

Electronic supplementary information

**Tailoring Molecular Geometry of Polyfluoride
Perylene Diimide Acceptor towards Efficient Organic
Solar Cells**

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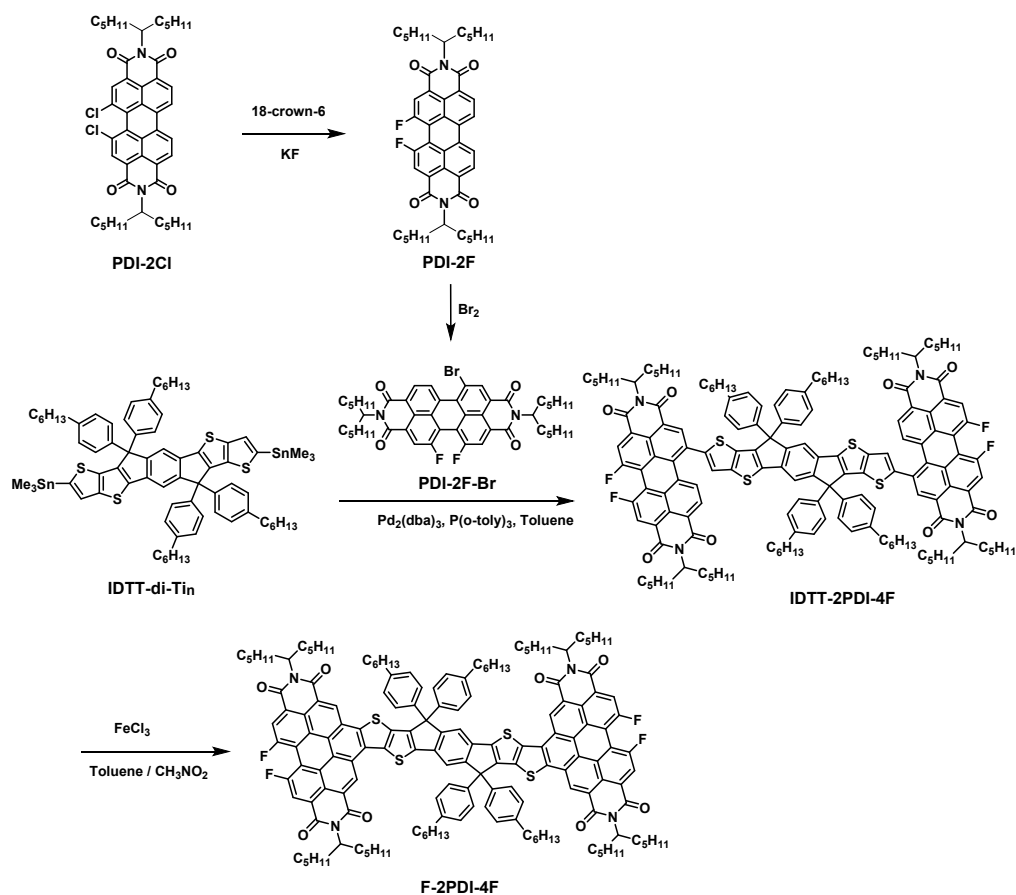
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1. Instruments and measurements

^1H and ^{13}C NMR spectra were measured by Bruker Avance-III HD 400 and Avance-III HD 500 spectrometer using *d*-chloroform (CDCl_3) as the solvent and tetramethylsilane (TMS) as internal standard at room temperature, respectively. Matrix-assisted laser desorption/ionization time of flight mass spectrometry (Maldi-Tof-MS) was measured by Bruker autoflex speed TOF/TOF with dichloromethane (CH_2Cl_2) at reflection mode utilizing DCTB (trans-2-[3(4-tert-butylphenyl)-2-methyl-2-propenyl]malononitrile) as matrix. UV-Vis absorption spectroscopy (UV-Vis) were recorded on a Lambda 750S UV-Vis spectrophotometer with dilute solution in chloroform or film. Electrochemical cyclic voltammetry (CV) was tested by a CHI660D electrochemical workstation at room temperature. The geometry of F-2PDI and F-2PDI-4F was optimized via Gaussian 09 software using density functional theory (DFT) at $\omega\text{B97X-D/6-31G(d,p)}$ level to provide rational and convincing theoretical results. The hexyl side chains of F-2PDI and F-2PDI-4F were replaced by methyl groups to simplify the calculation. Atomic force microscopy (AFM) measurement was conducted on a Bruker Multimode 8 in tapping mode. Transmission electron microscopy (TEM) measurement was conducted on a Talos L120C G2 from Thermo Fisher Scientific. The characterization of GIWAXS for the blend films was obtained from the Advanced Light Source (Lawrence Berkeley National Laboratory) on beamline 7.3.3. The incident angle and the beam energy were 0.16° and 10 keV, respectively. The samples were spin-coated on the Si/PEDOT:PSS substrates in optimized conditions.

2. Synthesis



Scheme S1. Synthetic route of F-2PDI-4F.

The F-2PDI was synthesized according to the reference.^{1, 2}

Synthesis of PDI-2F. The mixture solution of **PDI-2Cl** (1.00 g, 1.30 mmol) and KF (8.74 mmol) in 80 mL dry DMF was heated to 160 °C and kept stirring for 0.5 h, followed by the addition of 18-crown-6 (0.17 g, 0.65 mmol). The solution was kept vigorous stirring at 160 °C for 8 h. The reaction solution was cooled to room temperature and then poured into 1 L H₂O. After filtration, the precipitate was washed by water. The crude product was purified by silica gel column chromatography column chromatography on silica gel (petroleum ether:CH₂Cl₂, 1:1 to 1:2 v/v) to afford **PDI-2F** (267mg, yield: 28%.) as a red solid. ¹H NMR (400 MHz, CDCl₃) δ: 8.65 (m, 4H), 8.48 (m, 2H), 5.24- 5.12 (m, 2H), 2.31-2.17 (m, 4H), 1.85 (m, 4H), 1.35-1.19 (m, 24H), 0.83 (m, 12H). ¹³C NMR (100 MHz, CDCl₃) δ: 164.59, 163.76, 162.73, 133.89, 130.84, 130.14, 128.56, 126.03, 123.77, 123.04, 122.73, 117.13, 55.16, 32.39, 31.85, 29.85, 26.72, 22.69, 14.17. ¹⁹F NMR (376 MHz, CDCl₃) δ: -92.31 (s). MS (MALDI-TOF) m/z: Calculated for C₄₆H₅₂F₂N₂O₄, 735.39; Found, 735.27.

Synthesis of PDI-2F-Br. Bromine (10.66 g, 13.60 mmol) was added slowly **PDI-2F** (1.00 g, 0.14 mmol) in 60 mL dichloromethane. The mixture solution was stirred in

dark at room temperature for 5 h. The excess of bromine was quenched by aqueous Na₂SO₃ solution, followed by the extraction of dichloromethane. The organic phase was dried by anhydrous Na₂SO₄ and the solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel (petroleum ether:CH₂Cl₂, 1:1 v/v) to give **PDI-2F-Br** (0.95 g, yield: 86%) as a red solid. ¹H NMR (400 MHz, CDCl₃) δ: 9.55 (d, *J* = 8.2 Hz, 1H), 8.91 (s, 1H), 8.68 (s, 1H), 8.48 (s, 2H), 5.23-5.09 (m, 2H), 2.30-2.17 (m, 4H), 1.91-1.79 (m, 4H), 1.39-1.19 (m, 24H), 0.84 (m, 12H). ¹³C NMR (100 MHz, CDCl₃) δ: 164.30, 163.51, 162.64, 160.60, 158.09, 137.95, 137.33, 134.53, 134.02, 133.56, 132.73, 132.56, 130.70, 129.56, 129.00, 128.71, 127.80, 126.10, 125.09, 124.22, 123.09, 121.86, 121.32, 116.83, 115.94, 55.37, 55.17, 32.40, 32.33, 31.85, 31.82, 26.71, 26.88, 22.69, 14.17. ¹⁹F NMR (376 MHz, CDCl₃) δ: -94.57 (s), -94.76 (s). MS (MALDI-TOF) *m/z*: Calculated for C₄₆H₅₁F₂N₂O₄Br, 813.30; Found, 813.26.

Synthesis of IDTT-2PDI-4F: IDTT-di-Tin (0.22g, 0.16 mmol), PDI-2F-Br (0.30g, 0.37 mmol), Pd₂(dba)₃ (6.6mg, 0.006 mmol) and P(*o*-Tol)₃ (7.8 mg, 0.026 mmol) were dissolved in 15 mL toluene under argon. Then, the mixture was kept reflux overnight. After cooling to room temperature, the crude product was extracted with dichloromethane and washed with water. The organic phase was dried by anhydrous Na₂SO₄ and the solvent was removed under vacuum. The crude product was purified by silica gel column chromatography (petroleum ether:CH₂Cl₂, 2:1 v/v), affording a black solid (0.32g, yield: 81%). ¹H NMR (400 MHz, CDCl₃) δ: 8.70 (m, 2H), 8.46 (m, 4H), 8.32 (m, 2H), 8.22 (m, 2H), 7.58 (s, 2H), 7.52 (s, 2H), 7.16 (d, *J* = 8.3 Hz, 8H), 7.10 (d, *J* = 8.3 Hz, 8H), 5.15 (m, 4H), 2.58 (m, 8H), 2.25 (m, 8H), 1.93-1.79 (m, 8H), 1.61 (m, 8H), 1.35-1.21 (m, 72H), 0.87-0.82 (m, 36H). ¹³C NMR (100 MHz, CDCl₃) δ: 163.97, 163.04, 160.37, 153.83, 146.84, 145.02, 144.20, 143.94, 142.39, 142.33, 139.92, 136.26, 135.55, 134.59, 130.43, 130.01, 128.76, 128.06, 125.47, 124.94, 121.76, 121.19, 117.56, 63.12, 55.09, 35.72, 32.38, 31.88, 31.84, 31.52, 29.38, 26.68, 22.76, 22.71, 14.24, 14.22, 14.18. ¹⁹F NMR (376 MHz, CDCl₃) δ -94.38, -94.75, -95.04, -95.45. MS (MALDI-TOF) *m/z*: Calculated for C₁₆₀H₁₇₄F₄N₄O₈S₄, 2484.22; Found, 2484.65.

Synthesis of F-2PDI-4F: IDTT-2PDI-4F (0.23g, 0.09 mmol) was dissolved in 60 mL dry toluene, followed by the addition of a solution of FeCl₃ (0.22g, 0.139 mmol) in 0.2 mL CH₃NO₂. The mixture is heated to 45 °C and kept stirring for 30 min. After cooling to room temperature, the product was poured into methanol. The crude product was filtrated and washed with methanol. The crude product was purified by silica gel column chromatography (petroleum ether:CH₂Cl₂, 2:1 v/v), yielding a deep green solid (0.16g, 70%). ¹H NMR (400 MHz, CDCl₃) δ: 9.97 (br, 2H), 9.58 (br, 2H), 8.80 (br, 4H), 7.91 (s, 2H), 7.42 (d, 8H), 7.28 (d, 8H), 5.34 (m, 4H), 2.71-2.58 (m, 8H), 2.37 (m, 8H), 1.96 (m, 8H), 1.68 (m, 8H), 1.44-1.25 (m, 72H), 0.86 (m, 36H). ¹³C NMR (125 MHz, CDCl₃) δ 164.97, 164.20, 163.11, 154.71, 147.72, 147.29, 142.61, 142.64, 142.24, 149.75, 136.99, 136.57, 135.26, 131.33, 129.15, 128.19, 127.11, 124.50, 123.53, 122.90, 122.01, 118.15, 117.12, 68.13, 63.79, 55.48, 35.83, 32.57, 31.93, 31.88, 31.43, 29.31, 26.91, 26.83, 25.79, 2275, 22.74, 22.73, 14.22. ¹⁹F NMR (376 MHz, CDCl₃) δ -90.83. MS (MALDI-TOF) *m/z*: Calculated for C₁₆₀H₁₇₀F₄N₄O₈S₄, 2480.18; Found, 2480.07.

Table S1. The screening D/A ratio and additives of PTB7-Th:F-2PDI based devices.

PTB7-Th:F-2PDI	V_{oc} (V) ^a	J_{sc} (mA cm ⁻²) ^a	FF (%) ^a	PCE (%) ^a
D:A = 1:0.8	1.00±0.01	10.20±0.03	49.0±0.4	4.96±0.08 (5.03)
D:A = 1:1.0	1.00±0.01	10.50±0.02	52.0±0.1	5.46±0.02 (5.48)
D:A = 1:1.2	1.00±0.01	11.67±0.02	51.0±0.3	5.95±0.03 (5.98)
D:A = 1:1.5	1.00±0.01	11.00±0.05	50.8±0.4	5.59±0.03 (5.62)
As-cast	1.00±0.01	11.67±0.02	51.0±0.3	5.95±0.03 (5.98)
+1.0 vt% CN	1.01±0.01	12.91±0.02	51.7±0.6	6.74±0.07 (6.80)
+2.0 vt% CN	1.02±0.01	13.22±0.13	53.9±0.9	7.27±0.14 (7.44)
+3.0 vt% CN	1.02±0.01	13.14±0.12	51.2±0.9	6.86±0.12 (6.95)
+1.0 vt% DIO	1.00±0.01	11.96±0.02	51.0±0.3	6.10±0.03 (6.13)

^aThe average values and standard deviations in parentheses are statistical data from ten independent cells. CN represents 1-chloronaphthalene and DIO represents 1,8-diiodooctane.

Table S2. The screening D/A ratio and additives of PTB7-Th:F-2PDI-4F based devices.

PTB7-Th:F-2PDI-4F	V_{oc} (V) ^a	J_{sc} (mA cm ⁻²) ^a	FF (%) ^a	PCE (%) ^a
D:A = 1:1.0	0.94±0.01	9.76±0.04	45.0±0.2	4.13±0.02 (4.15)
D:A = 1:1.5	0.94±0.01	10.92±0.12	44.1±0.1	4.53±0.08 (4.60)
D:A = 1:2.0	0.93±0.02	9.55±0.08	43.9±0.5	3.90±0.10 (3.96)
As-cast	0.94±0.01	10.92±0.12	44.1±0.1	4.53±0.08 (4.60)
+2.0 vt% CN	0.95±0.01	11.90±0.18	46.0±0.4	5.20±0.04 (5.27)

^aThe average values and standard deviations in parentheses are statistical data from ten independent cells.

Table S3. The screening D/A ratio and additives of PBDB-T:F-2PDI based devices.

PBDB-T:F-2PDI	V_{oc} (V) ^a	J_{sc} (mA cm ⁻²) ^a	FF (%) ^a	PCE (%) ^a
D:A = 1:0.8	1.03±0.01	11.22±0.04	58.2±0.2	6.73±0.02 (6.75)
D:A = 1:1.0	1.02±0.01	11.48±0.02	56.3±0.1	6.29±0.03 (6.33)
As-cast	1.03±0.01	11.22±0.04	58.2±0.2	6.73±0.02 (6.75)
+0.5 vt% DIO	1.03±0.01	11.23±0.04	60.4±0.5	6.99±0.06 (7.07)
+1.0 vt% DIO	1.03±0.01	10.95±0.06	60.2±0.4	6.79±0.05 (6.85)

^aThe average values and standard deviations in parentheses are statistical data from ten independent cells.

Table S4. The screening D/A ratio, additives and TA of PBDB-T:F-2PDI-4F based devices.

PBDB-T:F-2PDI-4F	V_{oc} (V) ^a	J_{sc} (mA cm ⁻²) ^a	FF (%) ^a	PCE (%) ^a
D:A = 1:0.6	1.00±0.01	12.99±0.03	65.2±0.4	8.47±0.06 (8.52)
D:A = 1:0.8	1.00±0.01	13.28±0.03	64.7±0.1	8.59±0.04 (8.61)
D:A = 1:1.0	1.00±0.01	12.75±0.03	63.5±0.6	8.09±0.04 (8.11)
D:A = 1:1.2	1.00±0.01	12.91±0.02	62.0±0.1	8.01±0.02 (8.03)
As-cast	1.00±0.01	13.28±0.03	64.7±0.1	8.59±0.04 (8.61)
+0.5 vt% CN	1.00±0.01	11.50±0.02	63.9±0.6	7.06±0.07 (7.11)
+1.0 vt% CN	1.01±0.01	9.71±0.18	50.9±0.6	4.99±0.04 (5.03)
+0.5 vt% DIO	1.00±0.01	13.42±0.07	66.1±0.8	8.96±0.10 (9.05)
+1.0 vt% DIO	1.00±0.01	13.51±0.09	64.5±0.7	8.72±0.09 (8.79)
w/o TA	1.00±0.01	13.38±0.06	66.6±0.6	8.92±0.05 (9.03)
90°C TA	1.00±0.01	13.54±0.05	65.7±0.7	8.90±0.09 (8.98)

^aThe average values and standard deviations in parentheses are statistical data from ten independent cells. TA represents thermal annealing for 10 min.

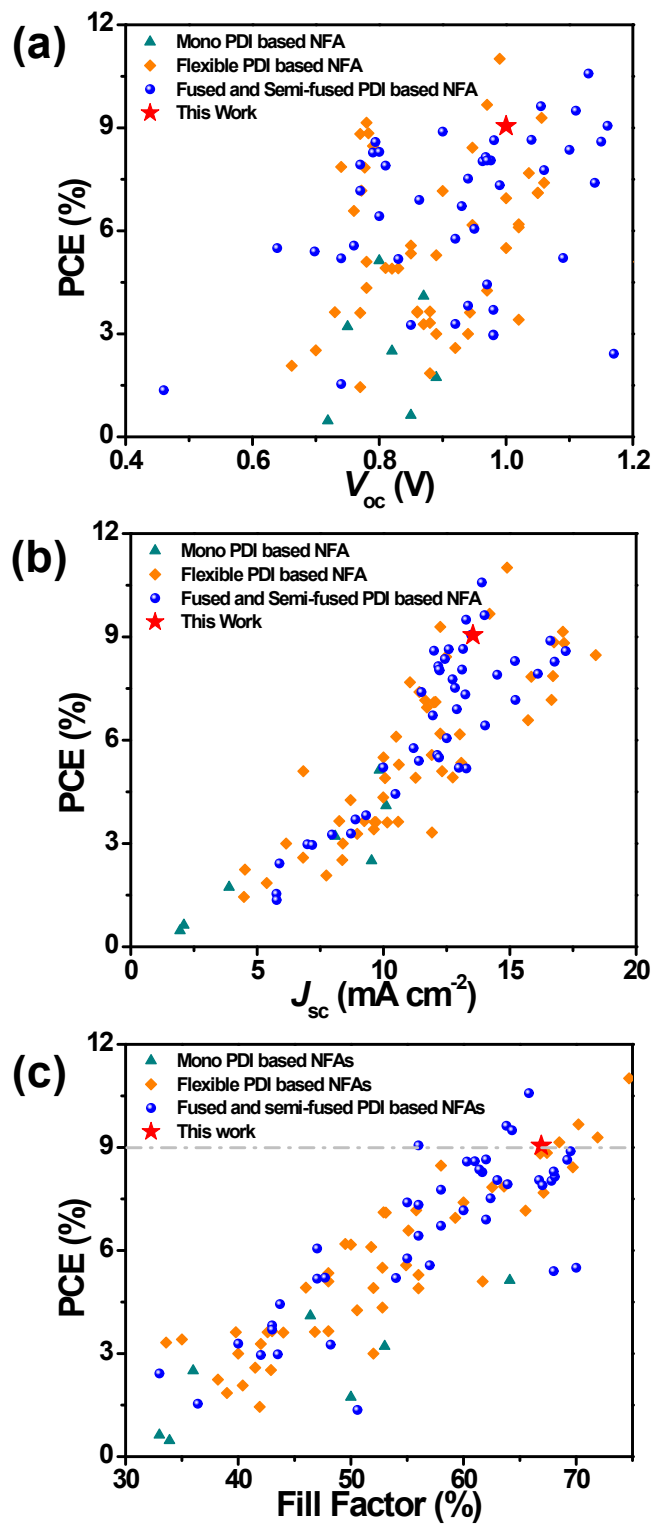


Fig. S1. Plots of (a) V_{oc} , (b) J_{sc} and (c) FF versus PCEs of the reported efficient OSCs with PDI-based NFAs¹⁻⁵⁴.

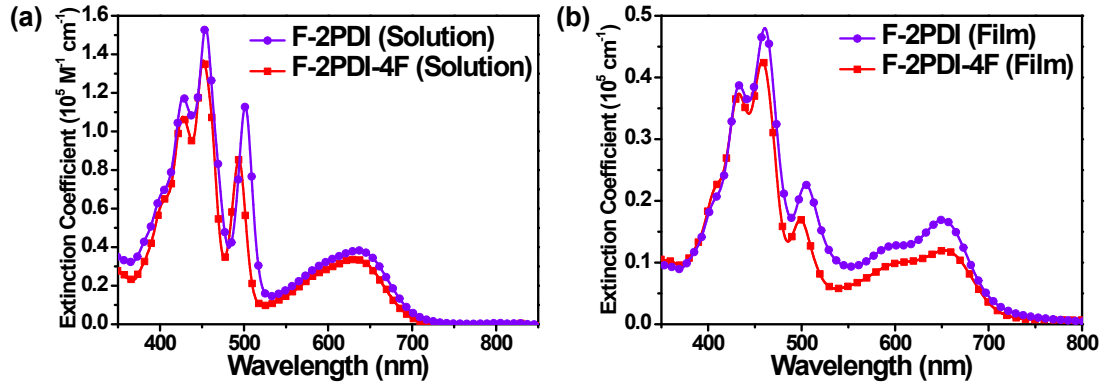


Fig. S2. UV-vis absorption spectra of F-2PDI and F-2PDI-4F (a) in chloroform solution and (b) in film.

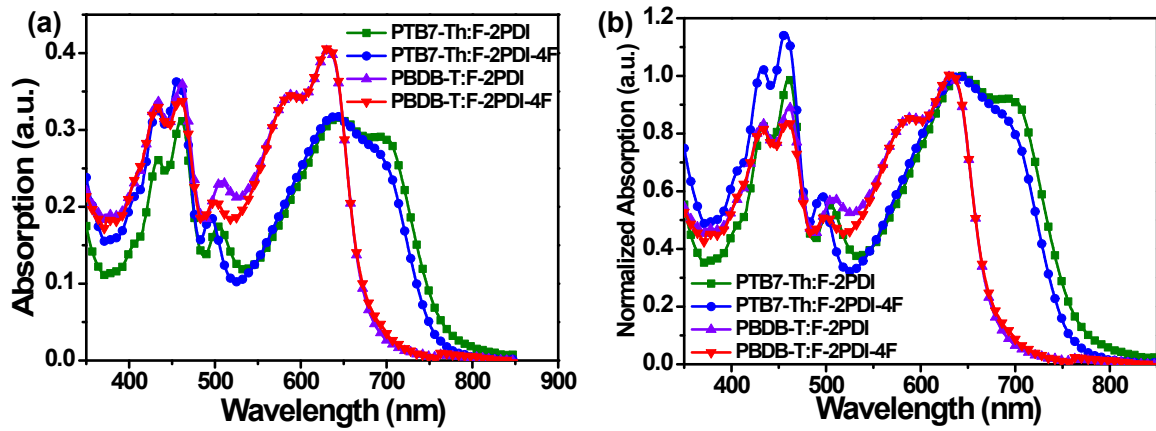


Fig. S3. (a) Absorption spectra and (b) normalized absorption spectra of varied active layers.

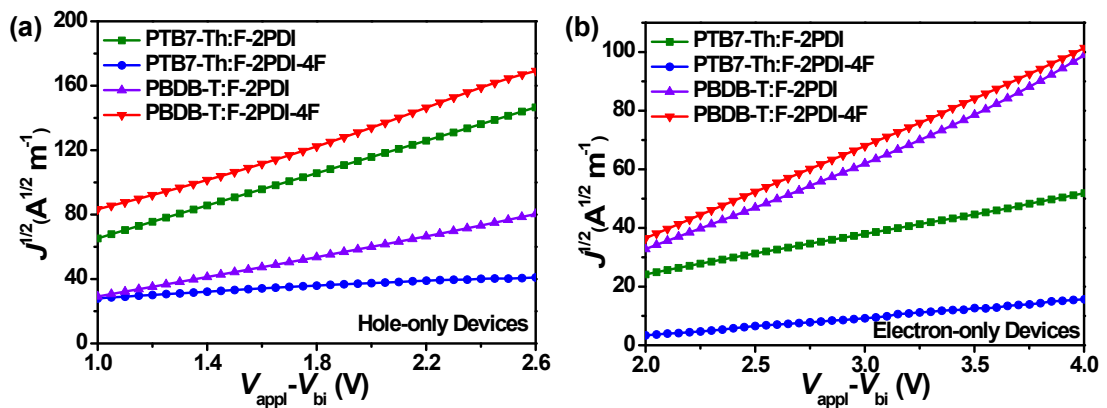


Fig. S4. Plots of $J^{1/2}$ as a function of $V_{\text{appl}} - V_{\text{bi}}$ for the (a) hole-only devices and (b) electron-only devices based on varied active layers.

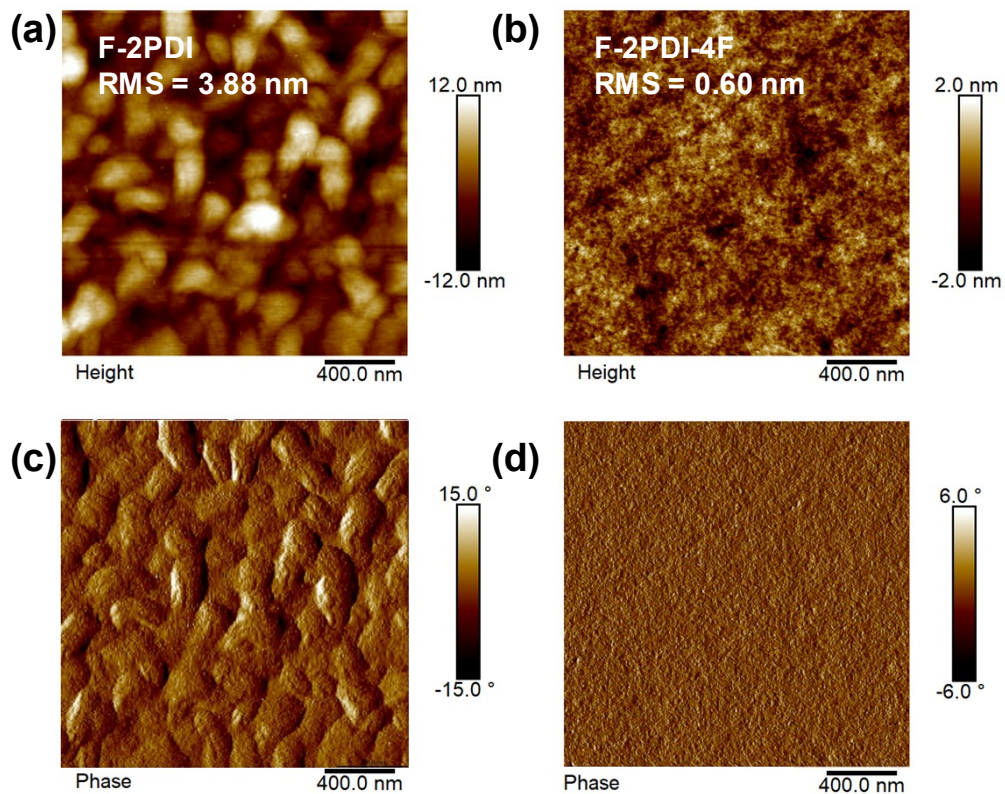


Fig. S5. Tapping-mode AFM height and phase images ($2 \times 2 \mu\text{m}$) of neat films based on F-2PDI (a, c), F-2PDI-4F (b, d).

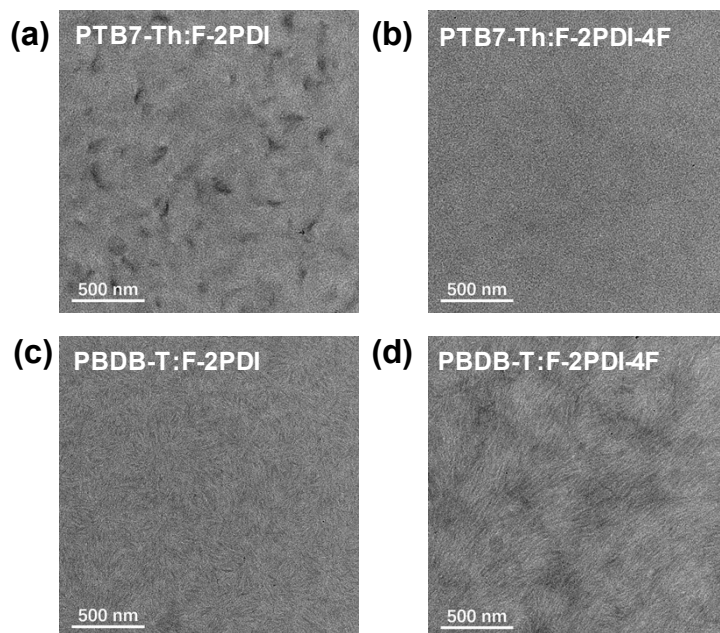


Fig. S6. TEM images ($2 \times 2 \mu\text{m}$) of blend films based on (a) PTB7-Th:F-2PDI, (b) PTB7-Th:F-2PDI-4F, (c) PBDB-T:F-2PDI, and (d) PBDB-T:F-2PDI-4F, respectively.

Table S5. Characteristic length scale of packing phenomenon in blend films of PTB7-Th:F-2PDI, PTB7-Th:F-2PDI-4F, PBDB-T:F-2PDI and PBDB-T:F-2PDI-4F, respectively.

active layer	Lamella Packing			π - π Stacking		
	(100) distance [Å]	FWHM[Å ⁻¹]	CCL [Å]	π - π distance [Å]	FWHM[Å ⁻¹]	CCL [Å]
PTB7-Th:F-2PDI	21.9 ^a	0.127	44.4	3.87 ^b	0.415	13.6
PTB7-Th:F-2PDI-4F	19.0 ^b	0.0773	73.2	3.90 ^b	0.442	12.8
PBDB-T:F-2PDI	21.5 ^a	0.0431	131	3.70 ^b	0.255	22.2
PBDB-T:F-2PDI-4F	20.3 ^a	0.0419	135	3.61 ^b	0.203	27.8

FWHM represents full-width at half maximum, CCL represents crystal coherence length, ^a Represents In-plane ^b represents Out-of-Plane.

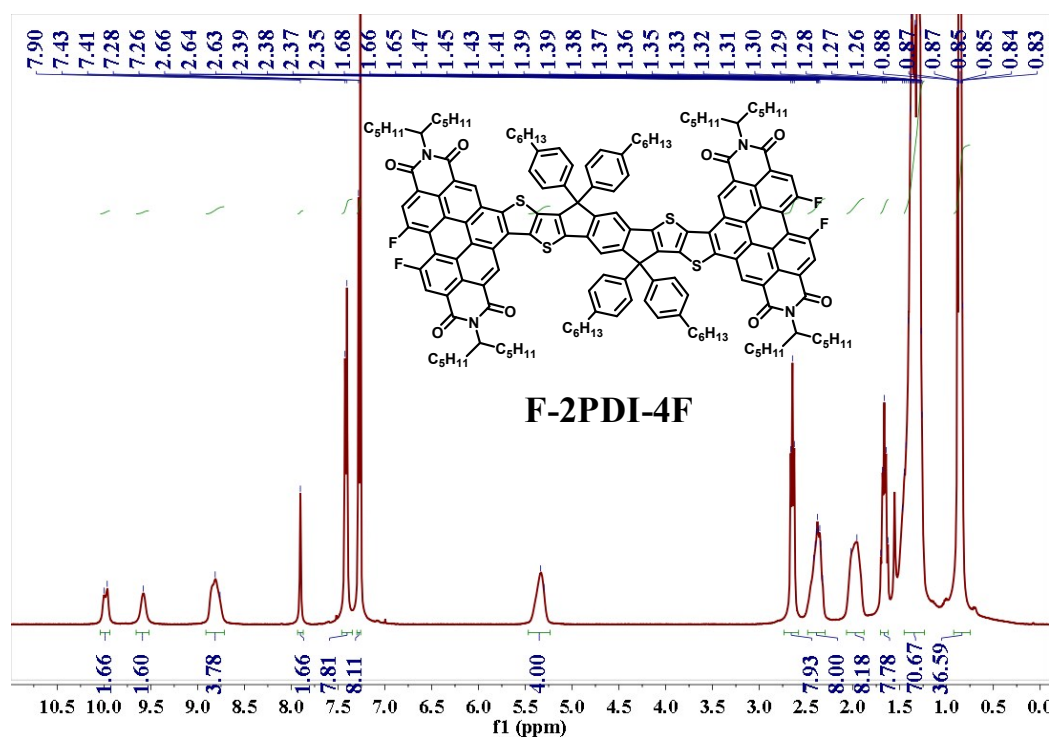


Fig. S7. ¹H NMR spectrum of F-2PDI-4F.

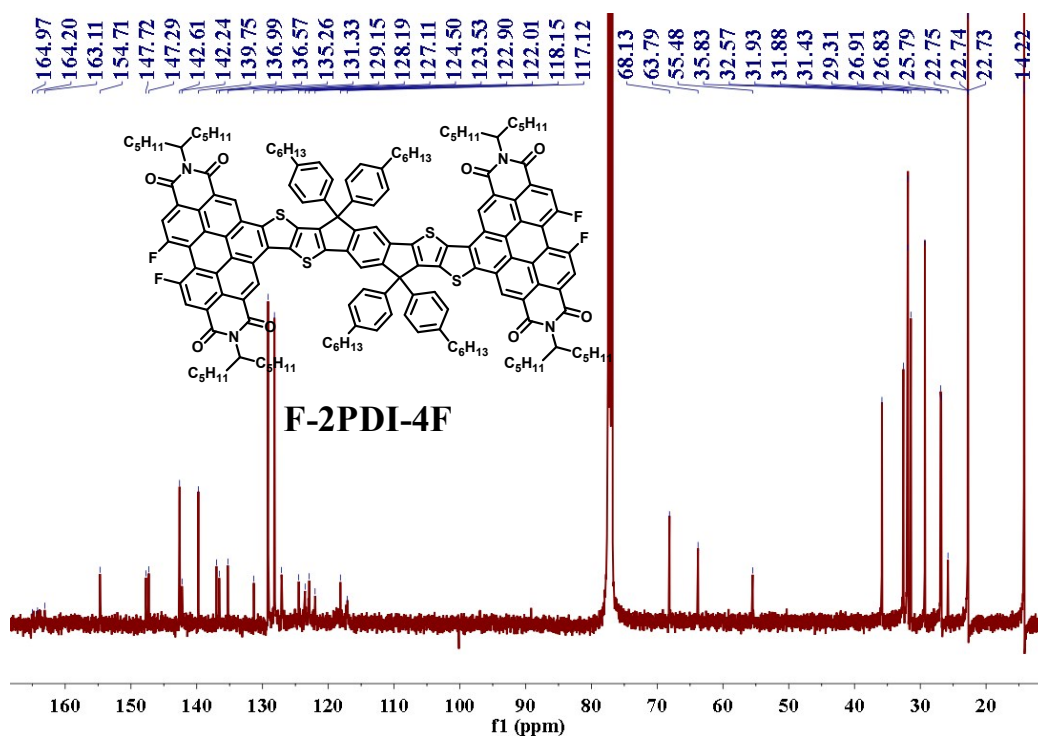


Fig. S8. ^{13}C NMR spectrum of F-2PDI-4F.

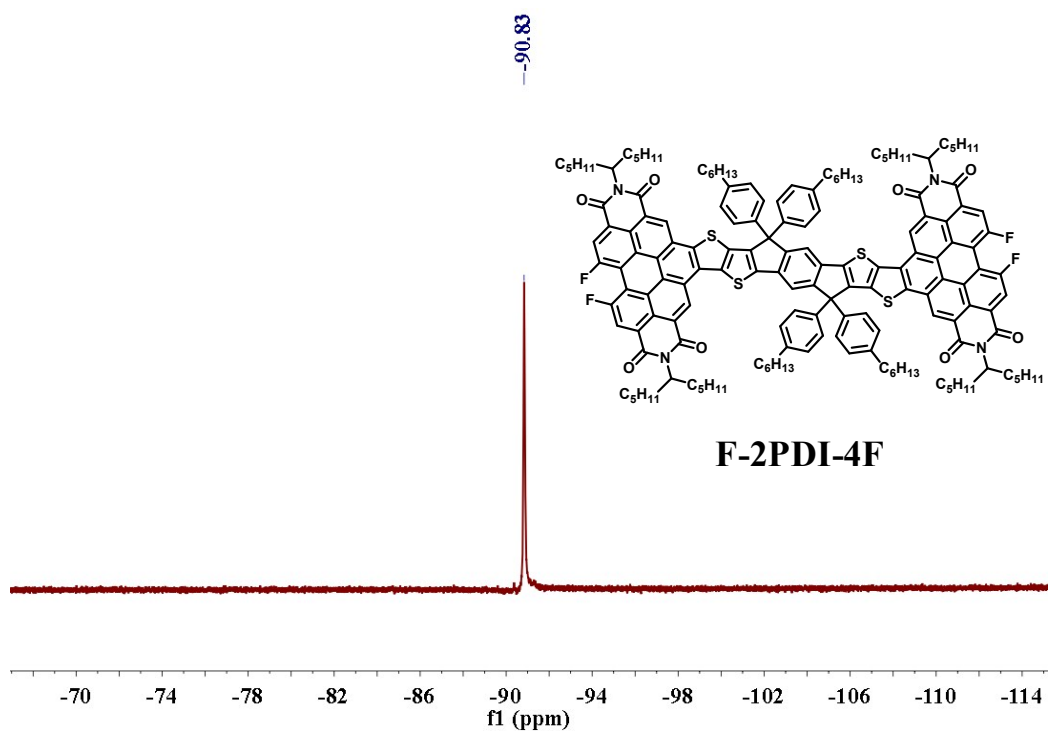


Fig. S9. ^{19}F NMR spectrum of F-2PDI-4F.

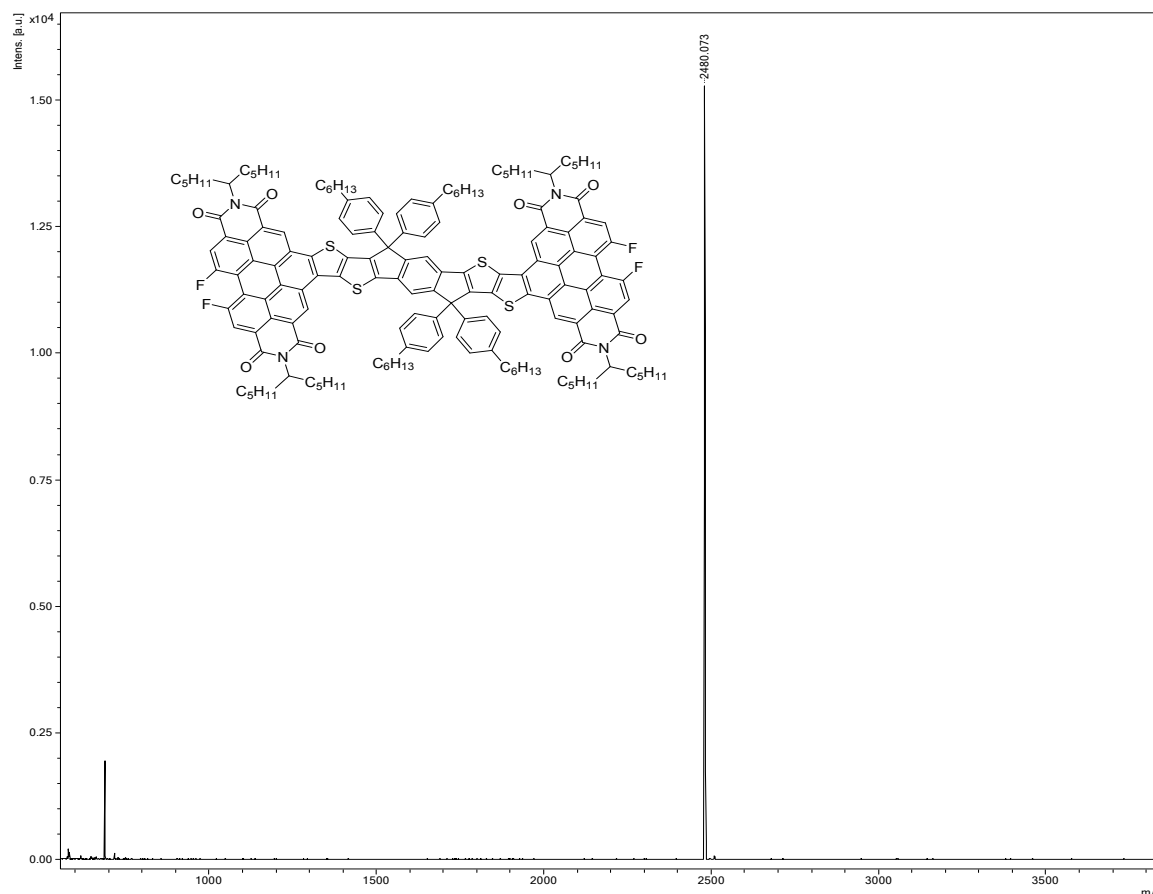


Fig. S10. Maldi-Tof-MS spectrum of F-2PDI-4F.

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