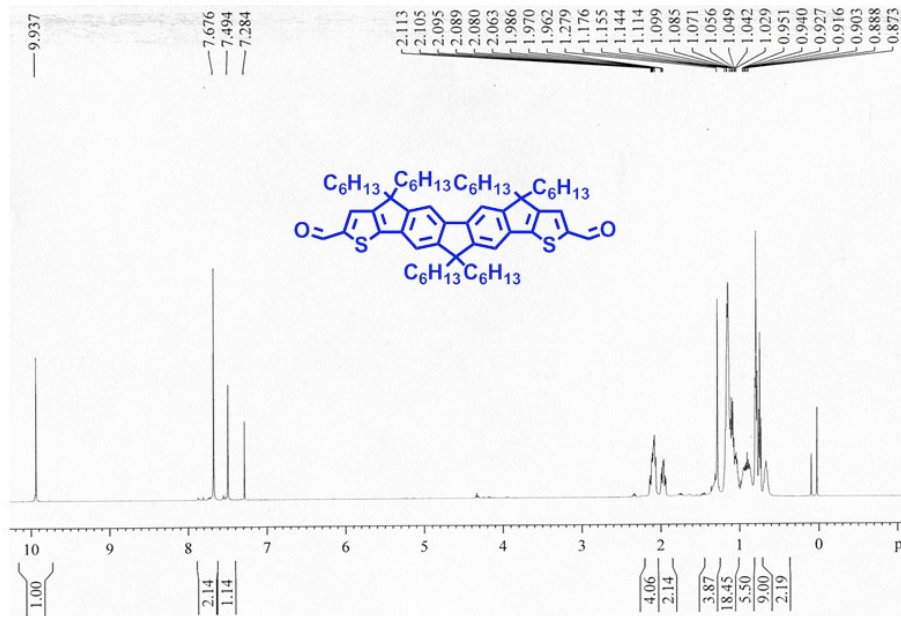
Compound FTIC-C6C6 and FTIC-C6C8 were synthesized by following the same procedure as FTIC-C8C6, yielding red-black solid (83%, 87%), respectively.

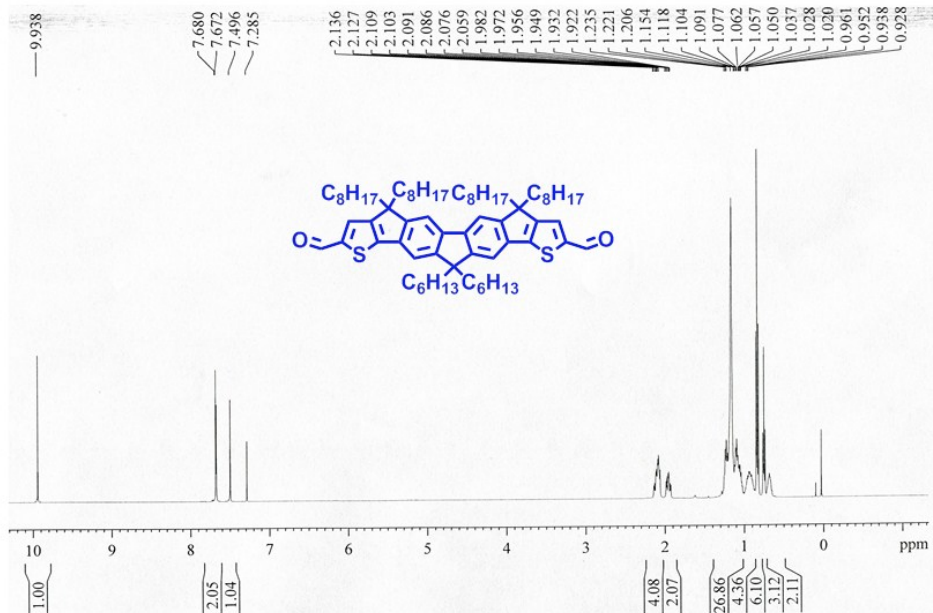
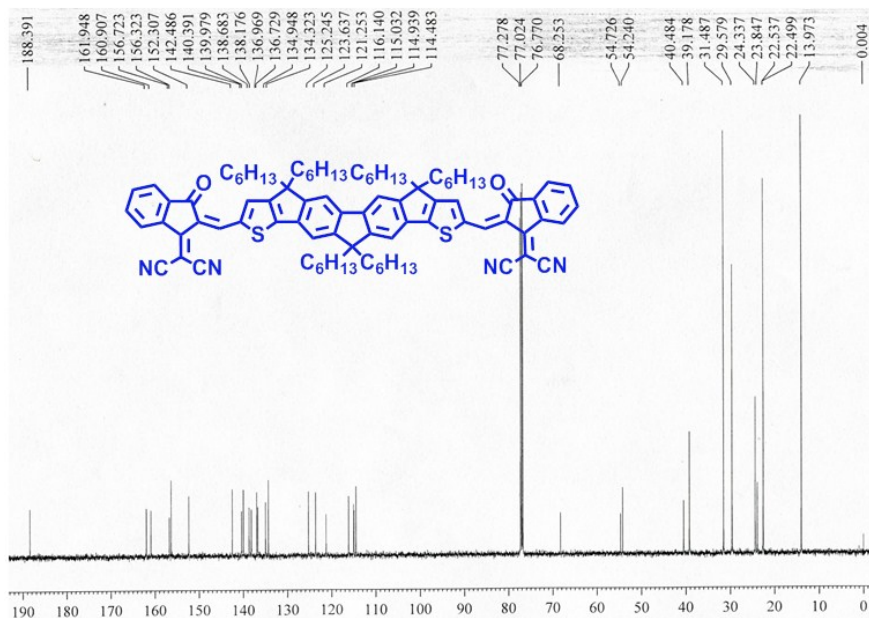
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- S 1 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. J. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and G. D. J. Fox, Gaussian 09W, Revision D.01; Gaussian, Inc., Wallingford, CT, 2013.
- S 2 D. Qian, L. Ye, M. Zhang, Y. Liang, L. Li, Y. Huang, X. Guo, S. Zhang, Z. Tan and J. Hou, *Macromolecules*, 2012, **45**, 9611-9617.
- S 3 C. Y. Chang, Y. J. Cheng, S. H. Hung, J. S. Wu, W. S. Kao, C. H. Lee and C. S. Hsu, *Adv. Mater.*, 2012, **24**, 549-553.









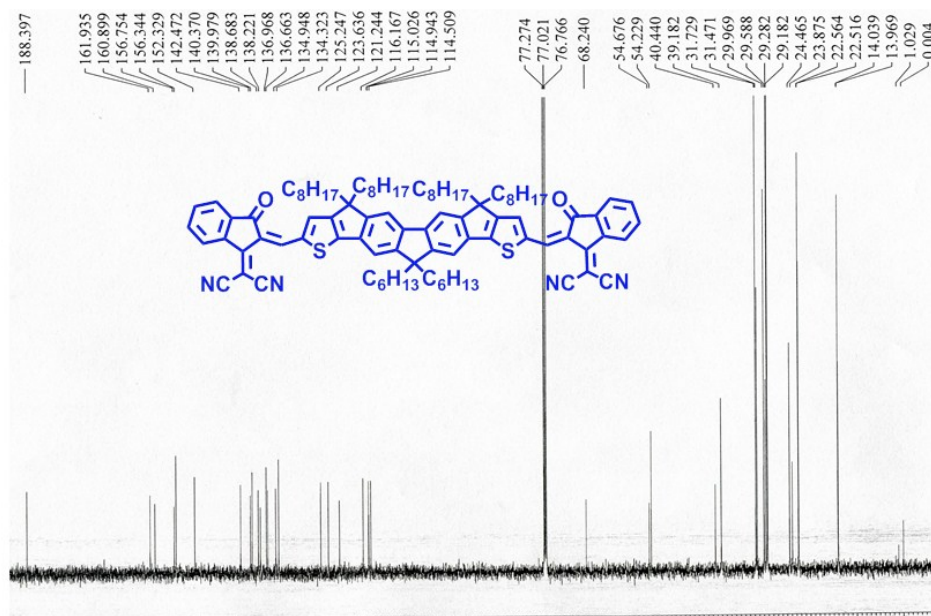
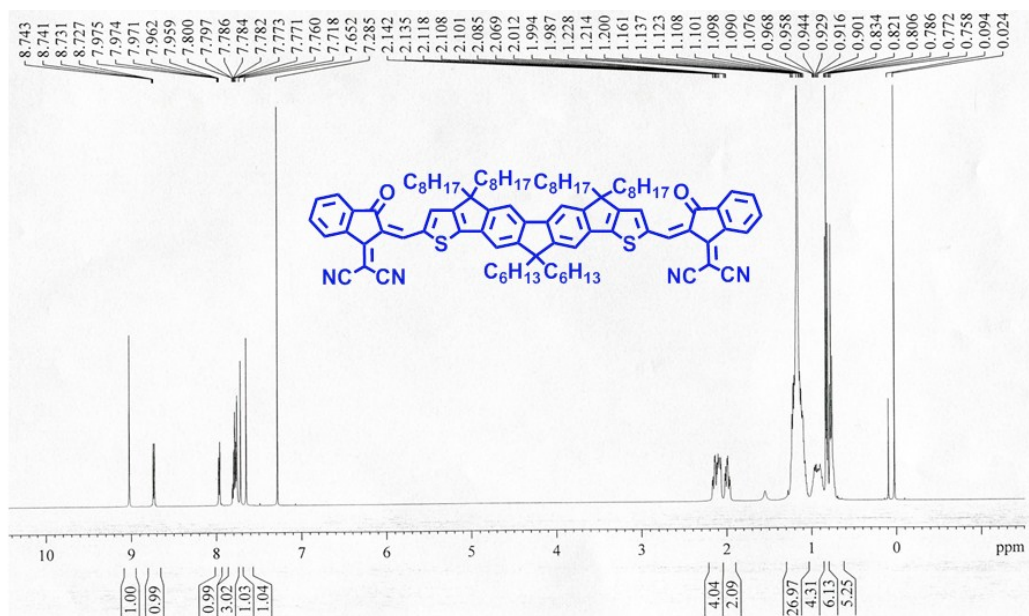


Fig. S1 1H and ^{13}C NMR spectras in $CDCl_3$.

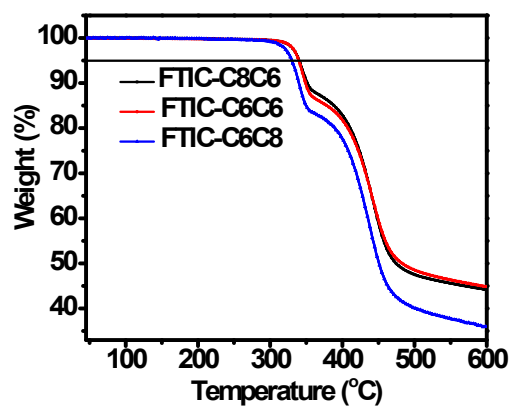


Fig. S2 Thermogravimetric analysis plot of three small molecules.

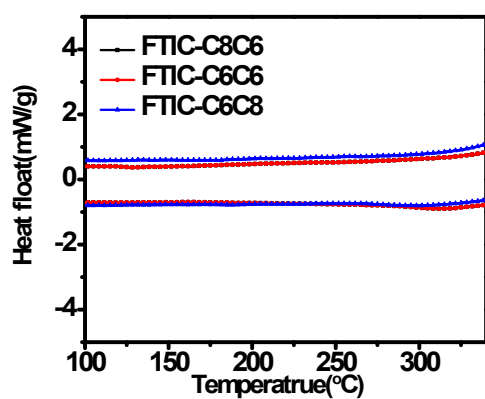


Fig. S3 DSC curves of three small molecules powdery samples.

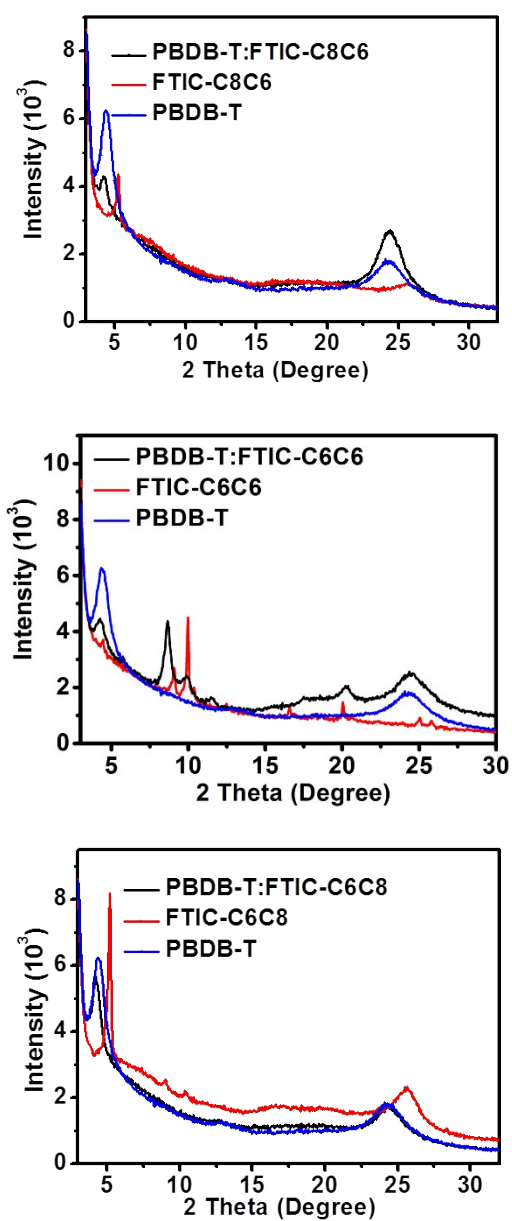


Fig. S4 Films XRD curves of PBDB-T, three small molecules and blend films.

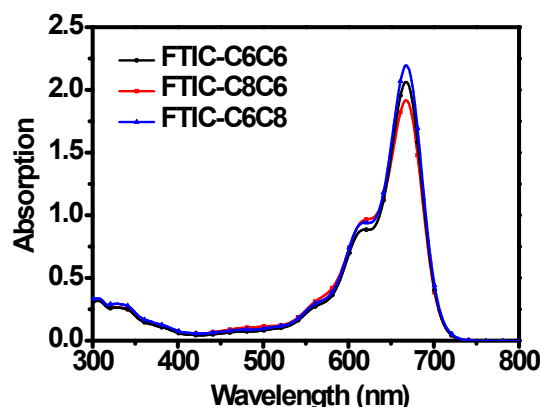


Fig. S5 UV-visible absorption spectra of FTIC-C8C6, FTIC-C6C6 and FTIC-C6C8 in chloroform.

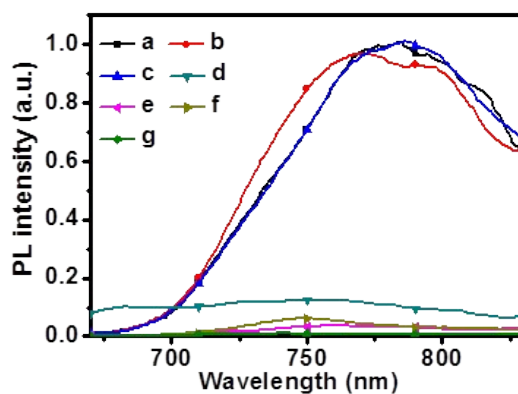


Fig. S6 Photoluminescence spectra (excitation wavelength 654 nm): (a) FTIC-C8C6, (b) FTIC-C6C6, (c) FTIC-C6C8, (d) **PBDB-T**, (e) **PBDB-T:FTIC-C8C6**, (f) **PBDB-T:FTIC-C6C6** and (g) **PBDB-T: FTIC-C6C8**.

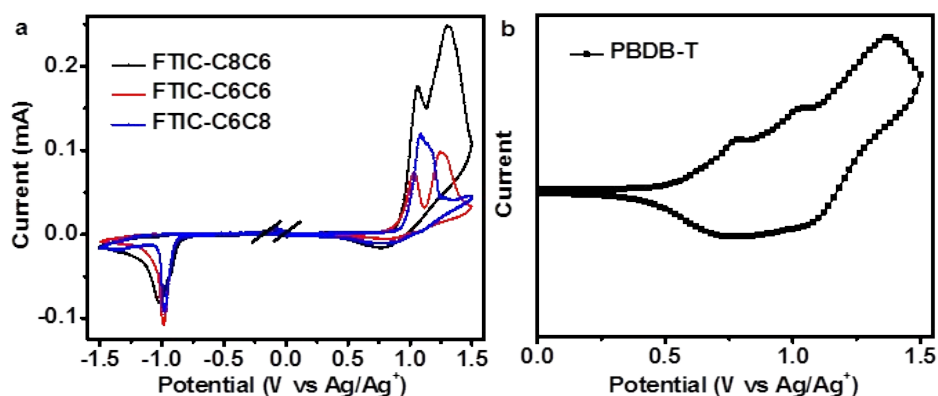


Fig. S7 Cyclic voltammetry plots of FTIC-C8C6, FTIC-C6C6 and FTIC-C6C8 thin films (a) and **PBDB-T** thin film (b)

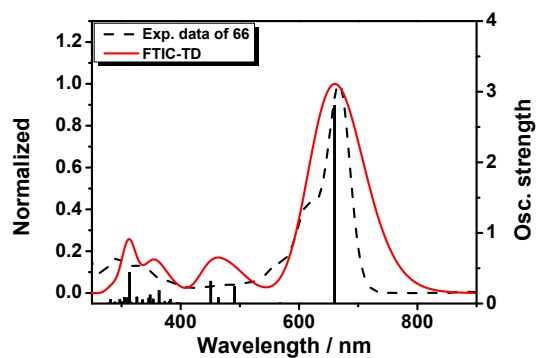


Fig. S8 Normalized optical absorption spectra of **FTIC-2** in chloroform solution: measured spectra (dash line); spectra computed within the TD-DFT/PCM approaches based on B3LYP (red solid line).

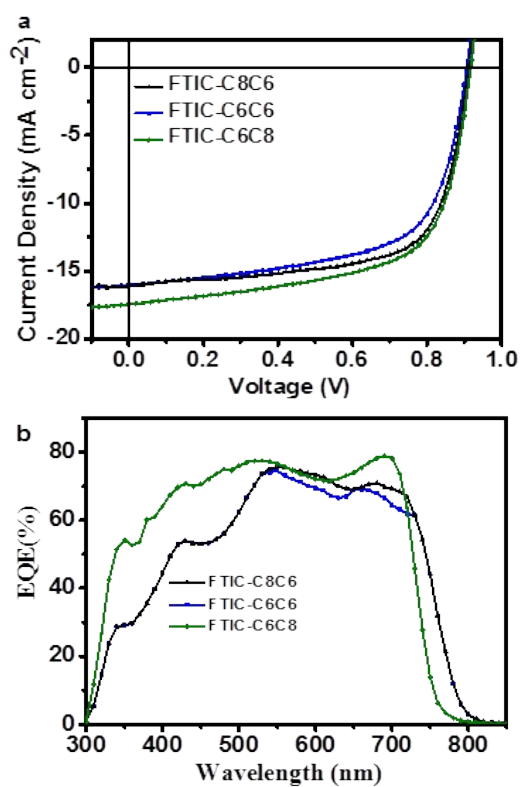


Fig. S9 *J-V* (a) and EQE (b) curves of FTIC-C8C6, FTIC-C6C6 and FTIC-C6C8 based devices without PFN-Br interlayer.

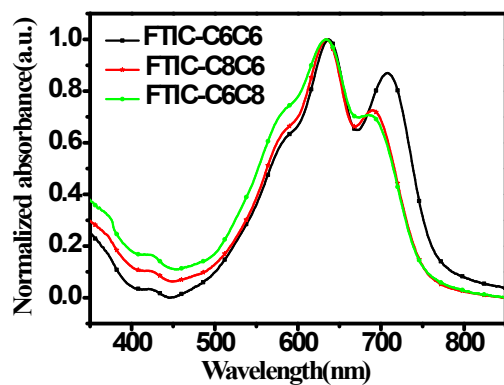


Fig. S10 UV-vis spectra of the blend films of PBDB-T with FTIC-C8C6, FTIC-C6C6 and FTIC-C6C8.

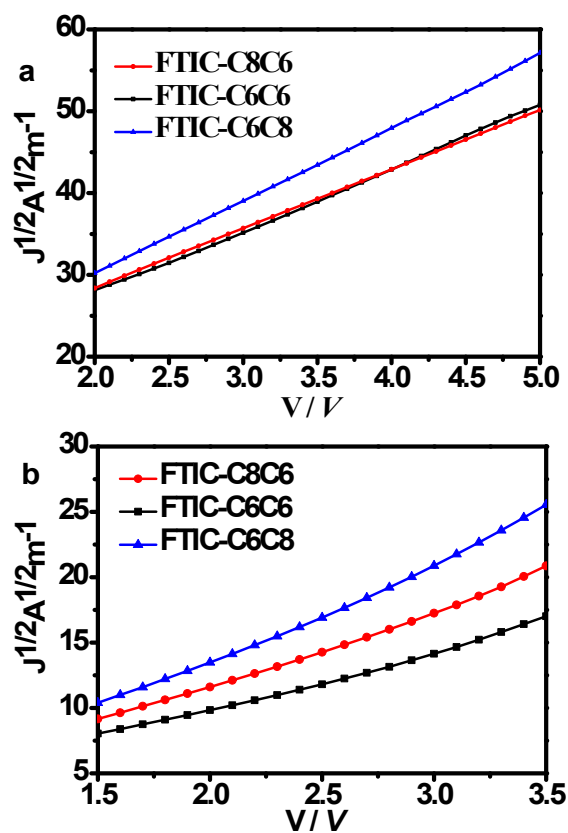


Fig. S11 $\ln(J^{1/2}/A^{1/2})$ vs (V) plot of the blends for the hole mobility (a) and electronic mobility (b) by SCLC method.

Table S1 Selected calculated absorption wavelength (nm), oscillator strength (f) and transition contributions of **FTIC** in chloroform solvent at TD-B3LYP/6-31 G(d,p) level of theory.

State	$\lambda_{\text{calc}}/\text{nm}$	Oscillator strength (f)	Major transition contributions
1	660.1	2.8012	HOMO→LUMO (98%)
3	491.1	0.2406	HOMO→L+2 (93%)
6	450.8	0.3146	H-1→L+1 (95%)
16	363.5	0.1811	H-4→LUMO (35%), H-3→LUMO (41%)
33	313.6	0.4382	H-3→L+2 (20%), H-2→L+3 (29%)

Table S2 Photovoltaic performance of the solar cells based on PBDB-T:FTIC-C8C6 blend films with different D:A ratio and DIO contents under illumination of AM 1.5 G, 100 mW cm⁻².

PBDB-T:FTIC-C8C6	Additive	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
1:0.8	/	0.93	13.03	66.22	8.02
1:1	/	0.93	14.55	65.12	8.79
1:1.5	/	0.93	14.29	64.66	8.58
1:2	/	0.93	13.02	60.77	7.40
1:1	0.3%DIO	0.91	15.24	67.83	9.39
1:1	0.5%DIO	0.92	16.10	67.46	9.91
1:1	0.7%DIO	0.92	16.29	64.80	9.66
1:1	1.0%DIO	0.91	15.57	64.49	9.10

Table S3 Photovoltaic performance of the solar cells based on PBDB-T:FTIC-C6C6 blend films with different D:A ratio and DIO contents under illumination of AM 1.5 G, 100 mW cm⁻².

PBDB-T:FTIC-C6C6	Additive	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
1:0.8	/	0.91	14.92	61.72	8.37
1:1	/	0.91	14.80	65.58	8.84
1:1.5	/	0.92	15.25	60.93	8.52
1:2	/	0.92	13.08	62.98	7.55
1:1	0.1%DIO	0.91	15.76	63.04	9.09
1:1	0.3%DIO	0.91	16.03	63.17	9.18
1:1	0.5%DIO	0.91	15.77	63.99	9.14
1:1	0.7%DIO	0.90	16.26	59.68	8.77

Table S4 Photovoltaic performance of the solar cells based on PBDB-T:FTIC-C6C8 blend films with different D:A ratio and DIO contents under illumination of AM 1.5 G, 100 mW cm⁻².

PBDB-T:FTIC-C6C8	Additive	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
1:0.8	/	0.92	15.88	52.03	7.60
1:1	/	0.94	14.73	65.18	9.02
1:1.5	/	0.94	14.89	61.36	8.56
1:2	/	0.94	14.54	59.24	8.13
1:1	0.3%DIO	0.92	17.17	62.86	9.86
1:1	0.5%DIO	0.92	17.44	64.10	10.26
1:1	0.7%DIO	0.91	16.54	63.36	9.58
1:1	1.0%DIO	0.90	16.50	61.72	9.20

Table S5 The optimized photovoltaic parameters of devices based on PBDB-T and other state-of-the-art NFAs under the illumination of AM 1.5G, 100 mW cm⁻².

Acceptors	Additive	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	PCE _{max} (%)
ITIC	/	0.87	15.80	63.78	8.73 ^{a)}
	0.5% DIO	0.86	19.00	61.30	10.04 ^{a)}
FDICTF	0.3% DIO	0.94±0.01	15.84±0.28	66±1	10.06 ^{b)}
IT-M	1% DIO	0.94	17.44	73.5	12.05 ^{c)}

^{a)} Tested in our laboratory.

^{b)} Data obtained from Ref. 40 (*Adv. Mater.*, 2016, DOI: 10.1002/adma.2016049644).

^{c)} Data obtained from Ref. 15 (*Adv. Mater.*, 2016, 28, 9423).