

Electronic Supplementary Information

New Small-Molecule Acceptors Based on Hexacyclic Naphthalene(cyclopentadithiophene) for Efficient Non-fullerene Organic Solar Cells

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Measurements and Instruments

The ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were taken on a Bruker AV400 Spectrometer. Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were performed on a Bruker Autoflex III instrument. The thermogravimetric analyses (TGA) were carried out on a NETZSCH STA 409PC instrument under purified nitrogen gas flow with a $10\text{ }^\circ\text{C min}^{-1}$ heating rate. UV-vis spectra were obtained with a JASCO V-570 spectrophotometer. Cyclic voltammetry (CV) experiments were performed with a LK98B II Microcomputerbased Electrochemical Analyzer in dichloromethane solutions. All CV measurements were carried out at room temperature with a conventional three-electrode configuration employing a glassy carbon electrode as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a Pt wire as the counter electrode. Dichloromethane was distilled from calcium hydride under dry argon immediately prior to use. Tetrabutylammonium phosphorus hexafluoride (Bu_4NPF_6 , 0.1 M) in dichloromethane was used as the supporting electrolyte, and the scan rate was 100 mV s^{-1} . Atomic force microscopy (AFM) was performed using Multimode 8 atomic force microscope in tapping mode. The transmission electron microscopy (TEM) investigation was performed on Philips Technical G2 F20 at 200 kV. The specimen for TEM measurement was prepared by spin casting the blend solution on ITO/PEDOT:PSS substrate, then floating the film on a water surface, and transferring to TEM grids.

The current density-voltage (J - V) curves of photovoltaic devices were obtained by a Keithley 2400 source-measure unit. All masked and unmasked tests gave consistent results with relative errors within 5%. The photocurrent was measured under illumination simulated 100 mW cm^{-2} AM 1.5G irradiation using an Oriel 96000 solar simulator, calibrated with a standard Si solar cell. The average PCE was obtained using 20 devices under the same conditions. External quantum efficiency (EQE) values of the

devices were measured using Stanford Research Systems SR810 lock-in amplifier. The thickness of the active layers in the photovoltaic devices was measured on a Veeco Dektak 150 profilometer.

SCLC mobility was measured using a diode configuration of ITO/PEDOT:PSS/Active layer/Au for hole and Al/Active layer/Al for electron by taking the dark current density in the range of 0-2 V and fitting the results to a space charge limited form, where SCLC is described by:

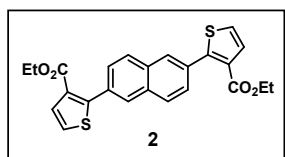
$$J = \frac{9\epsilon_0\epsilon_r\mu_0V^2}{8L^3} \exp(0.89\beta) \sqrt{\frac{V}{L}}$$

where J is the current density, L is the film thickness of the active layer, μ_0 is the hole or electron mobility, ϵ_r is the relative dielectric constant of the transport medium, ϵ_0 is the permittivity of free space (8.85×10^{-12} F m⁻¹), V ($= V_{\text{appl}} - V_{\text{bi}}$) is the internal voltage in the device, where V_{appl} is the applied voltage to the device and V_{bi} is the built-in voltage due to the relative work function difference of the two electrodes.

Material Synthesis and Characterization

All starting materials were purchased from commercial suppliers and used without further purification.

Synthesis of compound 2



A solution of compounds 1 (3.80 g, 10.0 mmol) and ethyl-2-bromothiophene-3-carboxylate (5.67 g, 24.0 mmol) in toluene (80 mL) and aqueous 2 M K₂CO₃ (25 mL) was degassed twice with argon. Then Pd(PPh₃)₄ (1.16 g, 1.00 mmol) was added and the mixture was stirred at 100 °C for 24 h under argon, after which the mixture was poured into water (200 mL), and extracted with CH₂Cl₂ (50 mL × 2). The organic layer was washed with water, and then dried over anhydrous Na₂SO₄. The solvent was removed by a rotating

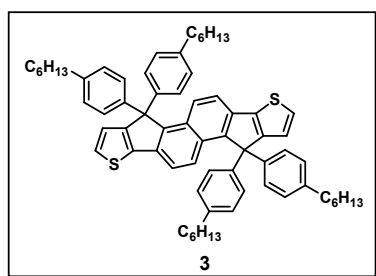
evaporator and the residue was purified by silica gel chromatography to obtain compound **2** (3.84 g, 88%).

¹H NMR (400 MHz, CDCl₃): δ 8.01 (d, *J* = 1.5 Hz, 2H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.67 (dd, *J* = 8.4, 1.5 Hz, 2H), 7.60 (d, *J* = 5.4 Hz, 2H), 7.32 (d, *J* = 5.4 Hz, 2H), 4.23 (q, *J* = 7.1 Hz, 4H), 1.19 (t, *J* = 7.1 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃): δ 163.36, 150.45, 132.51, 131.72, 130.24, 128.61, 128.55, 127.60, 124.40, 60.61, 14.12.

MS (MALDI-TOF): calcd for C₂₄H₂₀O₄S₂ [M⁺], 436.080; found: 436.721.

Synthesis of compound **3**



Step 1: To a argon-filled two-neck flash was added 1-(4-bromophenyl)hexane (1.92 g, 8.0 mmol) and then anhydrous THF (30 mL). The reaction mixture was stirred as -78 °C for 10 min, and *n*-BuLi (3.33 mL, 2.4 M in hexane) was added slowly to the mixture through funnel. The mixture was stirred at the same temperature for over one hour and then an anhydrous THF solution of compound **2** was added by syringe. The reaction mixture was allowed to warm to room temperature and stirred overnight. By the completion of the reaction, saturated aq. NH₄Cl (50 mL) was added and extracted with CH₂Cl₂ (50 mL × 2). The organic layer was washed with water, and then dried over anhydrous Na₂SO₄. The solvent was removed by a rotating evaporator and the residue was used in next step without further purification.

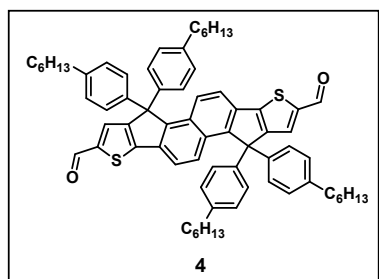
Step 2: The residue was dissolved in toluene (50 mL) and a drop of TfOH was added to the mixture. The reaction mixture was stirred and heated to 70 °C. After 30 min, the reaction was completed, then, quenched by water (50 mL) and extracted with CH₂Cl₂ (50 mL × 2). The organic layer was washed with water, and then dried over anhydrous Na₂SO₄. The solvent was removed by a rotating evaporator and the residue was purified by silica gel chromatography to obtain compound **3** (605.0 mg, 63%).

¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 10H), 7.00 (dd, *J* = 14.9, 5.4 Hz, 10H), 2.53 (m, 8H), 1.56 (m, 8H), 1.28 (m, 24H), 0.86 (m, 12H).

¹³C NMR (101 MHz, CDCl₃) δ 159.66, 149.62, 141.20, 140.76, 139.29, 134.12, 129.18, 128.91, 128.08, 127.24, 126.34, 122.62, 118.74, 63.88, 35.54, 31.71, 31.20, 29.16, 22.58, 14.08.

MS (MALDI-TOF): calcd for C₆₈H₇₆S₂ [M⁺], 956.538; found: 957.013.

Synthesis of compound 4



A Vilsmeier reagent, which was prepared with POCl₃ (0.50 mL) in DMF (4 mL), was added to a solution of compound 3 (0.46 g, 0.50 mmol) in 1,2-dichloroethane (40 mL) under the protection of argon. After refluxing at 80 °C overnight, the mixture was poured into ice water (100 mL), neutralized with aqueous AcONa, and then extracted with dichloromethane (50 ml x 2). The combined organic layer was washed with water and brine, dried over anhydrous Na₂SO₄. After removal of solvent, the crude product was purified by silica gel to obtain compound 4 (430 mg, 85%).

¹H NMR (400 MHz, CDCl₃) δ 9.76 (s, 2H), 7.90 (d, *J* = 8.6 Hz, 2H), 7.64 (s, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 7.16 (d, *J* = 8.3 Hz, 8H), 7.04 (d, *J* = 8.3 Hz, 8H), 2.58 – 2.49 (m, 8H), 1.56 (p, *J* = 7.9 Hz, 8H), 1.35 – 1.23 (m, 24H), 0.85 (t, *J* = 6.7 Hz, 12H).

¹³C NMR (101 MHz, CDCl₃) δ 182.89, 160.21, 151.91, 150.32, 146.01, 142.00, 137.84, 133.89, 131.58, 130.02, 128.77, 128.47, 127.51, 119.78, 64.20, 35.55, 31.72, 31.24, 29.15, 22.61, 14.12.

MS (MALDI-TOF): calcd for C₇₀H₇₆O₂S₂ [M⁺], 1012.528; found: 1014.178.

Synthesis of NTIC

Under the protection of argon, compound 4 (0.15 g, 0.15 mmol) and INCN (0.18 g, 0.90 mmol) was dissolved in a dry CHCl_3 (40 mL) solution, and then pyridine (0.5 mL) was added to the mixture. After stirring at room temperature for 12 h, the mixture was poured into water and then extracted with CHCl_3 (30 ml x 2), the organic layer was dried over anhydrous Na_2SO_4 for 0.5 h. After removal of solvent, the crude product was purified by silica gel and recrystallized from CHCl_3 and hexane to give NTIC as a dark blue solid (0.15 g, 73%).

^1H NMR (400 MHz, CDCl_3) δ 8.84 (s, 2H), 8.68 – 8.62 (m, 2H), 7.96 (d, $J = 8.7$ Hz, 2H), 7.93 – 7.87 (m, 2H), 7.72 – 7.64 (m, 8H), 7.20 (d, $J = 8.1$ Hz, 8H), 7.10 (d, $J = 8.1$ Hz, 8H), 2.62 – 2.51 (m, 8H), 1.62 – 1.55 (m, 8H), 1.29 (m, 24H), 0.85 (m, 12H).

^{13}C NMR (101 MHz, CDCl_3) δ 188.45, 161.22, 160.37, 159.24, 153.38, 142.20, 141.04, 139.91, 138.96, 138.71, 137.50, 136.83, 135.09, 134.81, 134.43, 130.67, 128.78, 128.58, 128.28, 125.30, 123.70, 121.87, 120.27, 114.65, 77.22, 68.98, 64.07, 35.54, 31.68, 31.21, 29.14, 22.58, 14.09.

MS (MALDI-TOF): calcd for $\text{C}_{94}\text{H}_{84}\text{N}_4\text{O}_2\text{S}_2$ [M^+], 1365.852; found: 1366.436.

Synthesis of NTIC-Me

Following the general procedure of NTIC synthesis, NTIC-Me was obtained as a dark blue solid (70%).

^1H NMR (400 MHz, CDCl_3) δ 8.81 (s, 2H), 8.54 (d, $J = 8.1$ Hz, 1H), 8.46 (s, 1H), 7.95 (d, $J = 8.7$ Hz, 2H), 7.79 (d, $J = 7.7$ Hz, 1H), 7.71 – 7.63 (m, 5H), 7.56 – 7.48 (m, 2H), 7.19 (d, $J = 8.3$ Hz, 8H), 7.09 (d, $J = 8.3$ Hz, 8H), 2.59 – 2.49 (m, 14H), 1.58 (m, 8H), 1.41 – 1.21 (m, 24H), 0.86 (t, $J = 6.7$ Hz, 12H).

^{13}C NMR (101 MHz, CDCl_3) δ 188.59, 188.22, 161.12, 160.52, 158.87, 158.75, 153.25, 146.73, 146.24, 142.17, 141.01, 140.34, 138.69, 138.36, 137.57, 137.21, 136.03, 135.48, 134.81, 134.74, 130.62, 128.80, 128.58, 128.22, 125.66, 125.27,

124.04, 123.61, 122.45, 120.25, 114.74, 68.69, 68.14, 64.07, 58.51, 35.56, 31.71, 31.24, 29.17, 22.60, 22.10, 18.47, 14.12.

MS (MALDI-TOF): calcd for C₉₆H₈₈N₄O₂S₂ [M⁺], 1393.906; found: 1394.434.

Synthesis of NTIC-OMe

Following the general procedure of NTIC synthesis, NTIC-Me was obtained as a dark blue solid (79%).

¹H NMR (400 MHz, CDCl₃) δ 8.80 (s, 2H), 8.18 (d, *J* = 1.9 Hz, 2H), 7.97 (d, *J* = 8.7 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.70 – 7.65 (m, 4H), 7.21 (d, *J* = 8.2 Hz, 8H), 7.12 (d, *J* = 8.3 Hz, 8H), 3.97 (s, 6H), 2.62 – 2.53 (m, 8H), 1.62 (dd, *J* = 12.7, 6.7 Hz, 8H), 1.37 – 1.26 (m, 24H), 0.89 (t, *J* = 6.6 Hz, 12H).

¹³C NMR (101 MHz, CDCl₃) δ 187.35, 165.43, 161.04, 160.40, 158.69, 153.15, 142.39, 142.14, 140.91, 138.48, 137.75, 137.62, 134.83, 130.58, 130.20, 128.80, 128.56, 128.18, 125.35, 122.80, 121.84, 120.19, 114.78, 114.55, 108.85, 68.81, 64.06, 58.49, 56.13, 31.69, 31.22, 29.15, 22.59, 18.45, 14.10.

MS (MALDI-TOF): calcd for C₉₆H₈₈N₄O₄S₂ [M⁺], 1425.904; found: 1425.430.

Synthesis of NTIC-F

Following the general procedure of NTIC synthesis, NTIC-Me was obtained as a dark blue solid (56%).

¹H NMR (400 MHz, CDCl₃) δ 8.84 (s, 2H), 8.69 (dd, *J* = 8.7, 4.2 Hz, 0.5H), 8.36 (dd, *J* = 9.0, 1.9 Hz, 1.5H), 8.00 – 7.87 (m, 4H), 7.72 – 7.65 (m, 4H), 7.45 – 7.36 (m, 2H), 7.19 (d, *J* = 8.3 Hz, 8H), 7.10 (d, *J* = 8.2 Hz, 8H), 2.63 – 2.50 (m, 8H), 1.62 – 1.56 (m, 8H), 1.36 – 1.24 (m, 24H), 0.86 (t, *J* = 6.6 Hz, 12H).

¹³C NMR (101 MHz, CDCl₃) δ 187.01, 168.02, 165.45, 161.41, 159.86, 159.71, 159.35, 159.05, 153.57, 142.41, 142.30, 142.22, 141.08, 141.04, 139.25, 138.87, 137.45, 134.86, 134.82, 133.12, 130.78, 128.81, 128.71, 128.64, 128.40, 125.95,

125.85, 121.95, 121.82, 121.74, 120.35, 114.34, 114.24, 112.99, 112.73, 64.27, 64.14, 35.58, 31.72, 31.25, 30.98, 29.18, 22.62, 14.12.

MS (MALDI-TOF): calcd for C₉₄H₈₂F₂N₄O₂S₂ [M⁺], 1401.833; found: 1402.109.

Fabrication of OPV Devices

The photovoltaic devices were fabricated with a structure of glass/ITO/PEDOT:PSS/Donor:Acceptor/PDINO/Al. The ITO coated glass substrates were cleaned by indetergent, deionized water, acetone, and isopropyl alcohol under ultrasonication for 15 min each and dried by a nitrogen blow. PEDOT:PSS layer was spin-coated (ca. 30 nm thick) onto the cleaned ITO surface. The substrates were then placed into an argon-filled glove box after being baked at 150 °C for 20 min. Subsequently, the active layer was spin-coated from donor (5 mg/mL) and acceptor (4 mg/mL) in chloroform solution at 1500 rpm for 20 s on the ITO/PEDOT:PSS substrate. The active layer thickness was measured using a Dektak150 profilometer. And then, PDIN, with the concentration of 1.5 mg/ml using CH₃OH/AcOH (v:v = 100:0.2%) as mixed solvent, was spin-coated at 3000 rpm for 40 s on the active layer. Finally, a 60 nm Al layer were deposited on the PDINO layer under high vacuum ($< 1.5 \times 10^{-4}$ Pa). The effective area of each cell was 4 mm², defined by masks for the solar cell devices.

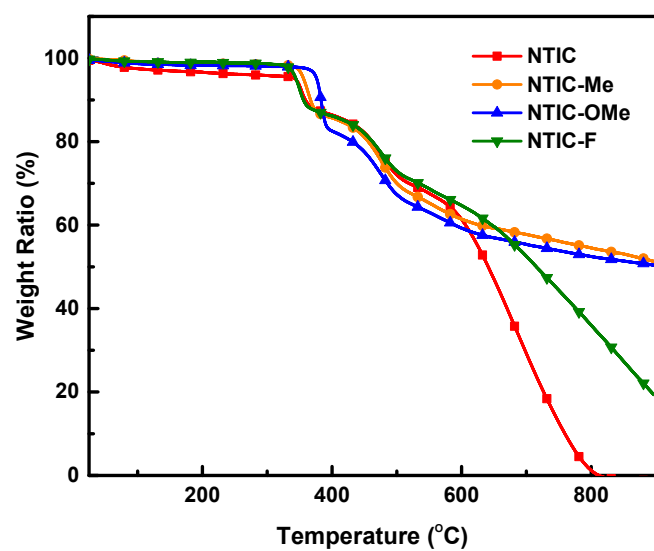


Fig. S1 TGA curves of acceptors with a heating rate of 10 °C/min under N₂ atmosphere.

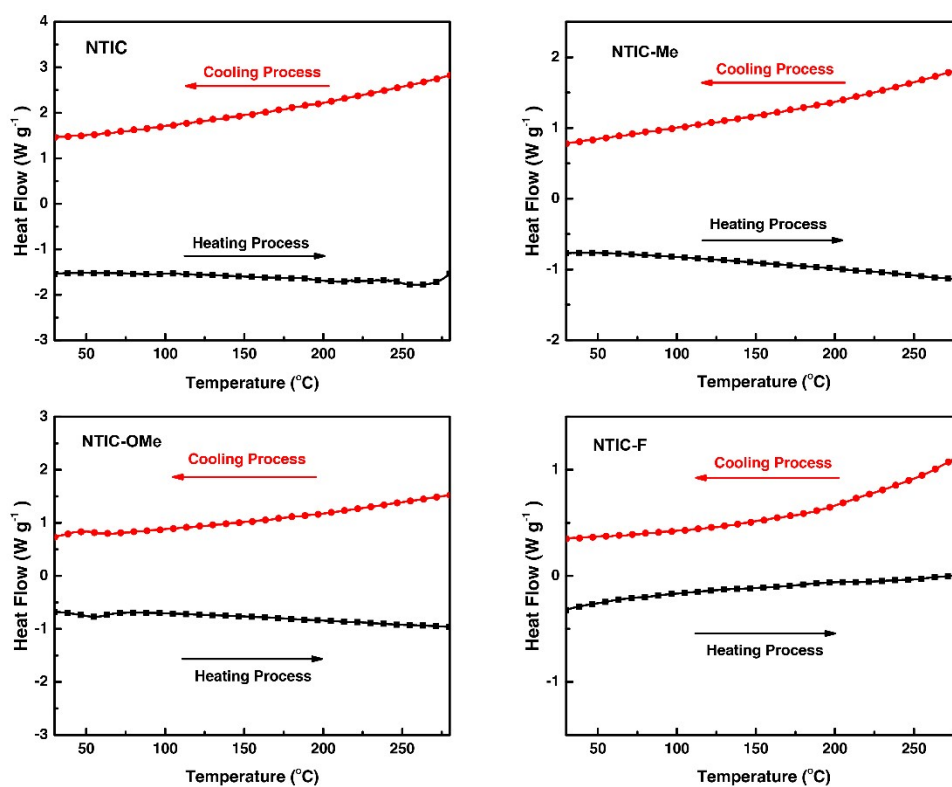


Fig. S2 DSC curves of acceptors.

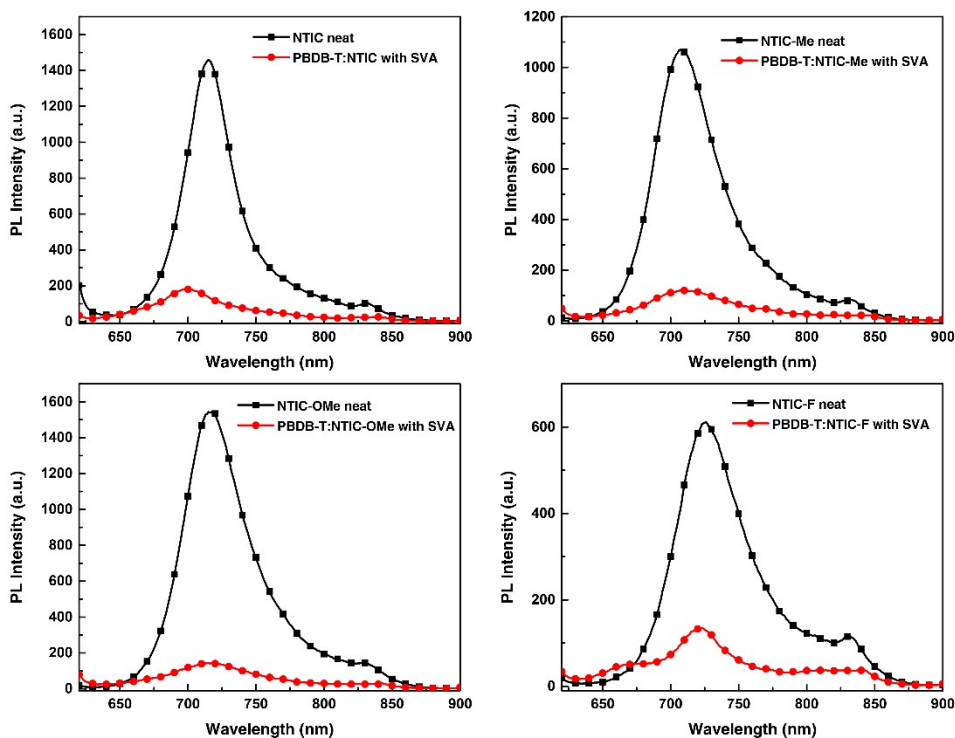


Fig. S3 Photoluminescence spectra of acceptor neat film and blend film with SVA.

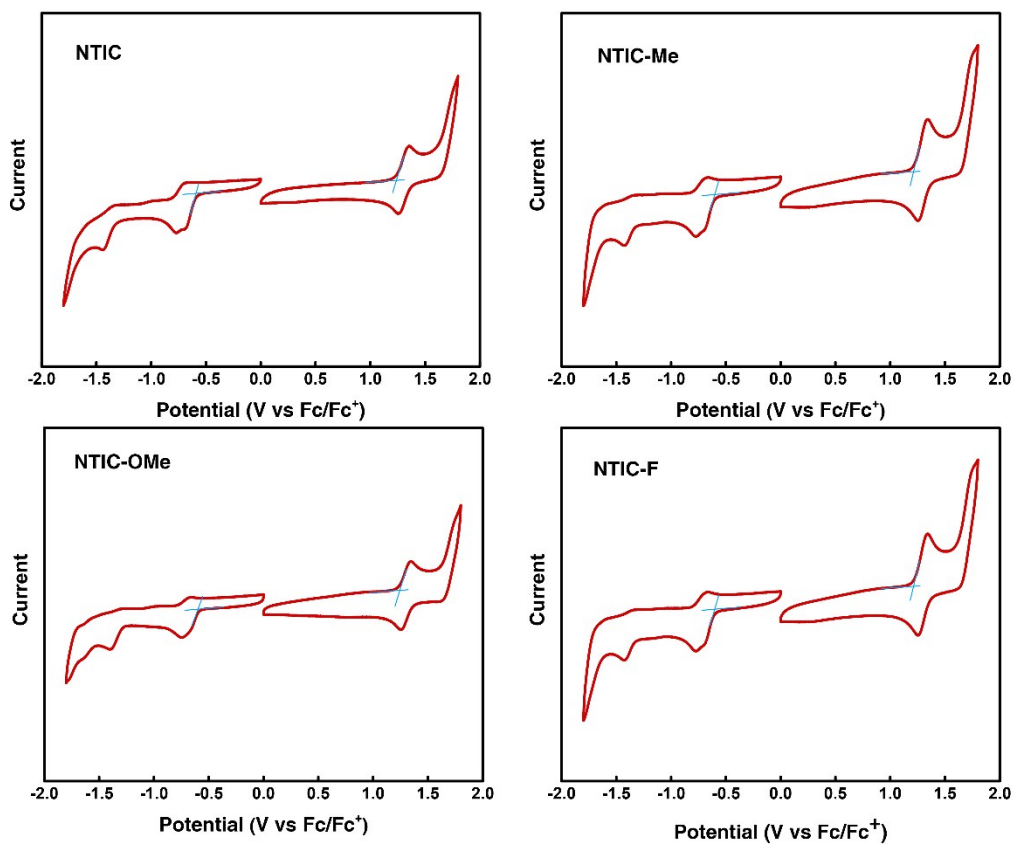


Fig. S4 Electrochemical properties of the acceptors.

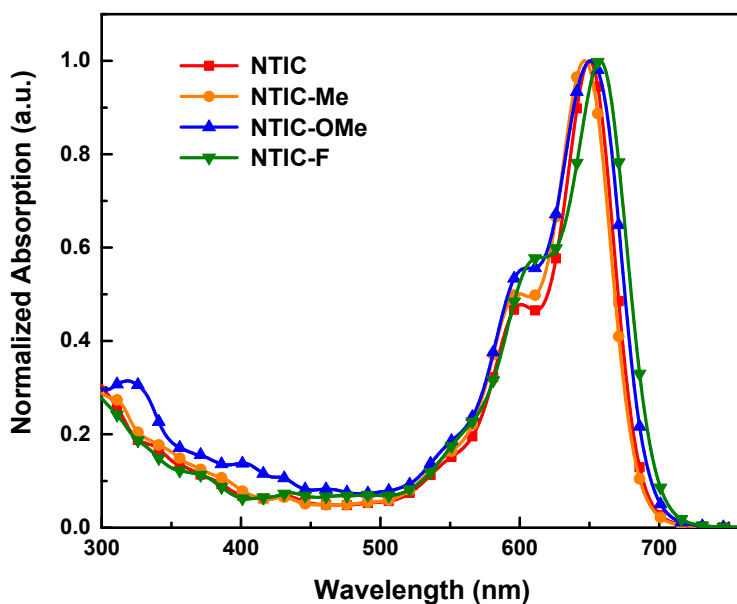


Fig. S5 UV-vis absorption of acceptors in CHCl_3 solution.

Table S1. Photovoltaic performance of the solar cells based on **PBDB-T:NTIC** (1:0.8, w/w) blend films with different SVA time under illumination of AM 1.5 G, 100 mW cm^{-2} . CHCl_3 as solvent.

SVA Time	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
As cast	0.926	13.19	60.8	7.43
60 s	0.920	13.74	62.5	7.91
120 s	0.916	13.61	64.3	8.02
150 s	0.935	13.55	68.1	8.63
240 s	0.926	13.74	66.6	8.48

Table S2. Photovoltaic performance of the solar cells based on **PBDB-T:NTIC-Me** (1:0.8, w/w) blend films with different SVA time under illumination of AM 1.5 G, 100 mW cm^{-2} . CHCl_3 as solvent.

SVA Time	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)
As cast	0.961	12.50	64.9	7.80
60	0.969	12.50	64.5	7.81
100	0.953	13.14	64.5	8.07
120	0.963	13.03	66.2	8.30
150	0.963	13.19	64.7	8.22

Table S3. Photovoltaic performance of the solar cells based on **PBDB-T:NTIC-OMe** (1:0.8, w/w) blend films with different SVA time under illumination of AM 1.5 G, 100 mW cm⁻². CHCl₃ as solvent.

SVA Time	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)
As cast	0.962	12.97	65.1	8.12
60	0.969	13.24	64.5	8.33
100	0.970	13.48	64.4	8.42
120	0.965	13.52	66.0	8.61
150	0.962	13.59	65.5	8.56

Table S4. Photovoltaic performance of the solar cells based on **PBDB-T:NTIC-F** (1:0.8, w/w) blend films with different SVA time under illumination of AM 1.5 G, 100 mW cm⁻². CHCl₃ as solvent.

SVA Time	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)
As cast	0.811	13.61	58.9	6.50
60	0.810	13.73	60.6	6.73
120	0.811	14.97	66.5	8.07
150	0.812	15.04	66.3	8.10
4 min	0.810	15.07	66.3	8.09

NMR Spectra

