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Supporting Information

Multi-component non-fullerene acceptors with tunable bandgap structures for efficient organic solar cells

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1. Materials:

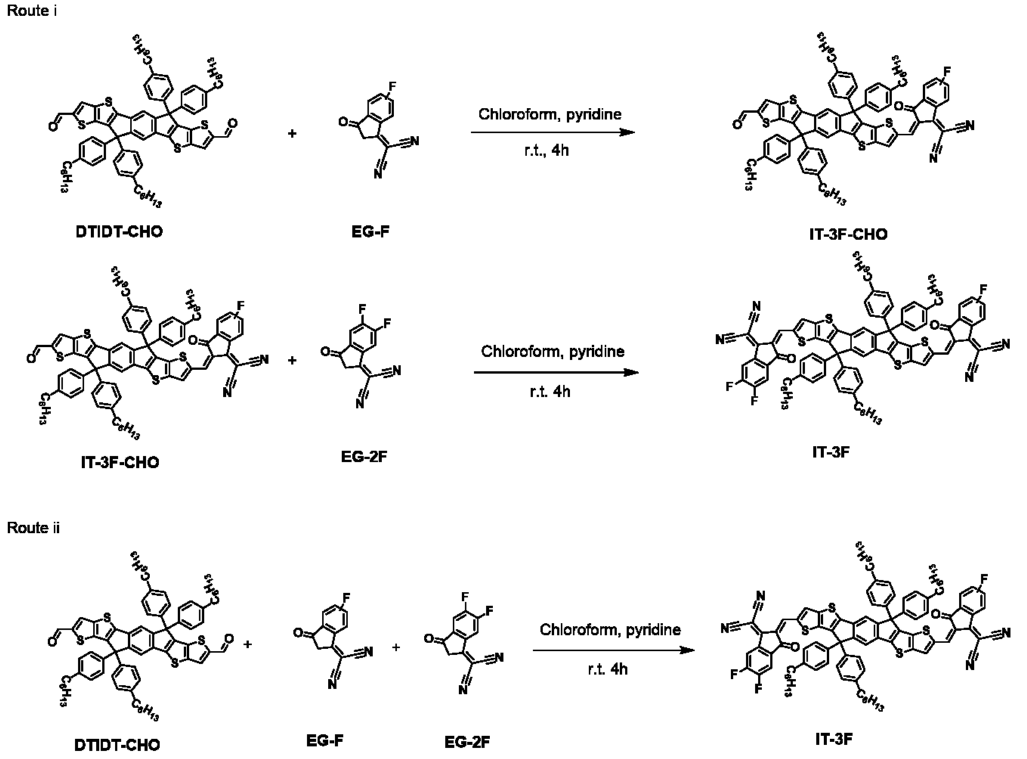
Polymer donor PBDB-TF, small molecules IT-2F, IT-4F were synthesized according to the reported literatures,[1,2] the compounds EG-2F, EG-F and DTIDT-CHO were purchased from Solar Materials Inc. (Beijing) The other reagents and solvents used were purchased from commercial sources and used as received.

Synthesis *of IT-3F-CHO*: DTIDT-CHO (0.250 g, 0.23 mmol) was added to a 100 ml two-necked flask. Solvent $CHCl_3$ (50 ml) was then added and the compound was fully dissolved by stirring for a while. After being flushed by a gentle stream of dry nitrogen for 15 min, pyridine (1.5 ml) was added as the catalyst. EG-F (48.76 mg, 0.23 mmol) was added in portions. After that, the solution was slowly turned into blue-green. The mixture was stirred at room temperature for 4 hours. After removing the solvent, the crude product was purified two times by silica gel column with toluene. The pure compound IT-3F-CHO was obtained dark purple solid. (85 mg, 30% yield). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 9.90 (s, 1H), 8.86 (s, 1H), 8.68-8.72 (dd, $J_1 = 9$ Hz, $J_2 = 4.2$ Hz, 0.25H), 8.35-8.38 (dd, $J_1 = 9$ Hz, $J_2 = 2.1$ Hz, 0.76H), 8.21-8.23 (d, $J = 5.4$ Hz, 0.98H), 7.95 (s, 1H), 7.89-7.93(dd, $J_1 = 8.4$ Hz, $J_2 = 5.4$ Hz, 0.82H), 7.65 (s, 1H), 7.60 (s, 1H), 7.53-7.56 (dd, $J_1 = 6.9$ Hz, $J_2 = 2.7$ Hz, 0.29H), 7.38-7.46(m, 1.16H), 7.20-7.23 (d, $J =$ 8.4 Hz, 4H), 7.09-7.16(m, 12H), 2.53-2.59(t, 8H), 1.54-1.58(m, 8H), 1.32(br, 24H), 0.83-0.88(m, 12H). ^{13}C NMR (300 MHz, $CDCl_3$, δ): 186.7, 182.9, 168.0, 165.4, 159.0, 155.6, 154.8, 153.6, 149.2, 147.7, 147.2, 144.7, 143.6, 142.5, 142.4, 142.3, 142.1, 140.1, 139.3, 139.0, 138.5, 138.4, 137.5, 137.3, 136.0, 133.1, 129.7, 128.9, 128.8, 127.9, 127.8, 125.9, 122.3, 121.9, 121.7, 118.6, 118.1, 114.3, 114.2, 112.9, 112.6, 70.0, 63.2, 35.6, 31.7, 31.3, 29.2, 29.1, 22.6, 14.1. MS (MALDI-TOF) m/z = 1269.1. Anal. calcd for $C_{82}H_{77}N_2O_2S_2F$ (%): C 77.54, H 6.11, N 2.20; found: C 77.48, H 6.25, N 2.18.

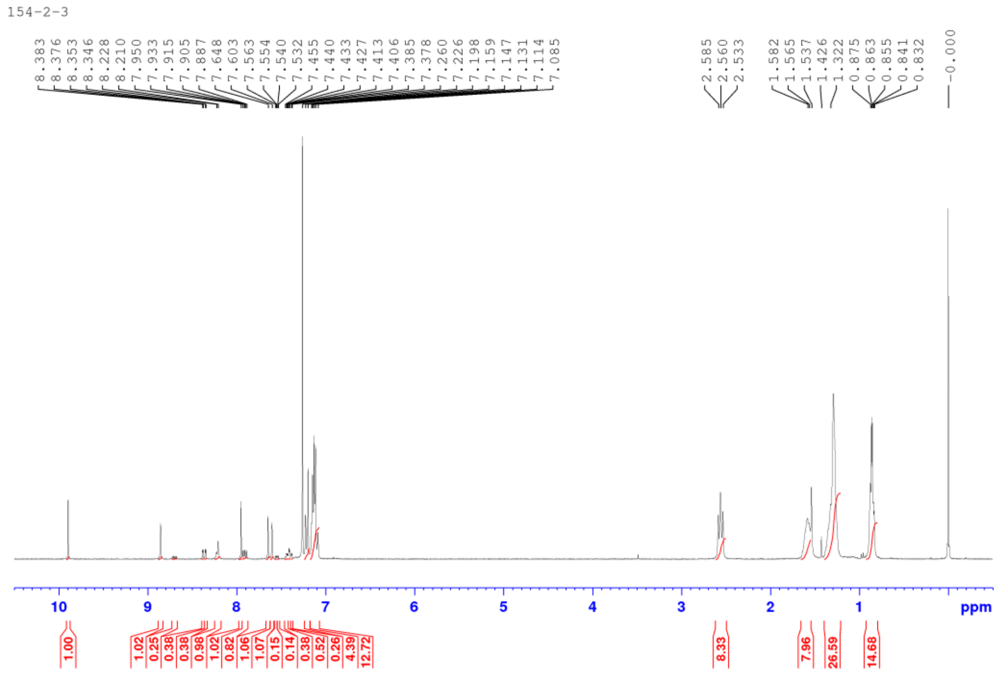
Synthesis of IT-3F: Route i: Materials IT-3F-CHO (102 mg, 0.08 mmol) and EG-2F (36.8 mg, 0.16 mmol) were added to a 100 ml two-necked flask. Solvent $CHCl_3$ (50 ml) was then added and the two compounds were fully dissolved by stirring for a while. After being flushed by nitrogen for 15 min, pyridine (0.8 ml) was added and the solution was slowly turned into blue-green. The mixture was stirred at room temperature for 4 hours. The product was purified two times by silica gel column with toluene:hexane = 3:2. The pure compound IT-3F was obtained as dark purple solid. (12.5 mg, 10% yield). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.85-8.86 (d, J = 2.1 Hz, 2H), 8.68-8.73 (dd, J_1 = 8.4 Hz, J_2 = 4.2 Hz, 0.24H), 8.51-8.56 (dd, J_1 = 9.9 Hz, J_2 = 6.6 Hz, 0.98H), 8.35-8.39 (dd, J_1 = 9 Hz, J_2 = 1.8 Hz, 0.68H), 8.22-8.23 (d, J = 4.2 Hz, 1.94H), 7.89-7.94(dd, J_1 = 8.4 Hz, J_2 = 5.4 Hz, 0.74H), 7.68-7.71 (d, J = 7.5 Hz, 0.81H), 7.64 (s, 2.29H), 7.39-7.45(m, 1.03H), 7.20-7.22 (d, J = 7.8 Hz, 8H), 7.13-7.15(d, J = 8.1 Hz, 8H), 2.54-2.59(t, 8H), 1.54-1.61(m, 8H), 1.27-1.36(m, 24H), 0.83-0.88(m, 12H). ^{13}C NMR (300 MHz, $CDCl_3$, δ): 186.7, 185.8, 158.2, 155.8, 153.7, 153.1, 147.8, 147.7, 147.4, 143.9, 143.8, 142.6, 139.6, 139.4, 138.8, 138.4, 138.3, 137.5, 137.1, 136.9, 128.9, 127.9, 122.5, 122.0, 121.7, 118.7, 114.2, 114.1, 112.8, 70.2, 69.8, 63.2, 35.6, 31.7, 31.3, 29.2, 22.6, 14.1. MS (MALDI-TOF) m/z = 1482.0.

Route ii: DTIDT-CHO (102 mg, 0.08 mmol), EG-F (20.3 mg, 0.096 mmol) and EG-2F (22.1 mg, 0.096 mmol) was added to a 100 ml two-necked flask. Solvent $CHCl_3$ (50 ml) was then added and the three compounds were fully dissolved by stirring for a while.

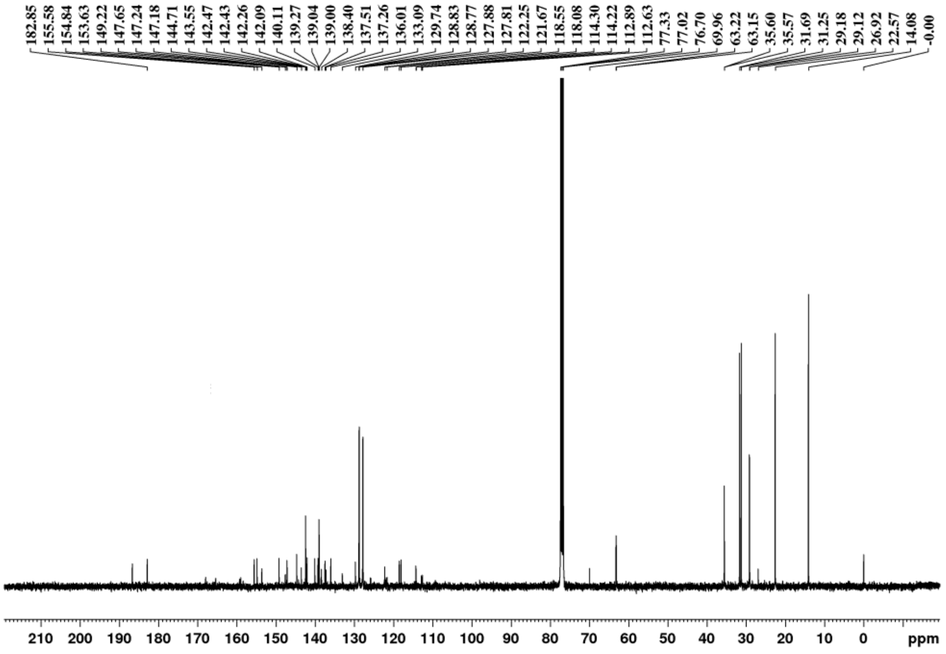
After being flushed with nitrogen for 15 min, pyridine (0.8 ml) was added and the solution was slowly turned into blue-green. The mixture was stirred at room temperature for 4 hours. The product was purified two times by a silica gel column with toluene:hexane = 3:2. The pure compound IT-3F was obtained as dark purple solid. (35.6 mg, 30% yield)



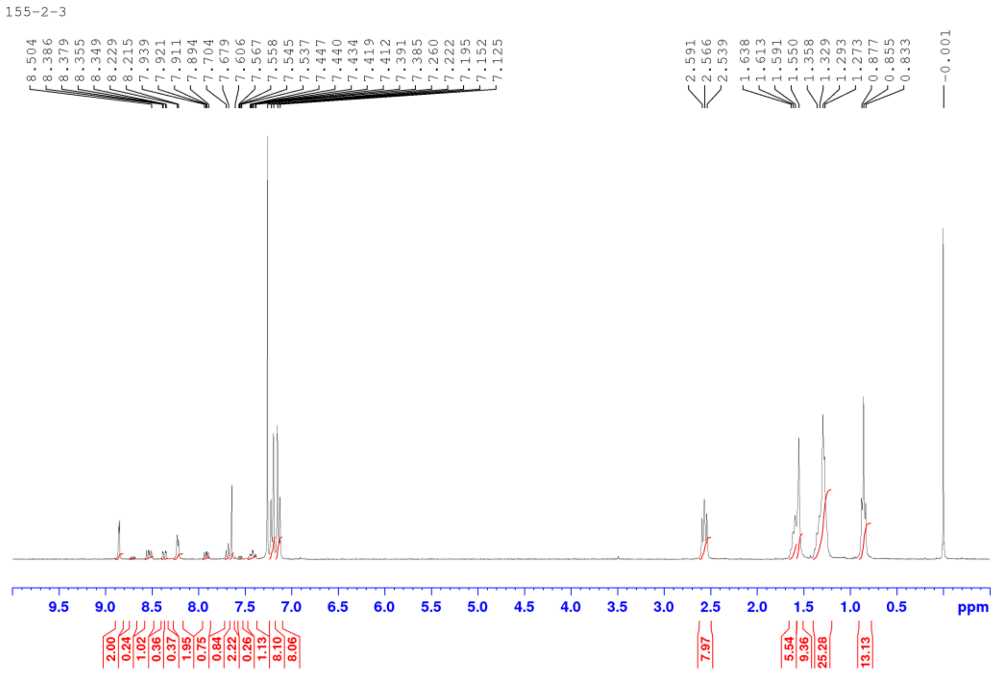
Scheme S1. Synthetic route of IT-3F.



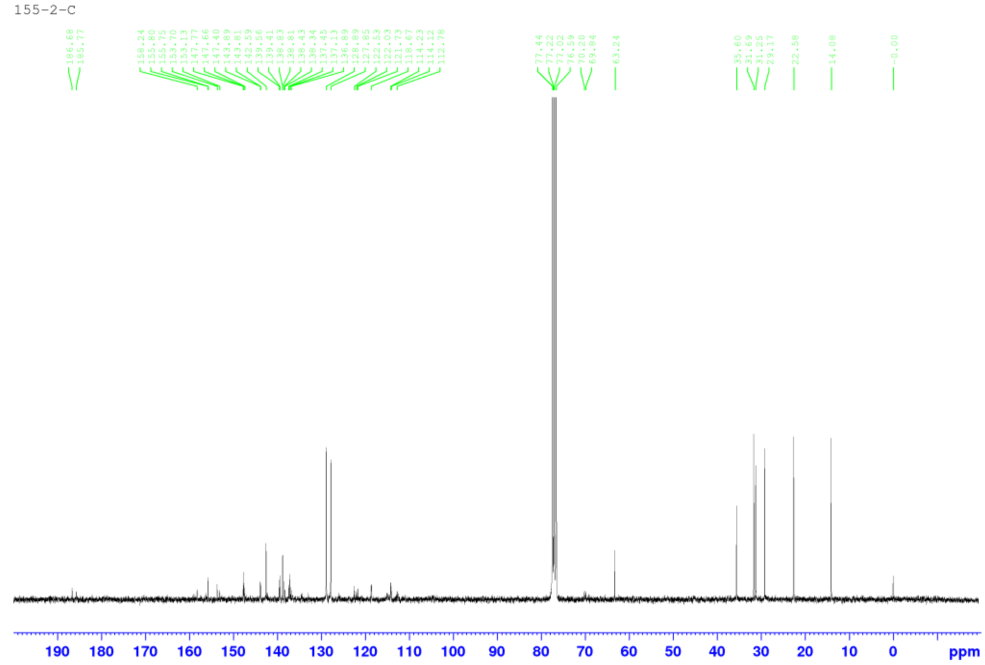
^{1}H NMR spectrum of IT-3F-CHO



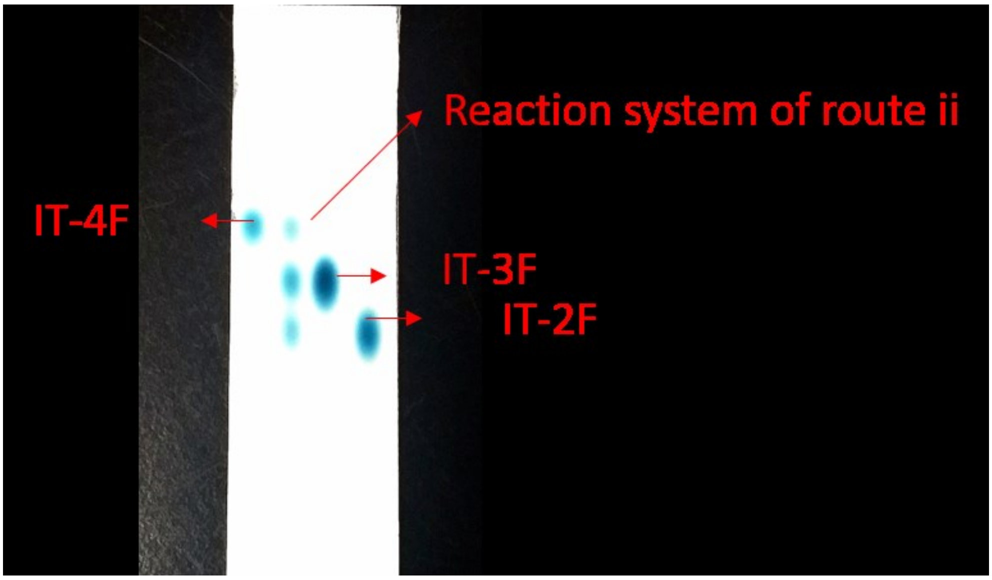
^{13}C NMR spectrum of IT-3F-CHO



^{1}H NMR spectrum of IT-3F



^{13}C NMR spectrum of IT-3F



TLC of Route ii

Fig. S1. NMR spectra of the target products and TLC of route ii.

2. Device fabrication and characterization:

Solar cell fabrication: ITO glasses were pre-cleaned by surface scrub and sonicated with water, acetone, and isopropanol for 15 min each. After UV-ozone treatment for 15 min, PEDOT:PSS were spin-coated on the surface of ITO glasses at 4000 rpm for 30 s. The PEDOT:PSS-coated ITO were annealed at 150 °C for 15 min and transferred to glove box. Then the blend solution of active layers was fully dissolved in chlorobenzene at a polymer weight concentration of 10 mg/mL, and a 0.5% volume ratio of 1,8-DIIODOOCTANE (DIO) was used as the solvent additive. The spin-coated active layer thickness was ~110 nm, as measured by a Bruker Dektak XT profilometer. Then, the active layer films were treated by thermal annealing at 100 °C for 10 min, followed by the coating of PFN-Br (~5 nm). Finally, approximately 80 nm of Al was deposited onto the active layer under high vacuum, giving an area of 4.15 mm^2.

Characterization: The $J-V$ measurement of all devices were performed via the solar simulator (SS-F5-3A, Enlitech) under AM 1.5G spectra at 100 mW cm^{-2} calibrating by the certified standard silicon solar cell (SRC-2020, Enlitech). The external quantum efficiency (EQE) data were obtained by using the solar-cell spectral-response measurement system (QE-R, Enlitech). Bruker AVANCE 300 or 400 MHz spectrometers was used to measure the ^{1}H and ^{13}C NMR spectra of the compounds in the synthetic procedure at room temperature. The UV-visible absorption spectra (in chloroform solution and as thin films) were conducted on a Hitachi UH4150 UV-Vis spectrophotometer. The molecular energy levels of the small molecular acceptors were measured on CHI650D Electrochemical Workstation in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile solution. The thickness of blend layers was measured via the surface profilometer Bruker Dektak XT. AFM and TEM images were obtained by Nanoscope V AFM and JEOL 2200FS instrument, respectively. The photo-CELIV and TPV measurements reported here were performed by the all-in-one characterization platform Paios developed and commercialized by Fluxim AG, Switzerland.

For photo-CELIV, the charge carrier mobility (μ) is calculated using Equation (1):

$$\mu = \frac{2d^2}{3At_{max}{}^2[1+0.36\frac{\Delta j}{j(0)}]} \qquad if\ \ \Delta j \leq j \ \ (1)$$

where d is the active layer thickness, A is the voltage rise speed, t_{max} is the time corresponding to the extraction peak maximum, and $j(0)$ is the displacement current.

For TPV, the TPV measurement is conducted by using a high resistor. So that the device is in open circuit condition in the whole measurement and the current is almost zero. A small light pulse intensity pulse is added to a constant offset light intensity and the voltage decay is analyzed.

It has been common to employ the relationships by equation 2 in organic photovoltaics:

$$V_{oc} = \frac{Eg}{q} - \frac{n_{eff}k_BT}{q}\ln\left(\frac{N^2}{np}\right) \qquad (2)$$

Where E_g is taken to be the difference between the lowest unoccupied molecular orbital of the fullerene and highest occupied molecular orbital of the polymer (LUMO $_{\text{acceptor}}$ – HOMO $_{\text{polymer}}$), n_{eff} is the effective non-ideality, k_B is Boltzmann's constant, T is absolute temperature, q is elementary charge, and n and p are the total density of electrons and holes, respectively.

The open-circuit voltage decay is governed by the electron-hole recombination, calculating the time derivative of Equation (2), following expressions can be obtained:

$$q\frac{dV_{oc}}{dt} = k_BT\frac{d}{dt}\ln(np) \qquad (3)$$

where$\frac{1}{\tau} = \frac{1}{np}\frac{\partial np}{\partial t}$ (4), Substituting equations (3) and (4), then the charge carrier lifetime can be calculated from photovoltage data through Equation(5):

$$\tau = -\frac{k_BT}{q}\left(\frac{dVoc}{dt}\right)^{-1} \qquad (5)$$

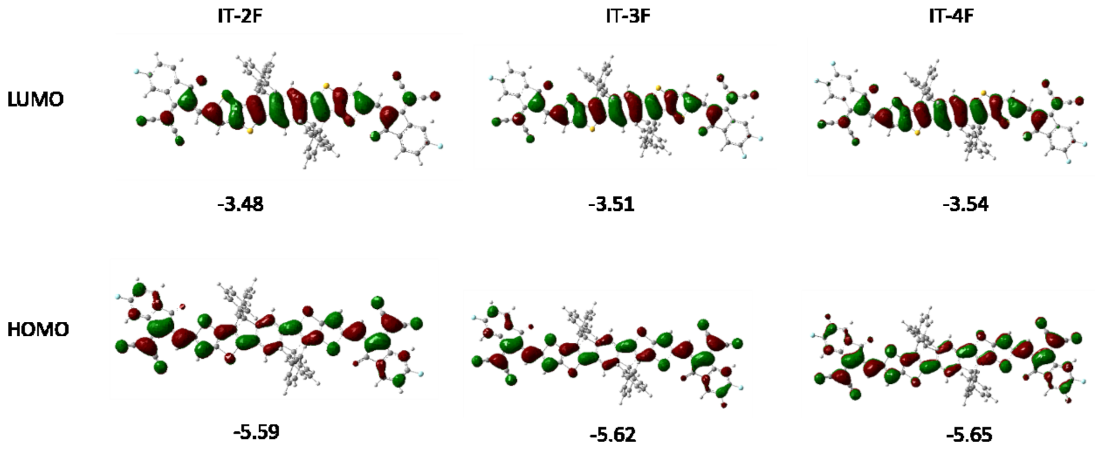


Fig. S2. HOMO and LUMO calculation results of IT-2F, IT-3F and IT-4F.

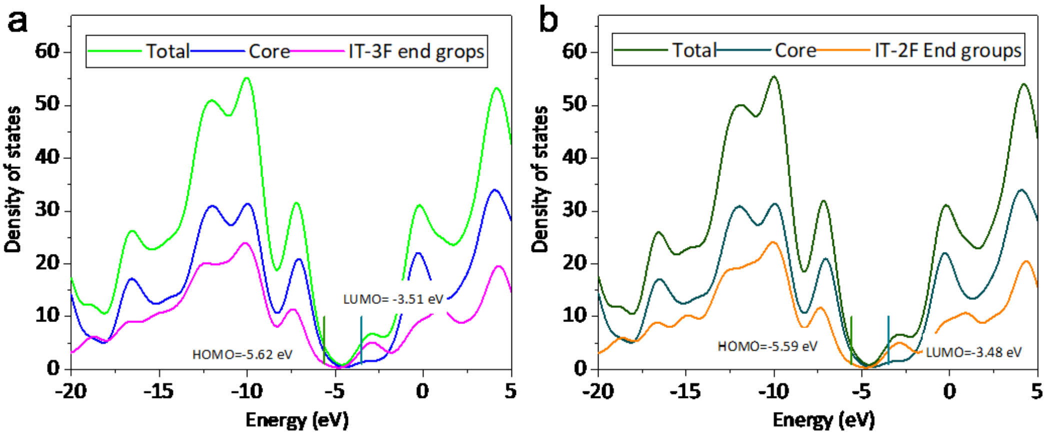


Fig. S3. DOS distributions of the a) IT-2F b) IT-3F.

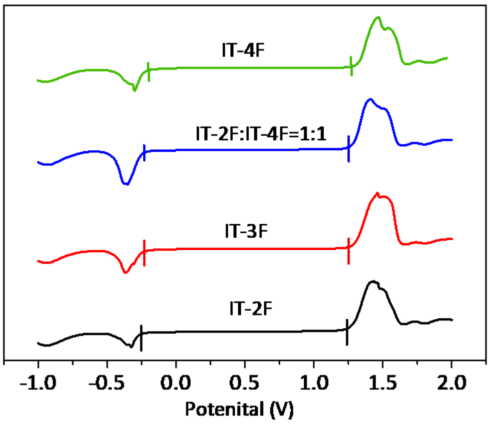
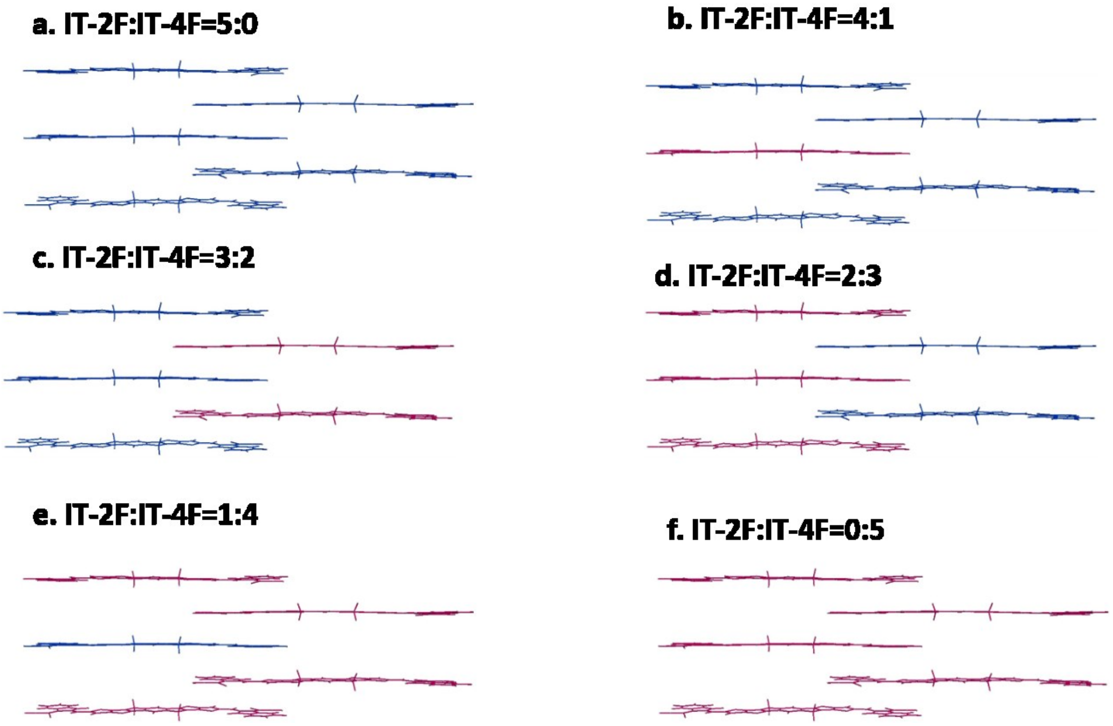


Fig. S4. Square wave voltammetry of acceptors and acceptor blends.



a. IT-2F:IT-4F=5:0

b. IT-2F:IT-4F=4:1

c. IT-2F:IT-4F=3:2

d. IT-2F:IT-4F=2:3

e. IT-2F:IT-4F=1:4

f. IT-2F:IT-4F=0:5

Fig. S5. Complexes of alloy-like packing patterns with different IT-2F:IT-4F ratios.

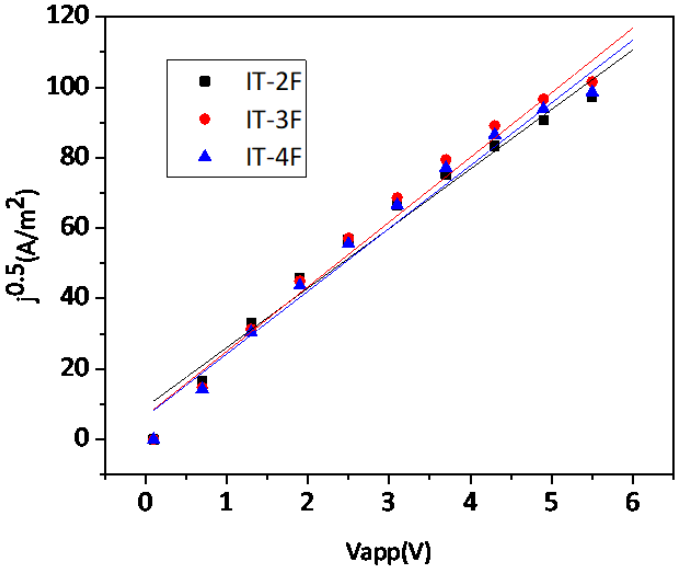


Fig. S6. Electron mobilities of acceptors.

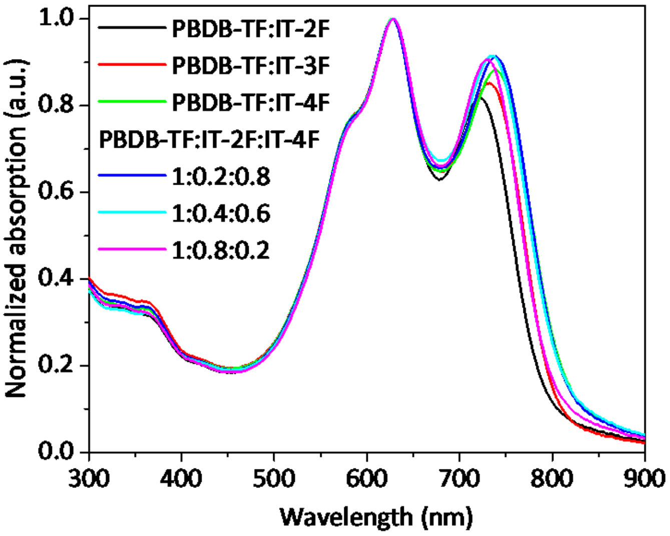


Fig. S7. Absorption spectra of the blended films.

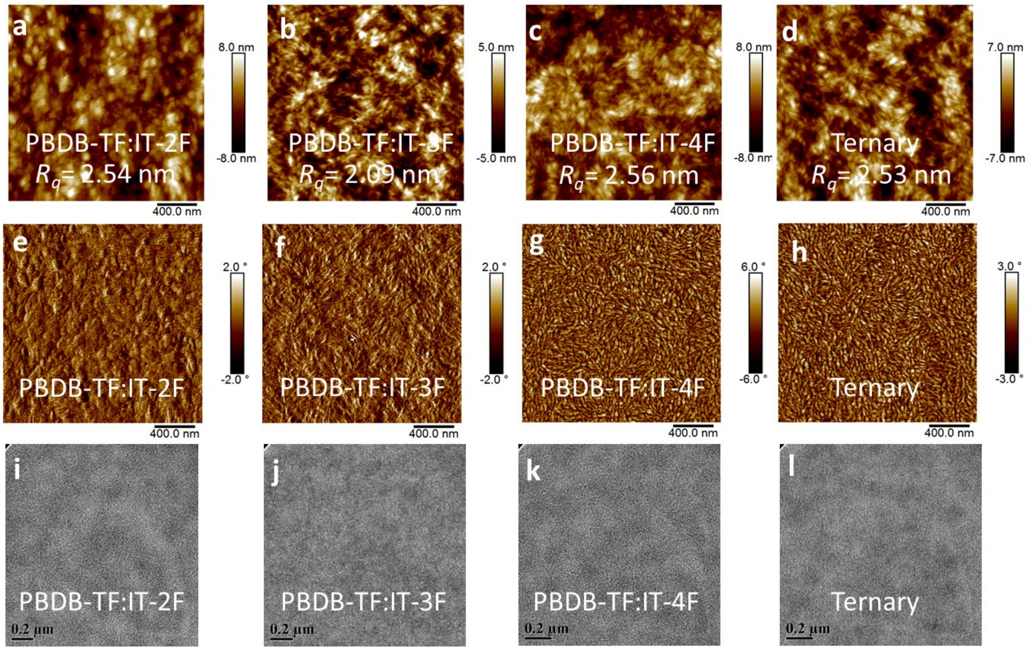


Fig. S8. a–d) AFM height images, e–f) AFM phase images, and i–l) TEM patterns of the binary and ternary films.

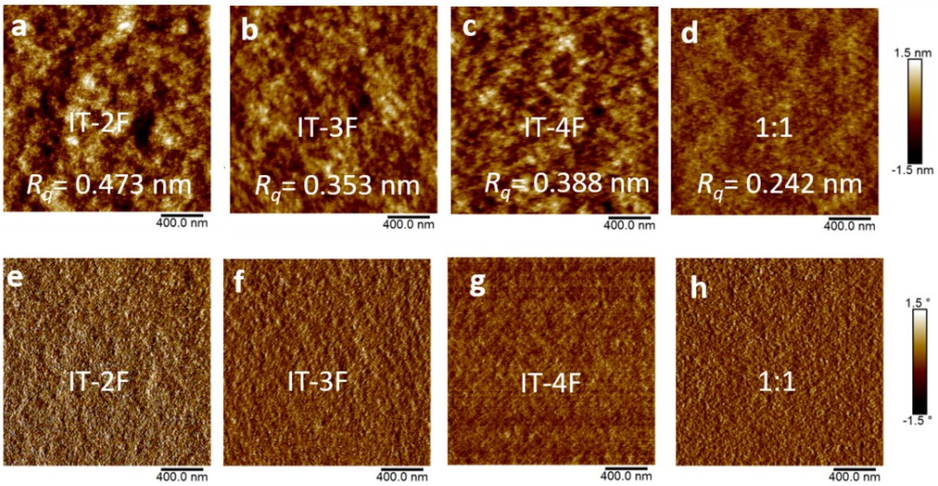


Fig. S9. a–d) AFM height images and e–f) AFM phase images of the neat and blended films.

Table S1. Photovoltaic parameters of PSCs with different IT-4F content in acceptors.

Devices (PBDB-TF:IT-2F:IT-4F weight ratio)	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF [%]	PCE [%]
1:0.2:0.8	0.88	20.70	77.1	14.04
1:0.4:0.6	0.88	20.83	76.0	13.93
1:0.5:0.5	0.89	20.67	75.5	13.89
1:0.6:0.4	0.90	20.35	74.2	13.58
1:0.8:0.2	0.91	20.04	72.9	13.29
1:0.505:0.495 (molar ratio of IT-2F:IT-4F = 1:1)	0.89	20.54	75.7	13.84

Table S2. Photovoltaic parameters of binary solar cells

Devices	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]

PBDB-TF:IT-M	1.01	16.38	60.9	10.07
PBDB-TF:ITIC	1.00	16.56	61.4	10.16
PBDB-TF:IT-4Cl[a]	0.78	22.23	73.1	12.67

[a] The solvent is chloroform.

Table S3. Photovoltaic parameters of multi-component solar cells

IT-M:ITIC:IT-2F:IT-4F:IT-4Cl	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
0.8:0.05:0.05:0.05:0.05	0.963	17.87	62.28	10.72

REFERENCES

(1) Zhao, W.; Li, S.; Yao, H.; Zhang, S.; Zhang, Y.; Yang, B.; Hou, J. *J. Am. Chem. Soc.* **2017**, *139*, 7148-7151.

(2) Zhang, M.; Guo, X.; Ma, W.; Ade, H.; Hou, J. *Adv. Mater.* **2015**, *27*, 4655-4660.