Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Supporting Information

Nonfullerene Acceptors with Carbon-Oxygen-Bridged Fused Nonacyclic Donor Units Enable Efficient Organic Solar Cells

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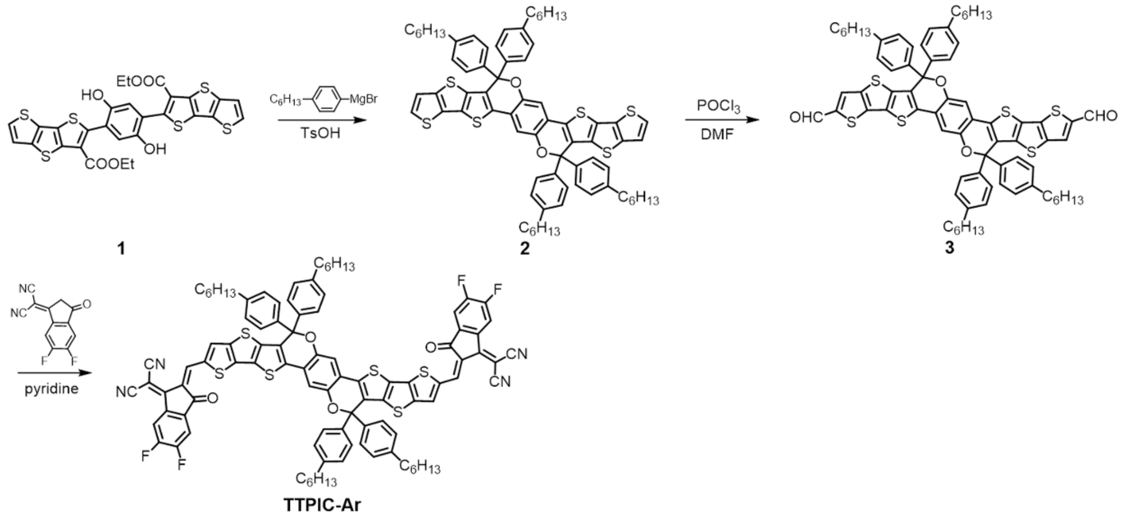
1. General characterization

^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance-400 spectrometer. Absorption spectra were recorded on a Lambda 950 spectrophotometer (PerkinElmer, U.S.A.). Cyclic voltammetry was done by using a Shanghai Chenhua CHI660C voltammetric analyzer under argon in acetonitrile of tetra-*n*-butylammonium hexafluorophosphate (0.1 M). A glassy-carbon electrode was used as the working electrode, a platinum-wire was used as the counter electrode, and a Ag/Ag$^+$ electrode was used as the reference electrode. All potentials were corrected against Fc/Fc$^+$ (Fc represents ferrocene.). AFM was performed on a Bruker Dimension icon using tapping mode. The EQE measurements of devices were carried out in the air with a solar cell spectral response measurement system (LST-QE, Lightsky Technology Co., Ltd). The light intensity at each wavelength was calibrated by a standard single-crystal Si photovoltaic cell.

2. Synthesis

All reagents were purchased from Innochem Co., HWRK Chem Co., SunaTech Inc., and other commercial suppliers, and used as received. The polymer donor, PM6, was purchased from Hyper Inc.. All reactions dealing with air- or moisture-sensitive compounds were carried out using standard Schlenk techniques. Compound **1** and **4** were synthesized, according to the reported literatures.[1,2]

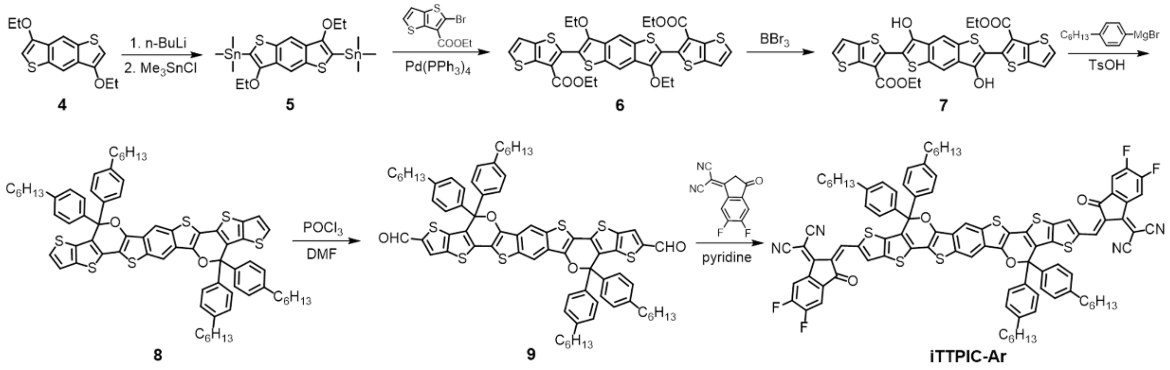


Scheme S1. Synthesis route of TTPIC-Ar.

Compound 2. To *p*-hexyl bromobenzene (3 g, 12.0 mmol) in dry THF (15 mL) was added magnesium chips (288 mg, 12.0 mmol) under argon at room temperature. The solution was heated to reflux for ~1 h until the magnesium chips almost disappeared to obtain the Grignard reagent. The fresh Grignard reagent was added into a suspension of compound **1** (642 mg, 1.0 mmol) in THF (15 mL) at room temperature under argon. The mixture was heated to reflux overnight and then allowed to cool down to room temperature. It was poured into water (150 mL) and extracted with CH_2Cl_2 three times. The organic phase was dried over anhydrous Na_2SO_4. After removing the solvent, the residue was resolved in toluene (20 mL), and 4-methylbenzenesulfonic acid (100 mg) was added. The solution was heated to 80 ^{o}C for ~1 h before cooling down to room temperature. It was extracted with petroleum ether three times and the combined organic phase was dried over anhydrous Na_2SO_4. After removing the solvent, the crude product was purified via column chromatography (silica gel) by using petroleum ether/CH_2Cl_2 (3:1, v/v) as eluent to give compound **2** as the yellow solid (428 mg, 37%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.29 (d, *J* = 5.2 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 8H), 7.12 (d, *J* = 8.1 Hz, 8H), 7.07 (d, *J* = 5.1 Hz, 2H), 6.99 (s, 2H), 2.59 (t, *J* = 7.6 Hz, 8H), 1.64-1.53 (m, 8H), 1.38-1.21 (m, 24H), 0.86 (t, *J* = 6.1 Hz, 12H). MALDI-TOF MS (m/z): 1161.941 [M^+], calcd. for $C_{72}H_{74}O_2S_6$ (1162.401).

Compound 3. Under argon, phosphorus oxychloride (0.2 mL) was dropped into DMF (1 mL) at 0 °C and stirred at room temperature for 2 h. Compound **2** (97 mg, 0.083 mmol) was dissolved in dry 1,2-dichloroethane (6 mL) and then added to the mixture to stir overnight at 85 °C. After cooling down to room temperature, the mixture was poured into water and extracted three times with dichloromethane. After removing the solvent, the crude product was purified via column chromatography (silica gel) by using petroleum ether/CH_2Cl_2 (1:1, v/v) as eluent to give compound **3** as the orange solid (77 mg, 75%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 9.89 (s, 2H), 7.73 (s, 2H), 7.21 (d, *J* = 8.2 Hz, 8H), 7.14 (d, *J* = 8.2 Hz, 8H), 7.02 (s, 2H), 2.60 (t, *J* = 7.7 Hz, 8H), 1.66-1.54 (m, 8H), 1.38-1.26 (m, 24H), 0.87 (t, *J* = 6.4 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 182.67, 146.84, 146.30, 143.97, 143.66, 142.19, 138.97, 137.77, 136.76, 131.77, 129.98, 128.62, 128.40, 128.31, 121.47, 111.62, 85.63, 35.66, 31.70, 31.20, 29.00, 22.62, 14.10. MALDI-TOF MS (m/z): 1218.905 [M^+], calcd. for $C_{74}H_{74}O_4S_6$ (1218.391).

TTPIC-Ar. Compound **3** (70 mg, 53 μmol) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malononitrile (53 mg, 0.23 mmol) were added to $CHCl_3$ (10 mL) and stirred at room temperature for 10 min. Then pyridine (1 mL) was added. It was heated to reflux for 1.5 h and then cooled down to room temperature. It was dropped into methanol and filtered to obtain the crude product. The crude product was purified via column chromatography (silica gel) by using $CHCl_3$/hexane (3:1, v/v) as eluent to give TTPIC-Ar as the dark solid (81 mg, 86%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.79 (s, 2H), 8.53 (dd, *J* = 9.6, 6.5 Hz, 2H), 7.81 (s, 2H), 7.69 (t, *J* = 7.4 Hz, 2H), 6.90 (s, 2H), 2.62 (t, *J* = 7.6 Hz, 8H), 1.69-1.54 (m, 8H), 1.39-1.25 (m, 24H), 0.87 (t, *J* = 6.4 Hz, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 185.82, 157.53, 155.97, 155.83, 153.37, 149.32, 147.05, 145.63, 143.83, 139.57, 138.74, 138.56, 137.92, 136.45, 134.41, 132.22, 128.77, 128.37, 121.70, 121.28, 115.07, 114.85, 113.96, 113.85, 112.84, 112.67, 111.67, 85.60, 69.72, 35.65, 31.68, 31.14, 29.01, 22.60, 14.07. MALDI-TOF MS (m/z): 1642.724 [M^+], calcd. for $C_{98}H_{78}F_4N_4O_4S_6$ (1643.432).



Scheme S2. Synthesis route of iTTPIC-Ar.

Compound 5. Compound **4** (500 mg, 1.8 mmol) was dissolved in 10 mL of anhydrous THF under argon. 1.6 M n-butyllithium (2.8 mL, 4.5 mmol) was added dropwise into the solution under -78 °C and then stirred for 1 h. Then 1 M trimethyltin chloride (5.4 mL, 5.4 mmol) was added dropwise and the solution further reacted for 2 h under the temperature. After reaction, the solution was extracted with water and petroleum ether. The organic phase was dried over anhydrous Na_2SO_4 and then filtered. After removing the solvent, the crude product was recrystallized by using methanol to obtain compound **5** as pale crystals (890 mg, 82%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.07 (s, 2H), 4.14 (q, J = 7.0 Hz, 4H), 1.48 (t, J = 7.0 Hz, 6H), 0.45 (s, 18H).

Compound 6. Compound **5** (689 mg, 1.14 mmol), ethyl 2-bromothieno[3,2-*b*]thiophene-3-carboxylate (728 mg, 2.5 mmol) and tetrakis(triphenylphosphine)palladium (95 mg, 0.08 mmol) were dissolved in dry toluene (10 mL) and stirred at 110 °C overnight. The reaction mixture was allowed to cool down to room temperature and then concentrated under reduced pressure. The crude product was purified via column chromatography (silica gel) by using petroleum ether/CH_2Cl_2 (2:1, v/v) as eluent to give compound **6** as the pale yellow solid (679 mg, 85%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.79 (s, 2H), 7.38 (d, J = 5.2 Hz, 2H), 7.31 (d, J = 5.2 Hz, 2H), 4.32 (q, J = 7.0 Hz, 4H), 4.21 (q, J = 6.9 Hz, 4H), 1.52 (t, J = 7.0 Hz, 6H), 1.28 (t, J = 6.6 Hz, 6H). MALDI-TOF MS (m/z): 697.504 [M$^+$], calcd. for $C_{32}H_{26}O_6S_6$ (698.005).

Compound 7. Compound **6** (530 mg, 0.76 mmol) was dissolved in dried dichloromethane (10.0 ml). 2M boron tribromide (1.9 mL, 3.8 mmol) was added dropwise under nitrogen and the reaction was further carried out for 4 h under room temperature. Then the solution was dropped into methanol and filtered to obtain compound **7** as dark yellow solid (464 mg, 95%). The compound **7** suffers from poor solubility in common solvent and was used for next step directly without further purification. MALDI-TOF MS (m/z): 664.735 [M+Na$^+$], calcd. for $C_{28}H_{18}O_6S_6$ (641.943).

Compound 8. To *p*-hexyl bromobenzene (840 mg, 3.5 mmol) in dry THF (12 mL) was added magnesium chips (96 mg, 4 mmol) under argon at room temperature. The solution was heated to reflux for ~1 h until the magnesium chips almost disappeared to obtain the Grignard reagent. The fresh Grignard reagent was added into a suspension of compound **7** (187 mg, 0.29 mmol) in THF (10 mL) at room temperature under argon. The mixture was heated to reflux overnight and then allowed to cool down to room temperature. It was poured into water (50 mL) and extracted with CH_2Cl_2 three times. The organic phase was dried over anhydrous Na_2SO_4. After removing the solvent, the residue was resolved in toluene (10 mL), and 4-methylbenzenesulfonic acid (50 mg) was added. The solution was heated to 80 °C for ~1 h under argon before cooling down to room temperature. It was extracted with petroleum ether three times and the combined organic phase was dried over anhydrous Na_2SO_4. After removing the solvent, the crude product was purified via flash column chromatography (silica gel) by using petroleum ether/CH_2Cl_2 (2:1, v/v) as eluent to give compound **8** as the dark yellow oil (139 mg, 41%). The compound **8** is not stable and no effective NMR data were obtained. MALDI-TOF MS (m/z): 1162.920 [M^+], calcd. for $C_{72}H_{74}O_2S_6$ (1162.401).

Compound 9. Under argon, phosphorus oxychloride (0.2 mL) was dropped into DMF (1 mL) at 0 °C and stirred at room temperature for 2 h. Compound **8** (100 mg, 0.086 mmol) was dissolved in dry 1,2-dichloroethane (6 mL) and then added to the mixture to stir overnight at 85 °C. After cooling down to room temperature, the mixture was poured into water and extracted three times with dichloromethane. After removing the solvent, the crude product was purified via column chromatography (silica gel) by using petroleum ether/CH_2Cl_2 (1:1, v/v) as eluent to give compound **9** as the dark red solid (69 mg, 66%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 9.81 (s, 2H), 8.19 (s, 2H), 7.84 (s, 2H), 7.25 (d, J = 8.1 Hz, 8H), 7.12 (d, J = 8.1 Hz, 8H), 2.59 (t, J = 7.7 Hz, 8H), 1.63-1.55 (m, 8H), 1.37-1.23 (m, 24H), 0.86 (t, J = 6.4 Hz, 12H). ^{13}C NMR ($CDCl_3$, 126 MHz, δ/ppm): 181.64, 145.12, 144.40, 143.29, 142.91, 137.54, 136.93, 134.71, 133.69, 128.82, 127.63, 127.31, 127.10, 124.93, 114.22, 111.90, 87.49, 34.61, 30.65, 30.11, 27.97, 21.54, 13.05. MALDI-TOF MS (m/z): 1218.915 [M^+], calcd. for $C_{74}H_{74}O_4S_6$ (1218.391).

iTTPIC-Ar. Compound **9** (70 mg, 57 μmol) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malononitrile (53 mg, 0.23 mmol) were added to $CHCl_3$ (10 mL) and stirred at room temperature for 10 min. Then pyridine (1 ml) was added. The solution was heated to reflux for 1.5 h and then cooled down to room temperature. It was dropped into methanol and filtered to collect the crude product. The crude product was purified via column chromatography (silica gel) by using $CHCl_3$/hexane (3:1, v/v) as eluent to give iTTPIC-Ar as the dark solid (87 mg, 92%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 8.66 (s, 2H), 8.46 (dd, J = 9.7, 6.6 Hz, 2H), 8.17 (s, 2H), 8.03 (s, 2H), 7.57 (t, J = 7.4 Hz, 2H), 7.30 (d, J = 8.0 Hz, 8H), 7.20 (d, J = 8.0 Hz, 8H), 2.61 (t, J = 7.5 Hz, 8H), 1.60 (d, J = 7.3 Hz, 8H), 1.37-1.20 (m, 24H), 0.82 (t, J = 6.2 Hz, 12H). ^{13}C NMR ($CDCl_3$, 126 MHz, δ/ppm): 184.12, 157.25, 152.71, 152.32, 152.24, 146.21, 143.23, 140.57, 138.42, 137.26, 136.74, 134.84, 134.39, 133.43, 129.06, 127.49, 127.16, 125.54, 120.63, 114.93, 113.89, 113.72, 113.31, 113.16, 112.84, 111.52, 111.36, 87.84, 68.46, 34.69, 30.73, 30.25, 28.03, 21.56, 13.02. MALDI-TOF MS (m/z): 1642.706 [M^+], calcd. for $C_{98}H_{78}F_4N_4O_4S_6$ (1643.432).

3. NMR spectra

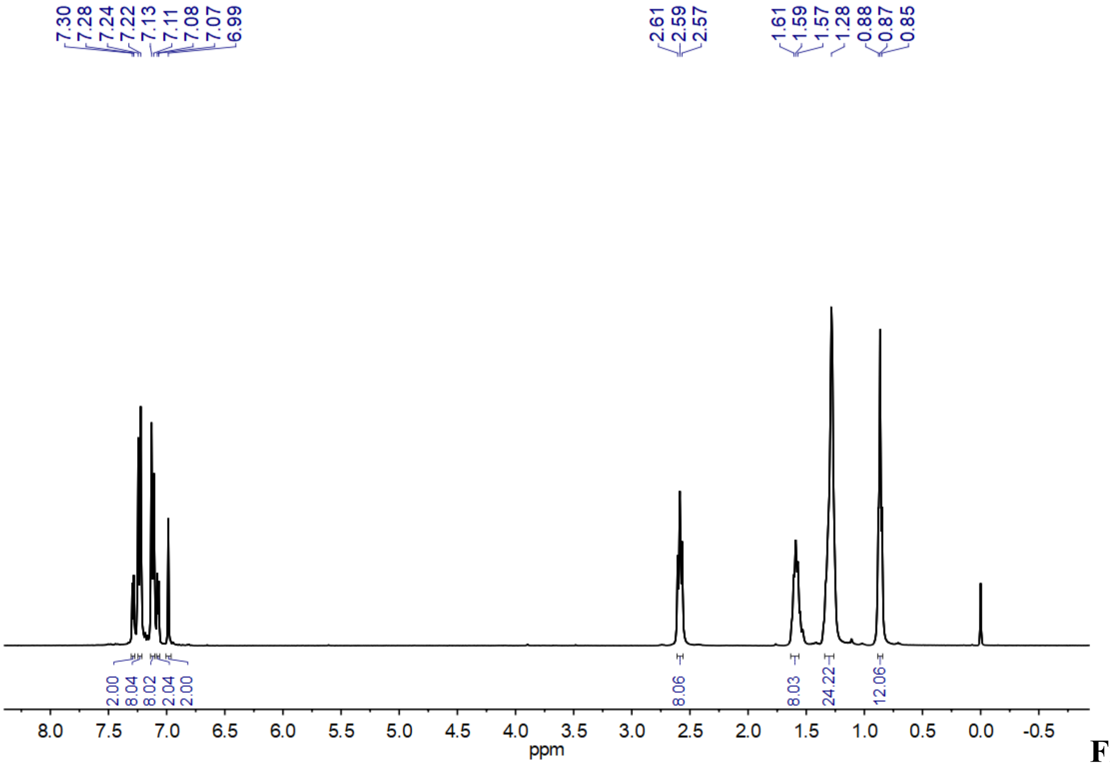
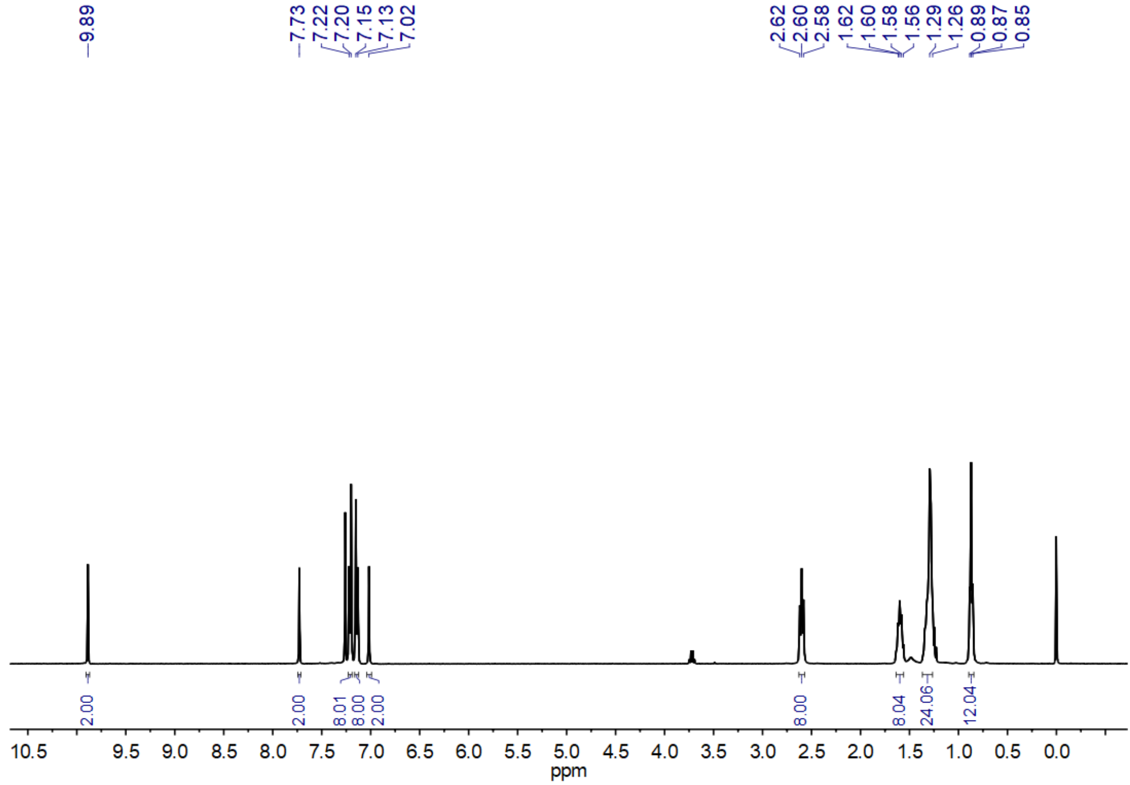


Figure S1. ^{1}H NMR spectrum of compound **2**.



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gure S2. ^{1}H NMR spectrum of compound **3**.

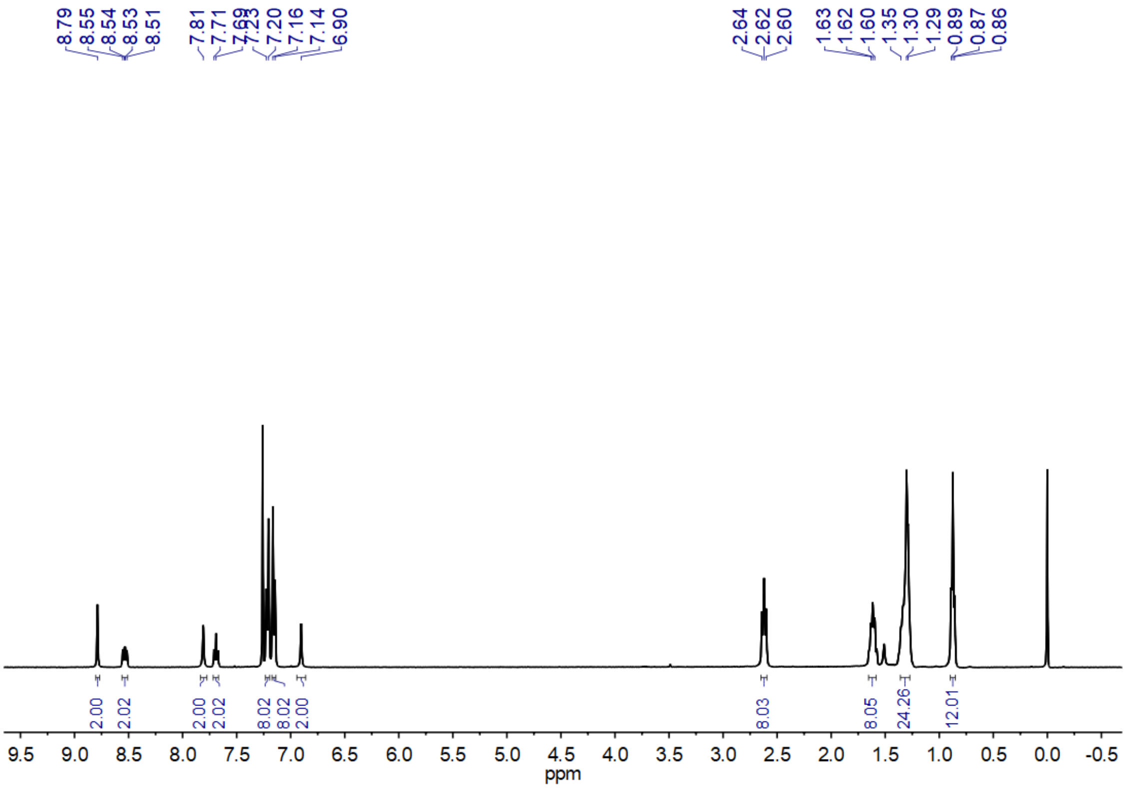

Figure S3. ^{1}H NMR spectrum of TTPIC-Ar.

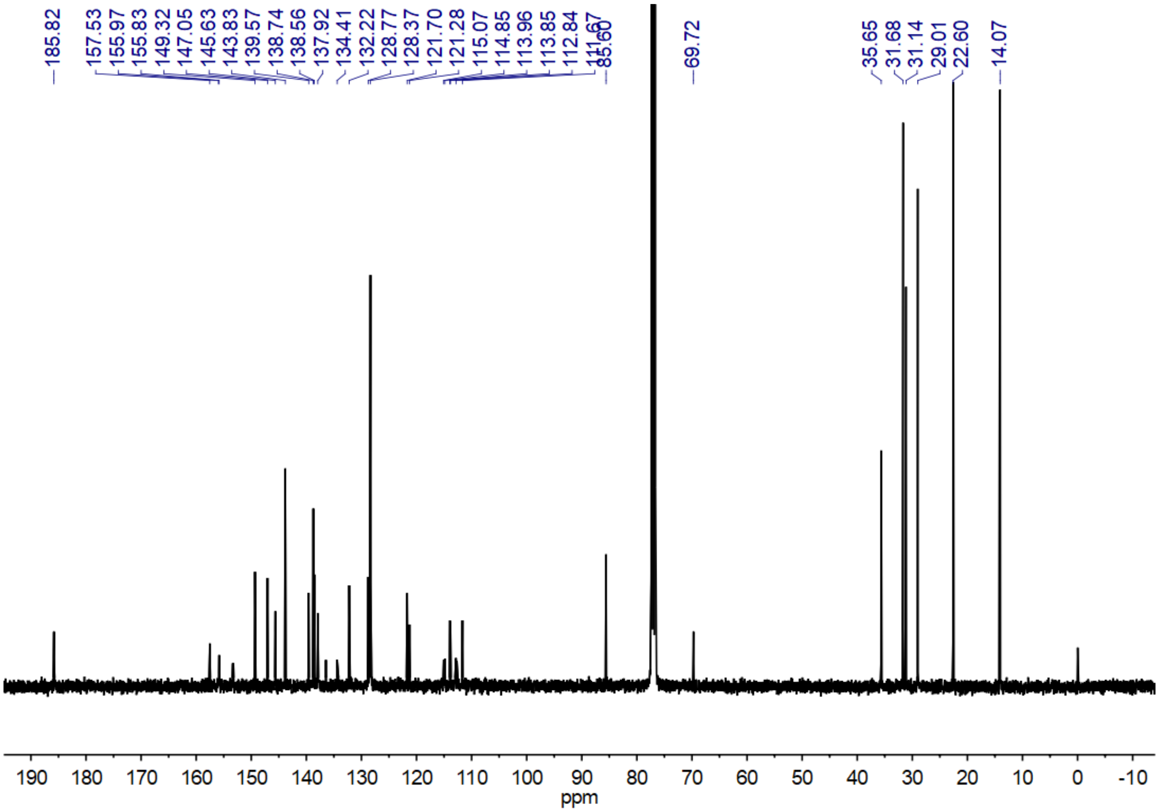

Figure S4. ^{13}C NMR spectrum of TTPIC-Ar.

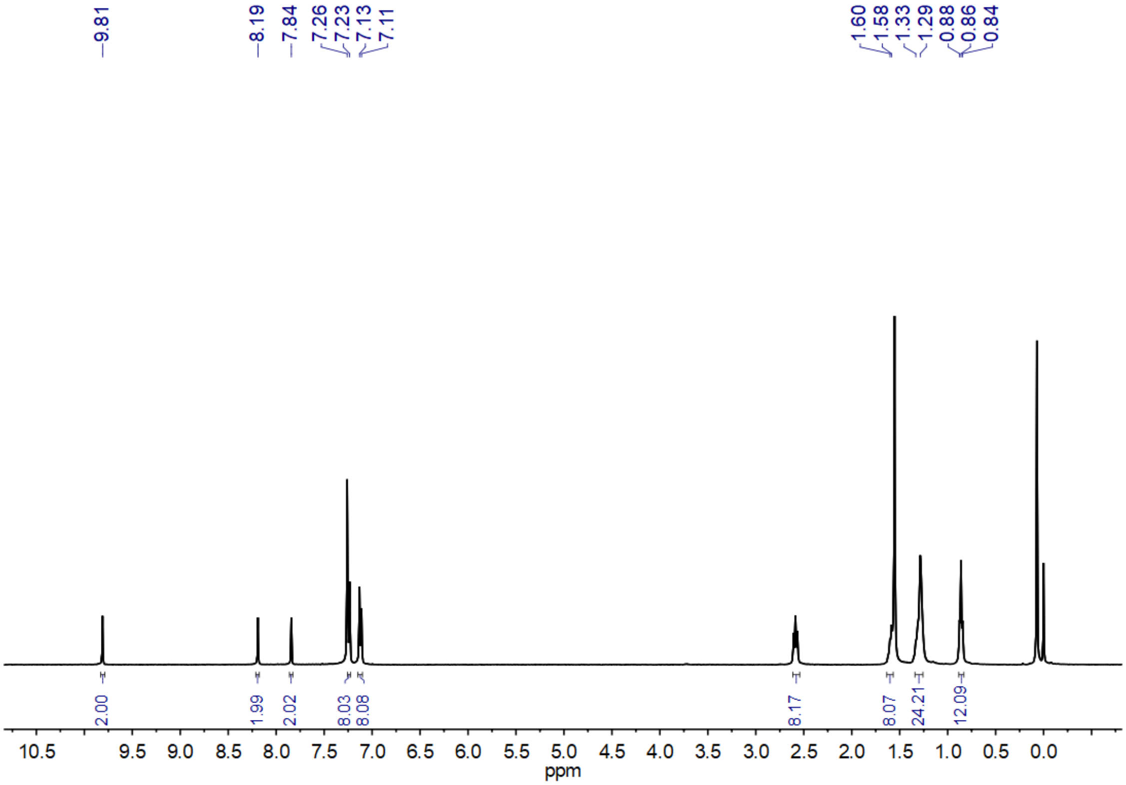

Figure S5. ^{1}H NMR spectrum of compound **9**.

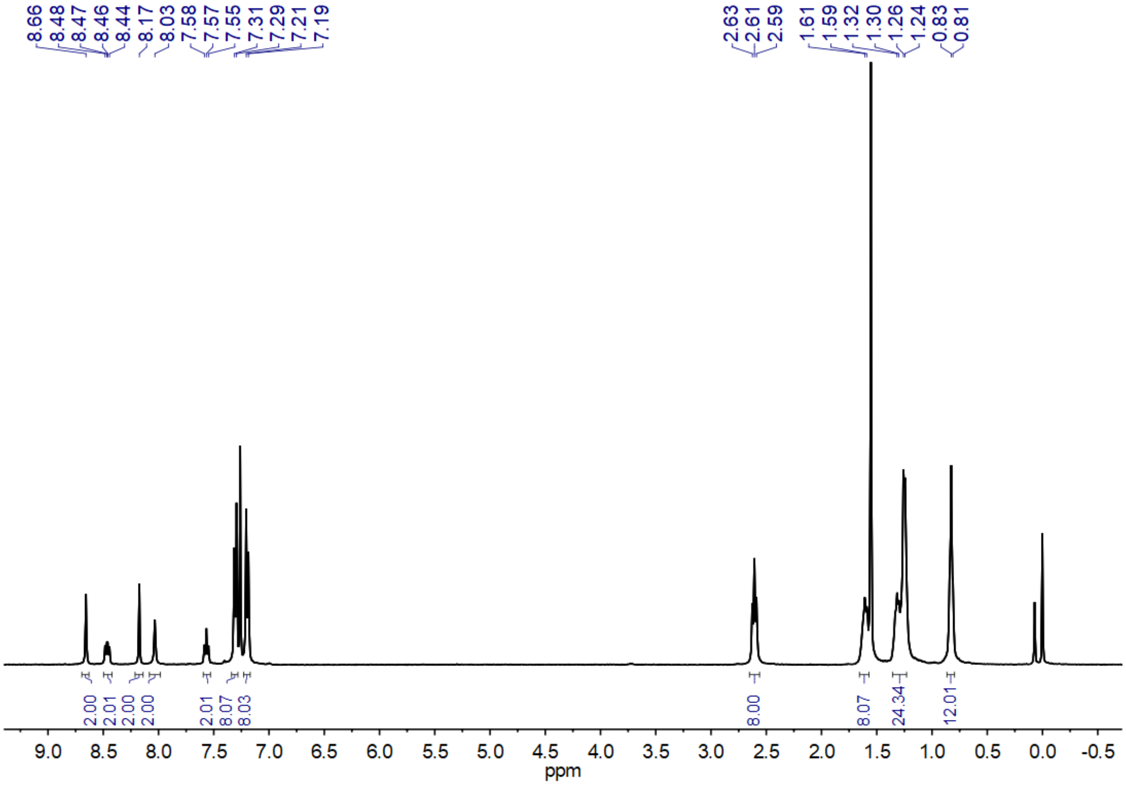

Figure S6. ^{1}H NMR spectrum of iTTPIC-Ar.

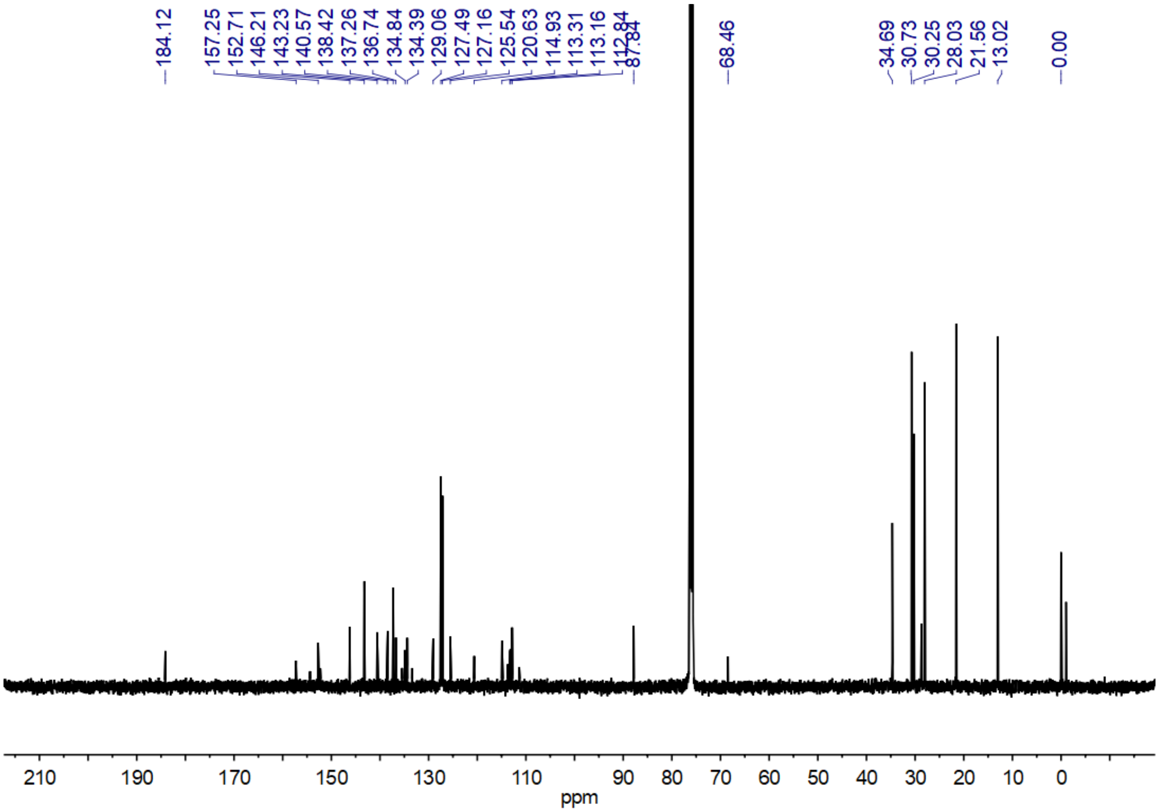

Figure S7. ^{13}C NMR spectrum of iTTPIC-Ar.

4. Cyclic voltammetry

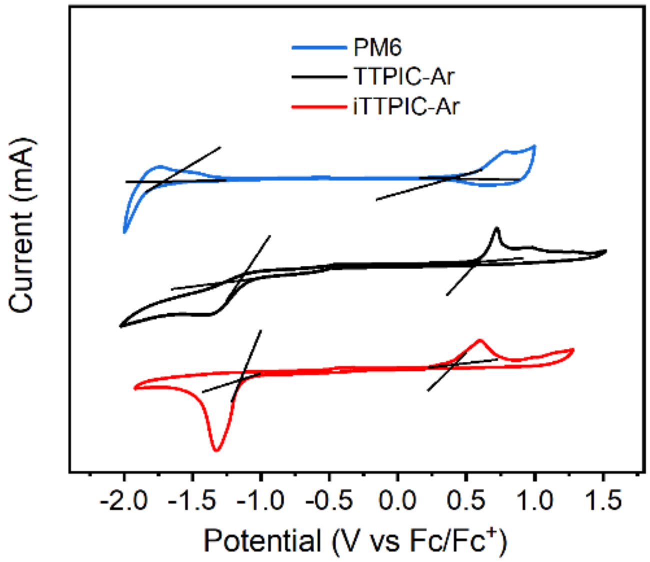

Figure S8. Cyclic voltammograms of PM6, TTPIC-Ar and iTTPIC-Ar .

Table S1. Optical and electrochemical data of PM6, TTPIC-Ar and iTTPIC-Ar.

	$\lambda_{sol.}$ [nm]	λ_{film} [nm]	λ_{onset} [nm]	E_g^{opt} [eV]^a	E_{ox}^{on}/E_{red}^{on} [V]	HOMO [eV]	LUMO [eV]	E_g^{ec} [eV]^b
PM6	-	614	674	1.84	0.38/-1.71	-5.18	-3.09	2.09
TTPIC-Ar	704	782	874	1.42	0.58/-1.17	-5.38	-3.63	1.75
iTTPIC-Ar	754	811	920	1.35	0.42/-1.12	-5.22	-3.68	1.54

$^aE_g^{opt} = 1240/\lambda_{onset}$; HOMO = $-(E_{ox}^{on} + 4.8)$; LUMO = $-(E_{red}^{on} + 4.8)$; $^bE_g^{ec}$ = LUMO-HOMO.

5. Device fabrication and measurements

The PEDOT:PSS layer was deposited onto the ITO glass via spin coating with 4000 rpm for 30 s. The films were annealed under 150 °C in air for 10 min. The PM6:NFA blend with/without 1-chloronaphthalene was dissolved in $CHCl_3$. The active layer was deposited onto PEDOT:PSS layer via spin coating with 3000 rpm for 30 s in nitrogen glove box. The films were annealed at 120 °C in N_2 for 15 min. Then PDINN in MeOH (1 mg/mL) was deposited onto the active layer with 4000 rpm for 20 s. Ag (~100 nm) was evaporated onto PDINN through a shadow mask (pressure ca. 10^{-4} Pa). The effective device area was 0.04 cm^2. The *J-V* curves were measured by using a Keithley 2450 source-measure unit. Photocurrent was measured under AM 1.5G illumination at 100 mW/cm^2 by using a 3A solar simulator (LSS-55, Lightsky Technology Co., Ltd). Light intensity is calibrated with a standard photovoltaic cell equipped with a KG5 filter (certificated by the National Institute of Metrology). The thickness of all films was measured by the Bruker Dektak-XT.

Electron-only devices

The structure for electron-only devices is ZnO/active layer/Ca/Al. The ZnO precursor was spin-coated onto ITO glass and annealed at 200 °C in air for 30 min. A PM6:NFA blend in $CHCl_3$ with additive was spin-coated onto ZnO. Then the film was annealed at 120 °C in N_2 for 15 min. Ca (~15 nm) and Al (~100 nm) were successively evaporated onto the active layer through a shadow mask (pressure ca. 10^{-4} Pa). *J-V* characteristics were measured by using a computerized Keithley 2450 SourceMeter in the dark.

Hole-only devices

The structure for hole-only devices is ITO/PEDOT:PSS/active layer/MoO_3/Al. A ~30 nm thick PEDOT:PSS layer was made by spin coating an aqueous dispersion onto ITO glass (4000 rpm for 30 s). PEDOT:PSS substrates were dried at 150 °C for 10 min. A PM6:NFA blend in $CHCl_3$ with additive was spin-coated onto PEDOT:PSS layer. Then the film was annealed at 120 °C in N_2 for 15 min. Finally, MoO_3 (~3 nm) and Al (~100 nm) was successively evaporated onto the active layer under a shadow mask (pressure ca. 10^{-4} Pa). *J-V* characteristics were measured by using a computerized Keithley 2450 SourceMeter in the dark.

6. Space charge limited current (SCLC)

Charge carrier mobility was obtained by using SCLC method. The mobility was determined by fitting the dark current to the model of a single charge carrier SCLC, which is described by

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu\frac{V^2}{d^3}$$

where *J* is the current density, μ is the zero-field mobility of electron (μ_e) or hole (μ_h), ε_0 is the permittivity of the vacuum, ε_r is the relative permittivity of the material, *d* is the thickness of the blend film, and *V* is the effective voltage, $V = V_{appl} - V_{bi}$, where V_{appl} is the applied voltage, and V_{bi} is the built-in potential determined by electrode work function difference.

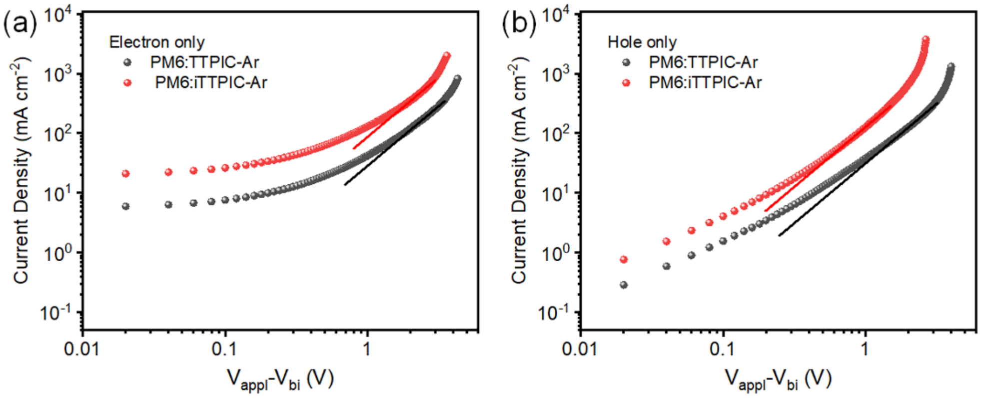

Figure S9. Typical current density-applied voltage semi-log plots for the electron-only devices (a) and hole-only devices (b) based on PM6:NFA blend film (in dark). Measured data are shown as symbols while the solid lines are the best fits to the SCLC model. Mobilities were extracted from the fitting.

Table S2. Electron and hole mobilities of PM6:NFA based devices.

	μ_h [cm^2 V^{-1} s^{-1}]	μ_e [cm^2 V^{-1} s^{-1}]
PM6:TTPIC-Ar	1.77×10^{-4}	1.26×10^{-4}
PM6:iTTPIC-Ar	6.72×10^{-4}	3.62×10^{-4}

Reference

[1] Zhou, J.; He, D.; Li, Y.; Huang, F.; Zhang, J.; Zhang, C.; Yuan, Y.; Lin, Y.; Wang, C.; Zhao, F. *Adv. Mater.* **2023**, *35*, 2207336.

[2] Ota, S.; Minami, S.; Hirano, K.; Satoh, T.; Ie, Y.; Seki, S.; Asob, Y.; Miura, M. *RSC Adv.* **2013**, *3*, 12356-12365.