Supporting Information

Significantly enhanced thermal stability from a new kind of n-type organic semiconductor DFA4: a fully fused F8IC

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1. General Experimental Details

All reactions were performed under nitrogen atmosphere. All solvents were purified and dried from appropriate drying agents using standard techniques prior to use. Reagents available from commercial sources were used without further purification unless otherwise stated. Flash chromatography was performed by using Silicycle Silica Flash P60 (particle sizes of 40-63 µm, pore size of 60 Å) silica gel. Silica gel on thin layer chromatography-polyethylene terephthalate (TLC-PET) foils was used for TLC. Di-brominated fused tris(thienothiophene) (1), 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (**IN2F**) and reference material **F8IC** were purchased from Derthon Optoelectronic Materials Science Technology Co., Ltd. All new compounds were characterized by NMR spectroscopy on a Bruker Avance III Ultrashield Plus instrument (400 MHz), the spectra were referenced on the internal standard tretramethylsilane (TMS). Matrix-Assisted Laser Desorption/Ionization Time of Flight Mass Spectrometry (MALDI-TOF-MS) data of **DFA4** was collected by using a Bruker ultrafleXtreme MALDI-TOF/TOF mass spectrometer

2. Synthetic Protocols and Characterizations



Scheme S1. Synthesis of fully fused acceptor DFA4.



Di-brominated dicarbaldehyde of fused tris(thienothiophene) (2): The aldehyde compound **2** was synthesized according to previous report^[1] with minor variation. To a solution of dibrominated fused tris(thienothiophene) (**1**, 5.00 g, 4.03 mmol) in THF (120 mL) at -50 °C, a solution of lithium diisopropylamide (LDA) (9.1 mL, 2 M in THF, 18.14 mmol) was added dropwise. The mixture was stirred for 30 min at -50 °C, and then warmed to room temperature (RT) for overnight. After the mixture was cooled to 0 °C, excess amount of anhydrous DMF (5 mL) was added in one portion and stirred at the same temperature for 30 min. Then the mixture was allowed to warm to RT for 1 h with water (200 mL) added, and extracted with chloroform (3×100 mL). The combined organic phase were dried under Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was washed with methanol and filtered, the solid was further purified by column chromatography over SiO₂ using petroleum either (PE)/chloroform (v/v = 2/1) as an eluent, affording pure product as a brown powder (3.24 g, yield: 62%). ¹H NMR (400 MHz, CDCl₃, δ ppm): 9.94 (s, 2H), 7.14-7.08 (m, 16H), 2.57-2.53 (t, *J* = 7.6 Hz, 8H), 1.55-

1.53 (m, 8H), 1.31-1.28 (m, 24H), 0.87 (t, J = 6.4 Hz, 12H). ¹³C NMR (101 MHz, CDCl₃, δ ppm): 182.52, 151.09, 147.86, 145.03, 142.91, 142.55, 138.46, 138.35, 136.87, 136.83, 135.66, 129.11, 127.59, 113.76, 62.67, 35.58, 31.65, 31.14, 29.09, 22.54, 14.03.



Fully-fused acceptor DFA4:

Step 1: To a solution of the aldehyde compound **2** (3.00 g, 2.32 mmol) in DMF (50 mL), sodium azide was (1.51 g, 23.2 mmol) added in portions. After the addition, this mixture was heated to 80 °C for 8 h. Then water (200 mL) was added and extracted with chloroform (3×100 mL). The combined organic phase were repeatedly washed with water (6×200 mL), dried with Na₂SO₄, filtered, and concentrated under reduced pressure. The resulting organic azide was obtained as a brown oil (3.12 g, crude product) and used without further purification.

Step 2: In a round flask, a solution of the $SnCl_2$ (1.76 g, 9.28 mmol) in methanol (25 mL) was cooled to 0 °C. A solution of the organic azide (3.12 g, crude product) that obtained in previous step (in THF, 20 mL) was added dropwise, the reaction was exothermic, releasing N₂ gas (bubbles). The cooling bath was then removed and the mixture was stirred for 4 h at RT. The reaction was quenched with brine (250 mL) and the aqueous phase was extracted with chloroform (3×150 mL). The organic phase was collected, dried over Na₂SO₄, concentrated under reduced pressure, and the amino-aldehyde (2.69 g, crude product) was obtained as a brown oil and subjected to the next step immediately without further purification.

Step 3: In a pre-dried round flask, the amino-aldehyde obtained in previous step (2.69 g, crude product) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (2.67 g, 11.6 mmol) were dissolved in chloroform (30 mL). To the mixuture, anhydrous pyridine (0.5 mL) was added. Then the reaction mixture was heated to 70 °C and stirred for 48 h under inner atmosphere. Next, the mixture was concentrated under reduced pressure, washed with methanol and filtered. The solid was collected and purified by column chromatography over SiO₂ using PE/chloroform (v/v = 1/3) as an eluent. The solvent was removed by rotary evaporation,

affording final product **DFA4** as a blue-brownish solid (241 mg, yield: 6.40% of total three steps). ¹H NMR (400 MHz, CDCl₃, δ ppm): 8.87 (s, 2H), 8.30-8.26 (m, 2H), 7.84-7.80 (m, 2H), 7.20-7.15 (m, 16H), 2.60 (t, J = 8.0 Hz, 8H), 1.63-1.57 (m, 8H), 1.35-1.25 (m, 24H), 0.87 (t, J = 6.8 Hz, 12H). ¹³C NMR (101 MHz, CHCl₃, δ ppm): 158.07, 156.49, 152.31, 151.35, 150.66, 148.50, 145.93, 143.01, 139.94, 138.77, 138.58, 137.01, 136.90, 136.00, 134.93, 131.85, 129.13, 128.41, 127.74, 123.13, 116.23, 116.02, 113.13, 112.94, 111.31, 75.16, 62.56, 35.63, 31.67, 31.18, 29.73, 29.13, 22.57, 14.05. ¹⁹F (¹H decoupled) NMR (376 MHz, CDCl₃, δ ppm): -124.870 (d, J = 18.80 Hz, 2F), -131.12 (d, J = 18.80 MHz, 2F). MALDI-TOF-MS: calcd. for C₉₄H₇₄F₄N₆S₆ [m/z]: 1555.427, found 1555.367.

3. Density Functional Theory (DFT) Calculations

All optimizations were done at PBE0/def2-SVP level with Grimme's D3BJ ^[2] empirical dispersion correction. Then the vertical excited states are calculated at optimally-tuned ^[3] LC- ω HPBE/def2-SVP^[4] level with Gaussian16 program. The electron-hole analyses of excited stated and UV-Vis spectra simulation were performed using Multiwfn program^[5].



Figure S1. Simulated absorption spectra of DFA4 (left) and F8IC (right)

| Table S1. | Excited | states wit | h oscillatoi | strength | greater | than | 0.2 | for | F8IC | and | DF | A4 |
|-----------|---------|------------|--------------|----------|----------|------|-----|-----|------|-----|----|-----------|
| | | | | <u> </u> | <u> </u> | | | | | | | |

| | ~ | Transition Wave length Osc. | | Orbital composition | |
|----------|-------|-----------------------------|--------|---------------------|--------------------------|
| Molecule | State | Energy (eV) | (nm) | strength | Orbital composition |
| F8IC | 1 | 1.8699 | 663.04 | 2.8631 | H-L:0.875; H1-L1:0.081 |
| DFA4 | 1 | 1.9994 | 620.12 | 1.3535 | H-L:0.705; H1-L1:0.169 |
| | 3 | 2.4866 | 498.62 | 1.003 | H2-L:0.319; H-L2:0.15 |
| | 14 | 3.4778 | 356.5 | 0.4365 | H11-L:0.173; H9-L1:0.165 |



Figure S2. Calculated HOMO and LUMO distribution and energy levels of DFA4 and F8IC



Figure S3. Calculated hole-electron distribution of **DFA4** and **F8IC**, where light blue area stands for hole and orange region represents electron.

Table S2. The transition properties (energy, oscillator strength, and orbital composition) of first30 excited singlet states of F8IC and DFA4.

| Molecule St | <u>.</u> | Transition | Wave length | Osc. | Orbital composition | |
|-------------|----------|------------------------|-------------|--------|-----------------------|--|
| | State | lecule State Energy | | (nm) | strength | |
| DFA4 | 1 | 1.9994 | 620.12 | 1.3535 | H-L:0.705;H1-L1:0.169 | |

| | 2 | 2.1489 | 576.96 | 0.0001 | H-L1:0.511;H1-L:0.261 |
|------|----|--------|--------|--------|--------------------------|
| | 3 | 2.4866 | 498.62 | 1.003 | H2-L:0.319;H-L2:0.15 |
| | 4 | 2.619 | 473.41 | 0 | H-L1:0.299;H2-L1:0.284 |
| | 5 | 2.8074 | 441.63 | 0.1822 | H-L2:0.577;H2-L:0.109 |
| | 6 | 3.0114 | 411.72 | 0 | H16-L:0.408;H17-L1:0.373 |
| | 7 | 3.0116 | 411.69 | 0.0003 | H17-L:0.406;H16-L1:0.38 |
| | 8 | 3.0503 | 406.47 | 0.0002 | H3-L:0.153;H7-L:0.122 |
| | 9 | 3.1341 | 395.6 | 0.1662 | H-L2:0.142;H6-L:0.123 |
| | 10 | 3.2685 | 379.33 | 0.0019 | H-L3:0.31;H1-L:0.197 |
| | 11 | 3.3833 | 366.46 | 0.0001 | H5-L:0.213;H-L3:0.195 |
| | 12 | 3.394 | 365.3 | 0.0984 | H4-L:0.569;H5-L1:0.141 |
| | 13 | 3.4338 | 361.07 | 0.0005 | H5-L:0.351;H-L3:0.12 |
| | 14 | 3.4778 | 356.5 | 0.4365 | H11-L:0.173;H9-L1:0.165 |
| | 15 | 3.5396 | 350.28 | 0.0018 | H11-L1:0.226;H9-L:0.211 |
| | 16 | 3.555 | 348.76 | 0.0235 | H1-L1:0.243;H6-L:0.236 |
| | 17 | 3.5891 | 345.45 | 0.018 | H8-L:0.171;H6-L:0.111 |
| | 18 | 3.6353 | 341.05 | 0.1767 | H-L4:0.461;H3-L3:0.089 |
| | 19 | 3.7096 | 334.23 | 0.0018 | H3-L2:0.182;H2-L3:0.117 |
| | 20 | 3.7417 | 331.36 | 0.1216 | H2-L2:0.367;H3-L1:0.108 |
| | 21 | 3.7659 | 329.23 | 0.0009 | H3-L2:0.148;H7-L:0.127 |
| | 22 | 3.8504 | 322 | 0.1444 | H1-L:0.127;H8-L:0.127 |
| | 23 | 3.8792 | 319.61 | 0.0011 | H-L5:0.315;H12-L:0.173 |
| | 24 | 3.8856 | 319.08 | 0.0023 | H-L5:0.286;H4-L1:0.217 |
| | 25 | 3.9204 | 316.25 | 0.0212 | H13-L:0.315;H12-L1:0.133 |
| | 26 | 3.9298 | 315.5 | 0.0005 | H12-L:0.267;H4-L1:0.183 |
| | 27 | 3.9597 | 313.12 | 0.0007 | H1-L2:0.302;H3-L2:0.152 |
| | 28 | 3.9697 | 312.33 | 0.0261 | H5-L1:0.513;H4-L2:0.203 |
| | 29 | 4.0266 | 307.91 | 0.1849 | H1-L1:0.14;H13-L:0.114 |
| | 30 | 4.037 | 307.12 | 0.0031 | H6-L1:0.424;H5-L2:0.158 |
| F8IC | 1 | 1.8699 | 663.04 | 2.8631 | H-L:0.875;H1-L1:0.081 |
| | 2 | 2.3242 | 533.44 | 0.0001 | H-L1:0.785;H1-L:0.145 |

| 3 | 2.5715 | 482.15 | 0.0391 | H-L2:0.683;H1-L3:0.163 |
|----|--------|--------|--------|--------------------------|
| 4 | 2.6505 | 467.78 | 0.0001 | H-L3:0.664;H1-L2:0.183 |
| 5 | 2.6575 | 466.54 | 0 | H8-L:0.386;H7-L1:0.283 |
| 6 | 2.6576 | 466.53 | 0 | H7-L:0.359;H8-L1:0.288 |
| 7 | 2.8399 | 436.58 | 0.0002 | H1-L:0.555;H-L1:0.113 |
| 8 | 2.8902 | 428.98 | 0.1038 | H2-L:0.245;H6-L:0.241 |
| 9 | 2.9187 | 424.79 | 0 | H3-L:0.312;H5-L:0.157 |
| 10 | 3.0233 | 410.1 | 0.0568 | H2-L:0.445;H6-L:0.232 |
| 11 | 3.0318 | 408.95 | 0.0005 | H3-L:0.358;H5-L:0.252 |
| 12 | 3.0949 | 400.61 | 0.0315 | H8-L2:0.301;H7-L3:0.286 |
| 13 | 3.0962 | 400.44 | 0 | H8-L3:0.33;H7-L2:0.314 |
| 14 | 3.1037 | 399.48 | 0.1567 | H4-L:0.412;H1-L1:0.177 |
| 15 | 3.231 | 383.74 | 0.0036 | H1-L:0.327;H7-L:0.157 |
| 16 | 3.2317 | 383.65 | 0.025 | H-L4:0.528;H9-L:0.106 |
| 17 | 3.2939 | 376.41 | 0.0991 | H9-L:0.288;H-L4:0.265 |
| 18 | 3.3095 | 374.63 | 0.058 | H1-L1:0.269;H13-L:0.138 |
| 19 | 3.3131 | 374.22 | 0.0012 | H11-L:0.453;H9-L1:0.094 |
| 20 | 3.4137 | 363.2 | 0.0011 | H12-L:0.546;H6-L:0.049 |
| 21 | 3.4747 | 356.82 | 0 | H14-L:0.677;H15-L1:0.088 |
| 22 | 3.5221 | 352.02 | 0.0073 | H15-L:0.364;H13-L:0.295 |
| 23 | 3.5826 | 346.07 | 0.0001 | H5-L2:0.146;H1-L2:0.094 |
| 24 | 3.5989 | 344.5 | 0.094 | H6-L2:0.208;H5-L3:0.109 |
| 25 | 3.6131 | 343.15 | 0.0002 | H16-L:0.565;H2-L1:0.115 |
| 26 | 3.6379 | 340.81 | 0.0022 | H17-L:0.702;H16-L1:0.135 |
| 27 | 3.6563 | 339.09 | 0 | H1-L2:0.205;H2-L1:0.114 |
| 28 | 3.7001 | 335.08 | 0.0008 | H2-L1:0.29;H16-L:0.089 |
| 29 | 3.7054 | 334.6 | 0.0206 | H15-L:0.119;H18-L1:0.107 |
| 30 | 3.7351 | 331.94 | 0.0255 | H1-L3:0.275;H-L2:0.095 |

4. UV-Vis Spectroscopy

UV-Vis spectra of solution and thin films were recorded on a PerkinElmer LAMBDA 365 UV-Vis spectrophotometer.



Figure S4. Normalized UV-vis spectra of (a) chloroform solution and (b) thin film of F8IC and DFA4; (c) Photos of diluted solution (*ca.* 5×10^{-6} mol L⁻¹) of F8IC and DFA4.

5. Cyclic Voltammograms and Energy Level Diagram

Electrochemical measurements were performed with a CIH660e electrochemical workstation, using a glassy carbon button electrode as the working electrode, a platinum wire as the auxiliary electrode, and an Ag/Ag^+ glass electrode as the reference electrode. The Ag/Ag^+ reference electrode was calibrated using the ferrocene/ferrocenium (Fc/Fc⁺) redox couple. Fc/Fc⁺ is taken to be 4.8 eV relative to the vacuum level.^[6]



Figure S5. (a) Cyclic voltammograms of the DFA4 and F8IC; (b) Energy level diagram of organic semiconductors used in this work.

| Table S3. Summary | y of electrochemical | parameters of organic | semiconductors | used in this work. |
|-------------------|----------------------|-----------------------|----------------|--------------------|
|-------------------|----------------------|-----------------------|----------------|--------------------|

| Materials | $E_{\text{onset,ox}}^{[a]}$ [V] | E _{onset,re} ^[a] [V] | $\lambda_{ m onset}$ [nm] | $E_{\mathrm{opt}}^{[\mathrm{b}]}$ [V] | HOMO ^[c] (eV) | LUMO ^[d] (eV) |
|---------------------------|---------------------------------|---|---------------------------|---------------------------------------|-----------------------------|-----------------------------|
| PM7 ^[7] | / | / | 688 | 1.80 | -5.45 | -3.65 ^[d] |
| F8IC | 1.05 | -0.38 | 976 | 1.27 | -5.53 | -4.10 ^[e] |
| DFA4 | 1.08 | -0.60 | 886 | 1.40 | -5.56 | -3.88 ^[e] |

[a] Onset oxidation/reduction potentials of organic semiconductors;

[b] E_{opt} is derived from the absorption onset of the neat film: $E_{opt} = 1240/\lambda_{onset}$;

[c]
$$E_{\text{HOMO}} = -[E_{\text{onset, ox}} + (4.8 - E_{\text{Fc/Fc+}})] \text{ eV};$$

[d] $E_{\text{LUMO}} = (E_{\text{HOMO}} + E_{\text{opt}}) \text{ eV};$

[e] $E_{\text{LUMO}} = -[E_{\text{onset, re}} + (4.8 - E_{\text{Fc/Fc+}})] \text{ eV}.$

6. Contact Angle Measurements

Contact angle was measured by DSA-100 drop shape analyzer (KRÜSS Scientific).

The miscibility of two components in the blend can be estimated from the solubility parameters (δ) of each material, which can be calculated with equation below:

 $\delta = K \sqrt{\gamma}$

Where γ is the surface energy of the material, and K is the proportionality constant (K = 116 × 10³ m^{1/2})



Figure S6. Contact angle with deionized water and formamid of PM7, DFA4 and F8IC films

Table S4. Contact angle of neat films and miscibility paramaters of blend films.

| Sample | Contact A | ngle (aver.) (°) | Surface Energy (γ) | Solubility parameter (δ) | Absolute difference of δ |
|-----------------------|-----------|------------------|-----------------------|-----------------------------|---------------------------------|
| | Water | Formamide | (mN/m) | (×K) | (×K) |
| DFA4 | 90.5 | 61.3 | 38.8 | 6.23 | \ |
| F8IC | 104.5 | 80.5 | 25.6 | 5.06 | / |
| PM7 | 94.2 | 65.8 | 36.25 | 6.02 | \ |
| PM7:DFA4 | / | / | / | \ | 1.37 |
| PM7:F8IC | \ | \ | \ | \ | 0.93 |
| PM6:Y6 ^[8] | \ | \ | \ | \ | 0.11 |

7. Chemical- and Photo-stability Evaluation

The chemical- and photo-stability of DFA4 and F8IC were preliminaryly evaluated.

It can be seen in **Figure S7a,b,f**, after adding the enthanolamine (EA) into the solution of **F8IC** (THF:H₂O, 96:4 in v/v), the original colour of **F8IC** faded away immediately, indicating a quick decomposition; **DFA4** is not immune to the base as well, but the whole decomposition process took much longer than **F8IC**, indicating its highly enhanced chemical stability. As to the photostability tests, surprisingly that **F8IC** outperformed **DFA4**. After 6 hours exposure to the irradiation (100 mW cm⁻²), the absorption spectra of **F8IC** barely changed while those of **DFA4** exhibited obviou decay.

Overall, with the fully-fused structure, both the thermal and chemical stability of **DFA4** were significantly enhanced compared with **F8IC**. On the other hand, the photo-stability of **DFA4** decreased. The intrinsic mechanism of this anomaly is still under investigation.



Figure S7. (a,b) Normalized UV-Vis absorption spectra of F8IC and DFA4 before and after adding enthanolamine (EA) in THF:H₂O mixtures (96:4, v/v). The concentration of NFAs is *ca*. 3×10^{-5} mol/L, while that of EA is *ca*. 3×10^{-3} mol/L. (c,d) Normalized UV-Vis absorption spectra of F8IC and DFA4 films in air under different irradiation time (100 mW cm⁻²). (e) The diagram of time-dependent sun bleaching ratio of F8IC and DFA4. (f). The photo of NFA solution (THF:H₂O mixtures, 96:4, v/v) with/without adding EA.

8. Device Fabrication of OFETs and OPVs

OFETs Device fabrication: Bottom-gate bottom-contact OFET architecture was utilized for performance extraction. All the OFET devices were fabricated on SiO₂/Si wafers. The n-type heavily-doped Si and the above 300 nm SiO₂ were used as gate electrode and gate dielectric, respectively. The source-drain electrodes (Au/Cr, 27 nm/3 nm) with channel length of 5 µm and width of 1400 µm were prepared via photolithography processes. These substrates with source-drain electrodes were cleaned in acetone, deionized water, and ethanol, and then treated with octadecyltrichlorosilane (OTS) at 120 °C in vacuum for 3 h. In semiconductor thin film fabrication, polymers were dissolved in chloroform and stirred for 3 h to form solutions with a concentration of 10 mg/mL. The solutions were spin-coated on the prepared substrates at 2000 rpm for 60 s, followed by thermal treatment at 120 °C for 10 min. Both the spin coating and thermal annealing processes were carried out in nitrogen atmosphere.

OPVs Device fabrication: The BHJ solar cells were prepared on the glass substrates with tin-doped indium oxide (ITO, $15\Omega/sq$) on part of the surface and the effective area of each device is 0.1cm^2 . The entire cleaning process of the substrates can be divided into four sections. At first, the substrates were prewashed with detergent in an ultrasonic cleaning machine for 15 min to remove the stains. Then deionized water was used to wash the remaining detergent on the substrates. Followed by this, the substrates were cleaned by using acetone for 15 min in the ultrasonic bath. At last, isopropanol was applied to remove organic residues before immersing in an ultrasonic bath for 15 min. Next, the samples were dried with pressurized nitrogen before being exposed to a UV-ozone plasma for 20 min. A thin layer (~35nm) of PEDOT:PSS was spin cast onto the UV-treated samples, dried on the hot plate at 110 °C for 10 minutes, and then transferred into a dry nitrogen glovebox (< 3 ppm O₂).

All solutions were prepared in the glovebox. Optimized devices were obtained by dissolving the polymer donor and **DFA4** in chloroform with 0.5 vol% of 1-Chloronaphthalene. The as-prepared solutions were stirred 3 hours at room temperature before being cast. The effects of blend ratios and different post-conditions such as thermal annealing (TA) and solvent vapor annealing (SVA) on the device performance were also examined.

Next, the samples were dealt with optimized conditions. The active layers were spin-cast from the solutions of PM7:**DFA4**. Then each substrate was exposed to chloroform steam (which

was put into a glass Petri dish of 6 cm diameter) for 10 sec. Next, the PDINO, as the electron transporting layer, was spin-coated on the active layer on a speed of 2000 rpm from methanol solution. At the final period, the substrates were pumped down in high vacuum at a pressure of 2 \times 10⁻⁶ Torr, and Ag layer (100 nm) was thermally evaporated onto the active layer. Shadow masks were used to define the OSC active area (0.1 cm²) of the devices. Following electrode deposition process, samples underwent *J*–*V* testing.

The current density–voltage (J–V) characteristics of un-encapsulated photovoltaic devices were measured under N₂ using a Keithley 2400 source meter. An AAA class solar simulator (Enli Technology Co., Ltd. SS-X50R) with an AM 1.5 global filter operated at 100 mW cm⁻² was used to simulate the AM 1.5G solar irradiation. The illumination intensity was corrected by using a silicon photodiode with a protective KG5 filter calibrated by the National Institute of Metrology, China (NIM). The external quantum efficiency (EQE) was performed using certified IPCE equipment (QE-R, Enli Technology Co., Ltd).

9. Additional PV Device Performance Data

| | $V_{\rm OC}$ (V) | $J_{\rm SC}$ (mA cm ⁻²) | FF (%) | PCE _{ave} (%) | PCE _{max} (%) |
|----------|------------------|-------------------------------------|----------|------------------------|------------------------|
| PM7:DFA4 | 0.87±0.01 | 13.2±0.1 | 65.8±0.8 | 7.58±0.15 | 7.73 |
| PM7:F8IC | 0.78±0.01 | 24.4±0.2 | 62.6±1.5 | 11.89±0.29 | 12.34 |

Table S5. Photovoltaic properties of the optimized PM7:DFA4 and PM7:F8IC devices.



Figure S8. (a) J-V curves of BHJ solar cells made with PM7:DFA4 and PM7:F8IC.

Table S6. Donor-Acceptor ratio dependence for PM7:DFA4 devices, treated by 120 °C thermal annealing. Performance includes standard deviation across at least 8 devices. (CN =1-Chloronaphthalene)

| D:A ratio | $V_{\rm OC}$ (V) | J _{SC} (mA | FF (%) | PCE _{ave} (%) | $PCE_{max}(\%)$ |
|-----------|------------------|---------------------|----------|------------------------|-----------------|
| (w/w) | | cm ⁻²) | | | |
| 1:1.1 | 0.89±0.0 | 7.8±0.1 | 61.3±0.6 | 4.24±0.07 | 4.35 |

| 1:1.3 | 0.89±0.0 | 6.9±0.1 | 64.2±0.3 | 3.96±0.03 | 4.01 |
|----------------|----------|---------|----------|------------|------|
| 1:1.6 | 0.89±0.0 | 6.5±0.1 | 64.5±2.6 | 3.73±0.17 | 3.88 |
| 1:1.3+0.75% CN | 0.9±0.0 | 8.2±0.1 | 67.1±0.7 | 4.94±0.131 | 5.13 |

Table S7. Annealing temperature dependence for PM7:DFA4 devices with D/A ratio at 1:1 and doped with 0.75% of CN. Performance includes standard deviation across at least 8 devices.

| TA temperature | $V_{\rm OC}\left({ m V} ight)$ | J _{SC} (mA cm ⁻²) | FF (%) | PCE _{ave} (%) | PCE _{max} (%) |
|----------------|--------------------------------|---|----------|------------------------|------------------------|
| 120 °C | 0.91±0.00 | 11.1±0.1 | 58.8±0.7 | 5.92±0.11 | 6.07 |
| 130 °C | 0.90±0.00 | 11.4±0.1 | 58.7±1.5 | 6.05±0.16 | 6.19 |
| 140 °C | 0.90±0.00 | 11.7±0.1 | 59.9±0.7 | 6.31±0.15 | 6.46 |
| 150 °C | 0.89±0.00 | 11.6±0.1 | 60.3±0.4 | 6.22±0.03 | 6.26 |

Table S8. Solvent vapor annealing (SVA) condition dependence for PM7:DFA4 devices. Performance includes standard deviation across at least 8 devices. Device fabrication condition is based on previous optimum protocol.

| SVA duration | $V_{\rm OC}$ (V) | J _{SC} (mA cm ⁻²) | FF (%) | PCE _{ave} (%) | PCE _{max} (%) |
|------------------|------------------|---|----------|------------------------|---------------------------|
| TA only (120 °C) | 0.90±0.00 | 10.2±0.1 | 62.3±0.8 | 5.75±0.1 | 5.88 |

| 10s SVA+TA | 0.89±0.00 | 11.5±0.1 | 66.8±0.7 | 6.82±0.11 | 6.94 |
|------------|-----------|----------|----------|-----------|------|
| 30s SVA+TA | 0.88±0.00 | 10.1±0.3 | 69.2±0.4 | 6.12±0.2 | 6.32 |
| 60s SVA+TA | 0.90±0.00 | 7.4±0.2 | 67.0±1.2 | 4.46±0.17 | 4.60 |

Table S9. Optimization of solvent additive at various concentrations. Performance includes standard deviation across at least 8 devices. Device fabrication condition is based on previous optimum protocol.

| Additive vol% | $V_{\rm OC}$ (V) | $J_{\rm SC}~({ m mA~cm^{-2}})$ | FF (%) | PCE _{ave} (%) | PCE _{max} (%) |
|---------------|------------------|--------------------------------|----------|------------------------|------------------------|
| 0.75%CN | 0.85±0.00 | 12.5±0.1 | 62.6±0.7 | 6.64±0.10 | 6.78 |
| 0.5%CN | 0.86±0.00 | 13.3±0.1 | 64.9±0.6 | 7.44±0.07 | 7.52 |
| 0.3%CN | 0.86±0.00 | 12.0±0.1 | 65.2±0.5 | 6.68±0.03 | 6.72 |

9. Carrier Recombination Analysis



Figure S9. (a) J_{ph} vs. V_{eff} (effective voltage). J_{ph} is defined as the photocurrent density difference between illuminated and dark conditions ($V_{eff} = V_0 - V$, where V_0 is the voltage when photocurrent reaches zero and V is the applied voltage). When J_{ph} reaches saturation (J_{sat}), the charge dissociation probability can be calculated from J_{ph}/J_{sat} . (b) J_{SC} vs. light intensity (under 1 sun) for optimized device. The solid lines correspond to the fits derived from the expression: $J_{SC} \propto I^{\alpha}$. With $\alpha = 0.977$ for **PM7:DFA4**. Note: bimolecular recombination is not the main limiting factor suppressing efficiency for the optimized blends. (c) V_{OC} vs. light intensity (1 sun) for optimized devices. The solid lines

corresponding to the fits derived from the expression: $V_{\rm OC} \propto n \frac{kT}{q} ln(I)$. With n = 1.31 for **PM7:DFA4**.

10. Carrier Mobility Measurements

The carrier mobility (hole and electron mobility) of photoactive active layer was obtained by fitting the dark current of hole/electron-only diodes to the space-chargelimited current (SCLC) model. Hole-only diode configuration: Glass/ITO/MoO₃/PM7:DFA4/MoO₃/Ag; here, $V_{bi} = 0$ V (flat band pattern formed by MoO_3-MoO_3). Electron-only diode configuration: Glass/ITO/ZnO/PDINO/PM7:DFA4/PDINO/Ag; here, $V_{bi} = 0V$ was used following the protocol reported.^[9] The active layer thickness was determined by a Tencor surface profilometer. The electric-field dependent SCLC mobility was estimated using the

following equation: $J(V) = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_0 exp \left(0.89\beta \sqrt{\frac{V - V_{bi}}{L}} \right) \frac{(V - V_{bi})^2}{L^3}$



Figure S10. Hole mobility and electron mobility fitting examples of (a,b) PM7:DFA4 and (c,d) PM7:F8IC

Table S10. Average mobility values of devices of PM7:DFA4 and PM7:F8IC.

| Blend | $\mu_{\rm h} ({\rm cm}^2 {\rm V}^{-1} {\rm s}^{-1})$ | $\mu_{\rm e} ({\rm cm}^2 {\rm V}^{-1} {\rm s}^{-1})$ | $\mu_{ m h}/\mu_{ m e}$ |
|----------|--|--|-------------------------|
| PM7:DFA4 | 2.9×10 ⁻⁴ | 3.0×10 ⁻⁵ | 9.67 |
| PM7:F8IC | 5.5×10 ⁻⁴ | 1.4×10-4 | 3.93 |

11. Atomic Force Microscopy (AFM) Imaging



Figure S11. Topography and phase images (tapping mode) of (**a-f**) pristine film of PM7, **DFA4** and **F8IC**; (**g-j**) optimized blend film of **PM7**:**DFA4** and **PM7**:**F8IC**.

12. Transmission Electron Microscope (TEM) Imaging



Figure S12. Bright-field TEM images of optimized BHJ thin film of PM7:DFA4 and PM7:F8IC. Scale bar is 200 nm.

13. GIWAXS Line Cutting Profiles

Si substrates were sonicated for 15 min in turn in successive baths of acetone and isopropanol. The substrates were then dried with pressurized nitrogen before being exposed to the UV-ozone plasma for 15 min. The BHJ layers were prepared following methods described in Section 7. Device Fabrication of OFETs and OPVs



Figure S13. GIWAXS Line Cutting Profiles: **(a-c)** out-of-plane (OOP) and in-plane (IP) for **neat** films PM7, DFA4, F8IC; **(d-e)** OOP and IP for blend films PM7:DFA4 and PM7:F8IC; **(f-g)** Overlapped profiles of neat films and blend films. All the films were spin coated on the Si/PEDOT:PSS substrate.

14. Solution NMR and MALDI-TOF Spectra



Figure S14. ¹H NMR spectrum of compound 2 in CDCl₃.

| | -182.518 | $\begin{array}{c} 145.028 \\ 142.909 \\ 142.548 \\ 138.349 \\ 138.349 \\ 136.873 \\ 136.873 \\ 135.656 \\ 123.562 \\ 123.562 \\ 123.562 \\ \end{array}$ | -62.675 -62.675 35.584 31.142 23.091 22.539 14.030 | |
|--|----------|---|--|--|
|--|----------|---|--|--|



Figure S15. ¹³C NMR spectrum of compound 2 in CDCl₃.



26

Figure S16. ¹H NMR spectrum of DFA4 in CDCl₃.



27

Figure S17. ¹⁹F NMR spectrum of DFA4 in CD₂Cl₂.



28

Figure S18. ¹³C NMR spectrum of DFA4 in CDCl₃.

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Figure S19. MALDI-TOF-MS spectra of DFA4.

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