

Electronic Supplementary Information for

Stabilizing resonance structure of nonfused-ring electron acceptor via closed-loop carbazole side chain for efficient and stable organic solar cells

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Materials and Methods

Instrument.

Proton (^1H) and carbon (^{13}C) NMR spectra were obtained on a Bruker Advance III 400 (400 MHz) nuclear magnetic resonance (NMR) spectroscope. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry were performed on a Walters MALDI-TOF Premier mass spectrometry. Thermogravimetric analysis (TGA) was carried out on a WCT-2 thermal balance under nitrogen protection at a heating rate of 10 °C/min. Ultraviolet-visible (UV-Vis) absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Cyclic voltammetry (CV) was done on a CHI600A electrochemical workstation with Pt disk, Pt plate, and standard calomel electrode (SCE) as working electrode, a counter electrode, and reference electrode, respectively, in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile solution. The CV curves were recorded versus the potential of SCE, which was calibrated by the ferrocene-ferrocenium (Fc/Fc^+) redox couple (4.8 eV below the vacuum level). AFM images were obtained on a VeecoMultiMode atomic force microscopy in the tapping mode.

Materials.

All reagents and solvents, unless otherwise specified, were purchased from J&K Scientific, Suna Tech, Aldrich and Energy Chemical Ltd., and were used without further purification. The polymer donor PM6 was purchased from Solarmer Materials Inc.

DFT Calculation.

Geometry optimizations were carried out by the density functional theory (DFT) method at the B3LYP/6-31G level. All the calculations were performed using Gaussian 03 program.

GIWAXS Measurements

GIWAXS measurements were conducted at a Xeuss 3.0 SAXS/WAXS laboratory beamline at Vacuum Interconnected Nanotech Workstation (Nano-X) in China with $\text{K}\alpha$ X-ray of Cu source (operated at 50kV, 0.06 mA, 1.542 Å). GIWAXS patterns were recorded by a two dimensional X-ray detector (Eiger2 R 1M, Dectris). The grazing incident angle were 0.18°. Samples were prepared by spin coating identical chloroform blend solutions as those used in OSCs on Si substrates.

Device fabrication and Characterization.

OSCs were fabricated on glass substrates commercially pre-coated with a layer of indium tin oxide (ITO) with the normal structure of ITO/PEDOT:PSS/active layer/PDINN/Ag. Before fabrication, the substrates were cleaned consecutively by an ultrasonic bath of detergent, deionized water, acetone, and isopropanol and then treated in an ultraviolet ozone generator for 7 min. After that, a layer of 20 nm thick PEDOT: PSS (Baytron P AI4083) was spin-coated onto the substrates at 4500 rpm for 20 s and annealed at 150 °C for 15 min. Then the substrates were transferred to a glovebox, the active layer was spin-coated from 17 mg/mL (PM6:3TTCz = 1:2, 2% vol CN; PM6:3TTDPA = 1:1, 1% vol DIO) chloroform solution at 3500 rpm. After annealing at 100 °C for 10 min, the PDINN layer was deposited from 1 mg/mL of methanol solution at 3800 rpm for 20s. 100 nm Ag electrode was deposited by thermal evaporation under a background pressure of approximately 1.5×10^{-4} Pa to complete the device with an active area of 9.25 mm².

The current density-voltage (*J-V*) curves of OSCs were measured in the glovebox with Keithley 2400 under AM 1.5G illumination at 100 mW cm⁻² irradiation using an Enli SS-X50 solar simulator, and the light intensity was calibrated with a standard Si solar cell with KG2 filter (made by Enli Technology Co., Ltd., Taiwan, and calibrated report can be traced to NREL).

The EQE spectrum was measured using a QE-R Solar Cell Spectral Response Measurement System (Enli Technology Co., Ltd., Taiwan). The *J-V* curves were measured from -0.2 to 1.2 V, yielding identical results. The scan speed and dwell times were fixed at 0.01 V/step and 20 ms, respectively. During the test, an aperture with an area of 4.7 mm² is used to calibrate the device area.

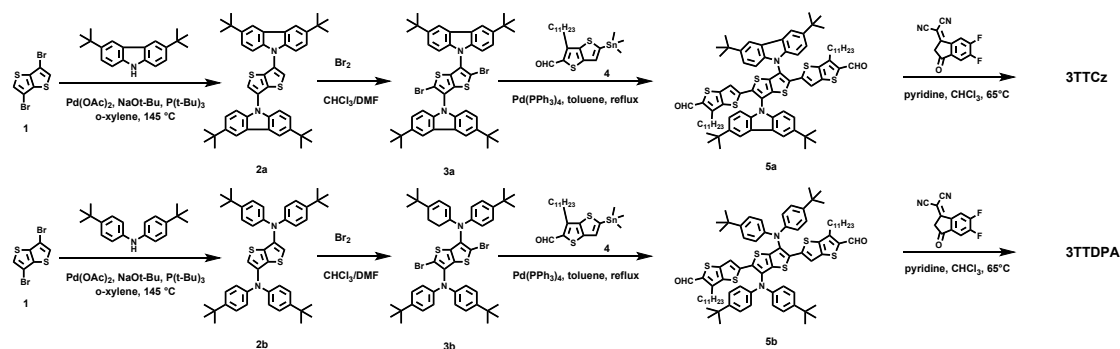
Photo-stability tests: The photo-stability of encapsulated devices were measured with ISOS-L-3 setup (Infinity PV) in air (Humidity: 45 ± 5 %; Temperature: 30 ± 5 °C). The photo-stability tests were conducted under continuous one sun equivalent illumination provided by a metal halide lamp (PHILIPS MSR 1200HR) without UV-filter.

The charge carrier mobilities of the donor:acceptor films were measured using the space charge limited current (SCLC) method. Hole-only devices were fabricated in a structure of ITO/PEDOT:PSS/blend film/MoO₃/Ag, electron-only devices were fabricated in a structure of ITO/ZnO/blend film/PDINN/Ag. The device characteristics were extracted by modelling the dark current under forward bias using the SCLC expression described by the Mott-Gurney law:

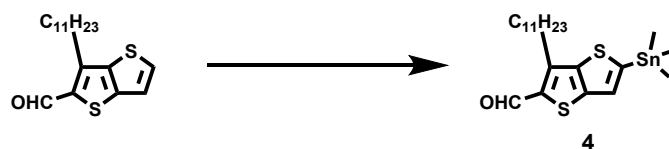
$$J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu \frac{V^2}{L^3}$$

where $\varepsilon_r \approx 3$ is the average dielectric constant of the blend film, ε_0 is the permittivity of the free space, μ is the carrier mobility, $L \approx 100$ nm is the thickness of the film, and V is the applied voltage.

Synthesis of 3TTDPA&3TTCz



5-(trimethylstannyl)-3-undecylthieno[3,2-*b*]thiophene-2-carbaldehyde (4)



3-undecylthieno[3,2-*b*]thiophene-2-carbaldehyde (5 g, 15.52 mmol) and dry THF (100 mL) were added to a 100 mL Schlenk tube under argon atmosphere, and the solution was cooled to -78 °C. Then N-methylpiperazine (1.713 g, 17.07 mmol) and n-butyllithium (6.83 mL, 2.5M in hexane, 17.07 mmol) were injected and the reaction mixture was stirred for 30min. The reaction was then warmed to -20 °C, and n-butyllithium (6.83 mL, 2.5M in hexane, 17.07 mmol) was injected secondly, after which the reaction was stirred for 30 min. Then trimethyltin chloride (17.07 mL, 1M in toluene, 17.07 mmol) was added and then the mixture was warmed to room temperature and stirred overnight. After pouring into water, the mixture was extracted with dichloromethane. The combined organic phase was evaporated under vacuum and the obtained product was used directly

in the next reaction without further purification, yielding a brown oil (6.0 g, 79.6%). ¹H NMR (400 MHz, CDCl₃): δ = 10.09 (s, 1H), 7.33 (s, 1H), 1.46-1.13 (m, 23H), 0.44 (s, 9H).

3,6-bis(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)thieno[3,2-*b*]thiophene (2a)

Compound **1** (1 g 3.35 mmol), 3,6-di-*tert*-butyl-9*H*-carbazole (3.74 g, 13.4 mmol), NaOtBu (1.93 g, 20.1 mmol) were dissolved in 40mL *o*-xylene. Then Pd(OAc)₂ (37.7 mg, 0.17 mmol) and tri-*tert*-butylphosphine (P(*t*-Bu)₃, 1.01 mL, 10% in Toluene, 1.01 mmol) were added under argon atmosphere and the solution was stirred at 145 °C for 36 h. After cooling and pouring into water, the reaction mixture was extracted with dichloromethane. The combined organic phase was evaporated under vacuum. The crude product was purified by washing with petroleum ether, yielding white solid compound **2a** (680.2 mg, 37.02%). ¹H NMR (400 MHz, CDCl₃): δ = 8.19 (s, 4H), 7.55 (s, 2H), 7.53 (dd, *J* = 8.7, 1.9 Hz, 4H), 7.44 (d, *J* = 8.6 Hz, 4H), 1.49 (s, 36H).

***N*³,*N*³,*N*⁶,*N*⁶-tetrakis(4-(*tert*-butyl)phenyl)thieno[3,2-*b*]thiophene-3,6-diamine (2b)**

Compound **1** (1 g 3.35 mmol), bis(4-(*tert*-butyl)phenyl)amine (3.77 g, 13.4 mmol), NaOtBu (1.93 g, 20.1 mmol) were dissolved in 40 mL *o*-xylene. Then Pd(OAc)₂ (37.7 mg, 0.17 mmol) and tri-*tert*-butylphosphine (P(*t*-Bu)₃, 1.01 mL, 10% in Toluene, 1.01 mmol) were added under argon atmosphere and the solution was stirred at 145 °C for 36 h. After cooling and pouring into water, the reaction mixture was extracted with dichloromethane. The combined organic phase was evaporated under vacuum. The crude product was purified on silica gel column chromatography with the mixture of petroleum ether and dichloromethane (1:1, v/v) as the eluent, yielding white solid compound **2b** (1.423 g, 60.77%). ¹H NMR (400 MHz, CDCl₃): δ = 7.27 (d, *J* = 6.1, 8H), 7.25 (s, 2H), 7.07 (d, *J* = 7.8Hz, 8H), 1.31 (s, 36H).

9,9'-(2,5-dibromothieno[3,2-*b*]thiophene-3,6-diyl)bis(3,6-di-*tert*-butyl-9*H*-carbazole) (3a)

Compound **2a** (200 mg, 0.288 mmol) and NBS (112.84 mg, 0.634mmol) were dissolved in the mixture solution of chloroform (20 mL) and N,N-dimethylformamide (5 mL). Then the reaction mixture was stirred at room temperature under darkness overnight. After pouring into water, the reaction mixture was extracted with dichloromethane and then the combined organic phase was evaporated under vacuum. The crude product was purified on silica gel column chromatography with the mixture of petroleum ether and dichloromethane (1:2, v/v) as the eluent, yielding white solid compound **3a** (218.14 mg, 89.1%). ¹H NMR (400 MHz, CDCl₃): δ = 8.17 (s, 4H), 7.52 (dd, *J* = 8.6, 1.9 Hz, 4H), 7.22 (d, *J* = 8.6 Hz, 4H), 1.36 (s, 36H).

2,5-dibromo-*N*³,*N*³,*N*⁶,*N*⁶-tetrakis(4-(*tert*-butyl)phenyl)thieno[3,2-*b*]thiophene-3,6-diamine (3b)

Compound **2b** (200 mg, 0.286 mmol) and NBS (112.84 mg, 0.634 mmol) were dissolved in the mixture solution of chloroform (20 mL) and N,N-dimethylformamide (5 mL). Then the reaction mixture was stirred at room temperature under darkness overnight. After pouring into water, the reaction mixture was extracted with dichloromethane and then the combined organic phase was evaporated under vacuum. The crude product was purified on silica gel column chromatography with the mixture of petroleum ether and dichloromethane (1:2, v/v) as the eluent, yielding white solid compound **3a** (218.14 mg, 89.1%). ¹H NMR (400 MHz, CDCl₃): δ = 7.28 (d, *J* = 8.7 Hz, 8H), 6.97 (d, *J* = 8.7 Hz, 8H), 1.32 (s, 36H).

3',6'-bis(3,6-di-*tert*-butyl-9H-carbazol-9-yl)-6,6''-diundecyl-[2,2':5',2''-terthieno[3,2-*b*]thiophene]-5,5''-dicarbaldehyde (5a)

Compound **3a** (200 mg, 0.235 mmol) and compound **4** (468.11 mg, 0.965 mmol) were dissolved in the mixture solution of toluene (20 mL) and N,N-dimethylformamide (2 mL). Then Pd(PPh₃)₄ (16.3 mg, 0.014 mmol) was added under argon atmosphere and the solution was refluxed at 110 °C for 24 h. After pouring into water, the mixture was extracted with dichloromethane and then the combined organic phase was evaporated under vacuum. The crude product was purified on silica gel column chromatography with the mixture of petroleum ether and dichloromethane (1:1, v/v) as the eluent, yielding red solid compound **5a** (261.3 mg, 84.2%). ¹H NMR (400 MHz, CDCl₃): δ = 9.94 (s, 2H), 8.23 (s, 4H), 7.46 (dd, *J* = 8.6, 1.9 Hz, 4H), 7.17 (d, *J* = 8.6 Hz, 4H), 6.99 (s, 2H), 1.46 (s, 36H), 1.11 - 1.32 (m, 46H).

3',6'-bis(bis(4-(*tert*-butyl)phenyl)amino)-6,6''-diundecyl-[2,2':5',2''-terthieno[3,2-*b*]thiophene]-5,5''-dicarbaldehyde (5b)

Compound **3b** (200 mg, 0.233 mmol) and compound **4** (462.13 mg, 0.953 mmol) were dissolved in the mixture solution of toluene (20 mL) and N,N-dimethylformamide (2 mL). Then Pd(PPh₃)₄ (16.3 mg, 0.014 mmol) was added under argon atmosphere and the solution was refluxed at 110 °C for 24 h. After pouring into water, the mixture was extracted with dichloromethane and then the combined organic phase was evaporated under vacuum. The crude product was purified on silica gel column chromatography with the mixture of petroleum ether and dichloromethane (1:1, v/v) as the eluent, yielding red solid compound **5b** (265 mg, 84.9%). ¹H NMR (400 MHz, CDCl₃):

δ = 9.98 (s, 2H), 7.26 (d, J = 8.7 Hz, 8H), 7.13 (s, 2H), 7.07 (d, J = 8.7 Hz, 8H), 1.28 (s, 36H), 1.26 - 1.22 (m, 46H).

2,2'-((2Z,2'Z)-((3',6'-bis(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-6,6''-diundecyl-[2,2':5',2''-terthieno[3,2-*b*]thiophene]-5,5''-diyl)bis(methaneylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1*H*-indene-2,1-diylidene))dimalononitrile (3TTCz)

Compound **5a** (150 mg, 0.112 mmol) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malononitrile (102.98 mg, 0.448 mmol) were dissolved in 20 mL chloroform under argon atmosphere and pyridine (0.2 mL) was added at 65 °C. Then the mixture was stirred and refluxed at 65 °C overnight, and the solvent was removed under reduced. The crude product was purified on silica gel chromatography using the mixture of petroleum ether and dichloromethane (2:1, v/v) as the eluent, yielding dark blue solid compound **3TTCz** (142.2 mg, 71.9%). ¹H NMR (500 MHz, CDCl₃): δ = 8.94 (s, 2H), 8.51 (dd, J = 9.9, 6.4 Hz, 2H), 8.26 (s, 4H), 7.62 (t, J = 7.5 Hz, 2H), 7.48 (dd, J = 8.6, 1.9 Hz, 4H), 7.18 (d, J = 8.5 Hz, 4H), 6.98 (s, 2H), 1.50 (s, 36H), 1.32 – 1.09 (m, 46H). MS (MALDI-TOF): Calcd for C₁₀₆H₁₀₂F₄N₆O₂S₆(M⁺): 1760.38, Found: 1759.56.

2,2'-((2Z,2'Z)-((3',6'-bis(bis(4-(*tert*-butyl)phenyl)amino)-6,6''-diundecyl-[2,2':5',2''-terthieno[3,2-*b*]thiophene]-5,5''-diyl)bis(methaneylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1*H*-indene-2,1-diylidene))dimalononitrile (3TTDPA)

Compound **5b** (150 mg, 0.112 mmol) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malononitrile (102.98 mg, 0.448 mmol) were dissolved in 20 mL chloroform under argon atmosphere and pyridine (0.2 mL) was added at 65 °C. Then the mixture was stirred and refluxed at 65 °C overnight, and the solvent was removed under reduced. The crude product was purified on silica gel chromatography using the mixture of petroleum ether and dichloromethane (2:1, v/v) as the eluent, yielding dark blue solid compound **3TTDPA** (138.6 mg, 70.2%). ¹H NMR (500 MHz, CDCl₃): δ = 8.99 (s, 2H), 8.52 (dd, J = 10.0, 6.4 Hz, 2H), 7.65 (t, J = 7.5 Hz, 2H), 7.31 (d, J = 8.7 Hz, 8H), 7.19 (s, 2H), 7.08 (d, J = 8.7 Hz, 8H), 1.60 (s, 36H), 1.32 – 1.21 (m, 46H). MS (MALDI-TOF): Calcd for C₁₀₆H₁₀₆F₄N₆O₂S₆(M⁺): 1764.41, Found: 1763.93.

Supporting Figures

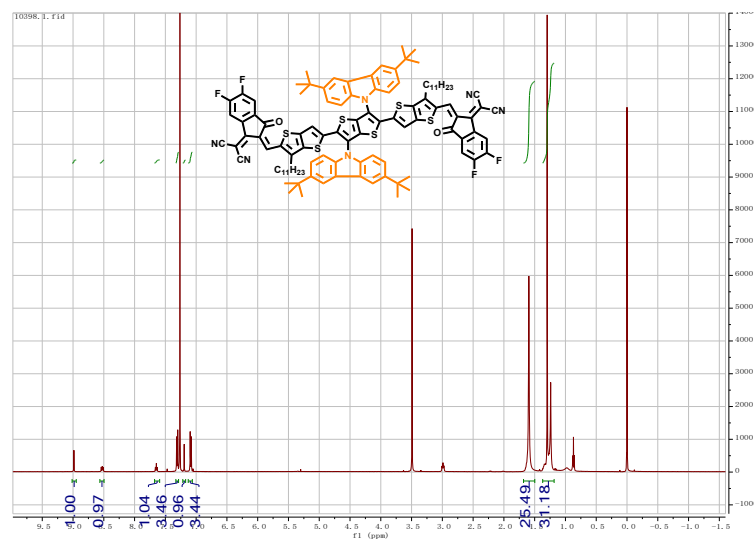


Fig. S1 The ¹H-NMR spectra of 3TTCz.

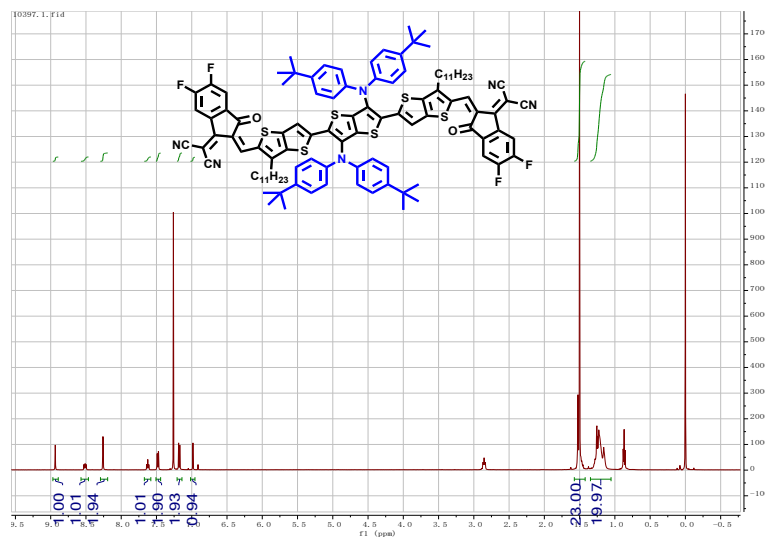


Fig. S2 The ¹H-NMR spectra of 3TTDPA.

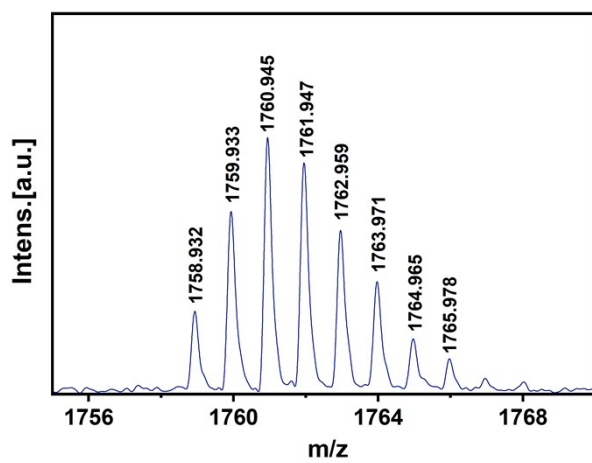
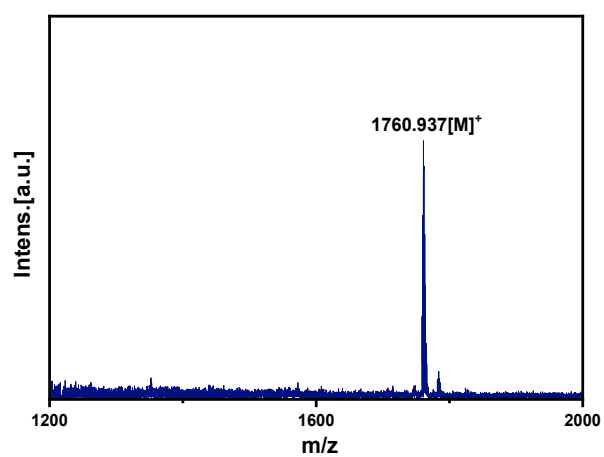
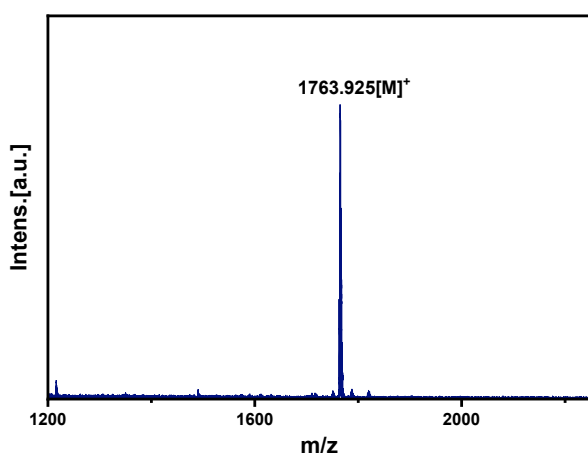


Fig. S3 The MALDI-TOF-MS spectra of 3TTCz.



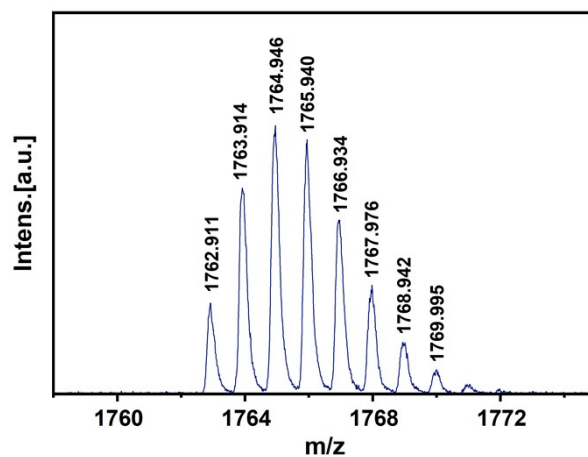


Fig. S4 The MALDI-TOF-MS spectra of 3TTDPA.

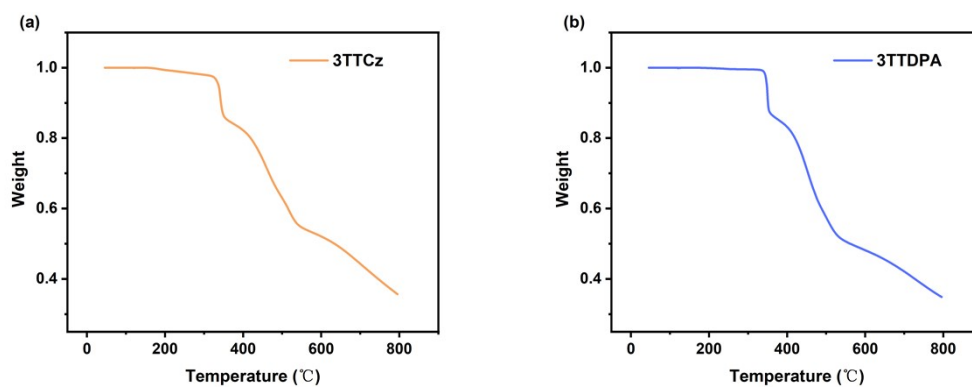


Fig. S5 TGA curves of (a) 3TTCz and (b) 3TTDPA.

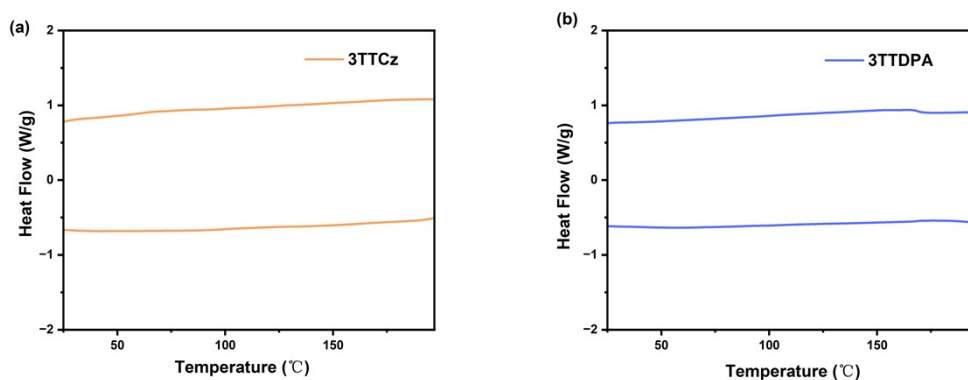


Fig. S6 DSC curves of (a) 3TTCz and (b) 3TTDPA.

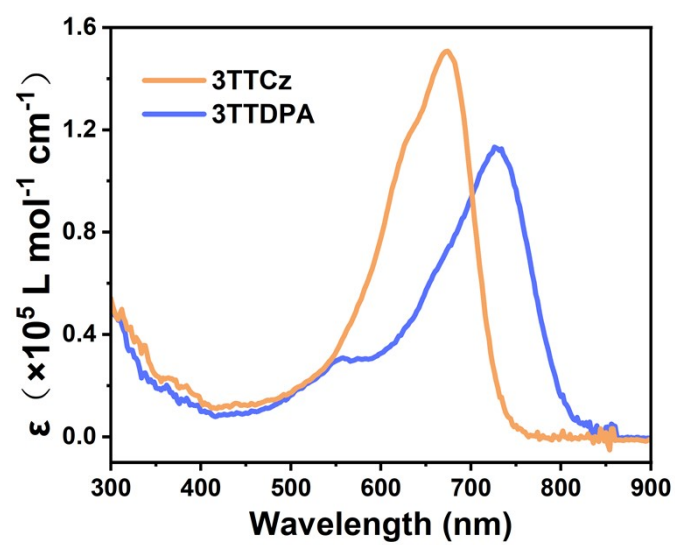


Fig. S7 The molar extinction coefficients of 3TTCz and 3TTDPA in chloroform solutions.

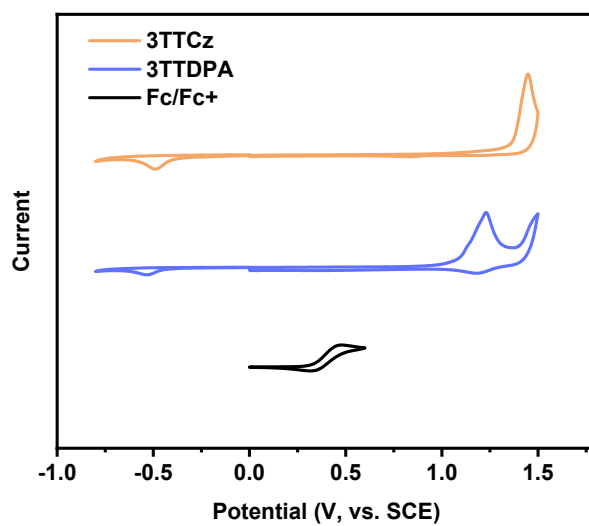


Fig. S8 The Cyclic Voltammograms of 3TTCz, 3TTDPA and Fc/Fc⁺ in acetonitrile solutions.

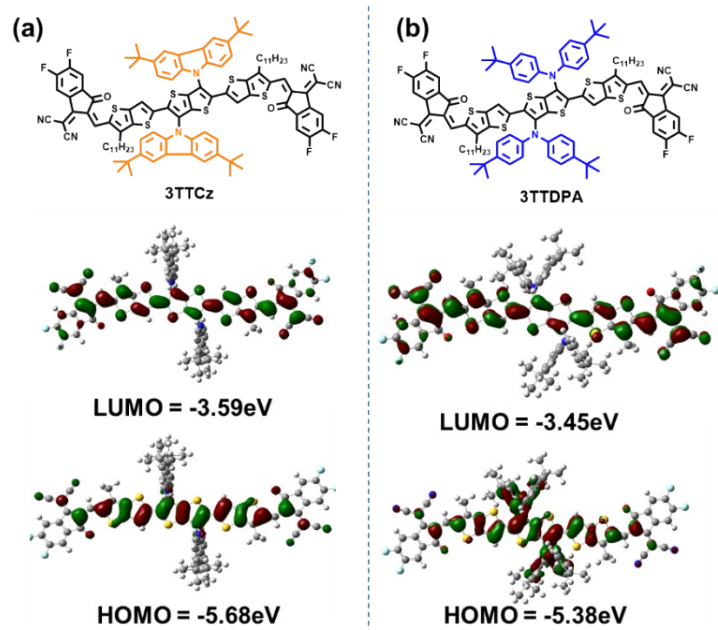


Fig. S9 Frontier molecular orbitals of (a) 3TTCz and (b) 3TTDPA calculated by density functional theory.

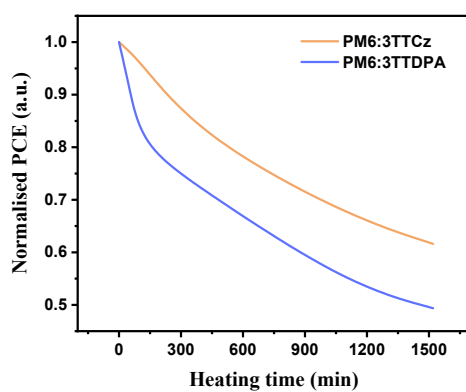


Fig. S10 Thermal-stabilities of PM6:3TTCz- and PM6:3TTDPA-based blends annealed at 80°C.

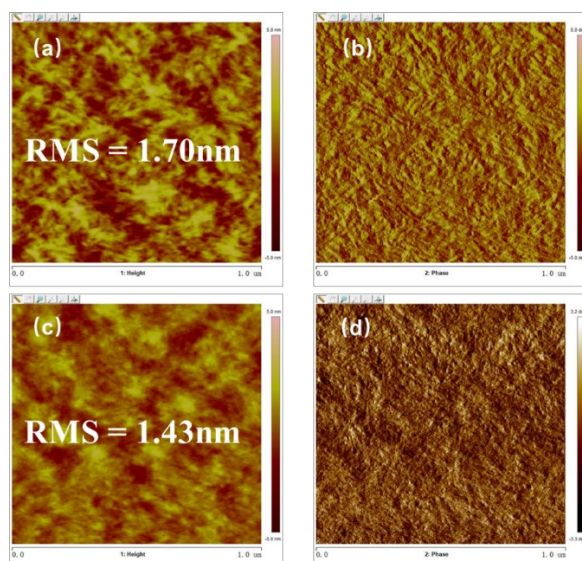


Fig. S11 AFM images for the optimal blend films of (a) and (b) PM6:3TTCz; (c) and (d) PM6:3TTDPA.

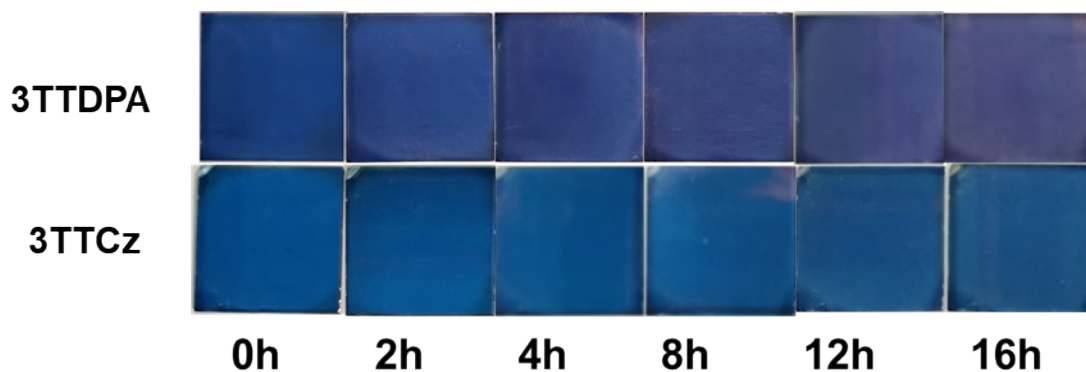


Fig. S12 Pictures of 3TTCz and 3TTDPA in films under 1.5 AM light illumination for various periods of time.

Supporting Tables

Table S1 Photovoltaic parameters of OPVs based on PM6:3TTCz films under various optimization conditions.

D:A	Annealing (°C)	Additive	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)
1:1	100	2%CN	0.943	18.15	73.79	12.63
1:1.5	100	2%CN	0.943	18.18	73.61	12.62
1:2	100	2%CN	0.941	18.90	78.78	14.00
1:2	100	3%CN	0.940	17.97	75.84	12.83
1:2	100	1%CN	0.944	17.73	75.00	12.57
1:2	100	0%CN	0.941	17.71	70.33	11.74
1:2	80	2%CN	0.941	17.50	75.04	12.36
1:2	120	2%CN	0.936	17.74	76.02	12.65

Table S2 Photovoltaic parameters of OPVs based on PM6:3TTDPA films under various optimization conditions.

D:A	Annealing (°C)	Additive	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)
1:1	100	0.3%DIO	0.928	21.32	64.61	12.78
1:1.2	100	0.3%DIO	0.939	21.71	63.95	13.03
1:1.5	100	0.3%DIO	0.932	20.19	63.30	11.92
1:1	80	0.3%DIO	0.937	21.14	64.36	12.92
1:1	120	0.3%DIO	0.927	20.26	66.80	12.55
1:1	100	/	0.925	20.07	60.89	11.29
1:1	100	0.5%DIO	0.942	20.63	64.96	12.51
1:1	100	1%DIO	0.937	21.97	66.93	13.85
1:1	100	1.5%DIO	0.935	20.46	65.27	12.41