

Supporting Information

Molecular engineering of *N*, *S*-heterarene-based small-molecule acceptors: Effects of side chains, backbone extension and end groups on structure, optoelectronic properties and solar cell performance

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Experimental section

Instruments and measure methods

¹H NMR and ¹³C NMR spectra were measured with Bruker AVANCE 400 spectrometer. Molecular mass was determined by flight mass spectrometry (MALDITOF MS) using a Bruker Aupoflex-III mass spectrometer. Ultraviolet-visible (UV-vis) absorption spectra were measured on Perkin Elmer Lamada 25 spectrometer with a dilute CHCl₃ solution or as a solid film casted from chlorobenzene. Photoluminescence (PL) spectrum was carried out on Edinburgh Instrument FLS 980. Thermal gravimetric analysis (TGA) was performed under nitrogen at a heating rate of 20 °C min⁻¹ with TGA Q50 analyzer. Differential scanning calorimetry (DSC) analysis was measured on a DSC instrument (DSC Q10) in a temperature range from 25 to 280 °C under N₂ with a heating rate of 5 °C min⁻¹. The cyclic voltammetry (CV) was measured on a electrochemistry work station (CHI830B, Chenhua Shanghai) with a Pt slice electrode (coated with a small acceptor film), a Pt ring, and a Ag/AgCl electrode as the working electrode, the auxiliary electrode and the reference electrode respectively, in a 0.1 M tetrabutylammonium hexafluorophosphate acetonitrile solution. The potentials were calibrated using a ferrocene/ferrocenium (Fc/Fc⁺) redox couple as an internal standard, whose redox potential is supposed at -4.8 eV relative to zero vacuum level. The HOMO/LUMO energy levels were obtained from the equation HOMO/LUMO = -(*E*_{ox/red}-*E*_{Fc/Fc⁺} + 4.8) (eV), where the redox potential (*E*_{Fc/Fc⁺}) of Fc/Fc⁺ was determined to be 0.42 V versus Ag/AgCl in this study. Therefore, the above

equation can be simplified as $\text{HOMO/LUMO} = -(E_{\text{ox/red}} + 4.38)$ (eV). Atomic force microscopy (AFM) measurement was carried out on a Digital Instruments Veeco Nanoscopy V using a tapping mode. Contact angles were measured with a contact angle meter (JC2000D1). Transmission electron microscopy (TEM, HITACHI H-7650 electron microscope) operating at an acceleration voltage of 100 kV. The solution of each pure organic material was spin-coated on cleaned ITO substrates. Droplets of two different liquids, water and ethylene glycol (EG) were cast onto the pure organic films with the drop size kept at 1 μL per drop. Contact angle images were taken at 4 s after the whole droplet was deposited onto the sample surface. At least 3 independent measurements were performed for each single liquid.

Materials synthesis and structural characterization

Synthesis of compound 1. 2,5-dibromonitrobenzene (2.8 g, 10 mmol) and thiophene-2-boronic acid pinacol ester (2.3 g, 11 mmol), K_2CO_3 (8.29 g, 60 mmol), toluene (150 mL), H_2O (30 mL), $\text{Pd}(\text{PPh}_3)_4$ (350 mg) and two drops of Aq336 were added into a 250 mL round bottom flask under Ar atmosphere. The resultant mixture was heated up to 120 $^\circ\text{C}$ and reacted for 48 h. The reaction system was allowed to drop to room temperature and extracted with dichloromethane. The organic layer was washed several times with water and dried over anhydrous MgSO_4 . After the removal of dichloromethane, compound **1** was obtained as brownish red oily (1.71 g, yield 54%) after the crude produce was subjected to treatment through silica gel column chromatography using petroleum ether as eluent. ^1H NMR (400 MHz, CDCl_3 , δ/ppm): 7.89 (s, 1H), 7.70 (d, $J = 8$ Hz, 1H), 7.44-7.41 (m, 2H), 7.08 (d, $J = 8$ Hz, 2H).

Synthesis of compound 2. Compound **1** (3.3 g, 11.67 mmol) and $\text{P}(\text{OEt})_3$ (20 mL) were added into a 50 mL round bottom flask. The resultant mixture was heated up to 160 $^\circ\text{C}$ and reacted for 8 h. Excessive $\text{P}(\text{OEt})_3$ was removed under reduced pressure and the residue was subjected silica gel column chromatography using petroleum ether/dichloromethane as eluent to obtain compound **2** as white crystal (1.1 g, yield 38%). ^1H NMR (400 MHz, CDCl_3 , δ/ppm): 8.24 (s, 1H), 7.60 (d, $J = 8$ Hz, 2H), 7.39 (d, $J = 4$ Hz, 1H), 7.29 (d, $J = 8$ Hz, 1H), 7.06 (d, $J = 4$ Hz, 1H).

Synthesis of compound 3a. Compound **2** (1.1 g, 3.89 mmol), NaH (0.47 g, 19.45 mmol), 8 mL dry DMF and 5 mL dry THF were added into a 100 mL round bottom flask under Ar atmosphere. After stirring at room temperature for 0.5 h, 1-bromo-2-hexyldecane (2.49 g, 8.169 mmol) was slowly added into this mixture and stirred for 1 h. The resultant mixture was heated up to 55 $^\circ\text{C}$ and stirred for overnight. The reaction system was allowed to drop to room temperature and quenched by adding water and extracted with dichloromethane. The organic layer was washed several times with water and dried over anhydrous MgSO_4 . After the removal of dichloromethane, compound **3a** was obtained as transparent viscous liquid (1.67 g, yield 90%) after the crude produce was subjected to treatment through silica gel column chromatography using petroleum ether as eluent. ^1H NMR (400 MHz, CDCl_3 , δ/ppm): 7.58 (d, $J = 8.0$ Hz, 1H), 7.48 (s, 1H),

7.37(d, $J = 8.0$ Hz, 1H), 7.25 (d, $J = 8.0$ Hz, 1H), 7.01 (d, $J = 8.0$ Hz, 1H), 4.03 (d, $J = 8.0$ Hz, 2H), 2.04-2.02 (m, 1H), 1.27-1.21 (m, 24H), 0.90-0.85 (m, 6H).

Compound 3b: This compound was prepared as a light yellow oily liquid (1.85 g, yield 82%) using Compound **2** (1.2 g, 4.78 mmol) and 1-bromo-2-octyldodecane (3.4 g, 7.17 mmol) according to the similar procedure with compound **3a**. ^1H NMR (400 MHz, CDCl_3 , δ/ppm): 7.59 (d, $J = 8$ Hz, 1H), 7.49 (s, 1H), 7.38 (d, $J = 4$ Hz, 1H), 7.24 (d, $J = 8$ Hz, 1H), 7.02 (d, $J = 8$ Hz, 1H), 4.06 (d, $J = 8$ Hz, 2H), 2.03 (s, 1H), 1.27-1.21 (m, 32H), 0.90-0.86 (m, 6H).

Synthesis of compound 4a. Compound **3a** (2.87 g, 6.03 mmol), pinacol diborate (1.84 g, 7.23 mmol), $\text{Pd}(\text{dppf})\text{Cl}_2$ (0.226 g, 0.18 mmol), potassium acetate (1.48 g, 15 mmol) were added into 100 mL round bottom flask. The reaction system was carried out vacuuming and backfilling with argon three times before the addition of dry 1,4-dioxane (20 mL). Then the reaction system allowed to heat up to 100 °C and kept stirring for 24 h. After cooling to room temperature, the mixture was extracted with dichloromethane. The organic layer was washed several times with water and dried over anhydrous MgSO_4 . Finally, compound **4a** was obtained as a light yellow oily liquid (2.84 g, yield 90%) after the crude produce was subjected to treatment through silica gel column chromatography using petroleum ether/dichloromethane as eluent. ^1H NMR (400 MHz, CDCl_3 , δ/ppm): 7.86 (s, 1H), 7.75 (d, $J = 8.0$ Hz, 1H), 7.62 (s, 1H), 7.39(d, $J = 8.0$ Hz, 1H), 7.04 (d, $J = 8.0$ Hz, 1H), 4.16 (d, $J = 8.0$ Hz, 2H), 2.12-2.10 (m, 1H), 1.39-1.21 (m, 36H), 0.89-0.84 (m, 6H).

Compound 4b: This compound was prepared by following the synthetic procedure of **4a**, obtained as a light yellow oily liquid (1.3 g, yield 74%); ^1H NMR (400 MHz, CDCl_3 , δ/ppm): 7.86 (s, 1H), 7.75 (d, $J = 8$ Hz, 1H), 7.61 (d, $J = 8$ Hz, 1H), 7.40 (d, $J = 4$ Hz, 1H), 7.05 (d, $J = 4$ Hz, 1H), 4.16 (d, $J = 8$ Hz, 2H), 2.15-2.04 (m, 1H), 1.41-1.13 (m, 44H), 0.90-0.86 (m, 6H).

Synthesis of compound 5a. Compound **5a** was synthesized by a Suzuki coupling reaction. Compound **4a** (2.26 g, 4.31 mmol), $\text{Pd}(\text{PPh}_3)_4$ (99 mg, 0.0862 mmol), ethyl 2-bromothiophene-3-carboxylate (1.51 g, 6.45 mmol), 13 mL K_2CO_3 aqueous solution (2 M) and two drops of trioctylmethylammonium chloride were added into a 100 mL round bottom flask. The reaction system was carried out vacuuming and backfilling with argon three times before the addition of dry toluene (30 mL). The resultant mixture was heated slowly to 115 °C and stirred for 20 h. The reaction system was allowed to drop to room temperature and the mixture was extracted with dichloromethane. The organic layer was washed several times with water and dried over anhydrous MgSO_4 . After the removal of dichloromethane, compound **5a** was obtained as a yellow oily liquid (1.73 g, yield 74%) after the crude produce was subjected to treatment through silica gel column chromatography using petroleum ether/dichloromethane as eluent. ^1H NMR (400 MHz, CDCl_3 , δ/ppm): 7.73 (d, $J = 8.0$ Hz, 1H), 7.54 (d, $J = 4.0$ Hz, 2H), 7.40 (d, $J = 4.0$ Hz, 1H), 7.30 (d, $J = 8.0$ Hz, 1H), 7.24 (d, $J =$

4.0 Hz, 1H), 7.05 (d, $J = 4.0$ Hz, 1H), 4.20 (t, $J = 8.0$ Hz, 2H), 4.13 (t, $J = 8.0$ Hz, 2H), 2.10-2.08 (m, 1H), 1.33-1.44 (m, 27H), 0.88-0.82 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3 , δ/ppm): 163.73, 152.46, 146.87, 141.33, 130.20, 127.98, 127.46, 127.37, 123.78, 121.89, 121.34, 118.26, 115.96, 111.61, 110.73, 77.48, 77.16, 76.84, 60.54, 49.90, 38.64, 32.00, 31.92, 31.83, 30.06, 29.74, 29.66, 29.40, 26.58, 26.55, 22.79, 22.75, 14.27, 14.23; MS (MALDI-TOF, m/z) $\text{C}_{33}\text{H}_{45}\text{N}_2\text{O}_4\text{S}_2$: calculated: 551.850; found: 551.549.

Compound 5b: This compound was prepared by following the synthetic procedure of compound **5a**, obtained as a light bluish oily liquid (1.3 g, yield 79%). ^1H NMR (400 MHz, CDCl_3 , δ/ppm): 7.73 (d, $J = 8$ Hz, 1H), 7.54 (s, 1H), 7.52 (s, 1H), 7.39 (d, $J = 4$ Hz, 1H), 7.30 (d, $J = 8$ Hz, 1H), 7.24 (d, $J = 8$ Hz, 1H), 7.05 (d, $J = 4$ Hz, 1H), 4.19 (m, 2H), 4.12 (d, $J = 8$ Hz, 2H), 2.09-2.06 (m, 1H), 1.36-1.09 (m, 35H), 0.89-0.85 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3 , δ/ppm): 163.73, 152.46, 146.86, 141.33, 130.20, 127.98, 137.46, 127.36, 123.78, 121.88, 121.34, 118.27, 115.96, 111.60, 110.74, 60.55, 49.91, 38.64, 32.06, 32.01, 31.82, 30.07, 29.76, 29.72, 29.48, 26.58, 22.84, 22.80, 14.28; MS (MALDI-TOF, m/z) $\text{C}_{37}\text{H}_{53}\text{NO}_2\text{S}_2$: calculated: 607.358; found: 607.415.

Compound 5b': This compound was prepared by following the synthetic procedure of compound **5a**, obtained as a dark yellow oily liquid (3.77 g, yield 70%). ^1H NMR (400 MHz, CDCl_3 , δ/ppm): 7.74 (d, $J = 8.0$ Hz, 1H), 7.59 (s, 1H), 7.42-7.37 (m, 3H), 7.23 (d, $J = 4.0$ Hz, 1H), 7.03 (d, $J = 4.0$ Hz, H), 4.30-4.28 (m, 2H), 4.09 (d, $J = 8.0$ Hz, 2H), 2.06 (m, 1H), 1.30-1.19 (m, 35H), 0.87-0.83 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3 , δ/ppm): 162.34, 155.21, 147.03, 141.19, 140.88, 135.82, 128.17, 127.68, 127.64, 122.15, 121.47, 120.34, 118.85, 118.20, 115.97, 111.87, 110.66, 77.48, 77.16, 76.84, 60.87, 49.84, 38.60, 32.02, 31.97, 31.80, 30.03, 29.72, 29.69, 29.64, 29.43, 29.38, 26.55, 22.80, 22.76, 14.26; MS (MALDI-TOF, m/z) $\text{C}_{39}\text{H}_{53}\text{NO}_2\text{S}_3$: calculated: 664.043; found: 663.654.

Synthesis of compound 6a. Under an Ar atmosphere, 3.16 mL $n\text{-BuLi}$ (2.4 M) was added into a solution of 1-bromo-4-hexylbenzene (1.77 g, 7.94 mmol) in THF (12 mL) at -78 °C. After this reaction system was stirred at -78 °C for 1.5 h, a THF solution of compound **5a** (1.90 g, 3.45 mmol) was slowly added and then the mixture was stirred overnight at room temperature. The reaction was quenched by adding water and extracted with dichloromethane. The organic layer was washed several times with water and dried over anhydrous MgSO_4 . Finally, the pure compound **6a** was obtained as a yellow viscous liquid (1.40 g, yield 50%) after the crude produce was subjected to treatment through silica gel column chromatography using an eluent of petroleum ether/dichloromethane. ^1H NMR (400 MHz, CDCl_3 , δ/ppm): 7.58 (d, $J = 8.0$ Hz, 1H), 7.37 (d, $J = 4.0$ Hz, 1H), 7.18-7.16 (m, 4H), 7.11-7.09 (m, 5H), 7.00 (d, $J = 4.0$ Hz, 2H), 6.44 (d, $J = 4.0$ Hz, 1H), 3.80 (d, $J = 8.0$ Hz, 2H), 2.59 (t, $J = 8.0$ Hz, 4H), 1.90-1.88 (m, 1H), 1.34-1.16 (m, 40H), 0.91-0.83 (m, 12H); ^{13}C NMR (100 MHz, CDCl_3 , δ/ppm): 155.96, 146.56, 146.11, 145.67, 144.14, 143.28, 141.92, 141.85, 141.58, 141.19, 140.06, 131.33, 122.33, 121.48, 121.20, 118.88, 117.10, 116.54, 116.03,

111.89, 110.73, 100.93, 80.92, 77.48, 77.16, 76.84, 62.35, 50.04, 49.49, 38.46, 35.78, 35.71, 32.03, 31.97, 31.93, 31.89, 31.68, 31.50, 30.08, 29.74, 29.71, 29.67, 29.43, 29.29, 29.25, 26.53, 26.50, 22.81, 22.78, 22.74, 14.25, 14.23; MS (MALDI-TOF, m/z) C₅₅H₇₃NS₂: calculated: 811.518; found: 812.658.

Compound 6b: This compound was prepared by following the synthetic procedure of **6a**, obtained as a transparent viscous liquid (0.93 g, yield 63%). ¹H NMR (400 MHz, CDCl₃, δ/ppm): 7.59 (d, *J* = 8 Hz, 1H), 7.37 (d, *J* = 4 Hz, 1H), 7.18-7.16 (m, 4H), 7.11-7.08 (m, 5H), 7.01-6.99 (m, 2H), 6.43 (d, *J* = 4 Hz, 2H), 3.79 (d, *J* = 8 Hz, 2H), 2.59 (t, *J* = 8 Hz, 4H), 1.89-1.87 (m, 1H), 1.35-1.16 (m, 48H), 0.91-0.85 (m, 12H); ¹³C NMR (100 MHz, CDCl₃, δ/ppm) 146.53, 145.63, 144.12, 141.86, 141.54, 139.97, 131.33, 128.14, 127.95, 127.75, 127.52, 122.34, 121.43, 121.14, 118.92, 115.94, 111.82, 110.74, 80.89, 49.42, 38.43, 35.77, 32.07, 32.03, 31.89, 31.85, 31.53, 30.08, 29.79, 29.74, 29.69, 29.50, 29.44, 29.27, 26.50, 22.85, 22.82, 22.79, 14.29, 14.28; MS (MALDI-TOF, m/z) C₅₉H₈₁NS₂: calculated: 867.586; found: 868.616.

Compound 6b': This compound was prepared by following the synthetic procedure of **6a**, obtained as a yellow viscous liquid (1.45 g, yield 65%). ¹H NMR (400 MHz, CDCl₃, δ/ppm): 7.56-7.54 (d, *J* = 8.0 Hz, 1H), 7.37-7.33 (m, 1H), 7.19-7.14 (m, 5H), 7.07-7.00 (m, 5H), 7.00-6.97 (m, 2H), 3.79 (d, *J* = 8.0 Hz, 2H), 2.59 (t, *J* = 8.0 Hz, 4H), 1.98-1.82 (m, 1H), 1.30-1.19 (m, 48H), 0.90-0.85 (m, 12H); ¹³C NMR (100 MHz, CDCl₃, δ/ppm): 146.49, 143.70, 142.35, 141.65, 141.14, 136.56, 135.93, 131.18, 130.11, 128.39, 128.34, 128.19, 127.92, 127.64, 127.46, 121.38, 120.98, 118.59, 118.13, 115.79, 111.85, 110.52, 77.28, 76.96, 76.65, 49.26, 35.59, 31.88, 31.84, 31.69, 31.32, 29.90, 29.59, 28.98, 26.87, 26.29, 22.65, 22.62, 14.08; MS (MALDI-TOF, m/z) C₆₁H₈₁NS₃: calculated: 924.510; found: 924.421.

Synthesis of compound 7a. Under an Ar atmosphere, A solution of compound **6a** (1.21 g, 1.49 mmol) in dry THF (10 mL) was added in to a 100 mL three-necked round bottom flask. This solution was cooled to -78 °C and stirred, then 2M LDA (1.64 mL, 3.28 mmol) was added dropwise. After stirring at -78 °C for 1 h, 1.1 mL DMF was added into this reaction system, and stirred for 10 minutes, then the mixture was stirred 2 h at room temperature. The reaction was quenched by adding water and extracted with dichloromethane. The organic layer was washed several times with water and dried over anhydrous MgSO₄. Finally, the pure compound **7a** was obtained as a yellow oily substance (646 mg, yield 50%) after the crude produce was subjected to treatment through silica gel column chromatography using an eluent of petroleum ether/dichloromethane. ¹H NMR (400 MHz, CDCl₃, δ/ppm): 9.95 (s, 1H), 9.86 (s, 1H), 7.77 (s, 1H), 7.70 (s, 1H), 7.66 (s, 1H), 7.53 (s, 1H), 7.16 (d, *J* = 8.0 Hz, 4H), 7.07 (d, *J* = 8.0 Hz, 4H), 4.18 (d, *J* = 8.0 Hz, 2H), 2.55 (t, *J* = 8.0 Hz, 4H), 2.13-2.10 (m, 1H), 1.33-1.23 (m, 40H), 0.88-0.84 (m, 12H); ¹³C NMR (100 MHz, CDCl₃, δ/ppm): 183.30, 182.96, 157.19, 151.06, 133.84, 132.51, 128.66, 127.74, 124.81, 121.15, 118.68, 102.91, 77.48, 77.16, 76.84, 62.56, 50.10, 38.62, 35.66, 31.95, 31.87, 31.81, 31.44, 30.04, 29.68, 29.63, 29.38, 29.22, 26.58, 26.54, 22.75, 22.70, 14.20; MS (MALDI-TOF, m/z) C₅₅H₇₃NO₂S₂: calculated: 868.341;

found: 868.416.

Compound 7b: This compound was prepared by following the synthetic procedure of **7a**, obtained as a yellow solid (300 mg, yield 36%); ¹H NMR (400 MHz, CDCl₃, δ/ppm): 9.94 (s, 1H), 9.85 (s, 1H), 7.77 (s, 1H), 7.70 (s, 1H), 7.65 (s, 1H), 7.53 (s, 1H), 7.16 (d, *J* = 8 Hz, 4H), 7.07 (d, *J* = 8 Hz, 4H), 4.17 (d, *J* = 8 Hz, 2H), 2.55 (t, *J* = 8 Hz, 4H), 2.11-2.08 (m, 1H), 1.41-1.17 (m, 48H), 0.90-0.82 (m, 12H); ¹³C NMR (100 MHz, CDCl₃, δ/ppm): 183.37, 183.02, 157.22, 151.10, 147.08, 146.28, 145.79, 144.07, 143.59, 142.05, 141.80, 133.86, 132.54, 128.68, 127.74, 124.90, 121.21, 118.76, 118.41, 102.97, 62.56, 50.18, 38.68, 35.68, 32.03, 31.98, 31.84, 31.80, 31.48, 30.07, 29.75, 29.66, 29.46, 29.41, 29.26, 26.59, 22.82, 22.78, 22.73, 14.26, 14.23; MS (MALDI-TOF, *m/z*) C₆₁H₈₁NO₂S₂: calculated: 923.575; found: 924.514.

Compound 7b': This compound was prepared by following the synthetic procedure of **7a**, obtained as an orange solid (635 mg, yield 65%); ¹H NMR (400 MHz, CDCl₃, δ/ppm): 9.95 (s, 1H), 9.91 (s, 1H), 7.98 (s, 1H), 7.85 (s, 1H), 7.67 (s, 1H), 7.47 (s, 1H), 7.18 (d, *J* = 8.0 Hz, 4H), 7.09 (d, *J* = 8.0 Hz, 4H), 4.19 (d, *J* = 4.0 Hz, 2H), 2.55 (t, *J* = 8.0 Hz, 4H), 2.15-2.10 (s, 1H), 1.35-1.25 (m, 48H), 0.89-0.86 (m, 12H); ¹³C NMR (100 MHz, CDCl₃, δ/ppm): 183.31, 182.99, 149.87, 147.12, 146.78, 145.56, 144.63, 143.73, 143.68, 142.25, 141.81, 140.63, 140.25, 135.20, 129.84, 128.78, 127.90, 125.17, 120.66, 118.49, 102.02, 77.48, 77.36, 77.16, 76.84, 62.74, 38.65, 35.71, 32.04, 32.00, 31.83, 31.42, 30.09, 29.77, 29.28, 27.06, 26.60, 22.83, 22.79, 22.72, 14.27, 14.24, 14.22; MS (MALDI-TOF, *m/z*) C₆₃H₈₁NO₂S₃: calculated: 980.531; found: 980.301.

Synthesis of compound 8. 2,5-dibromonitrobenzene (2.8 g, 10 mmol) and thieno[3,2-*b*]thiophene tin reagent (4.72 g, 11 mmol), and Pd(PPh₃)₄ (350 mg) were added into a 250 mL round bottom flask under Ar atmosphere. The resultant mixture was heated up to 120 °C and reacted for 24 h. The reaction system was allowed to drop to room temperature and extracted with dichloromethane. The organic layer was washed several times with water and dried over anhydrous MgSO₄. After the removal of dichloromethane, compound **1** was obtained as brownish red solid (1.55 g, yield 51%) after the crude produce was subjected to treatment through silica gel column chromatography. ¹H NMR (400 MHz, CDCl₃, δ/ppm): 7.92 (s, 1H), 7.73 (d, *J* = 8 Hz, 1H), 7.48 (d, *J* = 8 Hz, 1H), 7.44 (d, *J* = 8 Hz, 1H), 7.27 (d, *J* = 8 Hz, 2H).

Synthesis of compound 9. This compound was prepared by following the synthetic procedure of compound **2** using compound **8** (3.04 g, 10 mmol) as the raw material, obtained as a light yellow solid (1.35 g, yield 44%); ¹H NMR (400 MHz, CDCl₃, δ/ppm): 8.41 (s, 1H), 7.61 (s, 1H), 7.57 (d, *J* = 8 Hz, 1H), 7.38 (d, *J* = 8 Hz, 1H), 7.34-7.30 (m, 2H).

Synthesis of compound 10. This compound was prepared by following the synthetic procedure of compound **3a**, obtained as a light bluish oily liquid (1.8 g, yield 75%). ¹H NMR (400 MHz, CDCl₃, δ/ppm): 7.55 (d, *J* = 8 Hz, 1H), 7.52 (s, 1H), 7.38 (d, *J* = 8 Hz, 1H), 7.33 (d, *J* = 8 Hz, 1H), 7.27 (d, *J* = 8 Hz, 1H), 4.13 (d, *J* = 8 Hz, 2H), 2.12-2.08 (m, 1H), 1.35-1.12 (m, 24H), 0.88-0.81 (m, 6H); ¹³C NMR (100 MHz,

CDCl₃, δ/ppm): 141.79, 141.46, 137.21, 125.59, 123.00, 122.60, 121.48, 121.25, 119.75, 117.52, 115.52, 113.32, 50.43, 39.03, 31.87, 31.75, 31.65, 29.89, 29.59, 29.46, 29.26, 26.44, 26.42, 22.67, 22.62, 14.15, 14.11.

Synthesis of compound 11. This compound was prepared by following the synthetic procedure of compound **4a**, obtained as a light bluish oily liquid (1.5 g, yield 77%). ¹H NMR (400 MHz, CDCl₃, δ/ppm): 7.88 (s, 1H), 7.72 (d, *J* = 8 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 4 Hz, 1H), 7.35 (d, *J* = 4 Hz, 1H), 4.29 (d, *J* = 8 Hz, 2H), 2.23-2.17 (m, 1H), 1.37-1.33 (m, 16H), 1.25-1.19 (m, 20H), 0.88-0.80 (m, 6H); ¹³C NMR (100 MHz, CDCl₃, δ/ppm): 142.11, 140.48, 137.73, 125.61, 125.47, 124.91, 123.10, 121.28, 117.88, 117.67, 116.97, 83.63, 50.10, 39.15, 31.87, 31.75, 31.57, 29.90, 29.71, 29.58, 29.25, 29.39, 26.42, 26.37, 24.93, 22.66, 22.59, 14.13, 14.09.

Synthesis of compound 12. This compound was prepared by following the synthetic procedure of compound **5a**, obtained as a yellow oily liquid (1.2 g, yield 66%). ¹H NMR (400 MHz, CDCl₃, δ/ppm): 7.70 (d, *J* = 8 Hz, 1H), 7.56 (d, *J* = 4 Hz, 1H), 7.54 (s, 1H), 7.40 (d, *J* = 4 Hz, 1H), 7.36 (d, *J* = 8 Hz, 1H), 7.33 (d, *J* = 8 Hz, 1H), 7.25 (d, *J* = 4 Hz, 1H), 4.24-4.18 (m, 4H), 2.18-2.16 (m, 1H), 1.37-1.15 (m, 27H), 0.88-0.78 (m, 6H); ¹³C NMR (100 MHz, CDCl₃, δ/ppm): 163.57, 152.21, 141.91, 140.29, 137.79, 130.10, 127.92, 127.20, 125.47, 123.67, 123.07, 122.75, 121.81, 121.28, 117.90, 117.64, 111.77, 60.43, 50.46, 39.13, 31.86, 31.75, 29.92, 29.60, 29.48, 29.24, 26.51, 26.48, 22.65, 22.59, 14.15, 14.12, 14.07.

Synthesis of compound 13. This compound was prepared by following the synthetic procedure of compound **6a**, obtained as a bluish green oily liquid (0.8 g, yield 47%). ¹H NMR (400 MHz, CDCl₃, δ/ppm): 7.57 (d, *J* = 8 Hz, 1H), 7.39 (d, *J* = 8 Hz, 1H), 7.35 (d, *J* = 4 Hz, 1H), 7.19 (d, *J* = 8 Hz, 4H), 7.13 (d, *J* = 4 Hz, 4H), 7.10 (s, 1H), 7.05 (d, *J* = 8 Hz, 1H), 6.47 (d, *J* = 4 Hz, 1H), 3.93 (d, *J* = 8 Hz, 2H), 2.60 (t, *J* = 8 Hz, 4H), 2.04-1.97 (m, 1H), 1.34-1.27 (m, 40H), 0.91-0.80 (m, 12H); ¹³C NMR (100 MHz, CDCl₃, δ/ppm): 145.61, 144.09, 142.03, 141.91, 140.60, 137.63, 131.37, 128.54, 128.35, 128.25, 128.15, 127.96, 127.77, 127.65, 125.63, 123.18, 122.44, 122.37, 121.76, 118.62, 112.10, 80.91, 50.03, 39.27, 35.78, 32.02, 31.88, 31.51, 29.77, 29.64, 29.42, 29.27, 26.50, 22.79, 22.76, 14.25; MS (MALDI-TOF, *m/z*) C₅₇H₇₃NS₃: calculated: 867.496; found: 868.364.

Synthesis of compound 14. This compound was prepared by following the synthetic procedure of compound **7a**, obtained as as an yellow solid (0.21 g, yield 50%). ¹H NMR (400 MHz, CDCl₃, δ/ppm): 9.97 (s, 1H), 9.74 (s, 1H), 8.01 (s, 1H), 7.63 (d, *J* = 8 Hz, 1H), 7.16 (m, 8H), 7.12-7.07 (m, 2H), 3.95 (d, *J* = 8 Hz, 2H), 2.60 (t, *J* = 8 Hz, 4H), 2.00-1.95 (m, 1H), 1.39-1.10 (m, 40H), 0.90-0.78 (m, 12H); ¹³C NMR (100 MHz, CDCl₃, δ/ppm): 183.16, 183.03, 150.35, 145.88, 144.52, 143.64, 142.60, 141.64, 141.46, 140.11, 137.20, 130.95, 130.90, 129.51, 129.23, 128.32, 127.57, 123.21, 122.34, 121.69, 119.80, 112.18, 105.00, 80.72, 50.32, 39.27, 35.75, 32.00, 31.84, 31.58, 31.48, 30.07, 29.75, 29.59, 29.40, 29.24, 26.45, 26.42, 22.77,

22.75, 14.25, 14.22; MS (MALDI-TOF, m/z) C₅₉H₇₃NO₂S₃: calculated: 923.480; found: 924.476.

Preparation and performance test of OSCs

The OSC devices with an inverted structure of ITO/ZnO/polymer:SMA/MoO₃/Al were fabricated and characterized in an N₂-filled glovebox, where polymer means PBDB-T or PBDB-TF using as donor and NIT-based SMAs were used as acceptor materials. The indium tin oxide (ITO) patterned glass was cleaned with ultrasonic treatment in detergent, deionized water, acetone, ethanol, and isopropyl alcohol sequentially, and dried in an ultraviolet-ozone chamber for 15 min. The ZnO layer was deposited by spin-coating on top of a pre-cleaned ITO-coated glass substrate. And then, the active layer was spin-coated on the ZnO layer from a mixed solution containing polymer donor and SMA. The total concentration of the mixed solution was various according to the different donor:acceptor systems. Subsequently, a MoO₃ layer (~5 nm) and an Al layer (~100 nm) were evaporated through a shadow mask and form a top anode. The active area of the devices was defined by a shadow mask. The thicknesses of the active layer were controlled by varying the spin-coating speed and measured on an Ambios Technology XP-2 surface profilometer. Photovoltaic performance of solar cells was tested under illumination condition with an AM 1.5G (100 mW cm⁻²), and the current density-voltage (*J-V*) characteristics were measured by a computer controlled Keithley 2602 Source Meter. The incident light intensity was calibrated using a standard Si solar cell. The external quantum efficiency (EQE) was measured by using a Solar Cell Spectral Response Measurement System QE-R3011 (Enli Technology Co., Ltd.). The light intensity at each wavelength was calibrated by a standard single-crystal Si solar cell.

The charge mobility was measured by the space charge-limited current (SCLC) method with a hole only device configuration (ITO/PEDOT:PSS/active layer/MoO₃/Al) for hole mobility and an electron only device configuration (ITO/ZnO/active layer/PFN-Br/Al) for electron mobility. Both hole and electron mobilities were extracted by fitting measured *J-V* curves using the empirical Mott-Gurney formula in single carrier SCLC device with the equation of $\ln(JL^3/V^2) \approx 0.89(1/E_0)^{0.5} (V/L) + \ln(9\varepsilon_0\varepsilon_r\mu/8)$.

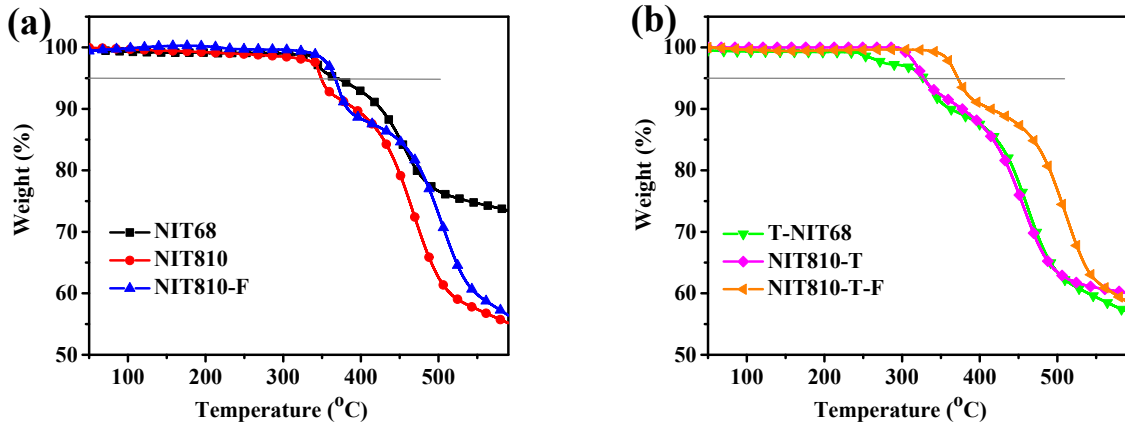


Fig. S1. TGA plots of six NIT-based SMAs: (a) NIT68, NIT810, and NIT810-F; (b) T-NIT68, NIT810-T, and NIT810-T-F

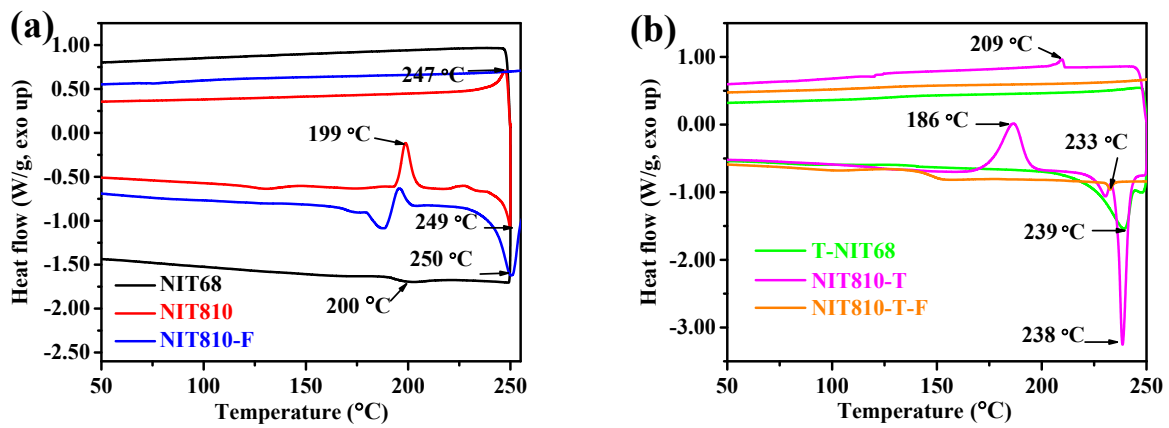


Fig. S2. The second heating and first cooling traces of DSC of six NIT-based SMAs: (a) NIT68, NIT810, and NIT810-F; (b) T-NIT68, NIT810-T, and NIT810-T-F.

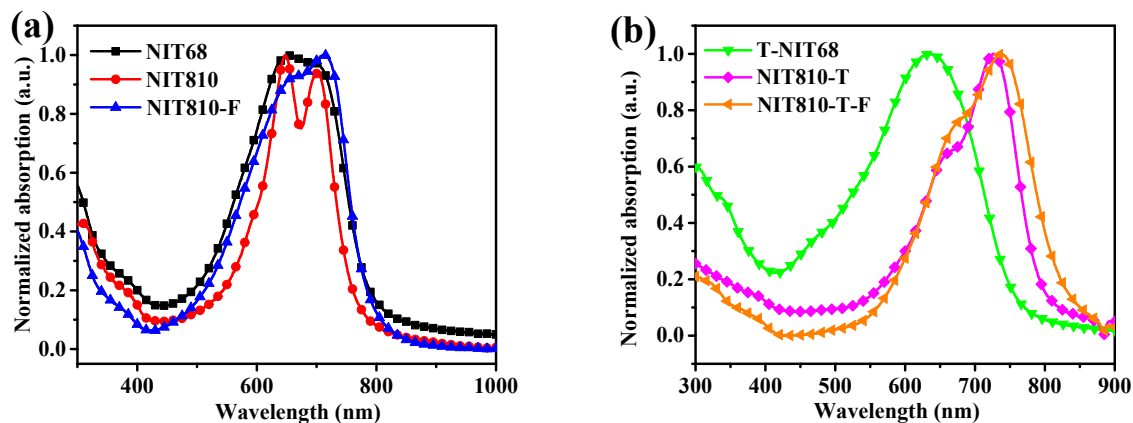


Fig. S3. Normalized absorption spectra of six NIT-based SMAs as solid films: (a) NIT68, NIT810, and NIT810-F; (b) T-NIT68, NIT810-T, and NIT810-T-F

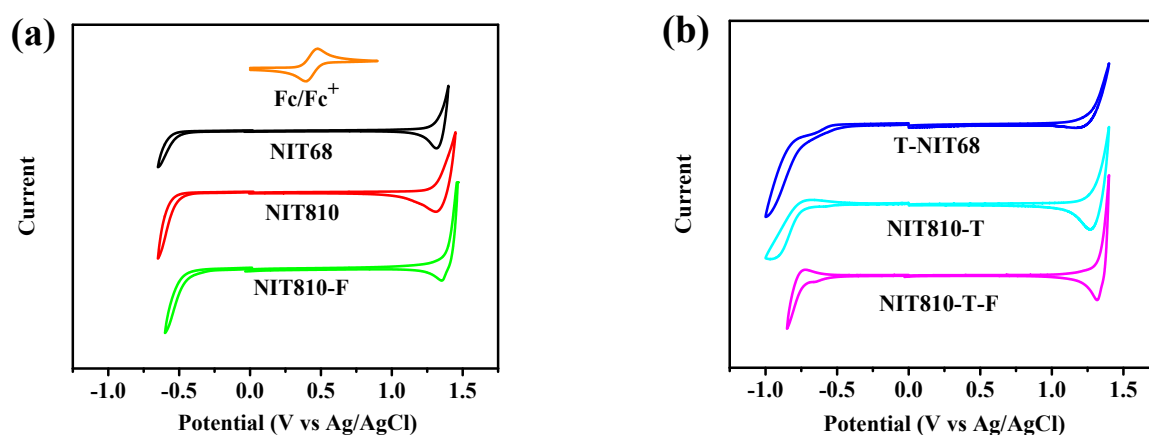


Fig. S4. CV curves of six NIT-based SMA films on platinum electrode and Fc/Fc⁺ versus Ag/AgCl: (a) NIT68, NIT810, and NIT810-F; (b) T-NIT68, NIT810-T, and NIT810-T-F.

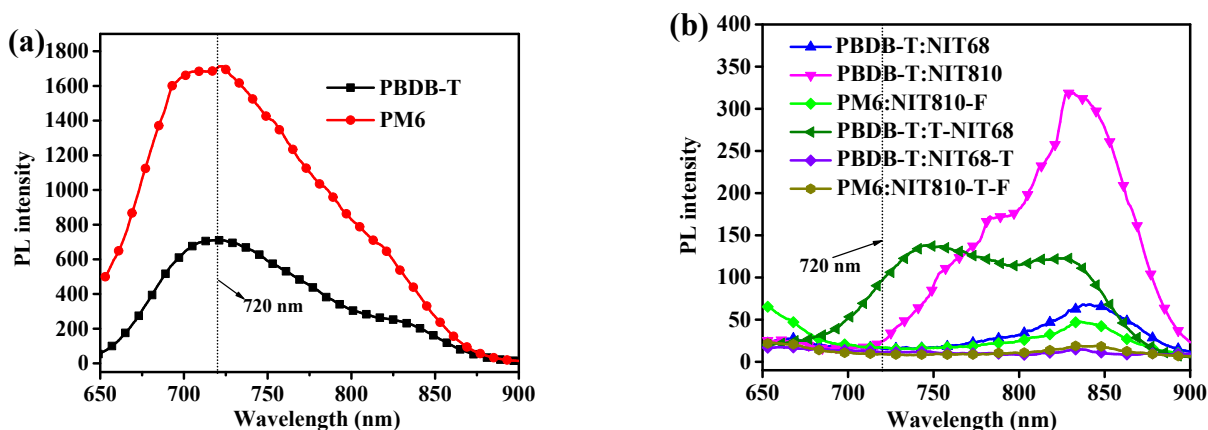


Fig. S5. PL spectra of (a) the pure polymer donors and (b) donor:SMA blend films.

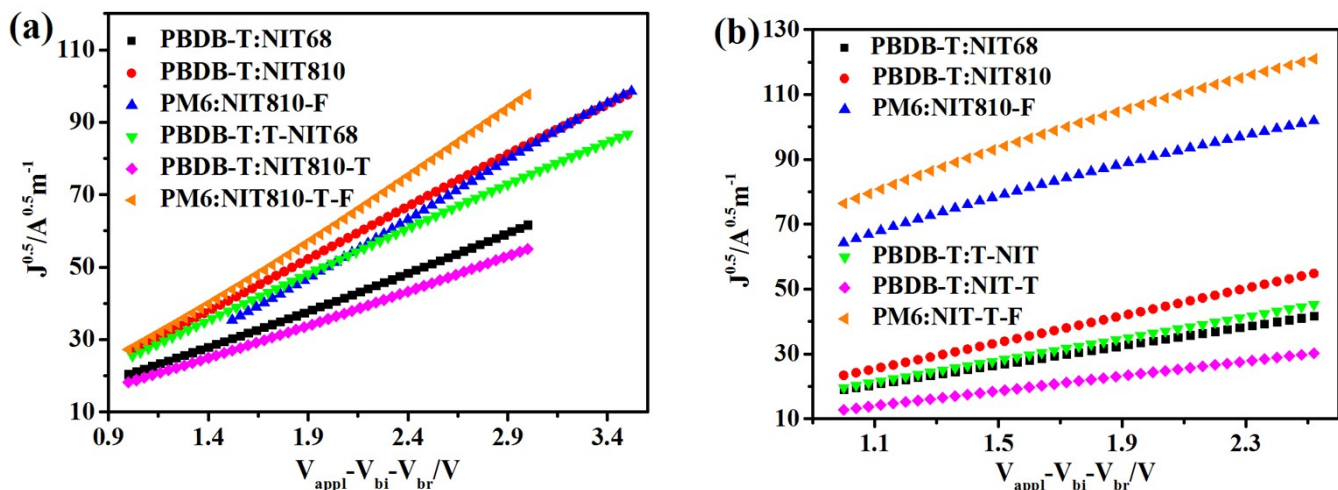


Fig. S6. The J - V plots for measuring the hole (a) and electron (b) mobilities by using SCLC method.

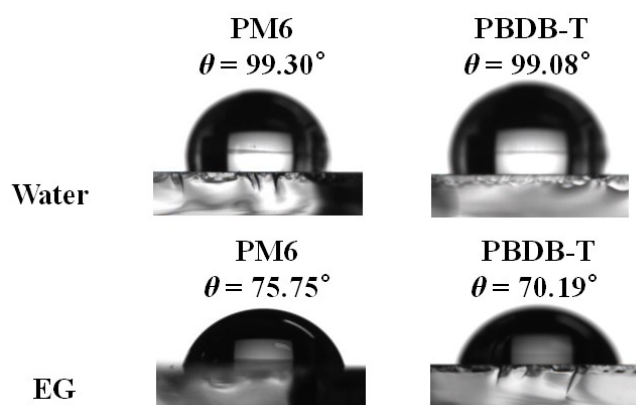


Fig. S7. Contact angle images and data of water (θ_{water}) and ethylene glycol (EG, θ_{EG}) on the pure film of PBDB-T and PM6.

Table S1. Photovoltaic properties of OSCs based on **NIT68** under various fabricated conditions.

Active layer	TA ($^{\circ}\text{C}$)	Additive (vol%)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
PBDB-T: NIT68 = 1:0.8	-	-	0.93	11.65	49.5	5.36
PBDB-T: NIT68 = 1:1	-	-	0.92	11.88	52.4	5.73
PBDB-T: NIT68 = 1:1.2	-	-	0.91	11.40	53.1	5.51
PBDB-T: NIT68 = 1:1.5	-	-	0.90	11.13	52.1	5.22
PBDB-T: NIT68 = 1:1	-	0.5% CN	0.93	11.12	54.4	5.63
PBDB-T: NIT68 = 1:1	90	-	0.92	12.12	54.5	6.08
PBDB-T: NIT68 = 1:1	110	-	0.90	12.73	57.9	6.63
PBDB-T: NIT68 = 1:1	130	-	0.91	12.69	53.6	6.19

Table S2. Photovoltaic properties of OSCs based on **NIT810** under various fabricated conditions.

Active layer	TA (°C)	Additive (vol%)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)
PBDB-T: NIT810 = 1:1	-	-	0.91	8.60	47.5	3.72
PBDB-T: NIT810 = 1:1.2	-	-	0.94	10.16	45.7	4.36
PBDB-T: NIT810 = 1:1.5	-	-	0.94	10.39	47.8	4.67
PBDB-T: NIT810 = 1:1.8	-	-	0.91	11.13	42.7	4.32
PBDB-T: NIT810 = 1:1.5	-	0.5% DIO	0.93	12.28	63.5	7.25
PBDB-T: NIT810 = 1:5	-	1% DIO	0.91	12.23	56.4	6.28
PBDB-T: NIT810 = 1:1.2	110	-	0.90	11.46	48.3	4.98
PM6: NIT810 = 1:1.5	-	-	0.98	11.11	40.8	4.44
PM6: NIT810 = 1:5	-	0.5% DIO	1.01	8.97	49.3	4.47
PM6: NIT810 = 1:1.5	110	-	0.97	12.51	44.8	5.44

Table S3. Photovoltaic properties of OSCs based on **NIT810-F** under various fabricated conditions.

Active layer	TA (°C)	Additive (vol%)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)
PBDB-T: NIT810-F = 1:0.8	-	-	0.84	3.52	32.6	0.96
PBDB-T: NIT810-F = 1:1	-	-	0.83	6.02	35.3	1.76
PBDB-T: NIT810-F = 1:1.2	-	-	0.83	6.57	35.0	1.91
PBDB-T: NIT810-F = 1:1.5	-	-	0.82	9.12	43.2	3.23
PBDB-T: NIT810-F = 1:1.8	-	-	0.81	9.52	38.3	2.95
PBDB-T: NIT810-F = 1:1.5	-	1%	0.75	7.42	45.8	2.55
PBDB-T: NIT810-F = 1:1.5	90	-	0.79	11.29	40.3	3.59
PBDB-T: NIT810-F = 1:1.5	110	-	0.79	12.17	43.4	4.17
PBDB-T: NIT810-F = 1:1.5	130	-	0.80	12.35	39.0	3.85
PM6: NIT810-F = 1:1.5	-	-	0.89	11.71	58.4	6.09
PM6: NIT810-F = 1:1.5	110	-	0.86	13.09	64.5	7.26
PM6: NIT810-F = 1:1.5	-	0.5% DIO	0.86	8.64	61.3	4.55
PM6: NIT810-F = 1:1.5	110	0.5% DIO	0.87	13.51	66.2	7.78

Table S4. Photovoltaic properties of OSCs based on **T-NIT68** under various fabricated conditions.

Active layer	TA (°C)	Additive (vol%)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)
PBDB-T:T-NIT68 = 1:1	-	-	0.96	12.29	52.8	6.23
PBDB-T:T-NIT68 = 1:1.2	-	-	0.97	12.02	54.2	6.32
PBDB-T:T-NIT68 = 1:1.5	-	-	0.96	12.13	52.7	6.14
PBDB-T:T-NIT68 = 1:1	110	-	0.97	12.03	51.1	5.96
PBDB-T:T-NIT68 = 1:1.2	-	0.5% DIO	1.00	11.75	58.2	6.84
PBDB-T:T-NIT68 = 1:1.2	-	1% DIO	1.01	10.32	56.0	5.84

Table S5. Photovoltaic properties of OSCs based on **NIT810-T** under various fabricated conditions.

Active layer	TA (°C)	Additive (vol%)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)
PBDB-T:NIT810-T = 1:1	-	-	0.95	11.87	40.4	4.56
PBDB-T:NIT810-T = 1:1	110	-	0.95	12.82	42.5	5.18
PBDB-T:NIT810-T = 1:1	-	0.5% DIO	0.95	12.22	41.8	4.85
PBDB-T:NIT810-T = 1:1	110	0.5% DIO	0.95	11.36	40.8	4.40
PBDB-T:NIT810-T = 1:1.2	-	-	0.95	13.32	41.8	5.30
PBDB-T:NIT810-T = 1:1.2	110	-	0.95	13.43	44.4	5.66
PBDB-T:NIT810-T = 1:1.5	110	-	0.93	13.59	39.6	5.00
PBDB-T:NIT810-T = 1:1.2	90	-	0.95	11.40	45.9	4.97
PBDB-T:NIT810-T = 1:1.2	130	-	0.95	11.91	42.7	4.83
PBDB-T:NIT810-T = 1:1.2	150	-	0.94	11.41	37.8	4.05
PBDB-T:NIT810-T = 1:1.2	-	0.5% CN	0.95	12.29	48.7	5.69
PBDB-T:NIT810-T = 1:1.2	-	1% CN	0.94	13.23	49.1	6.11
PBDB-T:NIT810-T = 1:1.2	-	2% CN	0.94	13.73	48.5	6.26
PBDB-T:NIT810-T = 1:1.2	-	3% CN	0.94	12.82	51.1	6.21

Table S6. Photovoltaic properties of OSCs based on **NIT810-T-F** under various fabricated conditions.

Active layer	TA (°C)	Additive (vol%)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)
PBDB-T: NIT810-T-F = 1:1	-	-	0.87	9.15	33.4	2.66
PBDB-T: NIT810-T-F = 1:1.2	-	-	0.85	9.77	33.7	2.80
PBDB-T: NIT810-T-F = 1:1.5	-	-	0.84	10.65	34.5	3.09
PBDB-T: NIT810-T-F = 1:1.8	-	-	0.84	10.27	34.6	2.98
PBDB-T: NIT810-T-F = 1:1.8	-	-	0.81	9.52	38.3	2.95
PBDB-T: NIT810-T-F = 1:1	-	0.5% DIO	0.86	9.87	33.7	2.86
PBDB-T: NIT810-T-F = 1:1.5	90		0.82	11.75	35.0	3.37
BDB-T: NIT810-T-F = 1:1.5	110		0.83	12.14	37.1	3.74
PBDB-T: NIT810-T-F = 1:1.5	130		0.84	12.90	35.9	3.89
PBDB-T: NIT810-T-F = 1:1.5	150		0.86	7.63	31.9	2.09
PM6: NIT810-T-F = 1:1	-	-	0.87	16.63	41.9	6.06
PM6: NIT810-T-F = 1:1.5	90	-	0.89	19.74	47.8	8.40
PM6: NIT810-T-F = 1:1.5	110	-	0.89	18.77	52.3	8.74
PM6: NIT810-T-F = 1:1.5	130	-	0.87	19.73	55.43	9.51
PM6: NIT810-T-F = 1:1.5	150	-	0.87	18.64	37.7	6.11

Table S7. Summarized electron and hole mobilities (μ_h and μ_e) data of the six blend films.

Blend films	μ_h (cm ² V ⁻¹ s ⁻¹)	μ_e (cm ² V ⁻¹ s ⁻¹)	μ_h/μ_e
PBDB-T: NIT68	1.42×10^{-4}	7.37×10^{-5}	1.93
PBDB-T: NIT810	2.75×10^{-4}	1.44×10^{-4}	1.91
PM6: NIT810-F	3.48×10^{-4}	2.01×10^{-4}	1.73
PBDB-T: T-NIT68	2.06×10^{-4}	9.41×10^{-5}	2.19
PBDB-T: NIT810-T	1.14×10^{-4}	4.40×10^{-5}	2.59
PM6: NIT810-T-F	4.21×10^{-4}	2.82×10^{-4}	1.49

Table S8. Summarized contact angles and surface free energy parameters of the polymer donors and NIT-based SMAs.

Film	θ_{Water} ($^{\circ}$)	θ_{EG} ($^{\circ}$)	γ (mJ cm^{-2})	$\chi_{\text{PM6-SMA}}$ (k)	$\chi_{\text{PBDB-T-SMA}}$ (k)
PM6	99.30	75.75	21.89		
PBDB-T	99.08	70.19	28.99		
NIT68	88.65	61.55	29.16	-	0.0002
NIT810	90.56	63.75	28.29	0.410	0.004
NIT810-F	92.25	68.75	24.20	0.058	0.216
T-NIT68	97.13	74.06	22.06	-	0.473
NIT810-T	95.44	69.25	26.18	0.192	0.072
NIT810-T-F	92.83	69.50	23.82	0.041	0.254