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Supporting Information

Tuning the Dipole Moments of Nonfullerene Acceptors with Facile Asymmetric Terminal Strategy for Highly Efficient Organic Solar Cells

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Table of Contents:

1. Materials and General Procedures

All commercial chemicals were used without further purification. UV-visible absorption spectra were recorded on a UV-1601pc spectrophotometer. Differential scanning calorimetry (DSC) measurements were performed on a Mettler Toledo DSC 822e with a heating and cooling rate of 10 °C/min. Electrochemical measurements were performed on a CHI 600E

Electrochemical Analyzer. Column chromatography was carried out on silica gel (300-400 mesh). Analytical thin-layer chromatography was performed on glass plates of Silica Gel GF-254 with detection by UV. ^{1}H and ^{13}C NMR spectra were obtained using chloroform-*d* ($CDCl_3$) as solvent and recorded on a 400 MHz spectrometer. HRMS spectra (MALDI/DHB) were recorded on mass spectrometer Thermo Fisher Scientific LTQ FT Ultra. GIWAXS measurements were conducted on a Xenocs-SAXS/WAXS system with X-ray wavelength of 1.5418 Å. The film samples were irradiated at a fixed angle of 0.2° and all film samples were prepared from with *o*-DCB.

Synthesis of *a*-IT-2F

To a schlenk flask were added **IDTT-CHO** (83.0 mg, 0.0772 mmol), IC (19.5 mg, 0.1003 mmol). the reactant was deoxygenated with argon for 30 min. Pyridine (0.1 mL) and chloroform (8 mL) was added under argon. after the mixture was stirred for 12 h at room temperature, 2F-IC (23.1 mg, 0.1003 mmol)was added for another 12 h. Then it was poured into methanol (100 mL). The filtrate was purified by column chromatography on silica gel using hexane/chloroform (1:1, v/v) as eluent yielding dark solids (45.2 mg, 39%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.87 (s, 1H), 8.85 (s, 1H), 8.69 (d, J = 7.6 Hz, 1H), 8.55-8.51 (m, 1H), 8.23 (s, 1H), 8.22 (s, 1H), 7.92 (d, J = 7.6 Hz, 1H), 7.82-7.66 (m, 3H), 7.65 (s, 1H), 7.64 (s, 1H), 7.24-7.17 (m, 8H), 7.17-7.11 (m, 8H), 2.57 (t, J = 7.6 Hz, 8H), 1.65-1.56 (m, 8H), 1.39-1.22 (m, 24H), 0.86 (t, J = 6.5 Hz, 12H). ^{13}CNMR ($CDCl_3$, 100 MHz): δ 188.32, 185.93, 160.50, 158.43, 156.04, 156.01, 155.91, 154.01, 153.46, 153.42, 153.33, 153.31, 153.28, 152.85, 148.02, 147.92, 147.82, 147.16, 144.08, 143.92, 142.78, 142.74, 140.22, 139.88, 139.58, 139.09, 139.04, 138.62, 138.39, 137.64, 137.45, 137.06, 136.95, 136.87, 136.84, 136.77, 135.40, 134.68, 129.08, 128.06, 125.52, 123.97, 123.06, 121.92, 118.88, 118.74, 115.29, 115.06, 114.78, 114.73, 114.43, 114.33, 112.96, 112.76, 70.04, 69.71, 63.48, 63.47, 35.81, 31.90, 31.45, 29.39, 22.79, 14.29. HRMS (ESI) m/z Calcd for $C_{94}H_{81}F_2N_4O_2S_4^+$ $[M+H]^+$ 1463.52049, Found 1463.52276.

Synthesis of *a*-IT-2OM

To a schlenk flask were added **IDTT-CHO** (42.6 mg, 0.0396 mmol), IC (11.5 mg, 0.0594 mmol). the reactant was deoxygenated with argon for 30 min. Pyridine (0.1 mL) and chloroform (8 mL) was added under argon. after the mixture was stirred for 12 h at room temperature, 2OM-IC (15.1 mg, 0.0594 mmol) was added for another 12 h. Then it was poured into methanol (100 mL). The filtrate was purified by column chromatography on silica gel using hexane/chloroform (1:1, v/v) as eluent yielding dark solids (31.6 mg, 54%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.87 (s, 1H), 8.74 (s, 1H) 8.68 (d, *J* = 7.6, 1H), 8.21 (s, 1H), 8.17 (s, 1H), 8.11 (s, 1H), 7.91 (d, *J* = 7.6 Hz, 2H), 7.80-7.70 (m, 2H), 7.62 (s, 1H), 7.61 (s, 1H), 7.34 (s, 1H), 7.24-7.19 (m, 8H), 7.17-7.10 (m, 8H), 4.05 (s, 3H), 4.03 (s, 3H), 2.56 (t, *J* = 7.6 Hz, 8H), 1.64-1.56 (m, 8H), 1.39-1.20 (m, 24H), 0.86 (t, *J* = 6.5 Hz, 12H). ^{13}C NMR($CDCl_3$, 100 MHz): δ 187.38, 185.87, 160.42, 156.11, 155.81, 155.49, 155.43, 154.18, 151.49, 148.22, 148.04, 147.83, 146.01, 144.10, 143.64, 142.79, 142.69, 139.79, 139.59, 139.28, 139.15, 138.59, 137.77, 137.45, 136.96, 136.93, 136.85, 136.66, 136.12, 135.67, 135.04, 134.88, 134.87, 134.84, 134.80, 134.79, 132.65, 129.12, 129.07, 128.19, 128.13, 124.19, 122.04, 118.90, 118.57, 115.44, 115.29, 115.07, 114.77, 114.46, 114.35, 112.95, 112.75, 106.98, 104.87, 70.10, 67.90, 63.58, 56.93, 56.89, 35.83, 31.92, 31.39, 29.38, 22.78, 14.22. HRMS (ESI) m/z Calcd for $C_{96}H_{87}N_4O_4S_4^+$ $[M+H]^+$ 1487.56047, Found 1487.55898.

2. NMR Spectra and HRMS results

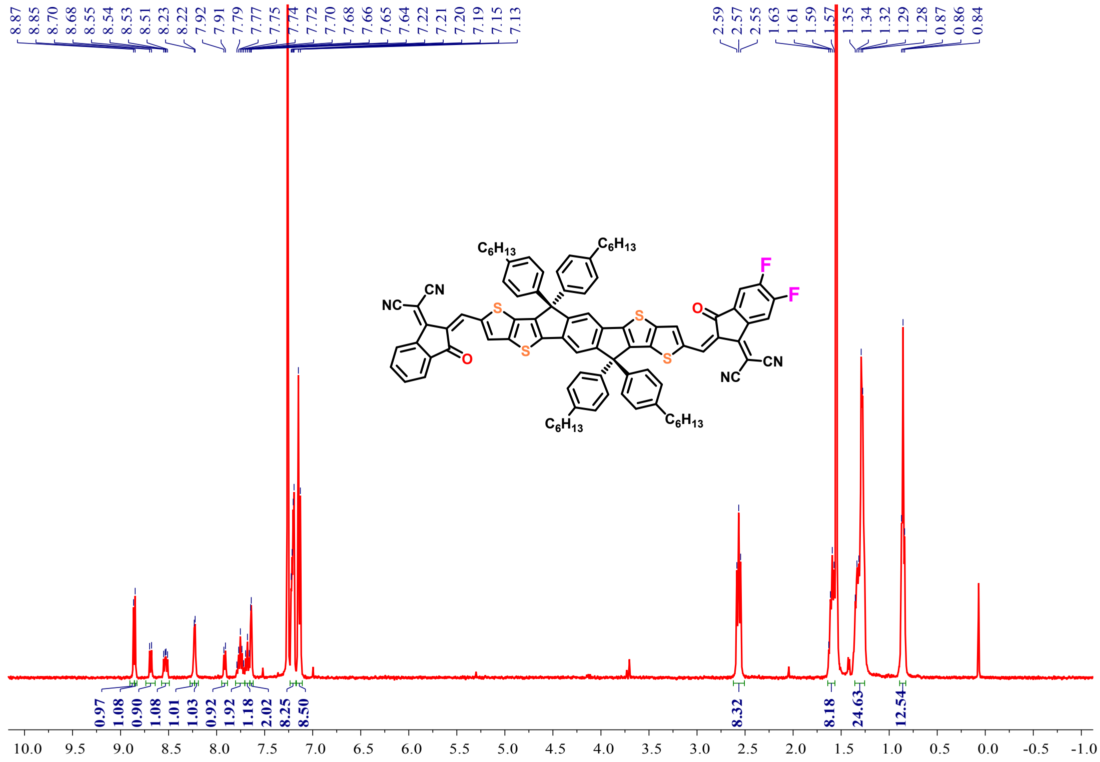


Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ***a*-IT-2F.**

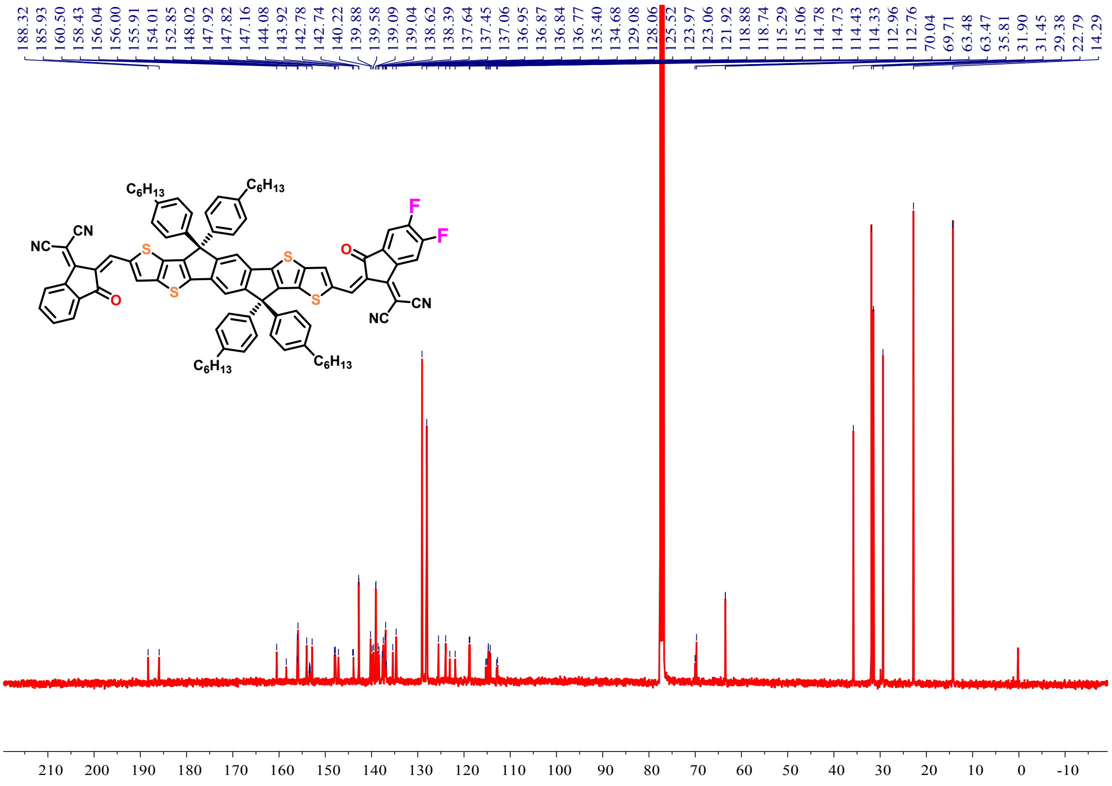
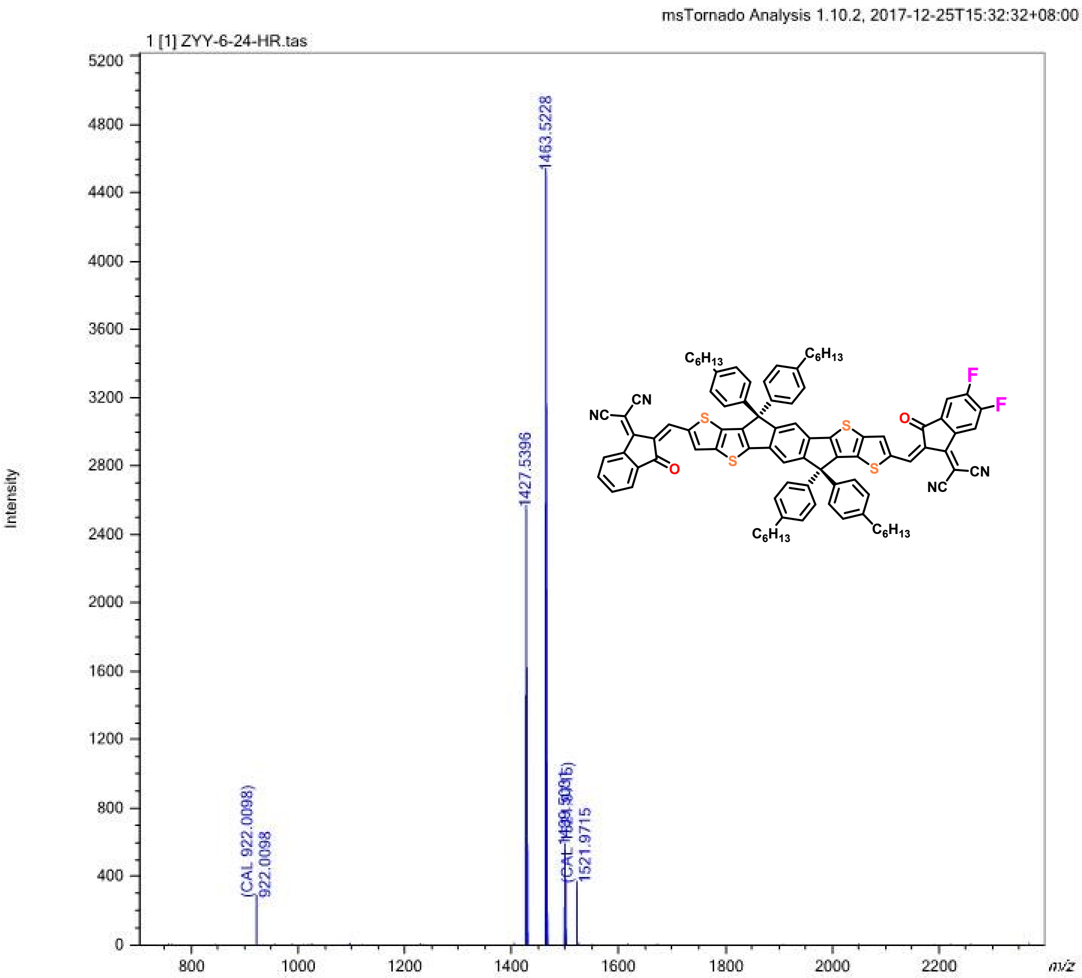


Figure S2. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of ***a*-IT-2F.**



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Elemental Composition Estimation

Parameters:

Mass                      Tolerance      Electron Mode      Charge      DBE Range       Max Results
 1463.52276 ± 0.00732      5.0 ppm        Odd/Even           +1          -0.5 - 200.0    100

Elements
 C    0 - 94      H    0 - 85      N    0 - 4      O    0 - 4      F    0 - 2      S    0 - 4

Results:
#      Formula                 Mass          DBE     Abs. Error (u)     Error (u)     Error (ppm)
  1    C94 H81 N4 O2 F2 S4     1463.52049    55.5          0.00227       0.00227            1.55
  2    C94 H82 N3 O4 F S4      1463.51667    55.0          0.00609       0.00609            4.16
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Figure S3. HRMS result of ***a*-IT-2F**.

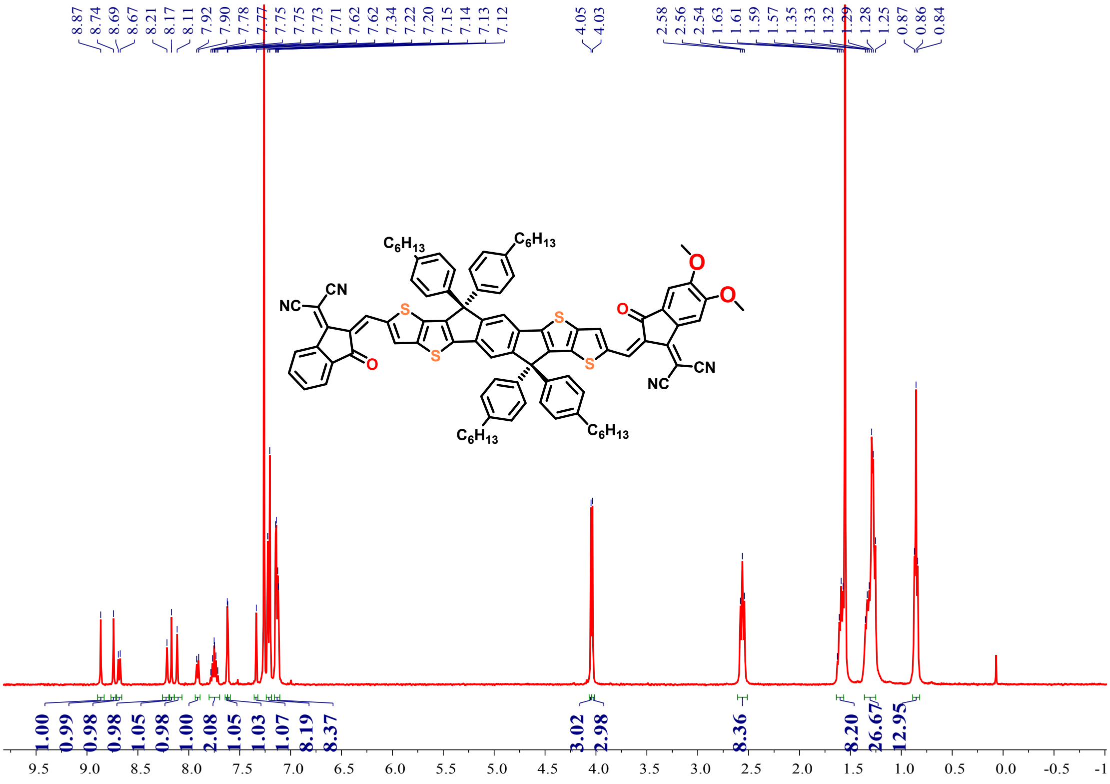


Figure S4. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of ***a*-IT-2OM.**

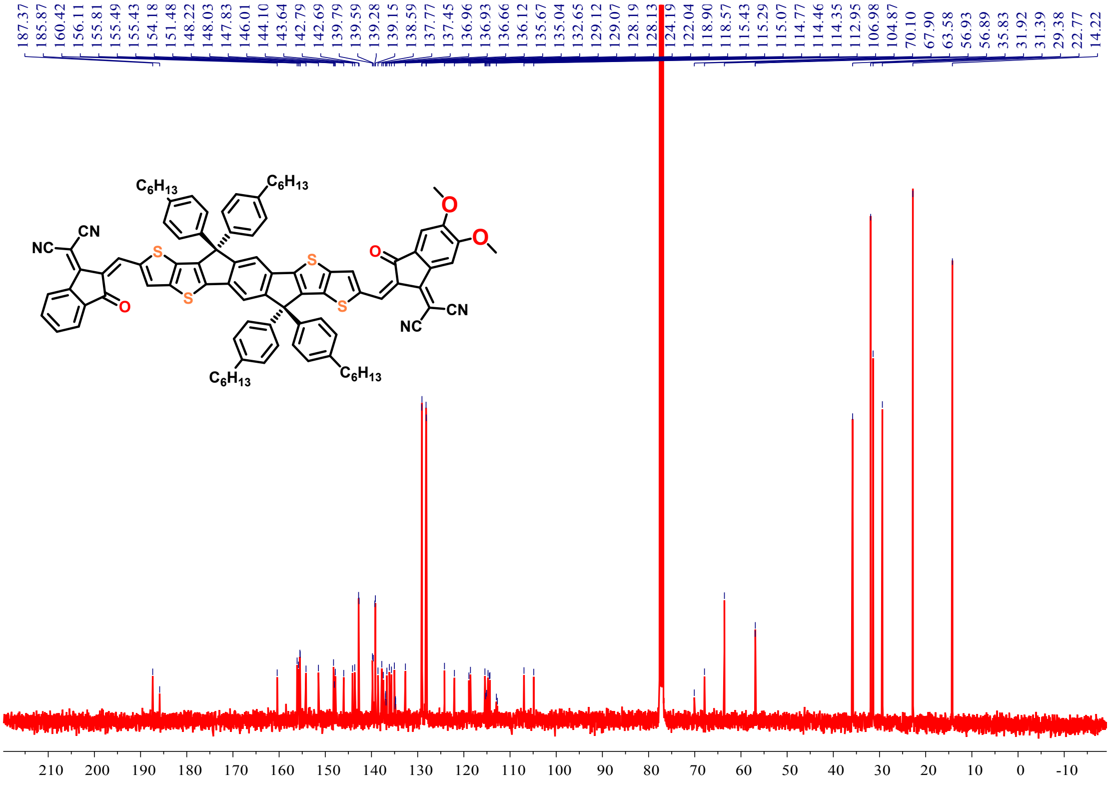
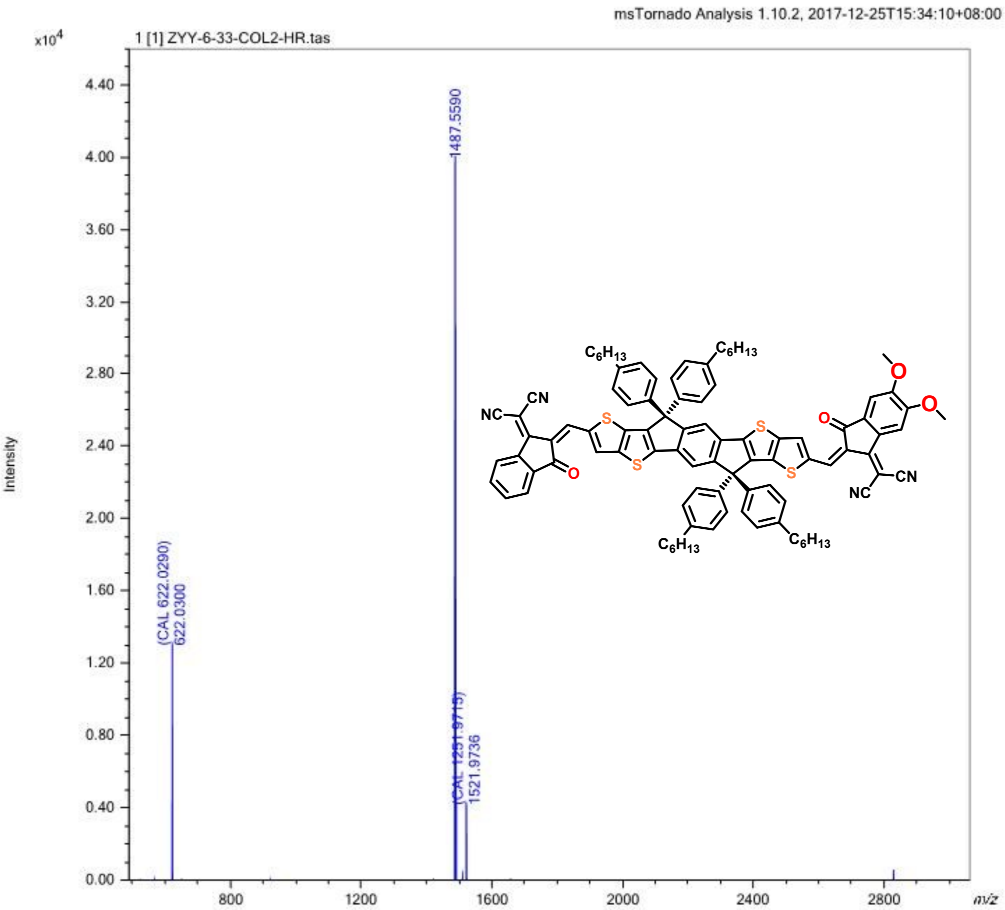


Figure S5. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of ***a*-IT-2OM.**



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Elemental Composition Estimation

Parameters:
Mass                    Tolerance    Electron Mode    Charge    DBE Range      Max Results
 1487.55898 ± 0.00744     5.0 ppm      Odd/Even         +1       -0.5 - 200.0    100

Elements
 C   0 - 96      H   0 - 88     N   0 - 4     O   0 - 4     F   0 - 2     S   0 - 4

Results:
#      Formula                  Mass          DBE    Abs. Error (u)    Error (u)    Error (ppm)
  1    C96 H87 N4 O4 S4         1487.56047    55.5          0.00149     -0.00149          -1.00
  2    C94 H87 N3 O4 F2 S4      1487.55420    52.0          0.00478      0.00478           3.21
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Figure S6. HRMS result of ***a*-IT-2OM.**

3. Additional DFT Calculation Results

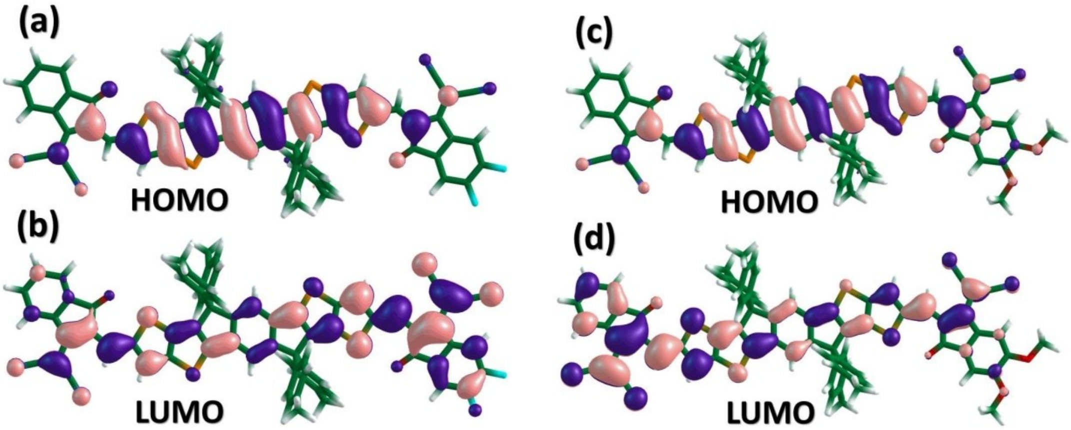

Figure S7. Frontier molecular orbitals (HOMO and LUMO) from DFT calculations of ***a*-IT-2F** (**a**, **b** and ***a*-IT-2OM** (**c**, **d**), respectively.

5. PSCs Optimization

OPV devices were made with a general configuration of ITO/ZnO/active layer/MoO_3/Ag. The conductivity of ITO was 15 Ω/sq. 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 10 minutes, thin layers of sol-gel ZnO (30 nm) were spin-coated on them and then annealed at 200 ˚C for 20 min in the air. The blend of polymers and small molecule was dissolved in DCB with the polymer concentration of 4 mg mL^{-1} (with or without additives) and heated at 110 ˚C at least 5 h to ensure a sufficient dissolution, and then spin-coated onto ZnO modified glass substrates. Followed 8.5nm thick MoO_3 film and 100 nm thick Ag layer were deposited sequentially to complete the inverted device. Six cells were fabricated on one substrate with an effective area of 0.04 cm^2 . 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.

Table S1. The PSC devices optimization based on ITO/ZnO/active layer/MoO_3/Ag by variation of the weight ratios of PBDB-T to acceptors and additive types.

Active layer	**additive**	**V_{oc}(V)**	**J_{sc}(mA/cm^2)**	***FF*** **(%)**	***PCE*** **(%)**
PBDB-T:*a*-IT-2OM=1:0.8	-	0.93	16.54	70.61	10.85
PBDB-T:*a*-IT-2OM=1:1	-	0.93	17.00	69.55	11.04
PBDB-T:*a*-IT-2OM=1:1.2	-	0.92	16.42	69.76	10.53
PBDB-T:*a*-IT-2OM=1:1.4	-	0.92	15.86	68.54	10.00
PBDB-T:*a*-IT-2OM=1:1	0.1%DIO	0.92	18.51	69.75	11.86
PBDB-T:*a*-IT-2OM=1:1	0.2%DIO	0.93	18.11	71.52	12.07
PBDB-T:*a*-IT-2OM=1:1	0.3%DIO	0.92	18.59	67.59	11.56
PBDB-T:*a*-IT-2OM=1:1	0.4%DIO	0.92	17.04	65.94	10.30
PBDB-T:*a*-IT-2OM=1:1	0.5%DIO	0.91	16.30	62.20	9.27
PBDB-T:*a*-IT-2OM=1:1	0.5%DIO	0.90	14.47	55.00	7.18
PBDB-T:*a*-IT-2F=1:0.8	-	0.80	15.56	66.66	8.79
PBDB-T:*a*-IT-2F=1:1	-	0.79	17.34	66.47	9.10
PBDB-T:*a*-IT-2F=1:1.2	-	0.79	17.11	64.50	8.71
PBDB-T:*a*-IT-2F=1:1.4	-	0.79	16.90	62.68	8.33
PBDB-T:*a*-IT-2F=1:1	0.1%DIO	0.77	18.83	69.17	10.03
PBDB-T:*a*-IT-2F=1:1	0.2%DIO	0.78	19.06	68.84	10.28
PBDB-T:*a*-IT-2F=1:1	0.3%DIO	0.77	19.01	67.79	9.80
PBDB-T:*a*-IT-2F=1:1	0.5%DIO	0.77	18.13	68.26	9.52

Table S2. The photovoltaic parameters of the optimization devices **PBDB-T:*a*-IT-2OM** with different active layer thickness.

Thickness (nm)	**additive**	V_{oc}**(V)**	J_{sc}**(mA/cm^2)**	***FF* (%)**	***PCE* (%)**
80	0.2%DIO	0.93 (0.92±0.01)	17.22 (17.45±0.15)	71.24 (69.88±0.92)	11.39 (11.23±0.18)
100	0.2%DIO	0.93 (0.92±0.01)	18.11 (18.02±0.54)	71.52 (70.01±0.91)	12.07 (11.87±0.22)
140	0.2%DIO	0.92 (0.92±0.01)	18.61 (18.56±0.22)	68.64 (66.90±1.19)	11.72 (11.40±0.20)
190	0.2%DIO	0.92 (0.92±0.01)	18.03 (17.73±0.17)	66.76 (65.83±1.28)	10.97 (10.65±0.22)
230	0.2%DIO	0.92 (0.91±0.01)	18.18 (17.71±0.66)	60.93 (61.06±1.01)	10.20 (9.96±0.30)
300	0.2%DIO	0.91 (0.91±0.01)	18.90 (18.33±0.53)	55.21 (54.41±1.19)	9.46 (9.05±0.38)
370	0.2%DIO	0.90 (0.90±0.01)	18.55 (17.97±0.54)	54.26 (53.56±1.41)	9.08 (8.72±0.41)
450	0.2%DIO	0.90 (0.90±0.01)	18.55 (17.70±0.99)	53.81 (52.59±1.56)	8.81 (8.44±0.31)

*The values in the parentheses are the statistical data from ten independent cells.

6. Space-Charge Limited Current Measurement

Hole/electron devices with a structure of ITO/PEDOT:PSS/active layer/Au and ITO/ZnO/active layer/Al were fabricated. Dark *J–V* curves of the hole/electron devices were measured by the space-charge limited current (SCLC) method. Hole and electron mobilities of devices were calculated according to the Mott-Gurney equation: $J = 9\varepsilon_o\varepsilon_r\mu V^2 /8d^3$, where J is the space charge limited current, ε_o is the vacuum permittivity (ε_o=8.85×10^{-12} F/m), ε_r is the permittivity of the active layer (ε_r = 3 F/m), μ is mobility, and d is the thickness of the active layer.

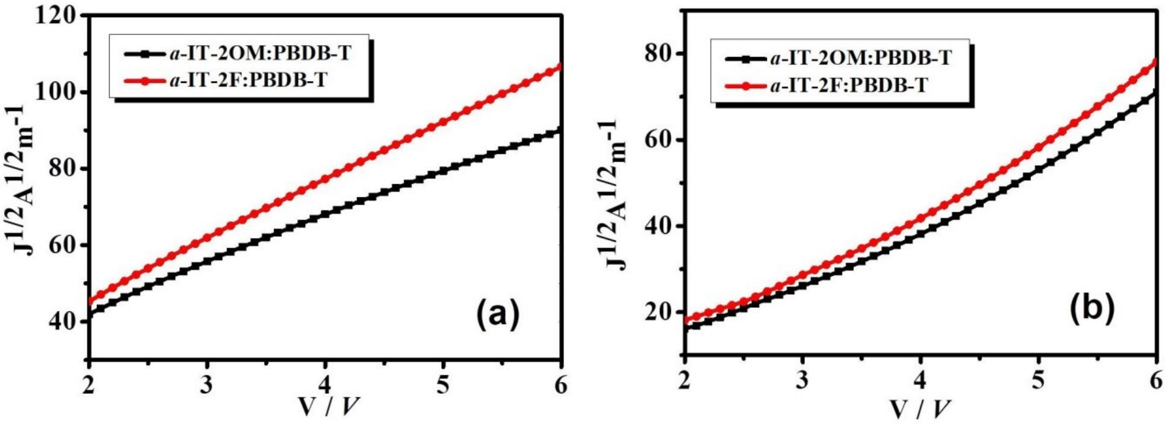

Figure S8. $J^{1/2}$–V curves for blended flms with **PBDB-T** and asymmetric acceptors: **(a)** hole-only devices and **(b)** electron-only devices.

Table S4. Charge transport properties of the PBDB-T:asymmetric acceptors at the optimized conditions.

Active layer	μ_h **(cm^{2}V^{-1} S^{-1})**	μ_e **(cm^{2}V^{-1} S^{-1})**	μ_h/μ_e	**Thickness (nm)**
PBDB-T:*a*-IT-2OM = 1:1	6.61×10^{-5}	3.89×10^{-5}	1.69	97
PBDB-T:*a*-IT-2F= 1:1	7.99×10^{-5}	3.95×10^{-5}	2.03	92