## Electronic Supplementary Information for:

## Pyrene-fused PDI based ternary solar cells: high power conversion efficiency

## over $10 \%$, and improved device thermal stability

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## 1. Materials and Measurements

Toluene for Stille coupling reactions was dried over and freshly distilled from K-Na alloy under an atmosphere of dry nitrogen. Three bis(trimethylstannyl) reagents and other chemicals and reagents were bought from commercial suppliers and used directly without purification. The important intermediates $\mathbf{1}$ and $\mathbf{2}$ were synthesized according to our previous work. ${ }^{1}$
${ }^{1} \mathrm{H}$ NMR spectra were recorded on a Bruker AVANCE III HD 400 MHz , using $\mathrm{CDCl}_{3}$ as solvent and tetramethylsilane (TMS) as an internal standard ( $\delta=0.00 \mathrm{ppm}$ ). ${ }^{13} \mathrm{C}$ NMR spectra were recorded on a Bruker AVANCE III HD 400 MHz , using $\mathrm{CDCl}_{3}$ as a solvent and an internal standard ( $\delta=77.09 \mathrm{ppm}$ ). MS spectra were recorded on a 5800MALDITOF mass spectrometer with trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) as the matrix. Elemental analysis measurements were recorded on a Vario EL III.

UV-visible absorption spectra were acquired on a Perkin Elmer Lambda 20 UV/VIS Spectrophotometer. Photoluminescence spectra were measured using a Renishaw RM 3000 Micro-Raman/Photoluminescence system with the excitation wavelength at either 514 or 633 nm . All film samples were spin-cast on ITO/ZnO substrates. Optical modeling was conducted using the transfer-matrix optical model. The optical constants, $n$ and $k$ values, for all materials except Al (literature value) were extracted from fitting the variable angle spectroscopic ellipsometry (VASE)
result in the wavelength range of $350-893 \mathrm{~nm}$ using various mathematical models built in the CompleteEASE software (J. A. Woollam Co.). All samples used for the optical characterizations were fabricated through the same way as the device without top electrode.

Cyclic voltammetry (CV) was carried out on a CHI voltammetric analyzer in a three-electrode cell with a Pt counter electrode, a $\mathrm{Ag} / \mathrm{AgCl}$ reference electrode, and a glassy carbon working electrode at a scan rate of $100 \mathrm{mVs}^{-1}$ with 0.1 M tetrabutylammonium perchlorate (purchased from Alfa Aesar) as the supporting electrolyte, in anhydrous $\mathrm{CH}_{3} \mathrm{CN}$ solution purged with nitrogen. Thin films of samples were deposited onto the glassy carbon working electrode from a dichloromethane solution. The potential values obtained in reference to the $\mathrm{Ag} / \mathrm{Ag}^{+}$electrode were converted to values versus the saturated calomel electrode (SCE) by means of an internal ferrocenium/ferrocene $\left(\mathrm{Fc}^{+} / \mathrm{Fc}\right)$ standard.

Geometrical and electronic properties were optimized at B3LYP/6-31G (d) level using Gaussian 09 program. Meanwhile, the molecular orbitals were obtained at the same level of theory.

Device Fabrication: Prepatterned ITO-coated glass substrates (purchased from South China Science \& Technology Company Limited ) were cleaned by successive sonication in toluene, deionized water, acetone, and isopropyl alcohol for 10 min each. After drying, a 30 min UV-ozone treatment was performed. Then a thin layer of PEDOT: PSS was deposited through spin-coating on the glass from a PEDOT: PSS aqueous solution (Xi'an Polymer Light Technology Corp 4083) at $4,000 \mathrm{rpm}$ and dried subsequently at $150^{\circ} \mathrm{C}$ for 15 min in air. Then the device was transferred to a nitrogen glove box, where the active blend layer was spin-coated onto the PEDOT:PSS layer from the chloroform solution of J71, ITIC and each PDI with different ratio. After spin-coating, the active layers were annealed at $150^{\circ} \mathrm{C}$ for 10 min . The thickness of the active layers is about 100 nm . Then methanol solution of PDINO at a concentration of $1.0 \mathrm{mg} \cdot \mathrm{mL}^{-1}$ was deposited atop the active layer at $3,000 \mathrm{rpm}$ for 30 s . Finally, top Al electrodes $(\approx 100 \mathrm{~nm})$ were thermally evaporated at a vacuum level of $\leq 1 \times 10^{-5} \mathrm{~Pa}$ at rates below $1 \AA \cdot \mathrm{~s}^{-1}$.

The current-voltage characteristics of the solar cells were measured under AM 1.5 G irradiation on an Enli Solar simulator ( $100 \mathrm{~mW} \mathrm{~cm}{ }^{-2}$ ). Before each test, the solar simulator was calibrated with a standard single-crystal Si solar cell (made by Enli Technology Co., Ltd., Taiwan, calibrated by The National Institute of Metrology (NIM) of China). External quantum efficiency (EQE) spectra was measured by Solar Cell Spectral Response Measurement System QE-R3011 (Enlitech Co.,

Ltd.).
Mobility Measurements: Hole mobilities and Electron mobilities were measured using the space charge limited current (SCLC) method. The structure of hole only devices was Glass/ITO/PEDOT:PSS/Active Layer/MoOx/Ag. As for electron only devices, the structure was Glass/ITO/ZnO/Active Layer/Ca/Al. The mobilities were obtained by taking current-voltage curves and fitting the results to a space charge limited form.

AFM: Atomic force microscopy (AFM) measurements were performed with a Nano Wizard 4 atomic force microscopy (JPK Inc. Germany) in Qi mode to observe the surface morphologies of the BHJ films deposited on glass substrates.

Contact Angle Measurements: Contact angles were measured with a Contact Angle System OCA20. 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 $10 \mu \mathrm{~L}$ per drop. Contact angle images were taken at 1 s after the whole droplet was deposited onto the sample surface. At least ten independent measurements were performed for each single liquid. The surface energy of each pure material was calculated directly by instrument using the model of $\mathrm{Wu} .^{2}$

GIWAXS patterns were collected with the highly customized Versatile Advanced X-ray Scattering instrument VAXSTER at the chair for Crystallography and Structural Physics (Universität Erlangen-Nürnberg, Germany). The system is equipped with a MetalJet D2 70 kV X-ray source from EXCILLUM, Sweden. The beam was shaped by a 150 mm Montel optics (INCOATEC, Geesthacht) and 2 of 4 double slit systems with the last slit system equipped with low scattering blades (JJXray/SAXSLAB). Aperture sizes were $\left(0.7 \times 0.7 \mathrm{~mm}^{2}, 0.4 \times 0.4 \mathrm{~mm}^{2}\right)$ for GIWAXS. The sample was located within the fully evacuated detector tube. The hybrid-pixel 2D Pilatus 300 K detector (Dectris Ltd., Baden, Switzerland) was used to collect the scattered radiation. The measurements were carried out at an energy of 9.28 keV . The collimation line was tilted and shifted with respect to the horizontal plane allowing grazing incidence angles which maximize the scattering volume and enhance the scattered intensity. The incidence angle $\alpha$ for GIWAXS measurements was between $0.183^{\circ}$ and $0.189^{\circ}$, which is smaller than the critical angle of total reflection of the glass substrate and PEDOT:PSS layer to limit the penetration depth and the scattering to the thin layer. Grazing incidence geometry of the incident X-ray with respect to the
sample surface is used here to enhance the scattered intensity, to maximize the scattering volume, and to access the 3D structure of the studied thin films (lateral and normal direction). The detector-to-sample distance (SDD) was calibrated with a silver behenate standard to 172.6699 mm for GIWAXS. Data were reduced with dpdak software. The samples have been probed at 3 different positions to check the repeatability and reproducibility of the measurements.

Thermal stability. After cleaning, spin-coating HTL (PEDOT:PSS) and active layer on the ITO-coated glass substrates in the same way, all substrates were put on the hot plate with the temperature of $80^{\circ} \mathrm{C}$ for different times ( 12 hours, 24 hours, 48 hours and 72 hours). Then, the PCE test was performed after spin-coating ETL (PDINO) and vacuum evaporating Al.

## 2. Synthesis and Characterization




TPDI


Th-PDI


O-PDI


ITIC


TPYPDI


Th-PYPDI


O-PYPDI

Chart S1. Molecular structure of J71, ITIC and six nonfullerene acceptors (NFAs).

Synthesis of TPDI. Under an atmosphere of dry nitrogen, a mixture of $\mathbf{1}(500 \mathrm{mg}, 0.44 \mathrm{mmol})$, 2,5-bis(trimethylstannyl)thiophene ( $\mathbf{3}, 82 \mathrm{mg}, 0.20 \mathrm{mmol}$ ), and $\operatorname{Pd}\left(\mathrm{PPh}_{3}\right)_{4}(30 \mathrm{mg})$ in anhydrous toluene ( 25 mL ) was stirred at $120{ }^{\circ} \mathrm{C}$ for 24 h . After cooling to room temperature. The organic parts are combined and dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$. The solution was filtered and concentrated via rotary evaporation. The crude product was purified by column chromatography on silica gel using $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ :petroleum ether (1:1) as eluent to afford dark purple product ( $91 \%, 401 \mathrm{mg}$ ). ${ }^{1} \mathrm{H}$ NMR ( 400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}, 298 \mathrm{~K}\right) \delta(\mathrm{ppm}): 8.67-8.61(\mathrm{~m}, 6 \mathrm{H}), 8.56-8.50(\mathrm{~m}, 6 \mathrm{H}), 8.40-8.38(\mathrm{~d}, 2 \mathrm{H}), 7.45(\mathrm{~s}$, $2 H), 4.12-4.00(\mathrm{~m}, 8 \mathrm{H}), 1.95(\mathrm{~m}, 4 \mathrm{H}), 1.42-1.17(\mathrm{~m}, 160 \mathrm{H}), 0.85-0.80(\mathrm{~m}, 24 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 100 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}, 298 \mathrm{~K}\right) \delta(\mathrm{ppm}): 163.57,163.41,163.28,146.68$, 136.23, 134.74, 133.98, 133.54,
132.48, 131.20, 129.77, 128.87, 128.54, 127.94, 127.36, 123.85, 123.36, 122.97, 122.33, 44.76, 36.62, 31.92, 30.07, 29.73, 29.70, 29.67, 29.38, 22.69, 14.13. MS (MALDI-TOF, m/z): 2205.3149 ([M+], calcd for $\mathrm{C}_{148} \mathrm{H}_{212} \mathrm{~N}_{4} \mathrm{O}_{8} \mathrm{~S}, 2205.6026$ ). Anal. Calcd: for TPDI $\left(\mathrm{C}_{148} \mathrm{H}_{212} \mathrm{~N}_{4} \mathrm{O}_{8} \mathrm{~S}\right): \mathrm{C}, 80.53 ; \mathrm{H}$, 9.68; N, 2.54. Found C, 80.23; H, 9.77; N, 2.44.

Synthesis of Th-PDI. The synthetic procedure was similar to that of TPDI. 1 ( $500 \mathrm{mg}, 0.44 \mathrm{mmol}$ ), (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstanna ne) $(\mathbf{4}, 181 \mathrm{mg}, 0.20 \mathrm{mmol})$, and $\mathrm{Pd}(\mathrm{PPh} 3) 4(30 \mathrm{mg})$. Dark purple product $(87 \%, 470 \mathrm{mg}) .{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}, 298 \mathrm{~K}$ ) $\delta(\mathrm{ppm}): 8.70-8.47(\mathrm{~m}, 14 \mathrm{H}), 8.30(\mathrm{~s}, 2 \mathrm{H}), 7.96(\mathrm{~m}, 2 \mathrm{H}), 6.88-6.87(\mathrm{~d}$, $2 \mathrm{H}), 4.10-4.00(\mathrm{~m}, 8 \mathrm{H}), 2.74-2.73(\mathrm{~d}, 4 \mathrm{H}), 1.98(\mathrm{~m}, 4 \mathrm{H}), 1.62-1.61$ (s, 2H), 1.32-1.19 (m, 170H), $0.85-0.70(\mathrm{~m}, 42 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}, 298 \mathrm{~K}$ ) $\delta(\mathrm{ppm}): 163.67,163.38,146.40,146.03$, $140.25,137.70,136.72,136.18,134.92,134.05,133.71,133.53,131.38,131.02,130.74,130.20$, 128.80 , 128.21, 127.81, 127.25, 125.52, 125.30, 123.64, 123.37, 122.96, 122.89, 122.12, 44.77, $41.20,32.37,31.93,31.77,31.64,30.06,29.72,29.68,29.37,28.76,26.45,25.53,22.90,22.60$, 14.13, 14.02, 10.70. MS (MALDI-TOF, m/z): 2699.3901 ([M+], calcd for $\mathrm{C}_{178} \mathrm{H}_{250} \mathrm{~N}_{4} \mathrm{O}_{8} \mathrm{~S}_{4}$, 2699.8162). Anal. Calcd: for Th-PDI ( $\mathrm{C}_{178} \mathrm{H}_{250} \mathrm{~N}_{4} \mathrm{O}_{8} \mathrm{~S}_{4}$ ): C, 79.12; H, 9.33; N, 2.07. Found C, 78.85; H, 9.60; N, 1.98.

Synthesis of O-PDI. The synthetic procedure was similar to that of TPDI. $1(500 \mathrm{mg}, 0.44 \mathrm{mmol})$, (4,8-bis((2-octyldodecyl)oxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (5, $222 \mathrm{mg}, 0.20 \mathrm{mmol})$, and $\mathrm{Pd}(\mathrm{PPh} 3) 4(30 \mathrm{mg})$. Dark purple product $(89 \%, 517 \mathrm{mg}) .{ }^{1} \mathrm{H}$ NMR ( 400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}, 298 \mathrm{~K}\right) \delta(\mathrm{ppm}): 8.83(\mathrm{~s}, 2 \mathrm{H}), 8.74-8.65(\mathrm{~m}, 8 \mathrm{H}), 8.40(\mathrm{~m}, 2 \mathrm{H}), 8.31(\mathrm{~m}, 2 \mathrm{H}), 7.76(\mathrm{~s}$, $2 H), ~ 4.24-4.08(m, 12 H), 2.03(m, 4 H), 1.77-1.76(m, 2 H), 1.42-1.04(m, 222 H), 0.87-0.68(m$, $38 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}, 298 \mathrm{~K}$ ) $\delta(\mathrm{ppm}): 163.46,145.61,144.29,136.47,133.35$, $132.64,131.24,130.51,130.23,128.81,128.68,127.69,127.08,123.32,122.85,122.16,120.33$, $44.60,39.19,38.74,36.68,36.59,31.95,31.81,30.12,29.74,29.70,29.40,22.70,22.67,22.61$, 14.13, 14.12, 14.06, 14.01, 10.98. MS (MALDI-TOF, m/z): 2904.9187 ([M+], calcd for $\mathrm{C}_{194} \mathrm{H}_{294} \mathrm{~N}_{4} \mathrm{O}_{10} \mathrm{~S}_{2}, 2904.2061$ ). Anal. Calcd: for O-PDI ( $\left.\mathrm{C}_{194} \mathrm{H}_{294} \mathrm{~N}_{4} \mathrm{O}_{10} \mathrm{~S}_{2}\right)$ : C, 80.17; H, 10.20; N , 1.93. Found C, 79.83 ; H, 10.45; N, 1.87.

Synthesis of TPYPDI. The synthetic procedure was similar to that of TPDI. 2 ( $300 \mathrm{mg}, 0.21 \mathrm{mmol}$ ), 3 (39 mg, 0.09 mmol ), and $\mathrm{Pd}(\mathrm{PPh} 3) 4(20 \mathrm{mg})$. Black product ( $90 \%$, 238 mg ). ${ }^{1} \mathrm{H}$ NMR ( 400 MHz , $\left.\mathrm{CDCl}_{3}, 298 \mathrm{~K}\right) \delta(\mathrm{ppm}): 10.45(\mathrm{~s}, 4 \mathrm{H}), 9.33(\mathrm{~s}, 2 \mathrm{H}), 9.13(\mathrm{~s}, 4 \mathrm{H}), 9.04(\mathrm{~s}, 2 \mathrm{H}), 8.82(\mathrm{~s}, 2 \mathrm{H}), 8.34$ (m,
$4 \mathrm{H}), 8.12(\mathrm{~m}, 4 \mathrm{H}), 7.65(\mathrm{~m}, 2 \mathrm{H}), 4.18(\mathrm{~m}, 8 \mathrm{H}), 2.08(\mathrm{~m}, 4 \mathrm{H}), 1.69-1.67(\mathrm{~d}, 36 \mathrm{H}), 1.28-1.12(\mathrm{~m}, 160$ H), 0.81-0.75 (m, 24H). ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}, 298 \mathrm{~K}$ ) $\delta(\mathrm{ppm}): 164.10,149.40,147.52$, 134.86, 134.29, 133.10, 132.49, 131.07, 129.80, 129.05, 127.66, 127.28, 127.04, 126.71, 126.12, $124.50,123.56,122.43,121.88,121.01,44.78,36.72,35.55,35.52,31.89,29.77,29.74,29.72$, 29.67, 22.67, 14.11, 14.09. MS (MALDI-TOF, m/z): 2825.5053 ([M+], calcd for $\mathrm{C}_{196} \mathrm{H}_{256} \mathrm{~N}_{4} \mathrm{O}_{8} \mathrm{~S}$, 2825.9469). Anal. Calcd: for TPYPDI ( $\left.\mathrm{C}_{196} \mathrm{H}_{256} \mathrm{~N}_{4} \mathrm{O}_{8} \mathrm{~S}\right)$ : C, 83.24; H, 9.12; N, 1.98. Found C, 82.85; H, 9.21; N, 1.94.

Synthesis of Th-PYPDI. The synthetic procedure was similar to that of TPDI. 2 ( $300 \mathrm{mg}, 0.21$ $\mathrm{mmol}), 4(85 \mathrm{mg}, 0.09 \mathrm{mmol})$, and $\mathrm{Pd}(\mathrm{PPh} 3) 4(20 \mathrm{mg})$. Black product $(86 \%, 267 \mathrm{mg}) .{ }^{1} \mathrm{H}$ NMR ( 400 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}, 298 \mathrm{~K}\right) \delta(\mathrm{ppm}): 10.49(\mathrm{~s}, 4 \mathrm{H}), 9.31-9.25(\mathrm{~m}, 4 \mathrm{H}), 9.05(\mathrm{~s}, 4 \mathrm{H}), 8.84(\mathrm{~m}, 2 \mathrm{H}), 8.37(\mathrm{~m}$, $4 \mathrm{H}), 8.26(\mathrm{~m}, 2 \mathrm{H}), 8.17(\mathrm{~m}, 4 \mathrm{H}), 7.49(\mathrm{~s}, 2 \mathrm{H}), 6.84 \mathrm{~s}, 2 \mathrm{H}), 4.27(\mathrm{~m}, 8 \mathrm{H}), 2.78-2.77(\mathrm{~m}, 4 \mathrm{H}), 2.11(\mathrm{~m}$, $4 \mathrm{H}), 1.87(\mathrm{~m}, 2 \mathrm{H}), 1.69-1.64(\mathrm{~d}, 36 \mathrm{H}), 1.26-1.16(\mathrm{~m}, 170 \mathrm{H}), 0.88-0.71(\mathrm{~m}, 42 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (100 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}, 298 \mathrm{~K}\right) \delta(\mathrm{ppm}): 164.27,149.34,147.12,146.30$, 140.61, 137.88, 136.55, 134.36, $133.39,133.10,132.68,131.08,129.66,129.14,128.36,127.68,127.19,127.01,126.79,126.04$, $125.61,125.39,124.75,123.85,123.52,122.86,121.74,121.31,120.97,41.25,31.92,31.89,31.87$, $30.15,30.11,29.73,29.67,29.39,28.78,26.70,26.59,22.94,22.60,14.13,14.06,10.74$. MS (MALDI-TOF, m/z): 3320.7036 ([M+], calcd for $\mathrm{C}_{226} \mathrm{H}_{294} \mathrm{~N}_{4} \mathrm{O}_{8} \mathrm{~S}_{4}, 3320.1605$ ). Anal. Calcd: for Th-PYPDI ( $\mathrm{C}_{226} \mathrm{H}_{294} \mathrm{~N}_{4} \mathrm{O}_{8} \mathrm{~S}_{4}$ ): C, 81.69; H, 8.92; N, 1.69. Found C, 81.37; H, 8.97; N, 1.66.

Synthesis of O-PYPDI. The synthetic procedure was similar to that of TPDI. 2 ( $300 \mathrm{mg}, 0.21$ $\mathrm{mmol})$, $5(104 \mathrm{mg}, 0.09 \mathrm{mmol})$, and $\mathrm{Pd}(\mathrm{PPh} 3) 4(20 \mathrm{mg})$. Black product $(87 \%, 287 \mathrm{mg}) .{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}, 298 \mathrm{~K}$ ) $\delta(\mathrm{ppm}): 10.48(\mathrm{~s}, 4 \mathrm{H}), 9.33(\mathrm{~s}, 2 \mathrm{H}), 9.25(\mathrm{~m}, 2 \mathrm{H}), 9.13(\mathrm{~m}, 2 \mathrm{H}), 9.04(\mathrm{~m}$, $2 \mathrm{H}), 8.84-8.77(\mathrm{~m}, 2 \mathrm{H}), 8.34(\mathrm{~m}, 4 \mathrm{H}), 8.15(\mathrm{~m}, 4 \mathrm{H}), 8.08(\mathrm{~m}, 2 \mathrm{H}), 4.41-4.27(\mathrm{~m}, 12 \mathrm{H}), 2.14(\mathrm{~m}$, $4 \mathrm{H}), 1.89(\mathrm{~m}, 4 \mathrm{H}), 1.69(\mathrm{~m}, 38), 1.29-0.93(\mathrm{~m}, 222 \mathrm{H}), 0.87-0.78(\mathrm{~m}, 24 \mathrm{H}), 0.64-0.57(\mathrm{~m}, 14 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}, 298 \mathrm{~K}$ ) $\delta$ (ppm): 164.21, 149.33, 145.70, 145.50, 134.87, 134.26, 133.19, $133.05,132.86,131.08,129.71,127.69$, 127.42, 127.07, 126.67, 126.08, 125.54, 124.74, 124.58, $123.84,123.53,122.58,121.94,121.05,120.28,44.86,31.95,31.88,31.76,30.20,30.17,30.07$, 29.78, 29.70, 29.42, 29.40, 22.71, 22.56, 22.53, 14.15, 13.97. MS (MALDI-TOF, m/z): 3524.0624 ( $[\mathrm{M}+]$, calcd for $\mathrm{C}_{242} \mathrm{H}_{338} \mathrm{~N}_{4} \mathrm{O}_{8} \mathrm{~S}_{2}, 3524.5504$ ). Anal. Calcd: for O-PYPDI $\left(\mathrm{C}_{242} \mathrm{H}_{338} \mathrm{~N}_{4} \mathrm{O}_{10} \mathrm{~S}_{2}\right)$ : C, 82.40; H, 9.66; N, 1.59. Found C, 82.09; H, 9.75; N, 1.54.

## 3. Photophysical properties



Figure S1. The absorption spectra of six NFAs in toluene solution.


Figure S2. CV curves of the six NFAs in thin film.

## 4. Theoretical calculations



Figure S3. The HOMO/LUMO distribution and optimal geometrics of six NFAs (the alkyl groups are simplified to the methyl one) calculated by the Gaussian 09 program at the B3LYP/6-31G* level.

## 5. Photovoltaic properties



Figure S4. (a) Device architecture of organic solar cells. (b) The energy level of J71 and ITIC.


Figure S5. $J-V$ curve and EQE spectra of these binary OSC devices based on J71:ITIC.

Table S1. Summary of device parameters of J71:ITIC:NFAs ternary OSCs devices with different NFAs content.

| mass ratio | $V_{\text {oc }}(\mathrm{V})$ | $J_{\text {sc }}\left(\mathrm{mA} / \mathrm{cm}^{2}\right)$ | FF | PCE ${ }_{\text {max }}$ (average) |
| :---: | :---: | :---: | :---: | :---: |
| J71:ITIC:TPDI (1:0.95:0.05) | 0.916 | 13.77 | 63.41 | 8.00 (7.88) |
| J71:ITIC:TPDI (1:0.9:0.1) | 0.913 | 13.55 | 62.03 | 7.67 (7.34) |
| J71:ITIC:TPDI (1:0.8:0.2) | 0.905 | 13.68 | 61.25 | 7.59 (7.44) |
| J71:ITIC:TPDI (1:0.5:0.5) | 0.872 | 11.28 | 51.68 | 5.10 (5.01) |
| J71:TPDI (1:1) | 0.703 | 1.41 | 48.8 | 0.47 (0.43) |
| J71:ITIC:TPYPDI (1:0.95:0.05) | 0.948 | 14.39 | 64.85 | 8.85 (8.56) |
| J71:ITIC:TPYPDI (1:0.9:0.1) | 0.951 | 15.54 | 66.27 | 9.80 (9.52) |
| J71:ITIC:TPYPDI (1:0.8:0.2) | 0.958 | 15.11 | 64.95 | 9.41 (9.38) |
| J71:ITIC:TPYPDI (1:0.5:0.5) | 0.965 | 13.06 | 47.59 | 6.00 (5.91) |
| J71:TPYPDI (1:1) | 1.047 | 3.19 | 29.73 | 0.99 (0.91) |
| J71:ITIC:Th-PDI (1:0.95:0.05) | 0.927 | 13.66 | 65.73 | 8.33 (7.96) |
| J71:ITIC:Th-PDI (1:0.9:0.1) | 0.93 | 15.23 | 62.82 | 8.91 (8.71) |
| J71:ITIC:Th-PDI (1:0.8:0.2) | 0.927 | 15.35 | 59.69 | 8.50 (8.46) |
| J71:ITIC:Th-PDI (1:0.5:0.5) | 0.918 | 13.19 | 42.97 | 5.19 (5.00) |
| J71:Th-PDI (1:1) | 0.833 | 1.33 | 33.01 | 0.36 (0.32) |
| J71:ITIC:Th-PYPDI (1:0.95:0.05) | 0.953 | 16.42 | 68.42 | 10.71 (10.57) |
| J71:ITIC:Th-PYPDI (1:0.9:0.1) | 0.955 | 16.66 | 65.34 | 10.63 (10.42) |
| J71:ITIC:Th-PYPDI (1:0.8:0.2) | 0.958 | 14.58 | 69.41 | 9.70 (9.30) |
| J71:ITIC:Th-PYPDI (1:0.5:0.5) | 0.965 | 13.93 | 52.12 | 7.01 (6.94) |
| J71:Th-PYPDI (1:1) | 1.023 | 1.26 | 28.71 | 0.37 (0.33) |
| J71:ITIC:O-PDI (1:0.95:0.05) | 0.918 | 12.34 | 61.18 | 6.94 (6.49) |
| J71:ITIC:O-PDI (1:0.9:0.1) | 0.916 | 11.96 | 59.46 | 6.46 (6.33) |
| J71:ITIC:O-PDI (1:0.8:0.2) | 0.907 | 9.83 | 58.81 | 5.25 (5.07) |
| J71:ITIC:O-PDI (1:0.5:0.5) | 0.892 | 9.17 | 54.81 | 4.48 (4.17) |
| J71:O-PDI (1:1) | 0.652 | 1.52 | 40.88 | 0.40 (0.39) |
| J71:ITIC:O-PYPDI (1:0.95:0.05) | 0.938 | 15.88 | 68.06 | 10.14 (9.81) |
| J71:ITIC:O-PYPDI (1:0.9:0.1) | 0.945 | 16.59 | 69.92 | 10.96 (10.71) |
| J71:ITIC:O-PYPDI (1:0.8:0.2) | 0.962 | 14.45 | 70.63 | 9.82 (9.73) |
| J71:ITIC:O-PYPDI (1:0.5:0.5) | 0.971 | 11.58 | 59.53 | 6.67 (6.46) |
| J71:O-PYPDI (1:1) | 1.013 | 4.22 | 34.42 | 1.47 (1.45) |
| J71:ITIC (1:1) | 0.939 | 17.55 | 67.28 | 11.08 (10.83) |



Figure S6. Photoluminescence spectra of neat films of pure J71 and ITIC and binary film of J71:ITIC.

Table S2. Charge mobility of six J71:ITIC:NFAs (1:0.9:0.1) ternary films.

| Devices | $\mu_{\mathrm{h}}\left[\mathrm{cm}^{2} \mathrm{~V}^{-1} \mathrm{~s}^{-1}\right]$ | $\mu_{\mathrm{e}}\left[\mathrm{cm}^{2} \mathrm{~V}^{-1} \mathrm{~s}^{-1}\right]$ | $\mu_{\mathrm{h}} / \mu_{\mathrm{e}}$ |
| :---: | :---: | :---: | :---: |
| J71:ITIC:TPDI (1:0.9:0.1) | $0.92 \times 10^{-3}$ | $1.89 \times 10^{-3}$ | 0.49 |
| J71:ITIC:TPyPDI (1:0.9:0.1) | $1.30 \times 10^{-3}$ | $1.02 \times 10^{-3}$ | 1.27 |
| J71:ITIC:Th-PDI (1:0.9:0.1) | $2.52 \times 10^{-3}$ | $1.50 \times 10^{-3}$ | 1.68 |
| J71:ITIC:Th-PyPDI (1:0.9:0.1) | $1.10 \times 10^{-3}$ | $1.38 \times 10^{-3}$ | 0.80 |
| J71:ITIC:O-PDI (1:0.9:0.1) | $1.97 \times 10^{-3}$ | $1.23 \times 10^{-3}$ | 1.60 |
| J71:ITIC:O-PyPDI (1:0.9:0.1) | $2.84 \times 10^{-3}$ | $2.39 \times 10^{-3}$ | 1.19 |
| J71:ITIC (1:1) | $1.75 \times 10^{-3}$ | $1.96 \times 10^{-3}$ | 0.89 |

## 6. Film morphology



RMS $=0.59$ nm

RMS: root-meansquare roughness


RMS $=0.55 \mathrm{~nm}$


RMS $=0.70$ nm


RMS= 0.57 nm


RMS $=0.62 \mathbf{n m}$


RMS $=0.57 \mathrm{~nm}$


RMS $=0.76$ nm

Figure S7. Atomic force microscopy (AFM) profiles of binary J71:ITIC film and J71:ITIC:NFAs (1:0.9:0.1) ternary films.
(a)

(b)

(c)


$Q$ vector $\left[\mathrm{A}^{-1}\right]$



Figure S8. GIWAXS patterns of J71:ITIC binary film (a), J71:ITIC:Th-PYPDI (1:0.9:0.1) ternary film (b) and J71:ITIC:Th-PDI (1:0.9:0.1) ternary film (c). Scattering profiles (horizontal and vertical) of J71:ITIC binary film (d), J71:ITIC:Th-PYPDI (1:0.9:0.1) ternary film (e), J71:ITIC:Th-PDI (1:0.9:0.1) ternary film (f)


Figure S9. GIWAXS patterns of J71:ITIC binary film (a), J71:ITIC:TPYPDI (1:0.9:0.1) ternary film (b) and J71:ITIC:TPDI (1:0.9:0.1) ternary film (c). Scattering profiles (horizontal and vertical) of J71:ITIC binary film (d), J71:ITIC:TPYPDI (1:0.9:0.1) ternary film (e), J71:ITIC:TPDI (1:0.9:0.1) ternary film (f).


Figure S10. GIWAXS patterns (a) and scattering profiles (b, horizontal and vertical) of each pure materials used in ternary OSCs devices.

## 7. NMR spectra



Figure S11. The ${ }^{1} \mathrm{H}$ NMR spectrum of TPDI recorded in $\mathrm{CDCl}_{3}$.


Figure S12. The ${ }^{13} \mathrm{C}$ NMR spectrum of TPDI recorded in $\mathrm{CDCl}_{3}$.


Figure S13. The ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathrm{Th}-\mathrm{PDI}$ recorded in $\mathrm{CDCl}_{3}$.


Figure S14. The ${ }^{13} \mathrm{C}$ NMR spectrum of Th-PDI recorded in $\mathrm{CDCl}_{3}$.


Figure S15. The ${ }^{1} \mathrm{H}$ NMR spectrum of O-PDI recorded in $\mathrm{CDCl}_{3}$.


Figure S16. The ${ }^{13} \mathrm{C}$ NMR spectrum of O-PDI recorded in $\mathrm{CDCl}_{3}$.


Figure S17. The ${ }^{1} \mathrm{H}$ NMR spectrum of TPYPDI recorded in $\mathrm{CDCl}_{3}$.


Figure S18. The ${ }^{13} \mathrm{C}$ NMR spectrum of TPYPDI recorded in $\mathrm{CDCl}_{3}$.


Figure S19. The ${ }^{1} \mathrm{H}$ NMR spectrum of Th-PYPDI recorded in $\mathrm{CDCl}_{3}$.


Figure S20. The ${ }^{13} \mathrm{C}$ NMR spectrum of Th-PYPDI recorded in $\mathrm{CDCl}_{3}$.


Figure S21. The ${ }^{1} \mathrm{H}$ NMR spectrum of O-PYPDI recorded in $\mathrm{CDCl}_{3}$.


Figure S22. The ${ }^{13} \mathrm{C}$ NMR spectrum of O-PYPDI recorded in $\mathrm{CDCl}_{3}$.

## 8. References

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