

Electronic Supplementary Information for:

A non-fullerene acceptor with a fully fused backbone for efficient polymer solar cells with high open-circuit voltage

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Materials and Methods

Instrument. ^1H NMR spectra were obtained on a Bruker Advance III 400 (400 MHz) nuclear magnetic resonance (NMR) spectroscope. UV-vis absorption spectra were recorded on a Shimadzu UV-2450 spectrophotometer. Elemental analysis was conducted on a Flash EA 1112 elemental analyzer. Thermogravimetric analysis (TGA) was carried out on a WCT-2 thermal balance under protection of nitrogen at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) was recorded on a Pekin-Elmer Pyris 1 differential scanning calorimeter. Cyclic voltammetry (CV) was done on a CHI600A electrochemical workstation with Pt disk, Pt plate, and standard calomel electrode (SCE) as working electrode, counter electrode, and reference electrode, respectively, in a 0.1 mol/L tetrabutylammoniumhexafluorophosphate (Bu_4NPF_6) CH_2Cl_2 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).

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. **PTB7-Th** was purchased from 1-Material Inc. **IDTT-di-Tin**¹ and **Br-PDI**² were synthesized according to reported procedure.

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. All 7-tridecane substituents were replaced with methyl groups in calculations.

2D-GIWAXS Measurements. The GIWAXS measurements were conducted at 23A SWAXS beamline of a superconductor wiggler at the National Synchrotron Radiation Research Center, Hsinchu, Taiwan. We probed the samples with 0.15° incident angle, using a 10 keV beam of 0.15 mm in height and 0.2 mm in width and C9728DK area detector.

Device fabrication and characterization. Polymer solar cells were fabricated on glass substrates commercially pre-coated with a layer of indium tin oxide (ITO) with the inverted structure of ITO/ZnO/PTB7-Th:FITP/MoO₃/Ag. Prior to fabrication, the substrates were cleaned using detergent, deionized water, acetone and isopropanol consecutively for every 15 min, and then treated in an ultraviolet ozone generator for 15 min. A thin layer of sol-gel ZnO (\approx 40 nm) was spin coated onto precleaned ITO-coated glass substrates and then annealed at 180 °C for 15 min. The PTB7-Th:FITP active layers were deposited from 20 mg mL⁻¹ solutions without or with CN as the additive in chlorobenzene by spin-coating at 2500 rpm, resulting in an active layer thickness of about 100 nm. MoO₃ (10 nm) and Ag (100 nm) were evaporated through a shadow mask, giving an active area of 5.2 mm² per device.

The current density-voltage (J - V) curves of PSCs were measured with Keithley 2400 measurement source units at room temperature in air. The photocurrent was

measured under a calibrated solar simulator (Abet 300W) at 100 mW cm⁻² and the light intensity was calibrated with a standard photovoltaic (PV) reference cell. External quantum efficiency (EQE) spectrum was measured with a Stanford lock-in amplifier 8300 unit.

The charge carrier mobilities of the PTB7-Th:FITP films were measured using the space-charge-limited current (SCLC) method. Hole-only devices were fabricated in a structure of ITO/PEDOT:PSS/PTB7-Th:FITP(1.2:1)/MoO₃/Al, electron-only devices were fabricated in a structure of ITO/PFN/ PTB7-Th:FITP(1.2:1)/PFN/Al. The device characteristics were extracted by modeling the dark current under forward bias using the SCLC expression described by the Mott-Gurney law:

$$J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu \frac{V^2}{L^3} \quad (1)$$

Here, $\varepsilon_r \approx 3$ 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

Synthesis of IDTT-PDI: To a two-necked round bottom flask was added IDTT-di-Tin (0.13g, 0.1 mmol), Br-PDI (0.21g, 0.25 mmol), toluene (15 mL) and dimethyl formamide (DMF, 2 mL). The mixture was frozen with liquid nitrogen, followed by three times of successive vacuum and nitrogen fill cycles, then under the protection of nitrogen, Pd(PPh₃)₄ (20mg, 0.017 mmol) was added, and another three times of successive vacuum and nitrogen fill cycles were performed. Then, the mixture was

refluxed at 110 °C for 48 h. The crude product was extracted with dichloromethane and washed with water. After removing the solvent, silica gel column chromatography was used to purify the product with the mixture of hexane and dichloromethane (1:1-1:2) as the eluent, yielding a black solid (0.24g, 95%). ¹H NMR (400 MHz, CDCl₃): δ= 8.76-8.57 (m, 10H), 8.38-8.30 (m, 2H), 8.29-8.19 (m, 2H), 7.61 (s, 2H), 7.55 (s, 2H), 7.18 (d, *J*=8.2 Hz, 8H), 7.11 (d, *J*=8.2 Hz, 8H), 5.22-5.13 (m, 4H), 2.64-2.51 (m, 8H), 2.31-2.16 (m, 8H), 1.93-1.78 (m, 8H), 1.66-1.53 (m, 8H), 1.42-1.12 (m, 88H), 0.90-0.78 (m, 36H).

Synthesis of FITP: IDTT-PDI (0.24, 0.1 mmol) was dissolved in 40 mL CHCl₃, the solution was frozen with liquid nitrogen, followed by three times of successive vacuum and nitrogen fill cycles, and under the protection of nitrogen, a solution of FeCl₃ (1.62g, 10 mmol) in 5 mL CH₃NO₂ was added quickly, then the mixture is refluxed at 50 °C for 8h. The crude product was extracted with dichloromethane and washed with water. After removing the solvent, the product was purified by silica gel column chromatography (eluent: hexane:dichloromethane=1:1-0:1), yielding a deep green solid (0.2g, 80%). ¹H NMR (400 MHz, CDCl₃): δ= 9.82 (sd, 2H), 9.43 (s, 2H), 9.17-8.79 (m, 8H), 7.95 (s, 2H), 7.51 (d, *J*=7.4 Hz, 8H), 7.34 (d, *J*=8.0 Hz, 8H), 5.46-5.27 (m, 4H), 2.76-2.60 (m, 8H), 2.57-2.30 (m, 8H), 2.15-1.92 (m, 8H), 1.77-1.63 (m, 8H), 1.51-1.21 (m, 88H), 0.94-0.75 (m, 36H). Elem. Anal. Cald for C₁₆₈H₁₉₀N₄O₈S₄: C, 80.02; H, 7.60; N, 2.22; Found: C, 79.72; H, 7.62; N, 1.97.

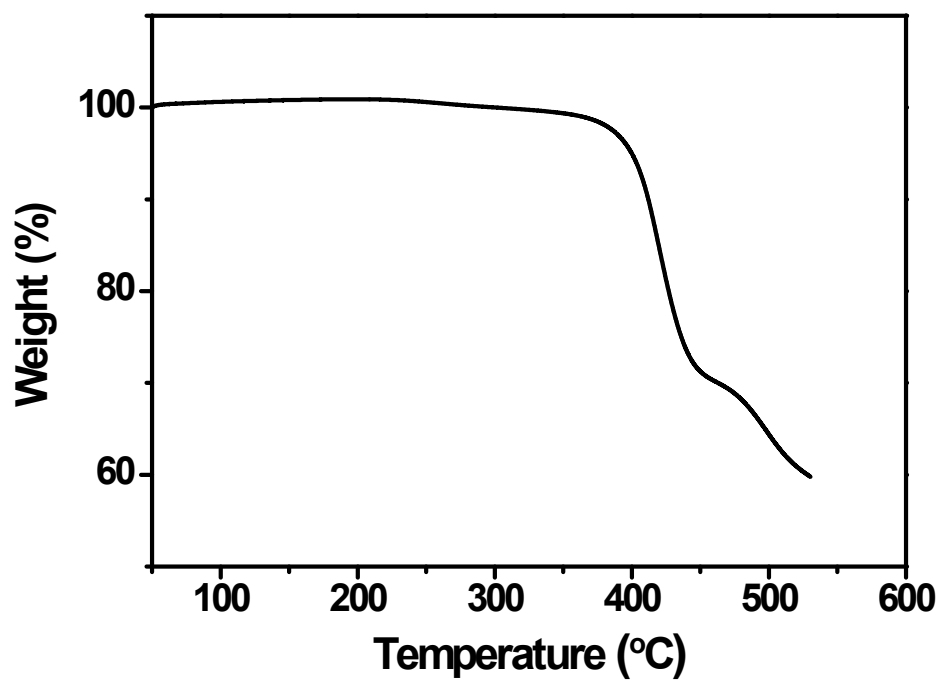


Fig. S3 TGA curve of FITP.

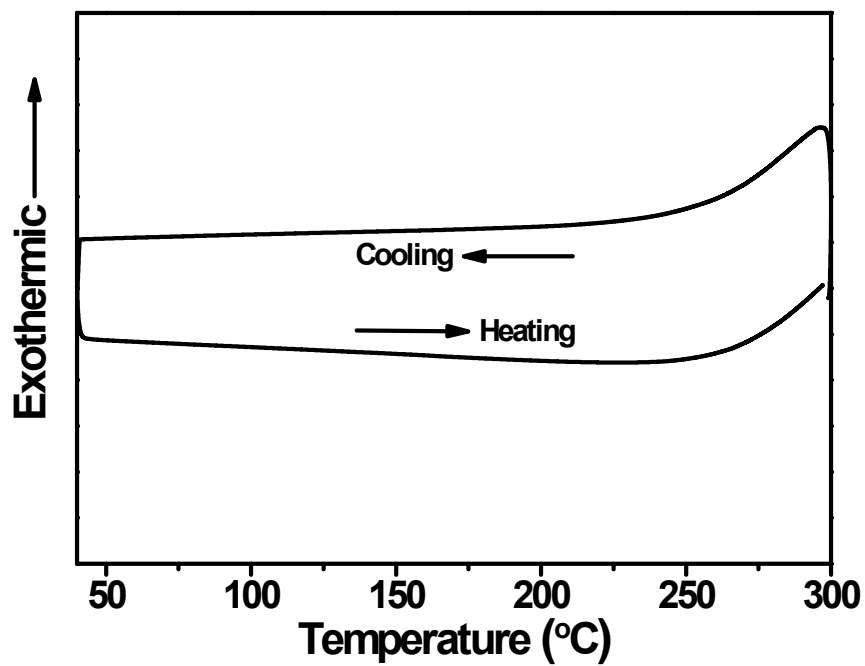


Fig. S4 DSC curve of FITP.

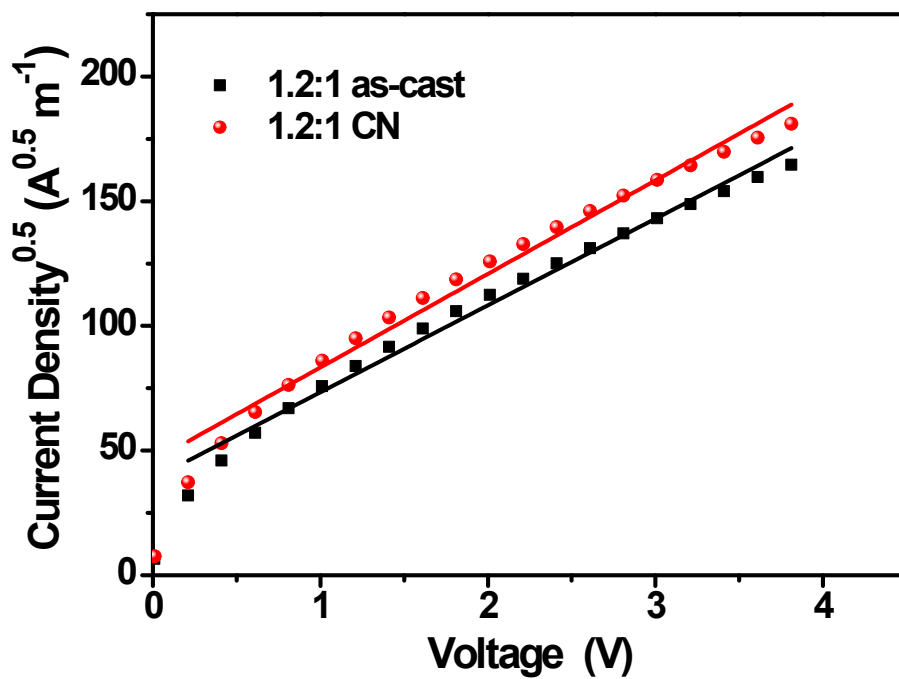


Fig. S5 $J^{0.5}$ - V curves of the hole-only devices based on PTB7-Th:FITP films.

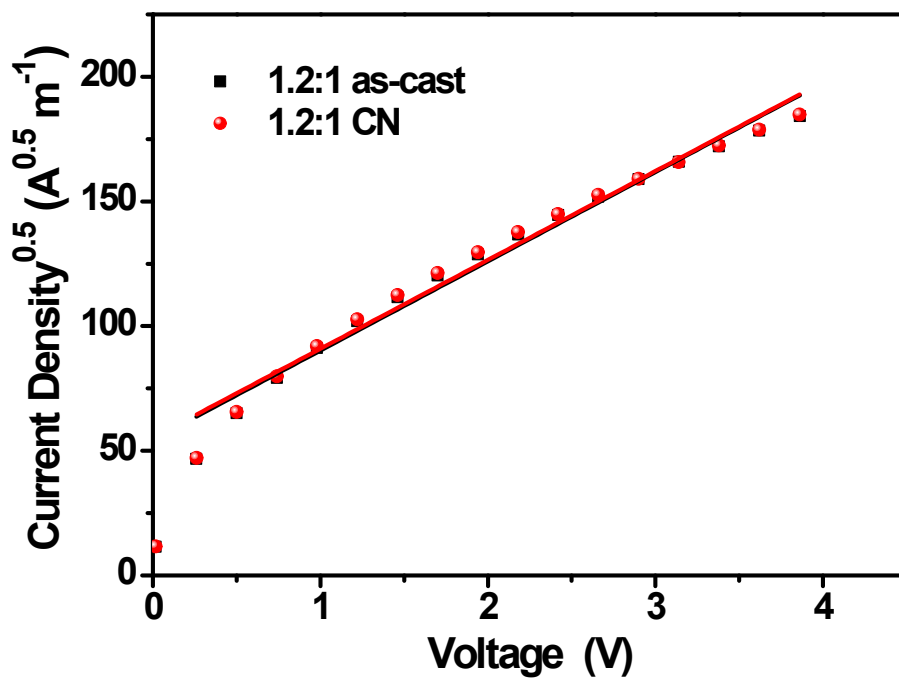


Fig. S6 $J^{0.5}$ - V curves of the electron-only devices based on PTB7-Th:FITP films.

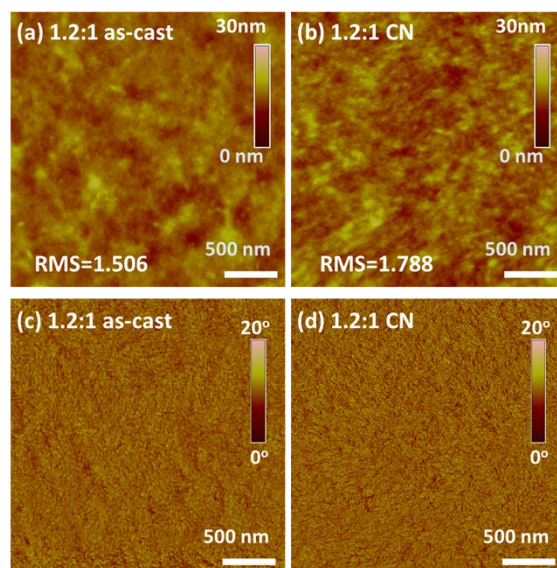


Fig. S7 AFM height images (a, b) and phase images (c, d) of 1.2:1 as-cast (a, c) and 1.2:1 CN (b, d) films.

References

1. Y.-X. Xu, C.-C. Chueh, H.-L. Yip, F.-Z. Ding, Y.-X. Li, C.-Z. Li, X. Li, W.-C. Chen and A. K. Y. Jen, *Adv. Mater.*, 2012, **24**, 6356-6361.
2. J. Lee, R. Singh, D. H. Sin, H. G. Kim, K. C. Song and K. Cho, *Adv. Mater.*, 2016, **28**, 69-76.