

Supporting Information

A small-molecule donor with thieno[3,2-c]isochromene unit to synchronously elevate efficiency and stability of ternary fullerene organic solar cells

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1. Materials

Chlorobenzene (CB) and 1, 8-diiodooctane (DIO) were purchased from Aldrich and used without further purification. PTB7-Th, PC₇₁BM and Ca were purchased from J&K Scientific Co., Ltd. Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) (Clevis PVP Al 4083) was obtained from H.C. Starck, Germany. Molybdenum oxide (MoO₃) and aluminum (Al) were purchased from Alfa Aesar Co., Ltd. All materials were used without further purification. TiC8 was synthesized by our research group.

2. General Measurements

UV-vis absorption spectra were obtained using a Shimadzu UV-1800 PC spectrometer. The electrochemical cyclic voltammetry (CV) was measured with a CHI630E electrochemical workstation with the working electrode dipped in an acetonitrile solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) under nitrogen at room temperature.

3. OSC Device Fabrication and Measurement

The organic solar cells were fabricated with a conventional configuration of ITO /PEDOT:PSS (30 nm) /active layer (100 nm) /Ca (20 nm) /Al (100 nm). The cell area is 0.06 cm². The used indium tin oxide (ITO)-glass substrates were sequentially washed by Decon90 dilution solution, deionized water, acetone and isopropyl alcohol using ultrasonic process for each 20 min, respectively, then were treated by UV-ozone for 15 min. PEDOT:PSS was spin-coated at 4800 rpm for 30 s on the cleaned ITO substrate and annealed at 150 °C for 15 min in air. The substrates were transferred into an N₂-filled glove box for preparing the photoactive layer. The PTB7-Th:PC₇₁BM blend solutions were prepared using chlorobenzene solvent. The PTB7-Th concentration in the blend solution was 10 mg mL⁻¹ (donor: acceptor = 1:1.5 by weight). The additive ratio of DIO was 3% by volume. The blend solutions were stirred for 12 h before use. In the ternary blends, the doping ratios of TiC8 in the PTB7-Th:TiC8 blend were 15%, 20% and 25% by weight. The binary and ternary active layers were spin-coated on PEDOT:PSS with the resulting thickness of 130 nm and stayed in a vacuum for half an hour. Finally, the Ca (20 nm) and Al (100 nm) electrodes were thermally deposited with a shadow

mask of 0.06 cm² at the pressure of 10⁻⁴ Pa. The current density-voltage (*J-V*) characteristics were performed using a programmable Keithley 2400 source measurement unit under simulated solar light (AM 1.5 G) (DM40S3, SAN-EI ELECTRIC, Japan). The light intensity was determined by the standardized mono-silicon cell (Oriol PN 91150V, Newport, USA). The external quantum efficiency (EQE) spectra were obtained by a photo-modulation spectroscopic setup (Newport monochromator).

Space charge limited current (SCLC) method was applied to determine the electron and hole mobilities in the electron-only device with a structure of ITO/ZnO/active layer/Ca/Al and hole-only device with a structure of ITO/PEDOT:PSS/active layer/MoO₃/Al, respectively. The mobility was determined by the following equation:

$$J = \frac{9}{8} \mu \epsilon \epsilon_0 \frac{V^2}{L^3} \quad (1)$$

Where ϵ is the dielectric permittivity of the polymer (generally taken to be about 3), ϵ_0 is the dielectric permittivity of free space, L is the film thickness, and V is the voltage, which is defined as $V = V_{\text{appl}} - V_{\text{bi}}$, where V_{appl} is the applied voltage, V_{bi} is the built-in voltage, which is related to the difference in the work function of the electrodes.

4.Characterization of Grazing Incidence Wide-Angle X-ray Scattering (GIWAXS)

GIWAXS measurements were performed on a XEUSS SAXS/WAXS system at the South China University of Technology (China, Guangzhou). The samples were initially dissolved in chloroform and then spin coated on the top of silicon wafer at 2000 rpm. The silicon wafers were treated with plasma in advance to optimize the film-forming property.

5. Additional OSC Device Performance Data

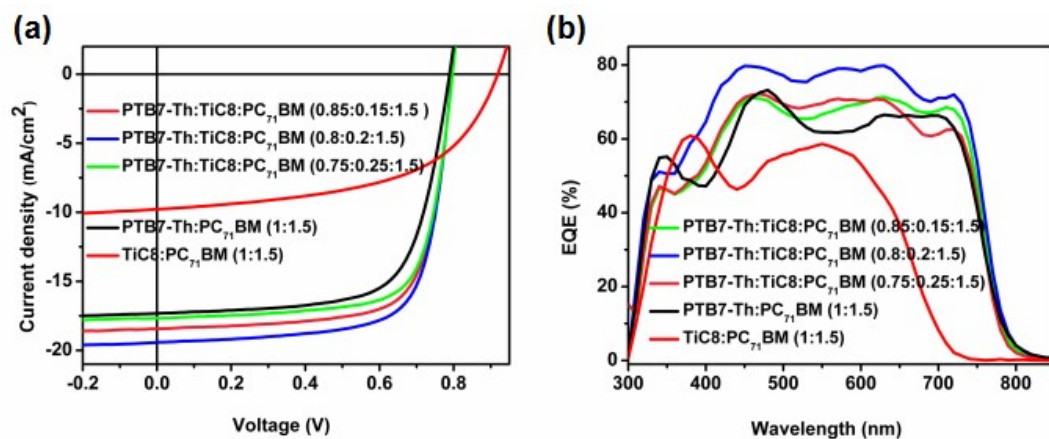


Fig. S1 a) J - V curves and b) EQE spectra of binary and ternary OSCs at various ratios of TiC8.

Table S1. Key photovoltaic parameters of all OPVs with different TiC8 content.

PTB7-Th: TiC8:PC ₇₁ BM	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]	R_s^a [Ω cm ²]	R_{sh}^a [k Ω cm ²]
1:0:1.5	0.789	17.31	68.8	9.39	9.1	16.74
0.85:0.15:1.5	0.796	18.43	72.3	10.61	6.2	17.33
0.8:0.2:1.5	0.789	19.42	72.1	11.12	5.6	14.82
0.75:0.25:1.5	0.796	17.64	72.8	10.22	6.4	20.4
0:1:1.5	0.918	9.76	54.2	4.85	24.5	9.42

6. SCLC Measurements

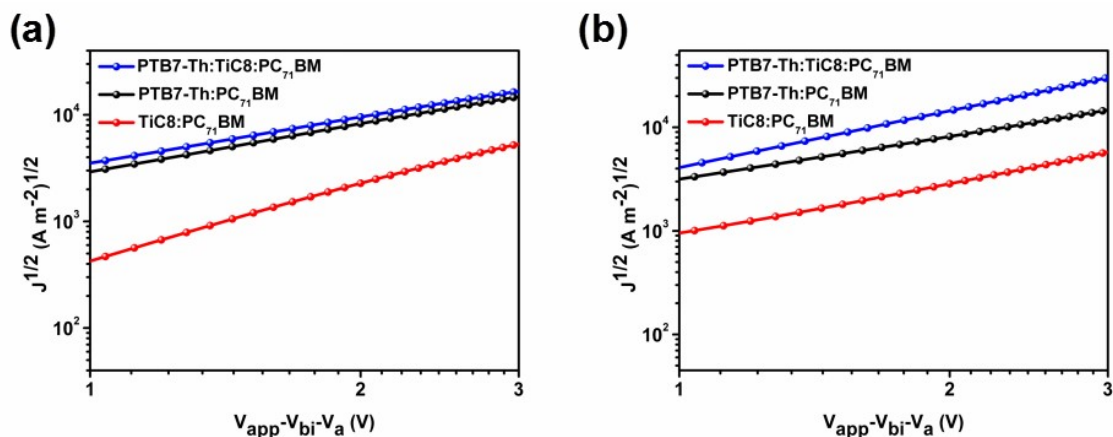
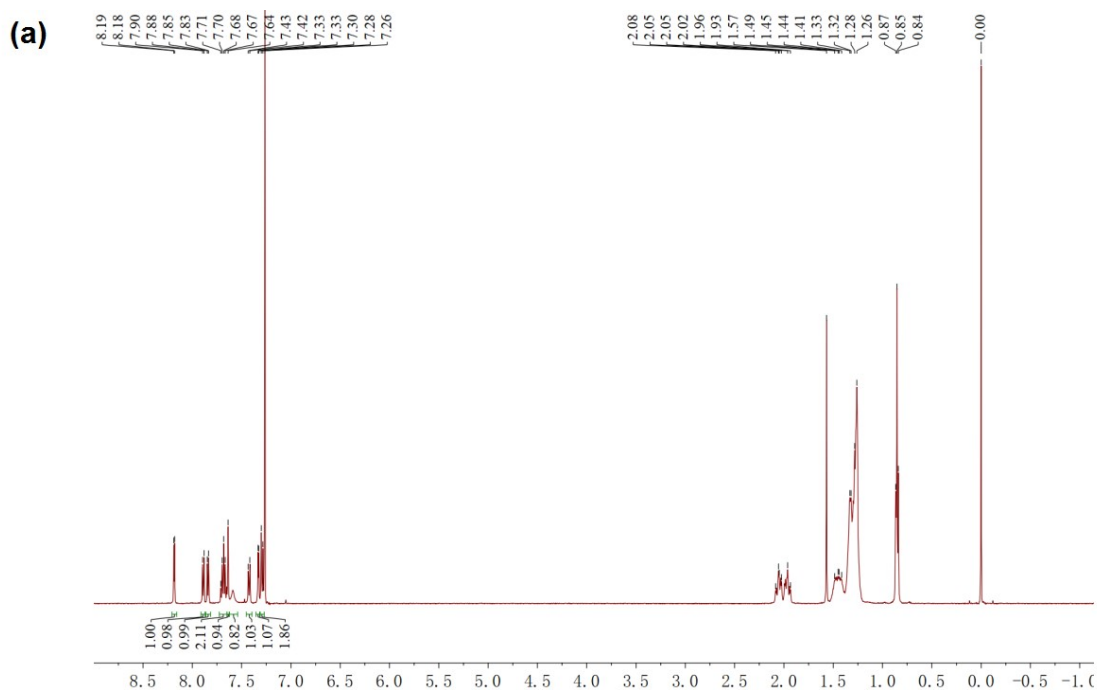


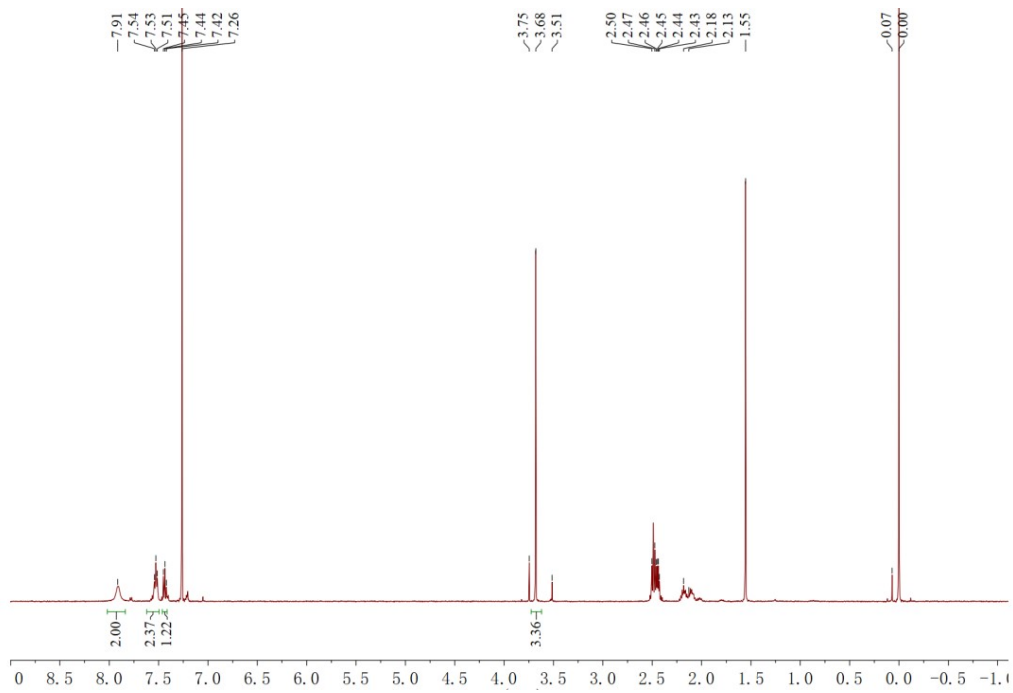
Fig. S2 $J^{1/2}$ - V plots of the hole-only devices a) and electron-only devices b) based on the PTB7-Th:TiC8:PC₇₁BM, PTB7-Th:PC₇₁BM and TiC8:PC₇₁BM systems, respectively.

7. ¹HNMR and 2D¹HNMR spectra of TiC8 and PC₇₁BM

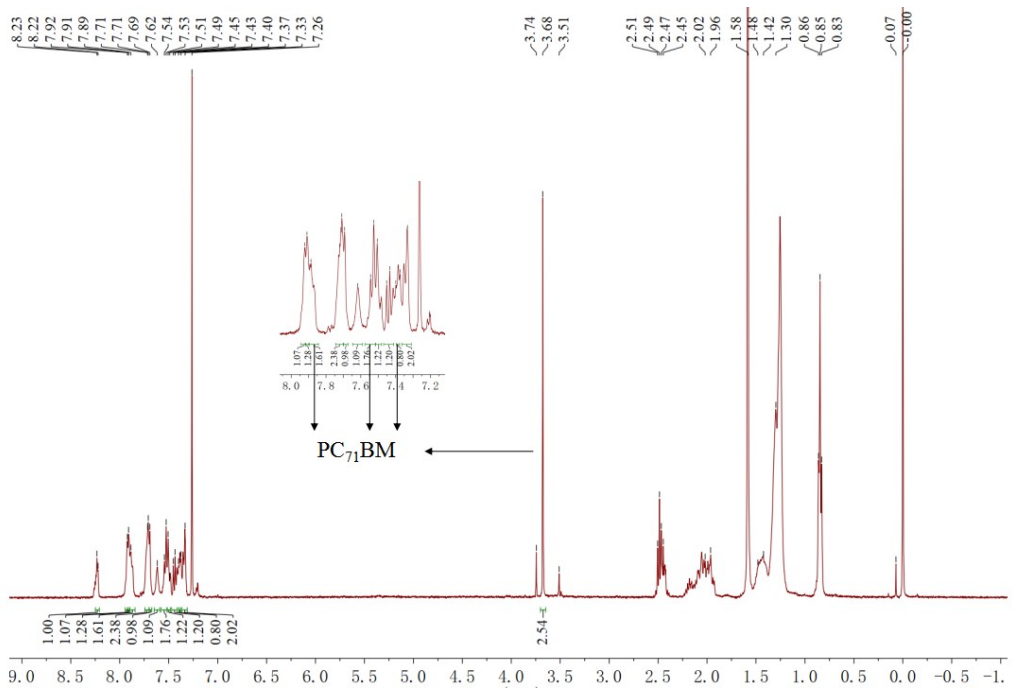
¹HNMR and 2D¹HNMR spectra were measured on a Bruker Dex-300/400 MHz NMR spectrometer using tetramethyl silane as a reference in deuterated chloroform solution at 298 K. Liquid chromatograph mass spectrometer were estimated on a Agilent 1100. The FT-IR and NMR spectra were performed by NICOLET IS 10 FT-IR spectrometer and Agilent DD2 (600M).



(b)



(c)



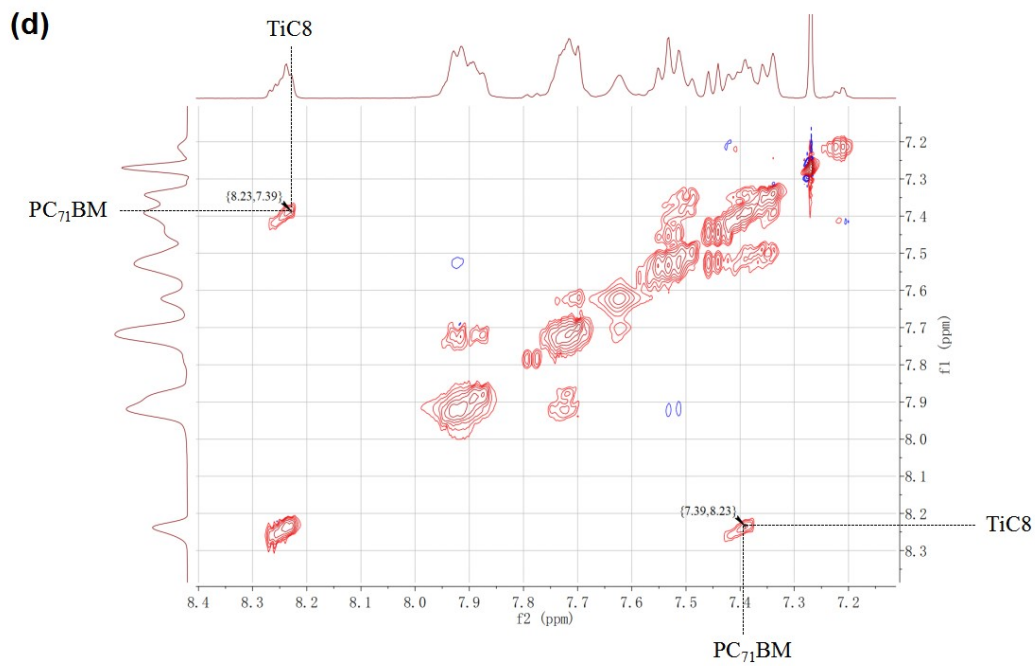


Fig. S3 a) The ^1H -NMR spectra of TiC8 and b) PC₇₁BM in CDCl_3 . c) The ^1H -NMR spectra of the mixture TiC8 and PC₇₁BM. d) 2D ^1H NMR spectrum of TiC8: PC₇₁BM blends.

8. Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM) Measurements

AFM measurements were performed in ambient on a SPID Bruker ICON using a TESPA probe. All the AFM images were flattened and exported from the NanoScope Analysis 1.9 software, the root-mean-square roughness (R_q) values of height images were obtained from the whole scan area ($2\ \mu\text{m} \times 2\ \mu\text{m}$). Transmission electron microscopy (TEM) images were obtained by using a HITACHI H-7650 electron microscope with an acceleration voltage of 100kV.

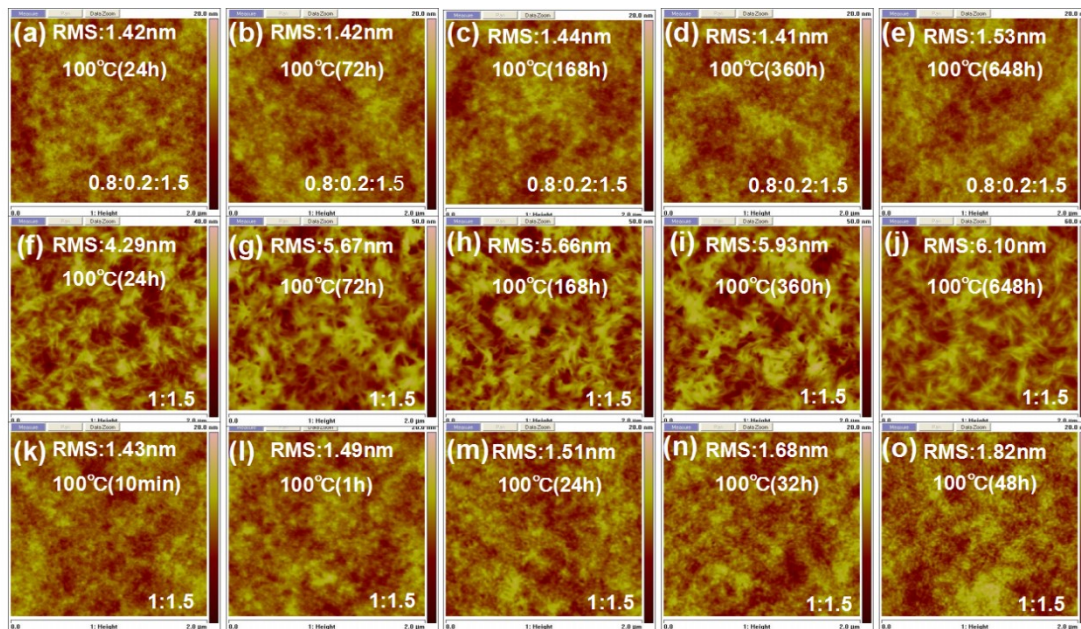


Fig. S4 a–e) AFM height images of PTB7-Th:TiC8:PC₇₁BM blend films under thermal annealing at 100 °C. f–j) AFM height images of TiC8:PC₇₁BM blend films under thermal annealing at 100 °C. k–o) AFM height images of PTB7-Th:PC₇₁BM blend films under thermal annealing at 100 °C.

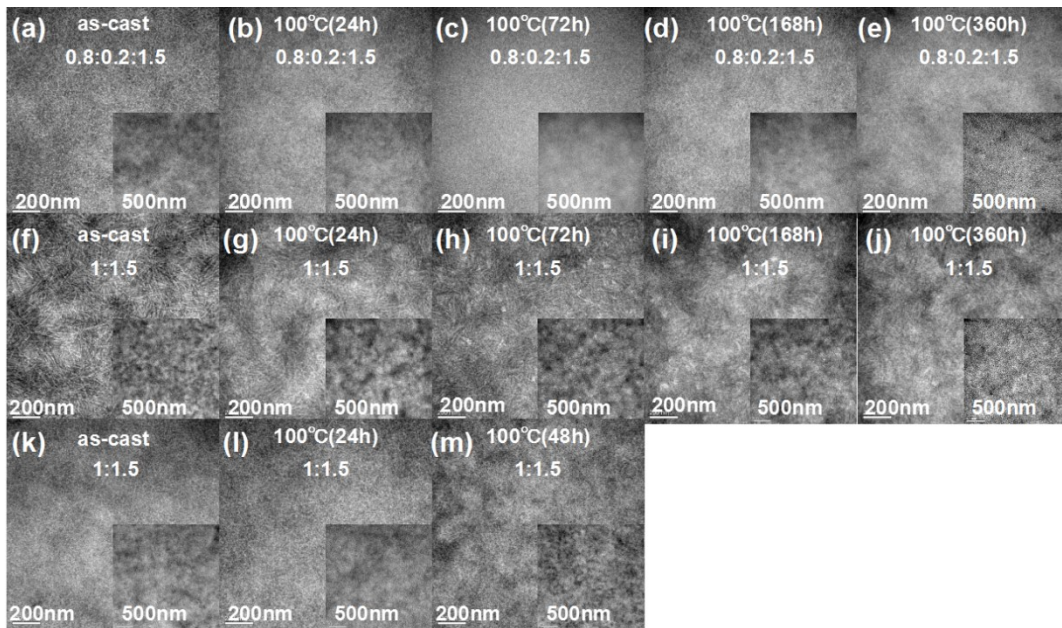


Fig. S5 a–e) TEM images of PTB7-Th:TiC8:PC₇₁BM blend films thermal annealing at 100 °C. f–j) TEM images of TiC8:PC₇₁BM blend films thermal annealing at 100 °C. k–m) TEM images of PTB7-Th:PC₇₁BM blend films thermal annealing at 100 °C.