Electronic Supporting Information for

High-performance NIR-sensitive fused tetrathienoacene electron acceptors†

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Materials

Unless stated otherwise, all the solvents and chemical reagents were obtained commercially and used without further purification. THF was distilled from sodium benzophenone under nitrogen before use. Starting materials 2,6-bis(trimethylstannyl)thieno[2',3':4,5]thieno[3,2-*b*]thieno[2,3-*d*]-thiophene and ethyl 2-bromothieno[3,2-*b*]thiophene-3-carboxylate were purchased from Sunatech Inc. Ethyl 2-bromothiophene-3-carboxylate was obtained from Bidepharm Inc. 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile[S1] and F6IC[S2] were synthesized according to our previously reported procedures. PTB7-Th (M_w = 124 kDa, M_w/M_n = 1.7) was purchased from 1-material Inc. Zinc acetate dihydrate, ethanolamine and MoO_3 were obtained from Aldrich Inc.

Synthesis

Compound 2. To a three-necked round bottom flask were added compound **1** (600 mg, 1.04 mmol), ethyl 2-bromothiophene-3-carboxylate (489 mg, 2.08 mmol), and toluene (30 mL). The mixture was deoxygenated with argon for 30 min. $Pd(PPh_3)_4$ (71 mg, 0.061 mmol) was added under argon. The mixture was refluxed at 110 °C for 48 h and then cooled down to room temperature. Brine (50 mL) was added and the mixture was extracted with dichloromethane (3 × 50 mL). After removing the solvent, the residue was washed using dichloromethane and filtered yielding an orange solid (554 mg, 95%). The crude product was directly used for next step without further purification due to the poor solubility in common organic solvents.

Compound 3. To a three-necked round bottom flask were added compound **2** (300 mg, 0.54 mmol) and THF (20 mL). The mixture was deoxygenated with argon for 30 min. A THF solution (10 mL) of fresh 4-hexylphenyl-1-magnesium bromide prepared from magnesium turnings (157 mg, 6.48 mmol) and 1-bromo-4-hexylbenzene (1.56 g, 6.48 mmol) was added dropwise to the mixture. The mixture was refluxed for 16 h and then cooled down to room temperature. A saturated NH_4Cl aqueous solution (10 mL) was added and the mixture was extracted with dichloromethane (3 × 50 mL). The organic phase was dried over anhydrous Na_2SO_4 and filtered. After removing the solvent, the residue was dissolved in dry dichloromethane (60 mL) and added into a three-necked round bottom flask. The mixture was deoxygenated with argon for 30 min. an excess of $BF_3 \cdot Et_2O$ (0.4 mL) was added at 0 °C under argon. The mixture was slowly warmed to room temperature and stirred overnight. The reaction was quenched with saturated $NaHCO_3$ aqueous solution. The mixture was extracted with dichloromethane (3 × 50 mL), the organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified using column chromatography on silica gel employing dichloromethane/petroleum ether (1:20, v/v) as eluent yielding a yellow sticky oil (170 mg, 29%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.24-7.12 (m, 20H), 2.61 (t, J = 7.2 Hz, 8H), 1.62 (m, 8H), 1.34 (m, 24H), 0.92 (t, J = 3.0 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.70, 149.08, 141.96, 139.45, 136.84, 134.69, 132.39, 132.28, 128.67, 127.80, 125.89, 123.35, 62.09, 35.68, 31.81, 31.40, 29.23, 22.71, 14.22. MS (MALDI-TOF): *m/z* 1081.3 (M^+).

Compound 4. To a Vilsmeier reagent prepared with $POCl_3$ (0.30 mL) in DMF (5 mL) was added a solution of compound **3** (170 mg, 0.16 mmol) in 1,2-dichloroethane (20 mL) under the protection of argon. The mixture was deoxygenated with argon for 30 min. After stirring at 80 °C overnight, the mixture was cooled down to room temperature and quenched with saturated CH_3COONa aqueous solution, and then extracted with dichloromethane (3 × 50 mL). The combined organic layer was washed with water and brine, and dried over anhydrous Na_2SO_4. After removal of solvent, the crude product was purified by silica gel using dichloromethane/petroleum ether (1:1, v/v) as eluent, yielding an orange solid (130 mg, 73%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 9.81 (s, 2H), 7.70 (s, 2H), 7.12 (m, 16H), 2.55 (m, 8H), 1.58 (m, 8H), 1.27 (m, 24H), 0.87 (m, 12H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 182.45, 158.05, 153.10, 147.05, 144.29, 142.72, 138.12, 136.34, 135.46, 134.17, 131.62, 129.00, 127.65, 62.44, 35.68, 31.80, 31.39, 29.20, 22.70, 14.20. MS (MALDI-TOF): *m/z* 1137.4 (M$^+$).

F8IC1. To a three-necked round bottom flask were added compound **4** (80 mg, 0.07 mmol), 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (80 mg, 0.35 mmol) and chloroform (20 mL). The mixture was deoxygenated with argon for 30 min. Pyridine (0.3 mL) was added under nitrogen. The mixture was refluxed for 16 h and then cooled down to room temperature. The mixture was poured into methanol (100 mL), and filtered. The residue was purified by column chromatography on silica gel using dichloromethane/petroleum ether (1:2, v/v) as eluent yielding a black solid (65 mg, 59%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.82 (s, 2H), 8.24 (m, 2H), 7.69 (s, 2H), 7.58 (m, 2H), 7.19 (m, 16H), 2.60 (m, 8H), 1.60 (m, 8H), 1.26 (m, 24H), 0.84 (m, 12H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 185.72, 158.92, 157.58, 155.53, 154.94, 153.09, 152.94, 143.31, 139.71, 137.85, 136.28, 135.13, 131.14, 129.29, 127.77, 119.53, 114.60, 114.40, 114.30 68.23, 62.56, 35.70, 31.76, 31.50, 29.23, 22.71, 14.21. MS (MALDI-TOF): *m/z* 1562.3 (M$^+$). Anal. calc. for $C_{94}H_{76}F_4N_4O_2S_6$: C, 72.28; H, 4.90; N, 3.59. Found: C, 72.42; H, 5.17; N, 3.38.

Compound 5. To a three-necked round bottom flask were added compound **1** (600 mg, 1.04 mmol), ethyl 2-bromothieno[3,2-b]thiophene-3-carboxylate (605 mg, 2.08 mmol), and toluene (40 mL). The mixture was deoxygenated with argon for 30 min. Pd(PPh$_3$)$_4$ (71 mg, 0.061 mmol) was added under argon. The mixture was refluxed at 110 °C for 48 h and then cooled down to room temperature. Brine (50 mL) was added and the mixture was extracted with dichloromethane (3 × 50 mL). After removing the solvent, the residue was washed using dichloromethane and filtered yielding an orange solid (630 mg, 90%). The crude product was directly used for next step without further purification due to poor solubility in common organic solvents. MS (MALDI-TOF): *m/z* 672.03 (M^+).

Compound 6. To a three-necked round bottom flask were added compound **5** (600 mg, 0.89 mmol) and THF (20 mL). The mixture was deoxygenated with argon for 30 min. A THF solution (15 mL) of fresh 4-hexylphenyl-1-magnesium bromide prepared from magnesium turnings (260 mg, 10.7 mmol) and 1-bromo-4-hexylbenzene (2.58 g, 10.7 mmol) was added dropwise to the mixture. The mixture was refluxed for 16 h and then cooled down to room temperature. A saturated NH_4Cl aqueous solution (10 mL) was added and the mixture was extracted with dichloromethane (3 × 50 mL). The organic phase was dried over anhydrous Na_2SO_4 and filtered. After removing the solvent, the residue was dissolved in dry dichloromethane (100 mL) and added into a three-necked round bottom flask. The mixture was deoxygenated with argon for 30 min. an excess of BF_3 Et_2O (1 mL) was added at 0 °C under argon. The mixture was slowly warmed to room temperature and stirred overnight. The reaction was quenched with saturated $NaHCO_3$ aqueous solution. The mixture was extracted with dichloromethane, the organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was purified on silica gel using dichloromethane/petroleum ether (1:20, v/v) as eluent yielding an orange sticky oil (160 mg, 15%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.26 (m, 2H), 7.24 (m, 2H), 7.16 (d, J =8.1 Hz, 8H), 7.08 (d, J = 7.8 Hz, 8H), 2.53 (t, J = 7.8 Hz, 8H), 1.54 (m, 8H), 1.26(s, 24H), 0.84 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.56, 147.45, 142.33, 140.72, 138.65, 137.99, 137.47, 134.67, 134.16, 132.54, 132.41, 128.87, 127.98, 125.97, 120.38, 62.44, 35.73, 31.80, 31.32, 29.26, 22.69, 14.18. MS (MALDI-TOF): *m/z* 1194.3 (M^+).

Compound 7. To a Vilsmeier reagent prepared with $POCl_3$ (0.20 mL) in DMF (3 mL) was added a solution of compound **6** (160 mg, 0.13 mmol) in 1,2-dichloroethane (20 mL) under the protection of argon. After stirring at 80 °C overnight, the mixture was quenched with saturated CH3COONa aqueous solution, and then extracted with dichloromethane (3 × 50 mL). The combined organic layer was washed with water and brine, and dried over anhydrous Na_2SO_4. After removal of solvent, the crude product was purified by silica gel using dichloromethane/petroleum ether (3:1, v/v) as eluent, yielding a red solid (140 mg, 86%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.88 (s, 2H), 7.90 (s, 2H), 7.13 (m, 16H), 2.56 (t, J = 7.8 Hz, 8H), 1.57 (m, 8H), 1.28(m, 24H), 0.84 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.62, 151.23, 147.38, 145.44, 143.62, 142.88, 140.47, 140.40, 137.03, 135.15, 134.23, 133.55, 129.79, 129.15, 127.79, 62.57, 35.71, 31.77, 31.31, 29.22, 22.67, 14.16. MS (MALDI-TOF): *m/z* 1249.3 (M^+).

F10IC1. To a three-necked round bottom flask were added compound **7** (70 mg, 0.06 mmol), 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (70 mg, 0.3 mmol) and chloroform (20 mL). The mixture was deoxygenated with nitrogen for 30 min. Pyridine (0.3 mL) was added under nitrogen. The mixture was refluxed for 12 h and then cooled down to room temperature. The mixture was poured into methanol (80 mL), and filtered. The residue was purified by column chromatography on silica gel using dichloromethane/petroleum ether (3:1, v/v) as eluent yielding a black solid (50 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.85 (s, 2H), 8.51 (m, 2H), 8.17 (s, 2H), 7.66 (m, 2H), 7.17 (m, 16H), 2.56 (m, 8H), 1.58 (m, 8H), 1.27 (m, 24H), 0.85 (m, 12H). ^{13}C NMR cannot be obtained due to limited solubility. MS (MALDI-TOF): *m/z* 1674.2 (M^+). Anal. calc. for $C_{98}H_{76}F_4N_4O_2S_8$: C, 70.31; H, 4.58; N, 3.35. Found: C, 70.12; H, 4.72; N,3.44.

Characterization

The ^1H and ^{13}C NMR spectra were measured using a Bruker AVANCE 300 or 400 MHz spectrometer. Mass spectra were measured using Bruker Daltonics Biflex III MALDI-TOF Analyzer in the MALDI mode. UV-vis absorption spectra in solution (chloroform) and as thin film (on a quartz substrate) were recorded using a Jasco V-570 spectrophotometer. Elemental analysis was carried out using an Elementar Vario EL CUBE (Germany) elemental analyzer. Electrochemical measurements were carried out under nitrogen in a deoxygenated solution of tetra-*n*-butylammoniumhexafluorophosphate (0.1 M) in acetonitrile using a potential scan rate of 100 mV s^{-1} employing a computer-controlled CHI660C electrochemical workstation, a glassy-carbon working electrode coated with F6IC, F8IC1, or F10IC1 film, a platinum-wire auxiliary electrode, and an Ag/AgCl electrode as a reference electrode. The potentials were referenced to a ferrocenium/ferrocene ($FeCp_2^{+/0}$) couple using ferrocene as an external standard. The HOMO and LUMO energies are estimated from the onset oxidation (E_{ox}) and reduction potentials (E_{red}) versus $FeCp_2^{+/0}$ (0.43 V vs. Ag/AgCl), respectively, assuming the absolute energy level of $FeCp_2^{+/0}$ to be 4.8 eV below vacuum.

$\mathrm{HOMO} = -e\,E_{ox} - 4.8\ (\mathrm{eV})$

$\mathrm{LUMO} = -e\,E_{red} - 4.8\ (\mathrm{eV})$

Thermogravimetric analysis (TGA) measurements were performed using a Shimadzu thermogravimetric analyzer (Model DTG-60) under flowing nitrogen gas at a heating rate of 10 °C min^{-1}. The nanoscale morphology of the blended films was observed using a Multimode 8 atomic force microscope (Bruker) in the tapping mode.

Grazing incidence wide-angle X-ray scattering

GIWAXS measurements were performed at beamline 7.3.3[S3] at the Advanced Light Source

(ALS). Samples were prepared on Si substrates using identical blend solutions as used in OSC devices. The 10 keV X-ray beam was incident at a grazing angle of 0.11^o –0.15^o, which maximized the scattering intensity from the samples. The scattered X-rays were detected using a Dectris Pilatus 2M photon counting detector.

Resonant soft X-ray scattering

R-SoXS transmission measurements were performed at beamline 11.0.1.2[S4] at the ALS. Samples for R-SoXS measurements were prepared on a PEDOT: PSS modified Si substrate under the same conditions as used for OSC device fabrication, and then transferred by floating in water to a 1.5 mm × 1.5 mm, 100-nm thick Si_3N_4 membrane supported by a 5 mm × 5 mm, 200 mm thick Si frame (Norcada Inc.). Two dimensional scattering patterns were collected on an in-vacuum CCD camera S7 (Princeton Instrument PI-MTE). The beam size at the sample is 100 μm × 200 μm. The photon energy of 284.8 eV was selected to acquire highly enhanced materials contrast. The composition variation (or relative domain purity) over the length scales probed can be extracted by integrating scattering profiles to yield the total scattering intensity. The purer the average domains, the higher the total scattering intensity.

Fabrication and characterization of organic solar cells

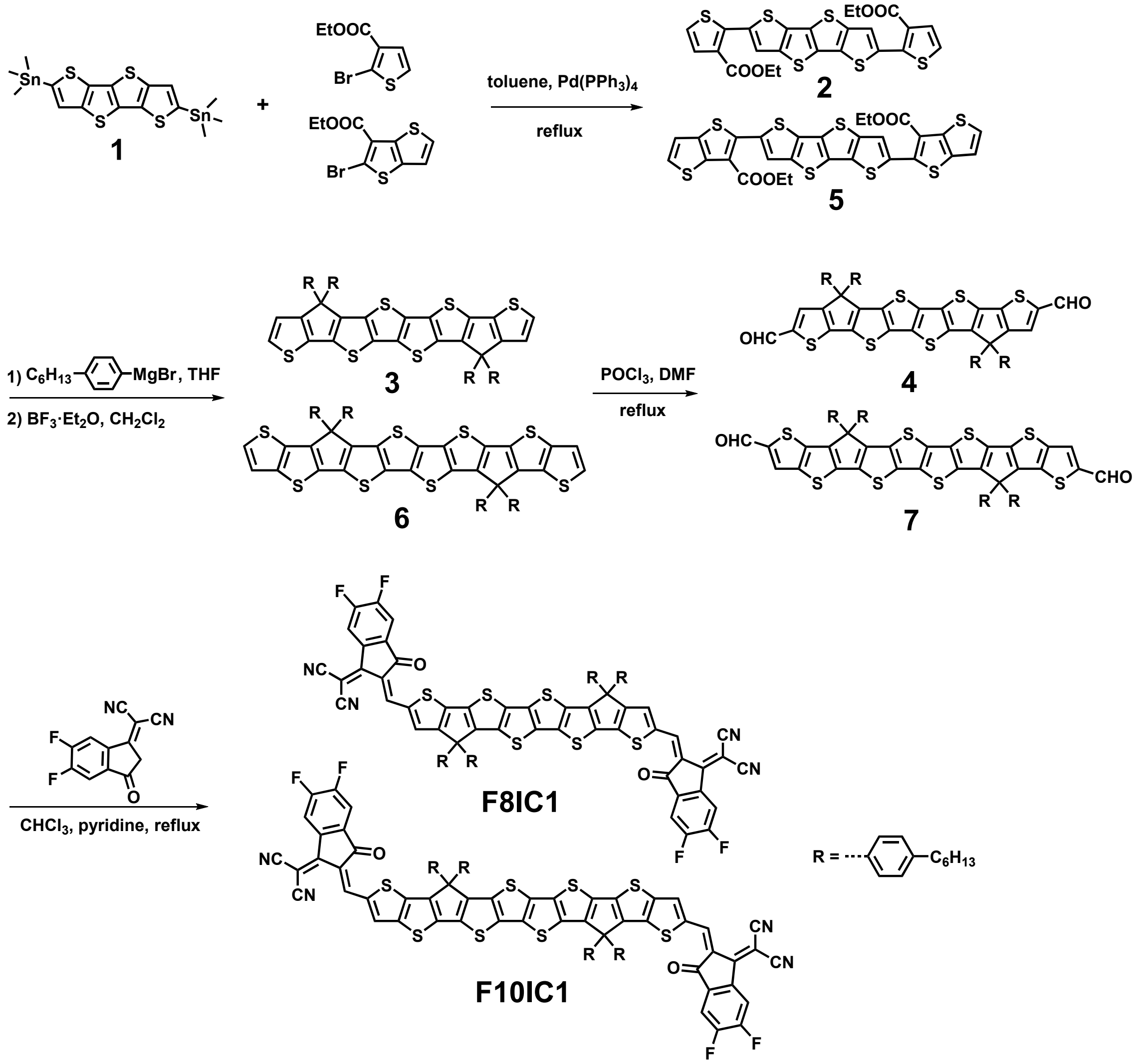
The structure of OSCs was ITO/ZnO/PTB7-Th:accpetor/MoO_3/Ag. Patterned ITO glass (sheet resistance = 15 Ω) was precleaned in an ultrasonic bath with deionized water, acetone and isopropanol, and treated in an ultraviolet–ozone chamber (Jelight Company, USA) for 20 min. ZnO layer (*ca.* 30 nm) was spin-coated at 4000 rpm onto the ITO glass from ZnO precursor solution, and then baked at 200 °C for 30 min. A PTB7-Th: acceptor mixture (11 mg mL^{-1} in total) in $CHCl_3$ was spin-coated at 1300 rpm on the ZnO layer to form a photoactive layer (*ca.* 100 nm). The MoO_3 layer (*ca*. 5 nm) and Ag electrode (*ca*. 80 nm) were slowly evaporated onto the surface of the photoactive layer under vacuum (*ca*. 10^{-5} Pa). The active area of the device was *ca.* 4 mm^2. The *J–V* curve was measured using a computer-controlled B2912A Precision Source/Measure Unit (Agilent Technologies). An XES-70S1 (SAN-EI Electric Co., Ltd.) solar simulator (AAA grade, 70 × 70 mm^2 photobeam size) coupled with AM 1.5 G solar spectrum filters was used as the light source, and the optical power at the sample was 100 mW cm^{-2}. A 2 × 2 cm^2 monocrystalline silicon reference cell (SRC–1000-TC-QZ) was purchased from VLSI Standards Inc. The EQE spectrum was measured using Solar Cell Spectral Response Measurement System QE-R3011 (Enlitech Co., Ltd.). The light intensity at each wavelength was calibrated using a standard single crystal Si photovoltaic cell.

Mobility measurements

Hole-only or electron-only devices were fabricated using the architectures of ITO/PEDOT: PSS/ PTB7-Th: acceptor/Au for holes and Al/PTB7-Th: acceptor/Al for electrons. For hole-only devices, the pre-cleaned ITO glass was spin-coated with PEDOT: PSS (*ca*. 35 nm), then PTB7-Th: acceptor blend was spin-coated as active layer, then Au (*ca*. 30 nm) was evaporated under vacuum (*ca*. 10^{-5} Pa) at a low speed (1 Å/5 s) to avoid the penetration of Au atoms into the active layer. For electron-only devices, Al (*ca*. 80 nm) was evaporated onto pre-cleaned glass under vacuum, PTB7-Th: acceptor blend was spin-coated, and then Al (*ca.* 80 nm) was evaporated under vacuum. The mobility was extracted by fitting the current density–voltage curves using space charge limited current (SCLC).[S5] The equation is as follows.

$$J = (9/8)\mu\varepsilon_r\varepsilon_0 V^2\exp(0.89(V/E_0 d)^{0.5})/d^3$$

where J is current density, μ is hole or electron mobility, ε_r is relative dielectric constant, ε_0 is permittivity of free space, $V = V_{appl} - V_{bi}$, where V_{appl} is the applied voltage to the device, and V_{bi} is the built-in voltage due to the difference in work function of the two electrodes (for hole-only diodes, V_{bi} is 0.2 V; for electron-only diodes, V_{bi} is 0 V). E_0 is characteristic field, d is the thickness of organic layer. The thickness of organic layer was measured on DektakXT (Bruker). The J–V curves of the devices are plotted as $\ln[Jd^3/(V_{\mathrm{appl}}-V_{\mathrm{bi}})^2]$ versus $[(V_{\mathrm{appl}}-V_{\mathrm{bi}})/d]^{0.5}$.



Scheme S1. Synthetic routes for F8IC1 and F10IC1.

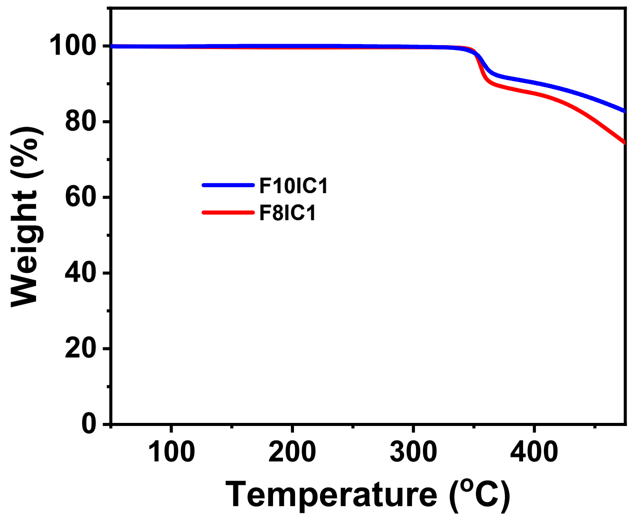


Fig. S1 TGA curves of F8IC1 and F10IC1.

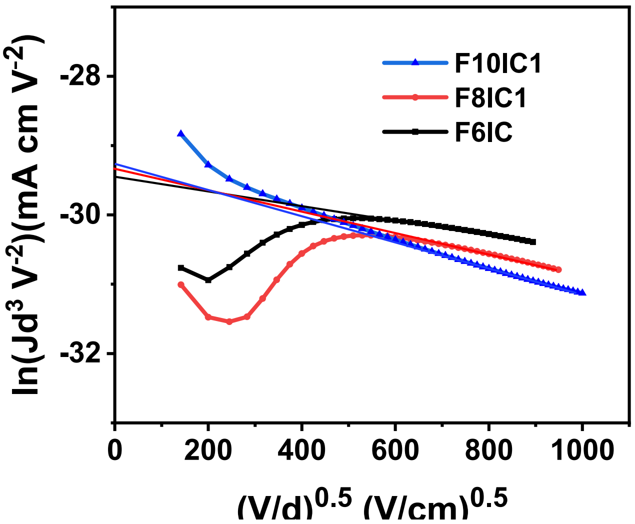


Fig. S2 *J-V* characteristics in the dark for electron-only devices based on F6IC, F8IC1 and F10IC1.

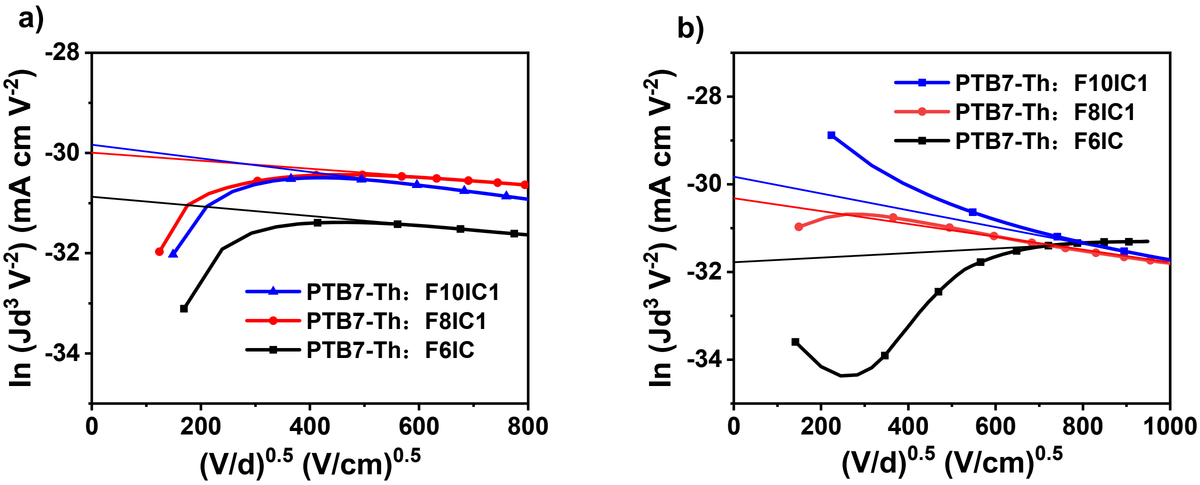


Fig. S3 *J-V* characteristics in the dark for (a) hole-only and (b) electron-only devices based on PTB7-Th: F6IC, PTB7-Th: F8IC1, and PTB7-Th: F10IC1.

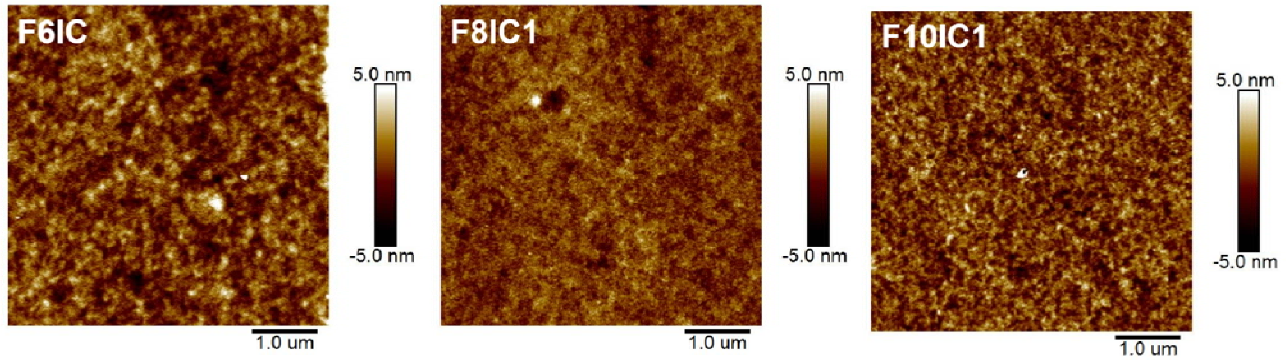


Fig. S4 AFM height images of PTB7-Th: F6IC, PTB7-Th: F8IC1, and PTB7-Th: F10IC1 blends.

Table S1. Device performance of OSCs based on PTB7-Th:F10IC1 blend with different donor/acceptor (D/A) ratio, annealing condition and spin-coating speed.

D/A (w/w)	annealing[a]	spin-coating (rpm)	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)	
						best	average[b]
1:0.9	no	1300	0.711	22.93	66.6	10.9	10.5
1:1.2	no	1300	0.718	23.39	70.1	11.8	11.6
1:1.5	no	1300	0.718	21.83	70.3	11.0	10.6
1:1.2	yes	1000	0.717	24.37	68.4	11.9	11.6
1:1.2	yes	1300	0.723	23.44	72.4	12.3	12.1
1:1.2	yes	1700	0.721	23.91	69.6	12.0	11.7
1:1.2	yes	2100	0.714	23.27	69.0	11.5	11.3

[a] 5 min at 80 °C. [b] Average PCEs are calculated based on 20 devices.

Table S2. Device performance of OSCs based on PTB7-Th:F8IC1 blend with different donor/acceptor (D/A) ratio, annealing condition and spin-coating speed.

D/A (w/w)	annealing[a]	spin-coating (rpm)	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)	
						best	average[b]
1:0.9	no	1600	0.680	22.13	69.0	10.4	10.2
1:1.2	no	1600	0.675	22.11	69.4	10.3	10.1
1:1.5	no	1600	0.683	22.25	70.4	10.7	10.4
1:1.8	no	1600	0.664	23.05	66.1	10.1	9.7
1:1.5	yes	1300	0.670	23.00	65.0	10.0	9.6
1:1.5	yes	1600	0.678	23.03	64.9	10.1	9.8
1:1.5	yes	2000	0.679	22.25	65.5	9.9	9.5

[a] 5 min at 80 °C. [b] Average PCEs are calculated based on 20 devices.

Table S3. Device performance of OSCs based on PTB7-Th:F6IC1 blend with different donor/acceptor (D/A) ratio, additive and spin-coating speed.

D/A (w/w)	additive	spin-coating (rpm)	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)	
						best	average[a]
1:0.9	no	1300	0.609	17.22	50.8	5.3	5.2
1:1.2	no	1300	0.603	17.42	64.1	6.7	6.5
1:1.5	no	1300	0.613	17.11	61.9	6.5	6.4
1:1.2	no	1000	0.588	19.06	55.9	6.3	6.1
1:1.2	0.5% DPE	1300	0.609	18.15	63.1	7.0	6.8
1:1.2	no	1700	0.604	16.84	59.6	6.1	6.0

[a] Average PCEs are calculated based on 20 devices.

Table S4. Hole and electron mobilities of the blends.

blend	μ_h (cm^2 V^{-1} s^{-1})	μ_e (cm^2 V^{-1} s^{-1})	μ_h/μ_e
PTB7-Th: F6IC	2.2×10^{-4}	9.1×10^{-5}	2.4
PTB7-Th: F8IC1	5.5×10^{-4}	3.9×10^{-4}	1.4
PTB7-Th: F10IC1	6.8×10^{-4}	6.1×10^{-4}	1.1

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