

Supporting Information

Enhancing Thermal Stability of Nonfullerene Organic Solar Cells via Fluoro-side-chains Engineering

Yue Xin, Guang Zeng, JinYang OuYang, Xiaoli Zhao, and Xiaoniu Yang**

Experimental Section

Materials: All reagents and chemicals were commercially available and were used as received without further purification unless otherwise stated. Chlorobenzene (CB, 99+% purity), acetonitrile (99.8%, purity) and 1,8-diiodooctane (DIO) were purchased from Sigma-Aldrich. PDINO was obtained from Suna Tech Inc.

Synthesis of 2a: To a degassed solution of 4-bromo-2-fluoro-1-hexylbenzene (5 g, 19 mmol) in anhydrous THF (30 ml), n-Buli (1.6 M in hexane, 6 ml) was added dropwise at -78 °C. After stirring for 30 min at -78 °C, diethyl 2,5-bis(thieno[3,2-b]thiophen-2-yl)terephthalate (1 g, 1.9 mmol) was added slowly into the mixture and then stirred for about 2 hours until the system warmed to room temperature. Water was added to quench the reaction, and the mixture was extracted with diethyl ether. After removing the solvent, the crude product was transferred into a 100 ml round bottom flask, and then acetic acid (30 mL) and concentrated sulfuric acid (1 mL) were added. The mixture was refluxed for 3 h at 130 °C. By quenching with water and then extracted with ether, the residue was purified with silica gel column chromatography to give pure product as yellow solid (0.9 g, 8%). ¹HNMR (400 MHz, CDCl₃, δ): 7.46 (s, 2H), 7.30 (s, 4H), 7.09 (t, 8.0 Hz, 4H), 6.99 – 6.86 (m, 8H), 2.63 – 2.50 (m, 8H), 1.67 – 1.19 (m, 49H), 0.86 (t, *J* = 6.6 Hz, 18H). HRMS (MALDI-TOF): *m/z* calcd. for C₆₄H₆₂F₂N₄O₂S₄Si₂ (M⁺) 1090.4; found 1090.4.

Synthesis of 2b: 2b was synthesized following the same procedure used for synthesizing 2a to give the product as a yellow solid (1.23 g, 12%). ¹HNMR (400 MHz, CDCl₃, δ): 7.75 (s, 2H), 7.29 (s, 4H), 6.91 (d, *J* = 12.6 Hz, 12H), 2.54 (s, 8H), 1.68 –

1.15 (m, 48H), 0.86 (s, 20H). HRMS (MALDI-TOF): m/z calcd. for $C_{64}H_{62}F_2N_4O_2S_4Si_2$ (M⁺) 1090.4; found 1090.4.

Synthesis of 3a: To dry DMF (10 ml) in a degassed flask, POCl₃ (1 ml) was added dropwise at 0 °C. After being stirred for 1 h at 0 °C, a solution of compound 2a (450 mg, 0.41 mmol) in 1,2-dichloroethane (30 ml) was added. Then the reactant was refluxed for 2 days. Then saturated sodium carbonate solution was added at room temperature, and the solution was stirred for 3 hours. The mixture was extracted with dichloromethane. After removing the solvent, the residue was purified by silica gel chromatography to give pure product as a yellow solid (264 mg, 56%). ¹HNMR (400 MHz, CDCl₃ δ): 9.92 (s, 2H), 7.98 (s, 2H), 7.58 (s, 2H), 7.14 (t, $J = 8.0$ Hz, 4H), 6.95 (dd, $J = 8.0, 1.8$ Hz, 4H), 6.86 (dd, $J = 11.1, 1.7$ Hz, 4H), 2.66 – 2.52 (m, 8H), 1.66 – 1.20 (m, 33H), 0.87 (t, $J = 6.7$ Hz, 12H). HRMS (MALDI-TOF): m/z calcd. for $C_{64}H_{62}F_2N_4O_2S_4Si_2$ (M⁺) 1146.4; found 1146.4.

Synthesis of 3b: 3b was synthesized following the same procedure used for synthesizing 3a to give the product a yellow solid (232 mg, 49%). ¹HNMR (400 MHz, CDCl₃, δ): 9.90 (s, 2H), 7.95 (s, 2H), 7.85 (s, 2H), 6.86 (d, $J = 53.7$ Hz, 12H), 2.55 (t, $J = 7.6$ Hz, 8H), 1.41 (dd, $J = 115.5, 9.9$ Hz, 39H), 0.86 (t, $J = 6.6$ Hz, 12H). HRMS (MALDI-TOF): m/z calcd. for $C_{64}H_{62}F_2N_4O_2S_4Si_2$ (M⁺) 1146.4; found 1146.4.

Synthesis of oF-ITIC: To a degassed solution of 3a (200 mg, 0.17 mmol) and 2-(3-oxo-2, 3-dihydro-1H-inden-1-ylidene) malononitrile (200 mg, 1 mmol) in CHCl₃ (40 mL), pyridine (1.5 mL) were added. After stirring the mixture at 45 °C for three days, water was poured into the reaction and the residue was extracted with dichloromethane.

After removing the solvent, the crude product was further purified by silica gel chromatography for two times to give pure products: a dark blue solid (105 mg, 40 %) ^1H NMR (400 MHz, CDCl_3 , δ): 8.88 (s, 2H), 8.70 (d, $J = 7.4$ Hz, 2H), 8.24 (s, 2H), 7.93 (d, $J = 6.8$ Hz, 2H), 7.82 – 7.68 (m, 4H), 7.60 (s, 2H), 7.18 (t, $J = 7.9$ Hz, 4H), 7.04 (d, $J = 8.0$ Hz, 4H), 6.91 (d, $J = 11.1$ Hz, 4H), 2.59 (t, $J = 7.6$ Hz, 8H), 1.66 – 1.18 (m, 38H), 0.85 (s, 12H). HRMS (MALDI-TOF): m/z calcd. for $\text{C}_{64}\text{H}_{62}\text{F}_2\text{N}_4\text{O}_2\text{S}_4\text{Si}_2$ (M^+) 1498.5; found 1498.5.

Synthesis of mF-ITIC: mF-ITIC was synthesized following the same procedure used for synthesizing oF-ITIC to give the product as a dark blue solid (103 mg, 39%) ^1H NMR (400 MHz, CDCl_3 , δ) 8.76 (s, 2H), 8.61 (d, $J = 7.5$ Hz, 2H), 8.24 (s, 2H), 7.91 – 7.78 (m, 4H), 7.67 (p, $J = 7.2$ Hz, 4H), 6.85 (d, $J = 60.8$ Hz, 12H), 2.59 – 2.37 (m, 8H), 1.61 – 1.12 (m, 37H), 0.78 (t, $J = 6.3$ Hz, 12H). HRMS (MALDI-TOF): m/z calcd. for $\text{C}_{64}\text{H}_{62}\text{F}_2\text{N}_4\text{O}_2\text{S}_4\text{Si}_2$ (M^+) 1498.5; found 1498.5.

Fabrication of OSCs: OSCs were fabricated with a conventional device architecture of ITO/PEDOT: PSS (30 nm)/active layer/PDINO (20 nm)/Al. ITO-coated glass (obtained from Lumtec, $7 \Omega \text{ sq}^{-1}$) was cleaned with detergent, deionized water, isopropyl alcohol and acetone. After complete drying, the ITO-coated glass was treated with UV-ozone for 20 min. PEDOT: PSS was spin coated onto the ITO with 30 nm in thickness, and then the PEDOT: PSS film was annealed at 150°C for 15 min in air. The substrates were transferred into a N_2 filled glove box to continue the rest operation after the procedure in air. Then, active layer was spin-coated from CB solution with a concentration of 12 mg ml^{-1} at a speed of $2000 \sim 3000 \text{ r min}^{-1}$. After depositing the

active layer, PDINO (2 mg ml⁻¹ in methanol) was spin-coated at a speed of 4000 r min⁻¹ on its top, and then Al (100 nm) was thermally deposited on the PDINO layer under high vacuum (< 10⁻⁴ Pa). The mask shadow area was 0.04 ~ 0.09 cm². The *J-V* characteristics of OSCs were measured in nitrogen atmosphere employing a Keithley-2400 source meter and a solar simulator (SAN-EI, XES-70S1, San-Ei. Electric Co. Ltd., Osaka, Japan) at AM 1.5 G illumination of 100 mW cm⁻² with a standard silicon solar cell as a reference to calibrate the light intensity.

Thermal stability test: The devices were fabricated under the same preparation conditions as described in device fabrication. After spin coating active layers, the films were heated at 150 °C on a hot plate for different periods of time in nitrogen filled glovebox. Then, the devices were quenched to room temperature before spin-coating PDINO (20 nm) and thermally depositing Al (100 nm).

EQE: The EQE spectra of devices were examined 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.

¹H and ¹³C nuclear magnetic resonance (NMR): The spectra were acquired on a Bruker AV-400 MHz spectrometer in *d*-chloroform with TMS as the internal standard. Chemical shifts were expressed in parts per million (ppm).

MALDI TOF MS: MALDI measurements were performed on MALDI-TOF MS Bruker Autoflex III instruments.

Cyclic voltammetry (CV) measurements: The electrochemical properties of three acceptors were performed on a CHI600D electrochemical instrument. The

measurements were carried out in anhydrous acetonitrile with tetrakis-(n-butyl)ammonium hexafluorophosphate (Bu_4NPF_6) (0.1 M) as the electrolyte under argon atmosphere. The scan rate is 50 mV s^{-1} . A glassy carbon electrode, a Ag/AgNO_3 electrode, and a Pt wire were employed as the working electrode, reference and counter electrode, respectively. The films were drop-casted onto the polished glassy carbon working electrode from a 5 mg ml^{-1} CHCl_3 solution. The potential of Ag/AgNO_3 reference electrode was internally calibrated by using the ferrocene/ferrocenium redox couple (Fc/Fc^+). The electrochemical onsets were determined at the position where the current begins to differ from the baseline. The HOMO energy levels were calculated from the equation: $\text{HOMO} = - (E_{\text{ox}}^{\text{onset}} + 4.8) \text{ eV}$, while the LUMO energy levels were obtained based on $\text{LUMO} = - (E_{\text{red}}^{\text{onset}} + 4.8) \text{ eV}$.

Space Charge Limited Current (SCLC): The hole and electron mobilities were measured by the SCLC method on a hole-only device with a structure of ITO/PEDOT:PSS/active layer/Au and electron-only device with a structure of ITO/ZnO/active layer/PDINO/Al. The SCLC mobility was estimated following the Mott-Gurney square law, $\ln(I/V)^2 = 0.89\beta(V/L)^{1/2} + \ln(9\mu\epsilon\epsilon_0 S/(8L^3))$, where I is the current, V is the applied voltage, β is the field activation factor, L is the thickness of polymer film, μ is the mobility, ϵ_0 is the permittivity of free space, ϵ is the relative permittivity, and S is the area of film. The measurement of hole and electron mobilities was conducted in the dark on a computer-controlled Keithley 2400 source-measure unit.

UV-Vis: UV-vis absorption spectra were recorded on a PerkinElmer Lambda 750 spectrophotometer (Wellesley, MA).

TEM: The TEM images were acquired with a Tecnai G2 F20 high resolution transmission electron microscope operated at an acceleration voltage of 200 KV.

Optical microscopy (OM): The OM images were carried out by using a Carl Zeiss A1m microscope equipped with an infinity 4-11 digital camera from Lumenera Corporation, Canada.

2D-GIWAXS: 2D-GIWAXS patterns were obtained at 1W2A at BL14B1 at Shanghai Synchrotron Radiation Facility (SSRF) ($\lambda=0.69 \text{ \AA}$). Samples were all prepared on top of Si (100) substrates.

Film thickness: Film thickness was measured by the profiler (D-100 Stylus Profilometer, KLA Tencor).

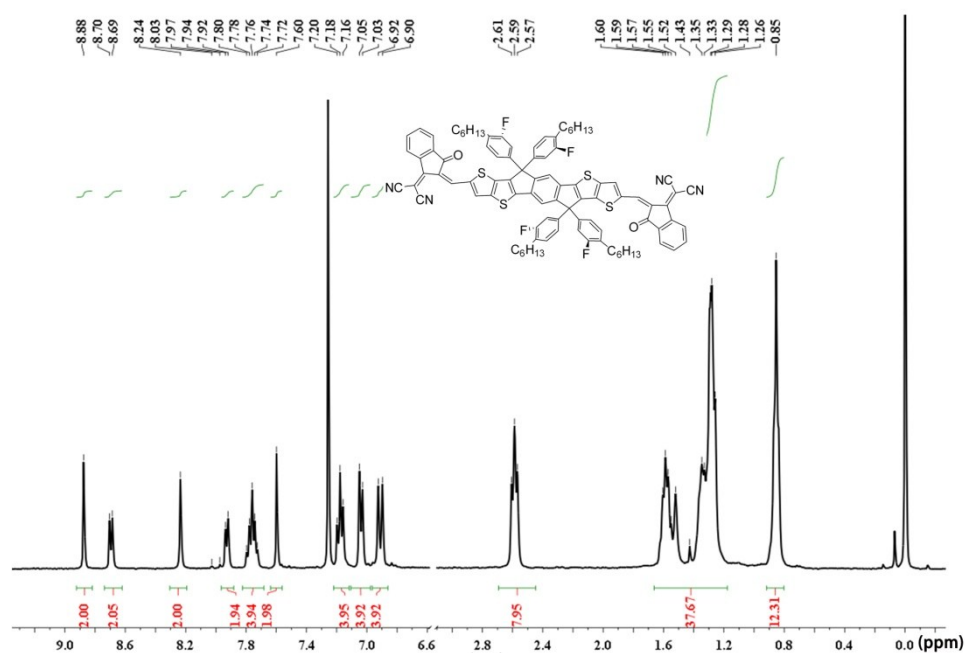


Figure S1. ^1H NMR spectrum of compound *o*-IFIC.

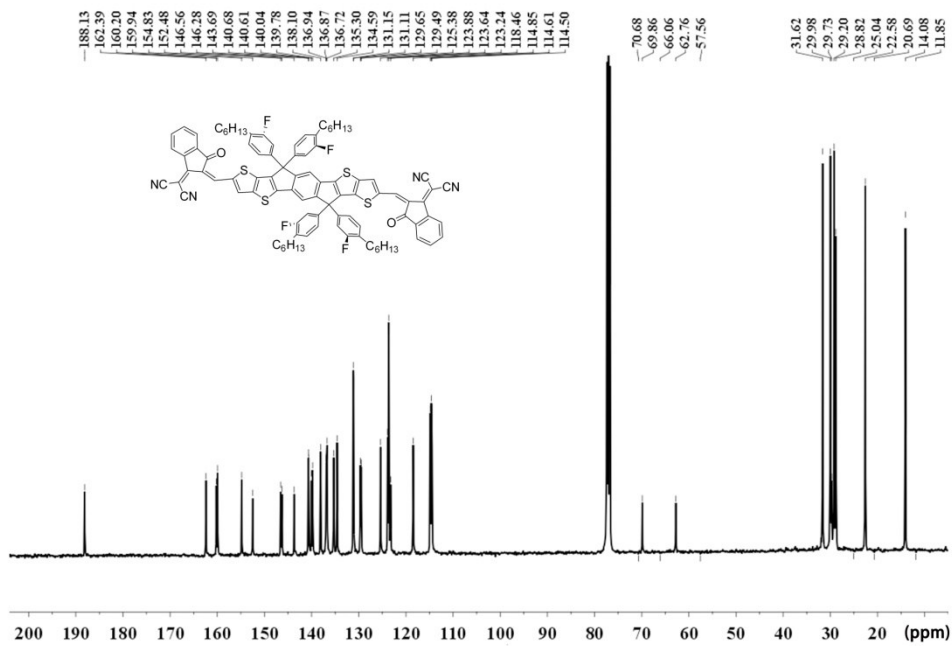


Figure S2. ^{13}C NMR spectrum of compound *oF*-ITIC.

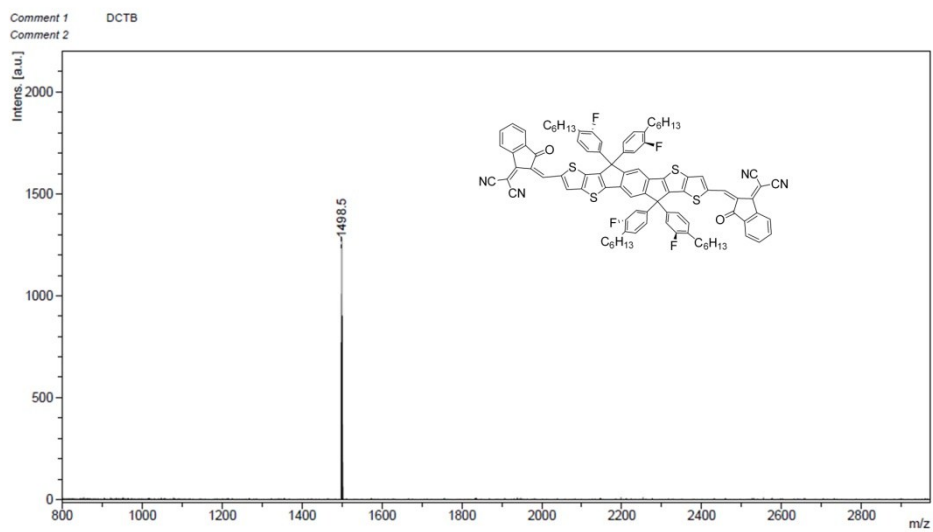
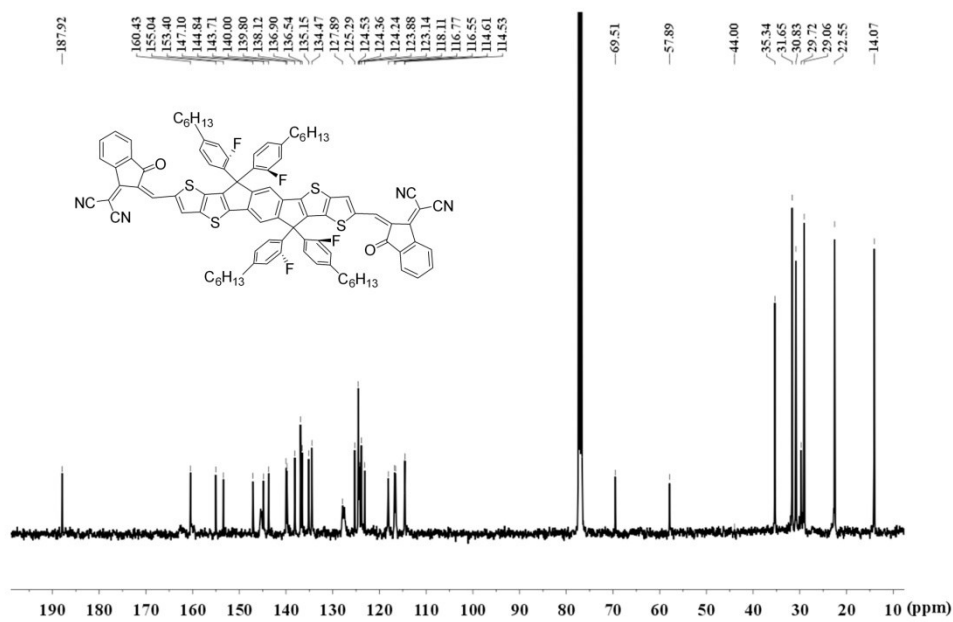
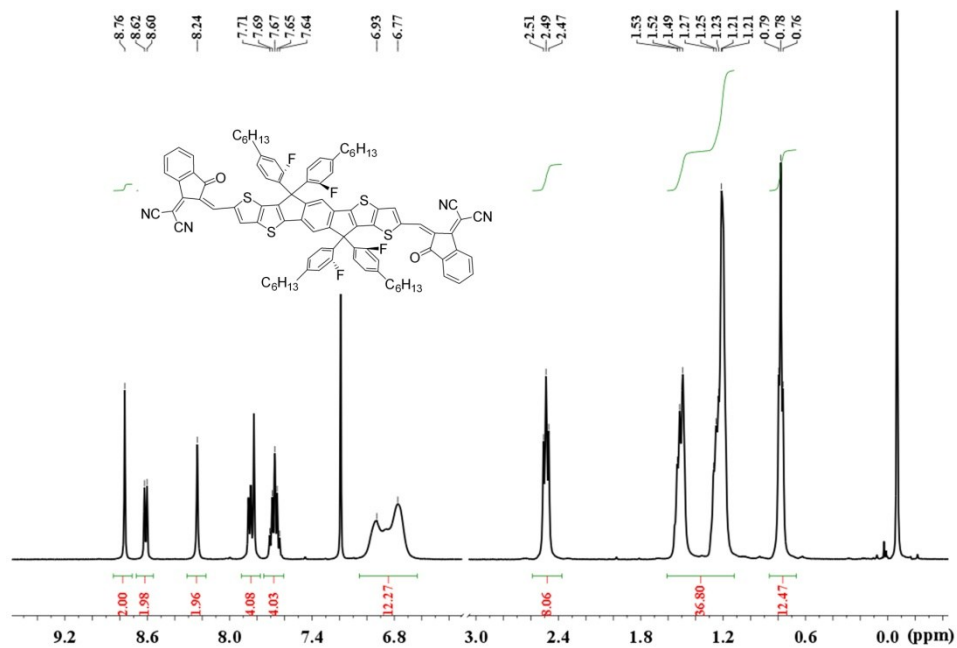


Figure S3. MALDI-TOF of *oF*-ITIC.



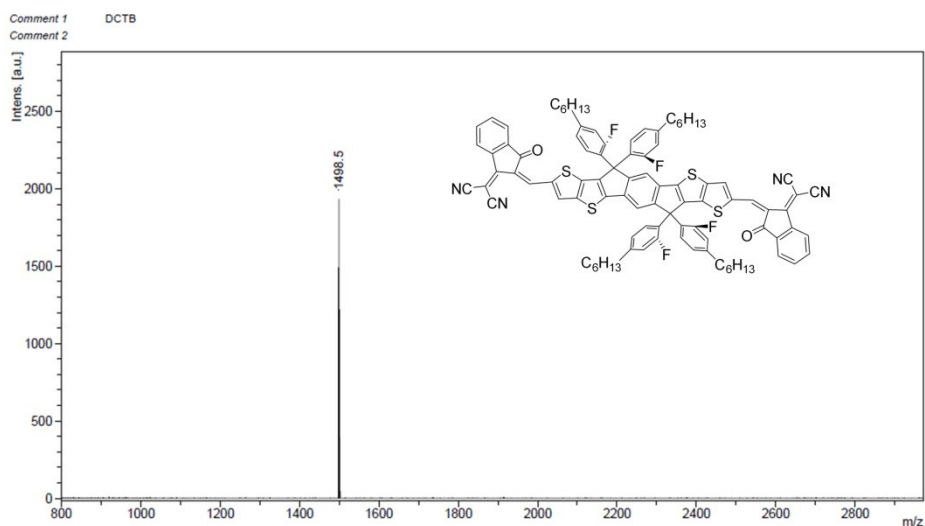


Figure S6. MALDI-TOF of *mF*-ITIC.

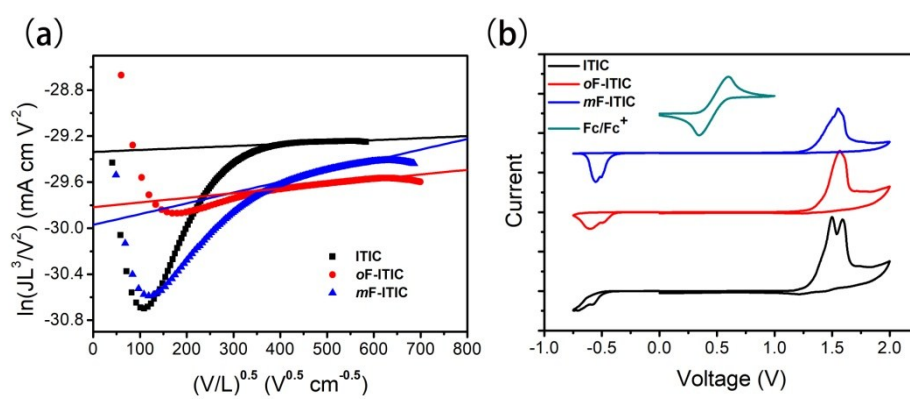


Figure S7. (a) Electron-only curves and (b) cyclic voltammograms (CV) curves of ITIC, *oF*-ITIC and *mF*-ITIC acceptors.

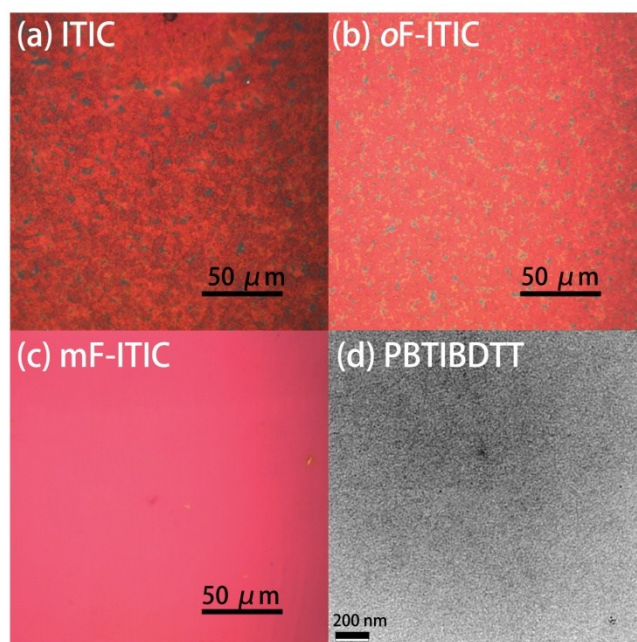


Figure S8. Optical microscopy images of (a) ITIC, (b) *o*F-ITIC and (c) *m*F-ITIC films spin-coated from CB. (d) TEM images of PBTIBDTT pure film after annealing for 96 hours at 150 °C

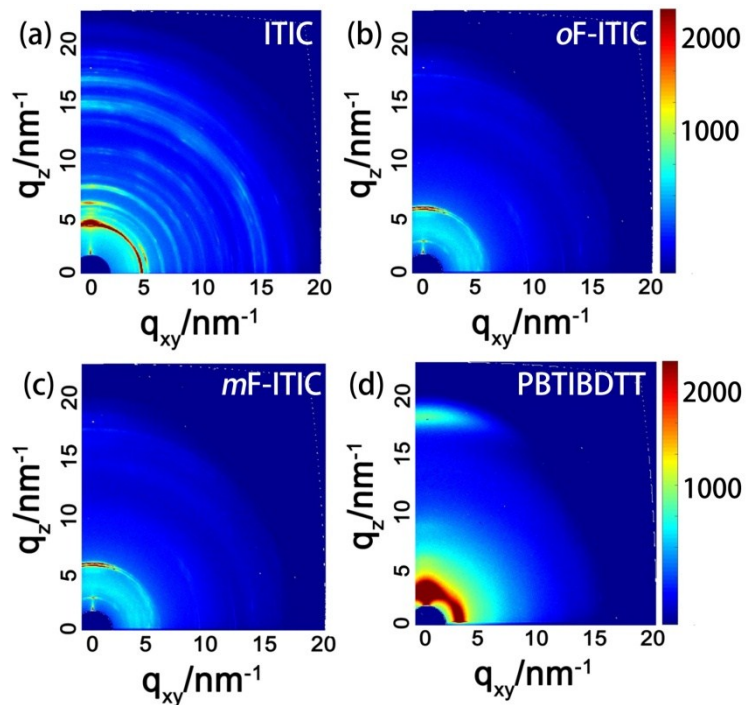


Figure S9. 2D-GIWAXS patterns of (a) ITIC, (b) *o*F-ITIC, (c) *m*F-ITIC and (d) PBTIBDTT pure films.

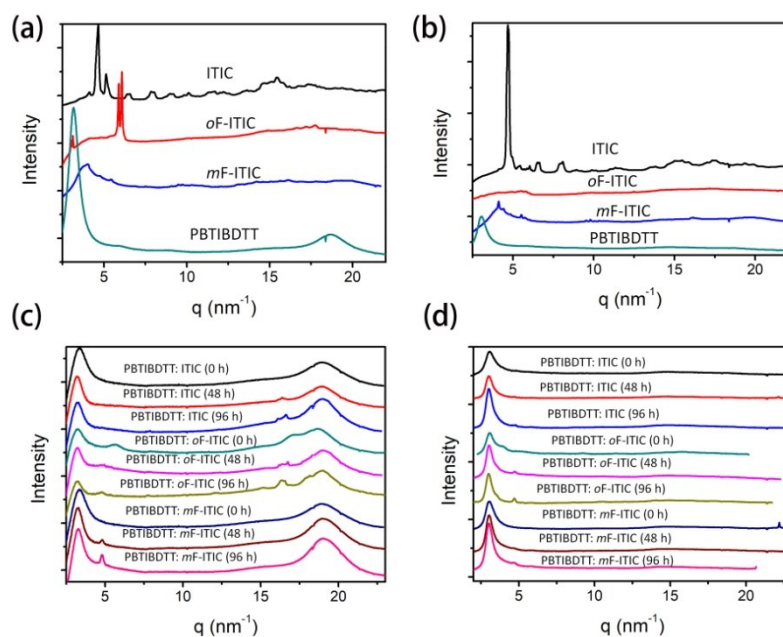


Figure S10. Line-cuts of the 2D-GIWAXS patterns of the (a, b) pure films and (c, d) blend films. (a, c) out of plane, (b, d) in plane.

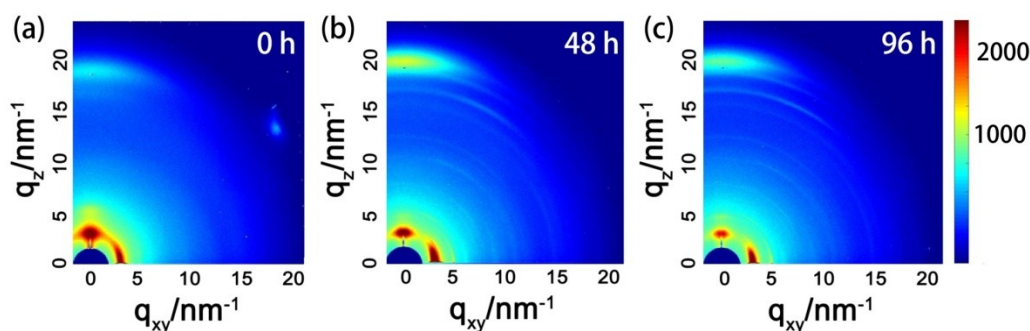


Figure S11. 2D-GIWAXS patterns of PBTIBDTT: *o*F-ITIC blend film with the D/A weight ratio of 1: 1 and 0% DIO, annealing for (a) 0 h, (b) 48 h, (c) 96 h.

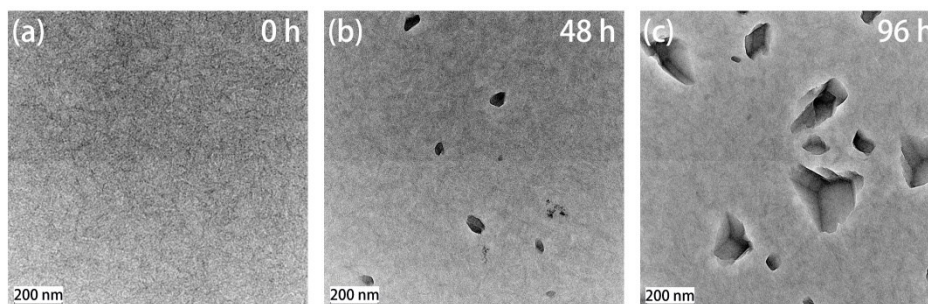


Figure S 12. TEM images of PBTIBDTT : *o*F-ITIC blend film with the D/A weight ratio of 1:1 and 0% DIO, annealing for (a) 0 h, (b) 48 h, (c) 96 h.

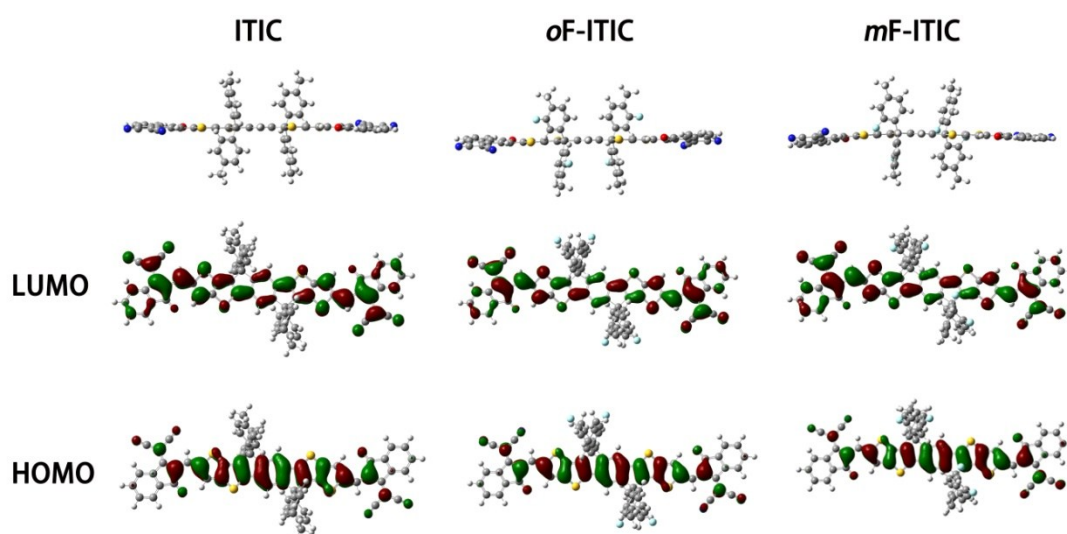


Figure S13. DFT-calculated HOMO and LUMO wave functions of the geometry optimized structures (B3LYP/6-31G*) of ITIC, *o*F-ITIC, *m*F-ITIC.

Table S1. Photovoltaic parameters of OSCs based on PBTIBDTT: ITIC, PBTIBDTT: *o*F-ITIC and PBTIBDTT: *m*F-ITIC with different annealing time (0 h, 1 h, 24 h, 48 h, 72 h, and 96 h) at 150 °C in glove box, under AM 1.5G solar spectrum.

Acceptors	Annealing time	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]
ITIC	0 h	0.97±0.01	13.65±0.37	66.30±1.03	8.74±0.08 (8.89)
	1 h	0.96±0	13.85±0.50	65.61±1.74	8.63±0.13 (8.79)
	24 h	0.94 ±0.01	13.40±0.39	65.10±2.22	8.22±0.24 (8.66)
	48 h	0.93±0.01	13.47±0.24	61.16±1.82	7.69±0.30 (8.04)
	72 h	0.93±0.01	13.27±0.21	61.58±0.79	7.62±0.19 (7.76)
	96 h	0.92 ±0	13.12±0.25	58.45±1.14	7.17±0.20 (7.50)
<i>o</i> F-ITIC	0 h	0.94 ±0.01	13.48 ±0.18	70.21±0.70	8.87±0.15 (9.01)
	1 h	0.94 ±0.01	12.71±0.44	65.58±1.30	7.83±0.10 (7.93)
	24 h	0.93±0.01	12.68±0.31	60.86±1.26	7.15±0.14 (7.31)
	48 h	0.92±0	12.22±0.29	62.03±2.46	6.97±0.29 (7.19)

	72 h	0.91±0.01	12.22±0.30	59.10±2.27	6.43±0.12 (6.61)
	96 h	0.90±0.01	11.15±0.35	57.56±0.83	5.94±0.17 (6.14)
<i>mF</i> -ITIC	0 h	0.96±0	14.38±0.13	67.79±0.71	9.39±0.09 (9.50)
	1 h	0.96±0	14.56±0.38	67.46±1.32	9.42 ±0.09 (9.55)
	24 h	0.96 ±0.01	14.42±0.11	69.28±0.28	9.58±0.19 (9.74)
	48 h	0.96±0	14.10±0.30	67.04±0.97	9.06±0.08 (9.16)
	72 h	0.95±0.01	13.76±0.23	67.62±0.49	8.87±0.09 (8.96)
	96 h	0.94±0	13.77±0.25	66.86±1.10	8.67±0.16 (8.90)

Table S2. Device characteristics of OSCs based on PBTIBDTT: *mF*-ITIC with various additive contents and D/A proportions under AM 1.5G solar spectrum.

D/A	DIO content	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]
1:0.8	none	0.96	14.08	66.16	8.94
1:1	none	0.96	14.75	67.45	9.55
1:1.2	none	0.96	14.19	65.12	8.87
1:1	0.25%	0.96	13.27	62.38	7.95

Table S3. Device characteristics of OSCs based on PBTIBDTT: *oF*-ITIC with various additive contents and D/A proportions under AM 1.5G solar spectrum.

D/A ratio	DIO content	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]
1:0.8	none	0.96	12.56	63.73	7.69
1:1	none	0.96	12.71	67.34	8.22

1:1.2	none	0.96	12.99	67.29	8.39
1:1.5	none	0.96	12.79	66.86	8.21
1:1.2	0.25%	0.94	13.70	66.41	8.55
1:1.2	0.5%	0.94	13.49	71.03	9.01
1:1.2	1%	0.96	12.39	58.50	6.96

Table S4. Device characteristics of OSCs based on PBTIBDTT: ITIC with various additive contents and D/A proportions under AM 1.5G solar spectrum.

D/A	DIO content	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]
1:0.8	none	0.96	13.34	62.1	7.95
1:1	none	0.96	14.39	64.39	8.89
1:1.2	none	0.96	13.83	63.40	8.42
1:1	0.25%	0.96	14.14	61.70	8.37

Table S5. Recombination parameters, P_{diss} and J_{sat} values of the blend films based on ITIC, *o*F-ITIC and *m*F-ITIC acceptors.

Blend films	recombination parameter α [%]	P_{diss} [%]	J_{sat} [mA cm ⁻²]
PBTIBDTT: ITIC	91.7	95.2	14.70
PBTIBDTT: <i>o</i> F-ITIC	92.5	95.7	14.60

PBTIBDTT: *m*F-ITIC 93.0 96.6 15.58

Table S6. Photovoltaic parameters of OSCs based on PBTIBDTT: *o*F-ITIC (D/A proportion of 1: 1 and none additive) with different annealing time (0 h, 24 h, 48 h, 72 h, and 96 h) at 150 °C in glove box, under AM 1.5G solar spectrum.

OSCs	Annealing time	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]
PBTIBDTT: <i>o</i> F-ITIC	0 h	0.96	12.71	67.34	8.22
	24 h	0.94	12.91	63.15	7.66
	48 h	0.92	11.28	66.56	6.91
	72 h	0.92	11.07	64.63	6.58
	96 h	0.92	10.69	63.70	6.26 (76 %)

Table S7: The thermal stability test of OSCs based on PBTIBDTT: ITIC, PBTIBDTT: *o*F-ITIC and PBTIBDTT: *m*F-ITIC at 85 °C.

Acceptors	Annealing time	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]
ITIC	0 h	0.96	14.12	64.87	8.79
	144 h	0.96	13.93	65.56	8.77
<i>m</i> -IFIC	0 h	0.96	14.25	68.71	9.40
	144 h	0.96	14.59	68.08	9.53
<i>o</i> -IFIC	0 h	0.94	13.55	68.74	8.76
	144 h	0.94	12.72	69.51	8.31