

Supporting Information

Synthesis and photovoltaic properties of novel 3, 4-ethylene-dithiathophene-based copolymers for organic solar cells

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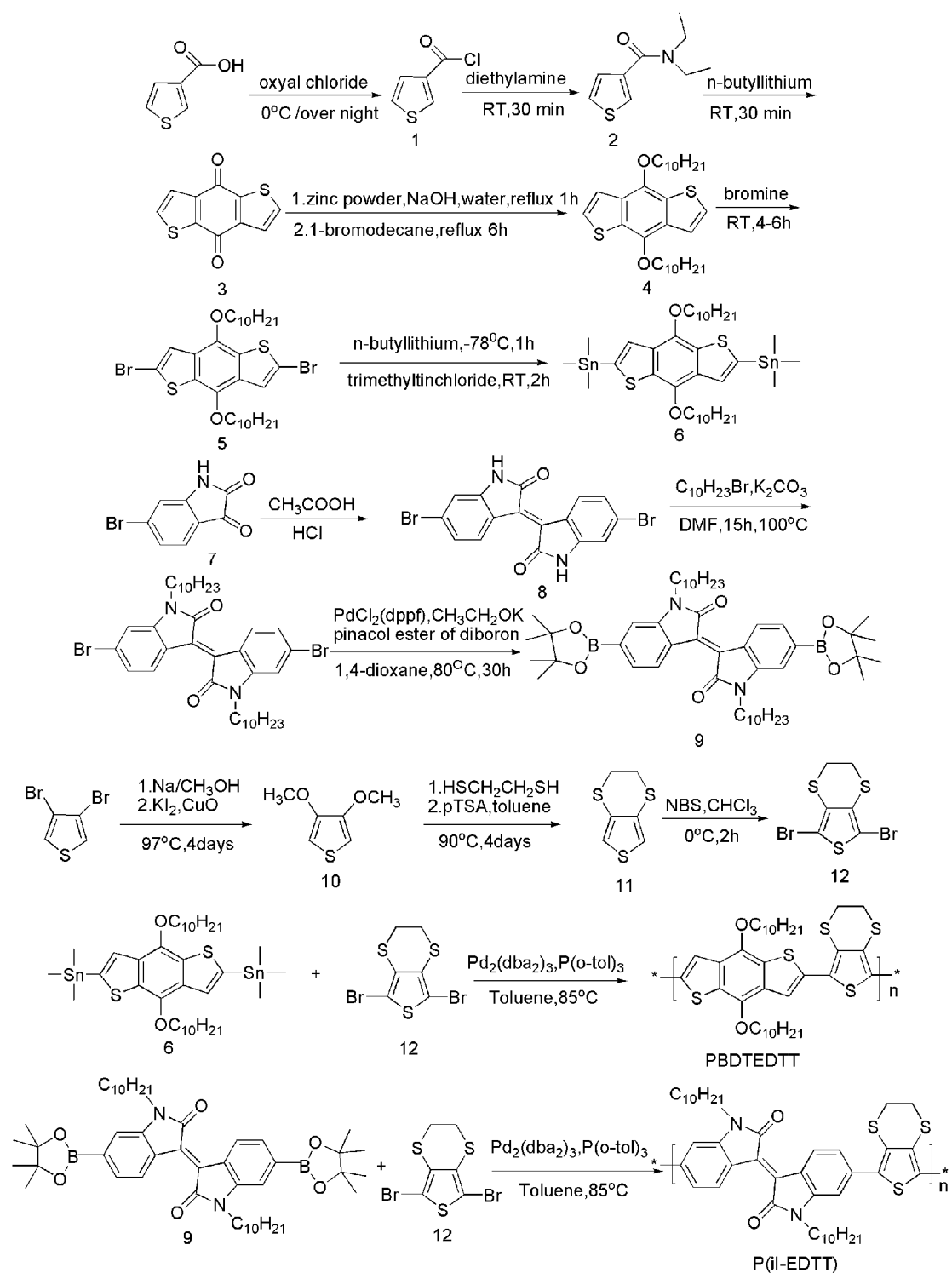
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Experimental Details

All reagents and starting materials were purchased from commercial sources and used without further purification, unless otherwise noted. All air and water sensitive reactions were performed under nitrogen atmosphere. Reaction mixtures were stirred magnetically. Solvents were transferred via syringe and were introduced into the reaction vessels through a rubber septum. The reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica-gel (60-F254). The TLC plates were visualized with UV light. Column chromatography was carried out on a column packed with silica-gel 60N spherical neutral size 50-74 μm . Toluene and tetrahydrofuran (THF) were distilled from sodium, with benzophenone as indicator. ^1H and ^{13}C NMR spectra were recorded on a Bruker Advance III 600 (600 MHz). UV-vis absorption spectra were recorded at room temperature using Hitachi U-4100 spectrophotometer. Cyclic voltammetry (CV) measurements were performed on a CHI660D electrochemical workstation. It is equipped with a three-electrode cell consisting of a glassy carbon working electrode, a saturated calomel reference electrode (SCE) and a platinum wire counter electrode. The measurements were done in anhydrous acetonitrile containing 0.1 M nBu_4NPF_6 as a supporting electrolyte under argon atmosphere at a scan rate of 100 mV/s. Thin films were deposited from chloroform solution onto the working electrodes and dried under nitrogen prior to measurement. The redox potential of the Fc/Fc^+ internal reference is 0.38 V vs. SCE. The highest occupied molecular orbit (HOMO) and the lowest unoccupied molecular orbit (LUMO) energy levels, were determined by calculating the empirical formula of $E_{\text{HOMO}} = -e(E_{\text{ox}} + 4.8 - E_{1/2,(\text{Fc}/\text{Fc}^+)})$, $E_{\text{LUMO}} = E_{\text{HOMO}} + E_g$, where E_{ox} and E_g were the onset oxidation potential and the optical band gap, respectively. AFM images were acquired with Agilent-5400 scanning probe microscope with a Nanodrive controller in tapping mode with

MikroMasch NSC-15 AFM tips with resonant frequencies ~300 kHz. Thermogravimetric analysis (TGA) and Differential scanning calorimetric (DSC) measurements was performed by a STA-409 at a heating rate of 10 °C/min. Gel permeation chromatography (GPC) was performed using an ELEOS System. FT-IR spectra were taken on a Nicolet 6700 spectrophotometer by using KBr pellets. X-ray diffraction (XRD) spectra were recorded on a Bruker D8 Advance. Scanning Electron Microscopy (SEM) measurements were acquired using a Hitachi S-4800.



Scheme S1 Synthetic routes of the polymers

Synthetic details

Synthesis of 2,5-dibromo-3,4-ethylenedithiathiothiophene, 2,6-bis(trimethyltin)-4,8-didecyloxybenzo [1,2-b;3,4-b]dithiophene, 6,6'-(N,N'-2-decyl)-pinacoldiboronisoindigo, were prepared according to the published procedures.^{1, 2, 3, 4}

Synthesis of PBDTEDITT

In a 25 mL flame-dried Schlenk flask, 2,6-bis(trimethyltin)-4,8-didecyloxybenzo [1,2-b;3,4-b]dithiophene (416mg, 0.5 mmol, 1 equiv.), 2,5-dibromo-3,4-ethylenedithiathiothiophene (166 mg, 0.5 mmol, 1 equiv.), Pd₂(dba)₃ (15 mg) and P(o-tol)₃ (10 mg) were subjected to three cycles of evacuation/argon purging and then dissolved with 5 mL of degassed toluene (the toluene was flushed with argon for 20 min). The oil bath was heated to 85 °C carefully, and the reactant was stirred for 36 hours at this temperature under an argon atmosphere. The reaction mixture was cooled down to room temperature and precipitated in 100 mL of methanol and filtered. The crude polymer was purified by silica gel column chromatography using chloroform as the eluent. The solid was dried under vacuum for 1 day to obtain the final product (188 mg, yield: 56%, M_n = 22 kDa, PDI 2.1). ¹H NMR (600MHz, CDCl₃, δ ppm): 7.75-7.45 (br, 2H), 4.45-4.21 (br, 4H), 3.50-3.26 (br, 4H), 2.06-1.88 (br, 4H), 1.80-1.16 (28H), 0.99-0.83 (br, 6H). FT-IR (KBr, cm⁻¹): 3107, 3076, 2922, 2852, 1530, 1464, 1434, 1362, 1263, 1176, 1047, 721.

Synthesis of P(iI-EDTT)

In a 25 mL flame-dried Schlenk flask, 6,6'-(N,N'-2-decyl)-pinacoldiboronisoindigo (399mg, 0.5 mmol, 1 equiv.), 2,5-dibromo-3,4-ethylenedithiathiothiophene (166 mg, 0.5 mmol, 1 equiv.), Pd₂(dba)₃ (15 mg), P(o-tol)₃ (10 mg) and several drops of Aliquat 336 were subjected to three cycles of evacuation/argon purging and then dissolved with 5 mL of degassed toluene after which 1.5 mL (1M) of degassed aqueous solution of Na₂CO₃ was added (both the aqueous solution and toluene were flushed with argon for 20 min). The oil bath was heated to 85 °C carefully, and the reactant was stirred for 36 hours at this temperature under an argon atmosphere. The reaction mixture was cooled down to room temperature and precipitated in 100 mL of methanol and filtered. The crude polymer was purified by silica gel column chromatography using chloroform as the eluent. The solid was dried under vacuum for 1 day to obtain the final product (196 mg, yield: 54%, M_n = 19 kDa, PDI 2.3) ¹H NMR (600MHz, CDCl₃, δ ppm): 9.36-8.80 (br, 2H),

7.34-6.63 (br, 4H), 3.98-3.65 (br, 4H), 3.46-3.09 (br, 4H), 2.11-0.64 (br, 38H). FT-IR (KBr, cm^{-1}):
3132, 3052, 2952, 2922, 2851, 1693, 1608, 1457, 1359, 1113, 1083, 880.

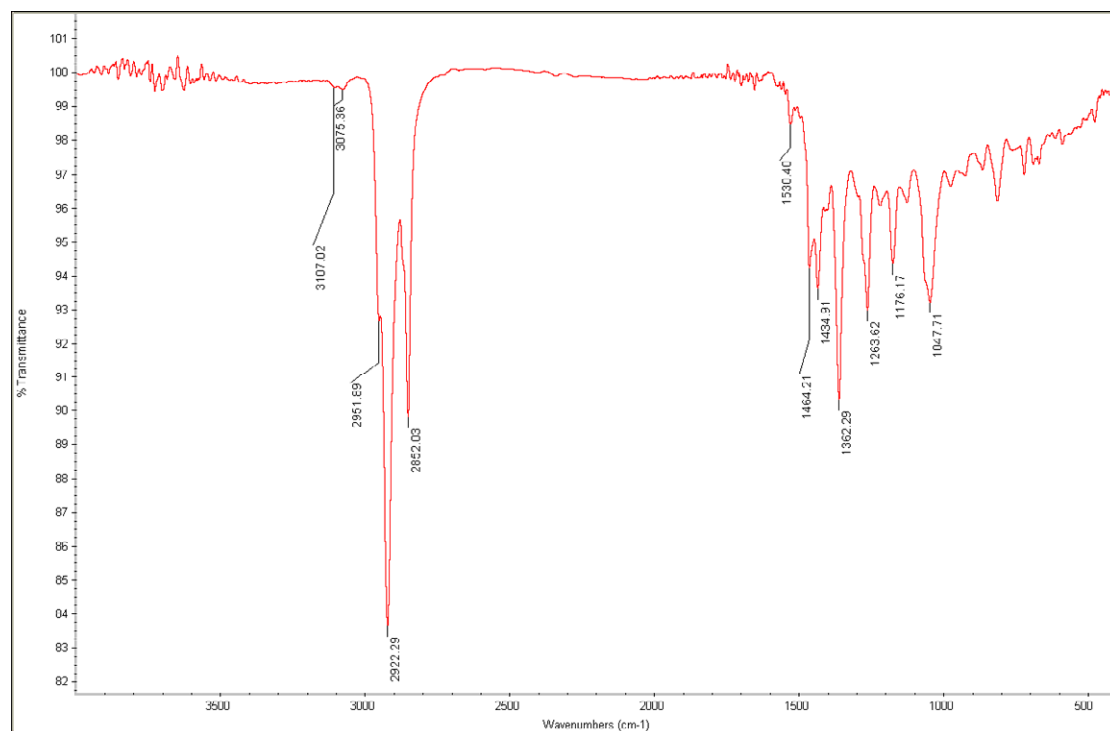


Figure S1 FT-IR spectra of PBDTDDTT.

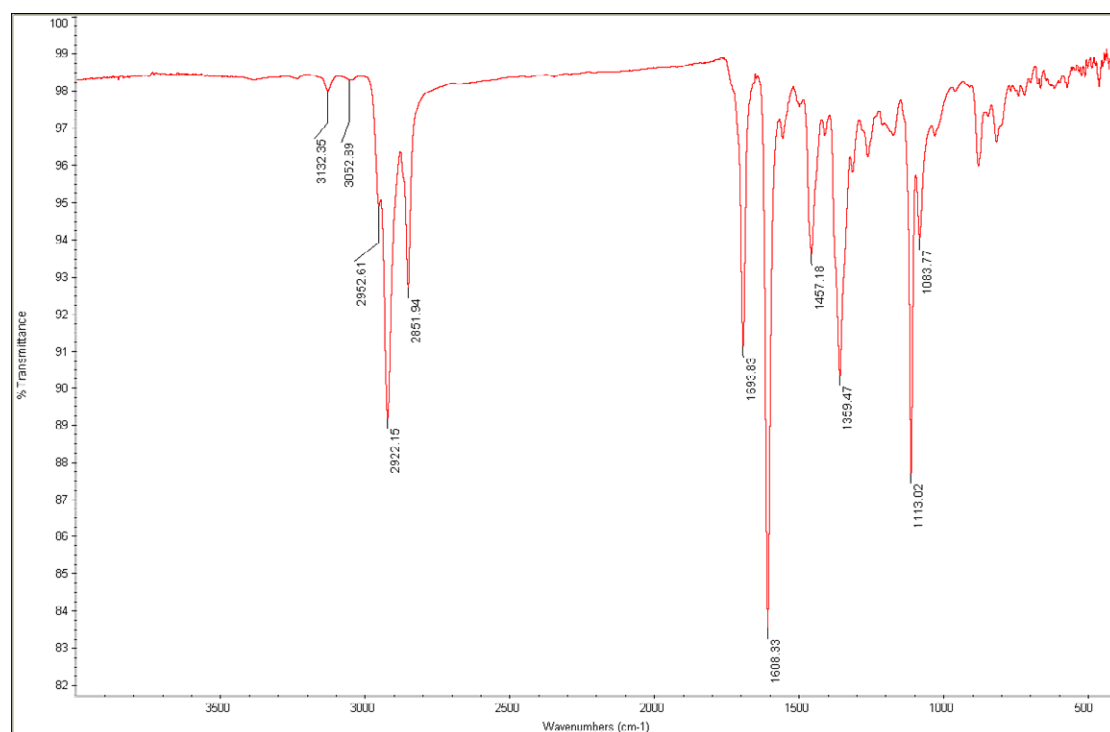


Figure S2 FT-IR spectra of P(iL-EDTT).

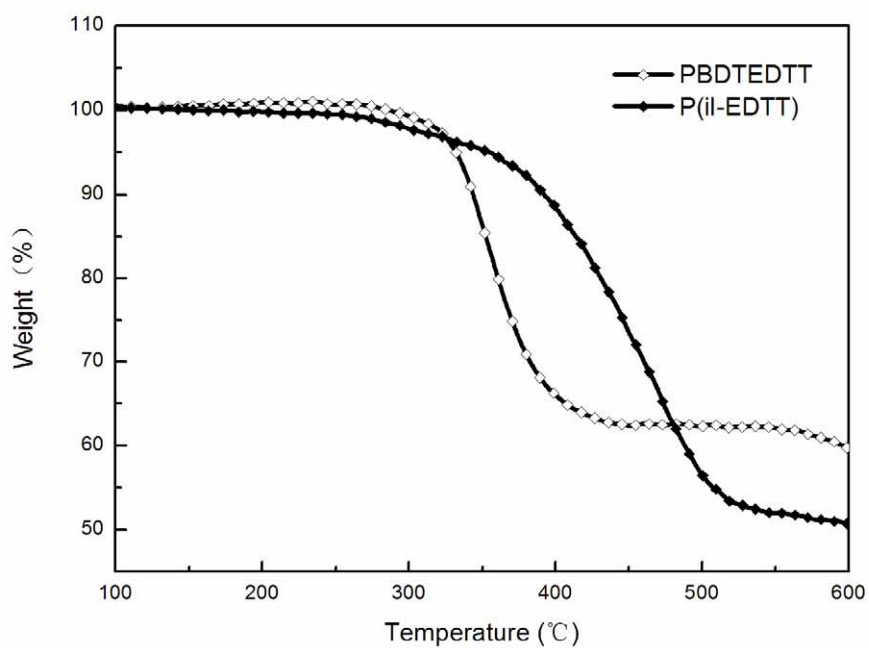


Figure S3 TGA thermogram of PBDTEDTT and P(iI-EDTT) with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under inert atmosphere.

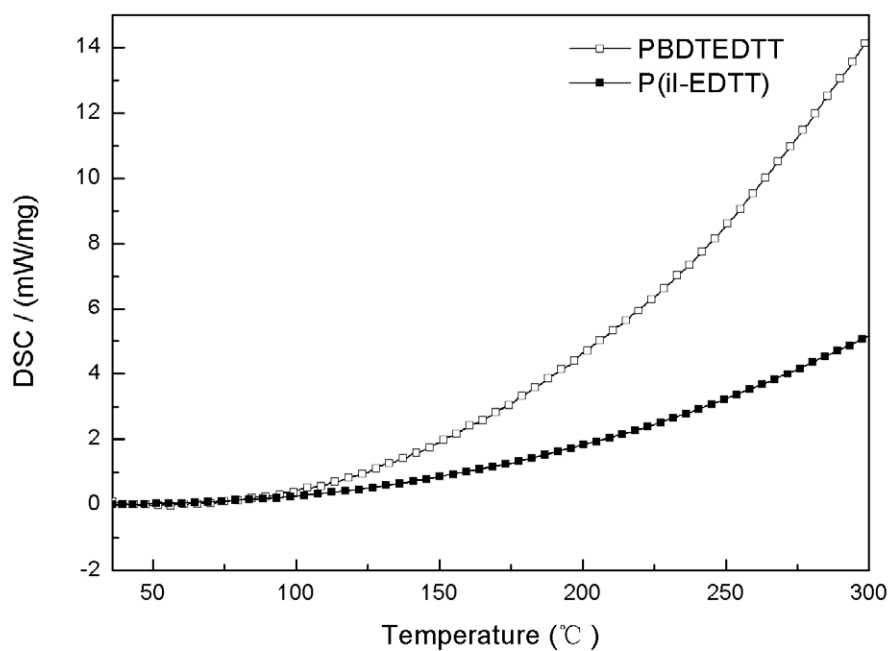


Figure S4 DSC measurements of PBDTEDTT and P(iI-EDTT) with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under nitrogen atmosphere.

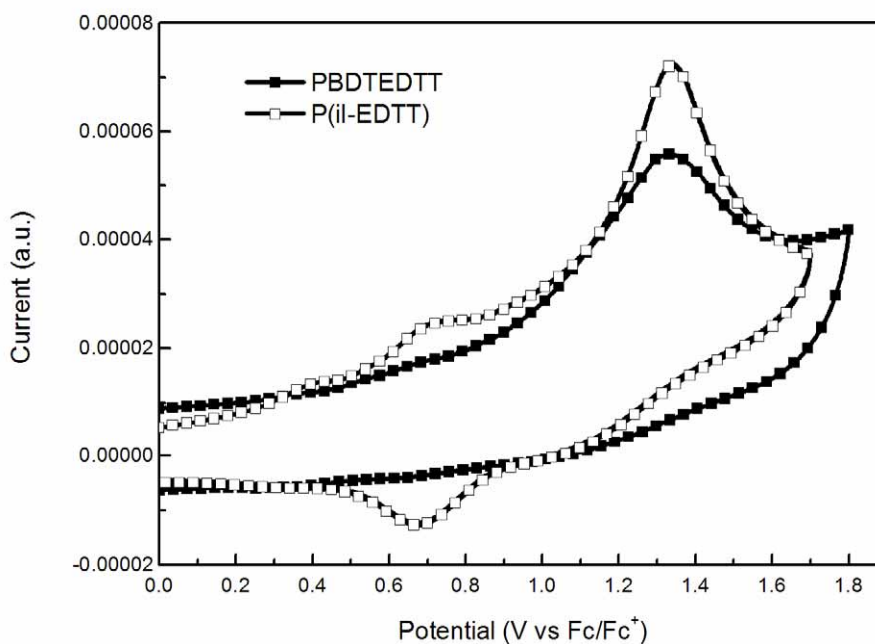


Figure S5 Cyclic voltammogram of PBDTEDTT and P(iI-EDTT) in film.

Fabrication of polymer solar cell devices

Before fabrication of the device, the indium tin oxide (ITO)-coated substrates were patterned by photolithography and cleaned in ultrasonic bath in acetone, toluene, methanol and isopropyl alcohol sequentially.

Polymer solar cell devices with the structure of ITO/PEDOT:PSS/copolymer:PC₆₀BM/LiF/Al were fabricated under conditions as follows: after spin coating a 40-nm-thick layer of poly(3,4-ethy lenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) on a ITO-coated substrates, followed by baking on a hot plate at 160 °C for 30 min. The PBDTEDTT polymer and PC₆₀BM were co-dissolved in chlorobenzene with or without 1,8-diiodoctane (DIO) in the weight ratios from 2.5:1, 2:1, 1.7:1, 1.3:1, 1:1, 1:2, and 1:3, respectively. An active layer of the device consisting of the blend of copolymers and PC₆₀BM was then spin coated from solution with a thickness of 100 nm. Typical concentration of the copolymer/PC₆₀BM blending solution used in this study for spin-coating active layer was 10 mg/ml. The device was subsequently heated on a hot plate at 120 °C for 10 min. LiF (1 nm) and aluminum (100 nm) were thermally evaporated at a vacuum of $\sim 2 \times 10^{-4}$ Pa on top of active layer as a cathode (Figure S6).

The inverted cells based on the structure of ITO/ZnO/PBDTEDTT:PC₆₀BM/MoO₃/Ag were also fabricated and the device fabrication procedures were as follows: a thin layer of sol-gel ZnO (45nm) was spin coated onto ITO-coated glass. The ZnO sol-gel film was then annealed in air for 10 h at 120 °C. The same process for the active layer in the conventional architecture was used for the inverted device. After annealing the active layer, a thin layer of MoO₃ (5 nm) was thermally evaporated and then Ag electrode was deposited to complete the inverted device structure. The active area of device was defined by shadow mask and was 0.1 cm².

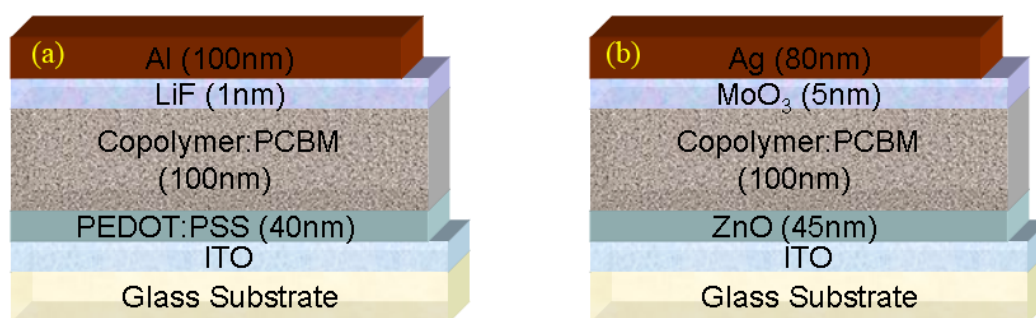


Figure S6 Schematic diagram of the polymer solar cells with conventional (a) and inverted geometry (b).

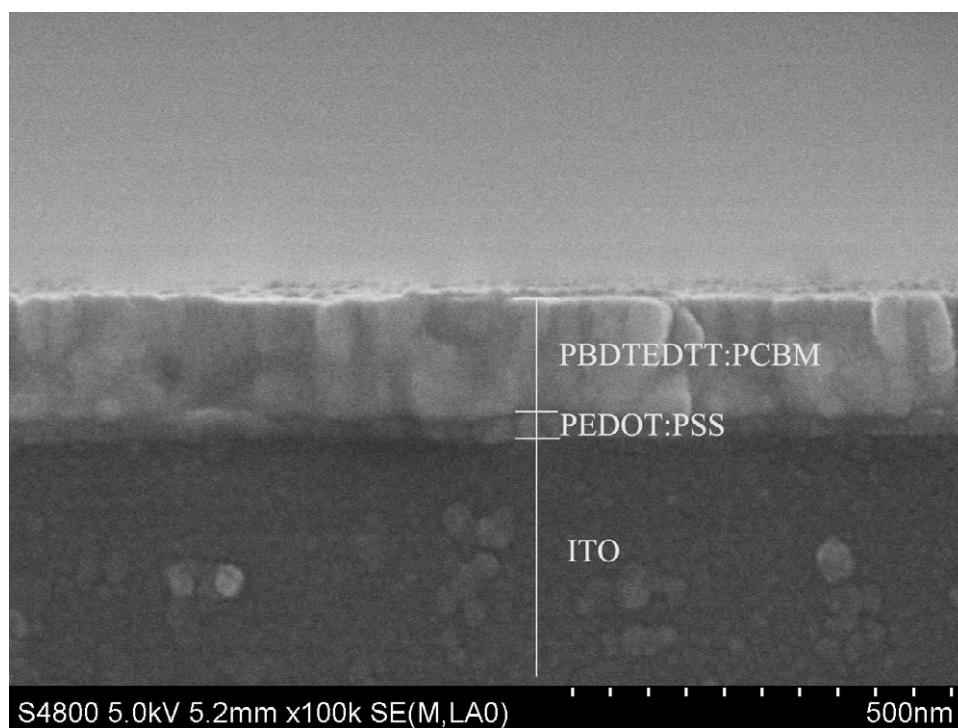


Figure S7 SEM side views (cross-sections) of PBDTEDTT:PC₆₀BM (2:1) film.

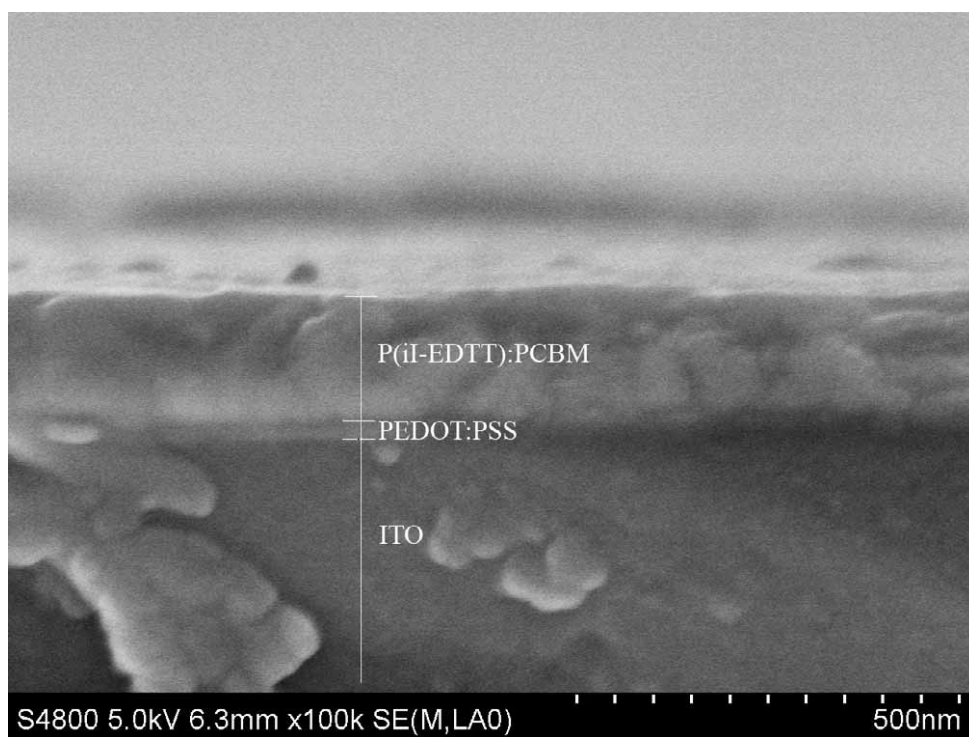


Figure S8 SEM side views (cross-sections) of P(iI-EDTT):PC₆₀BM (1:1) film.

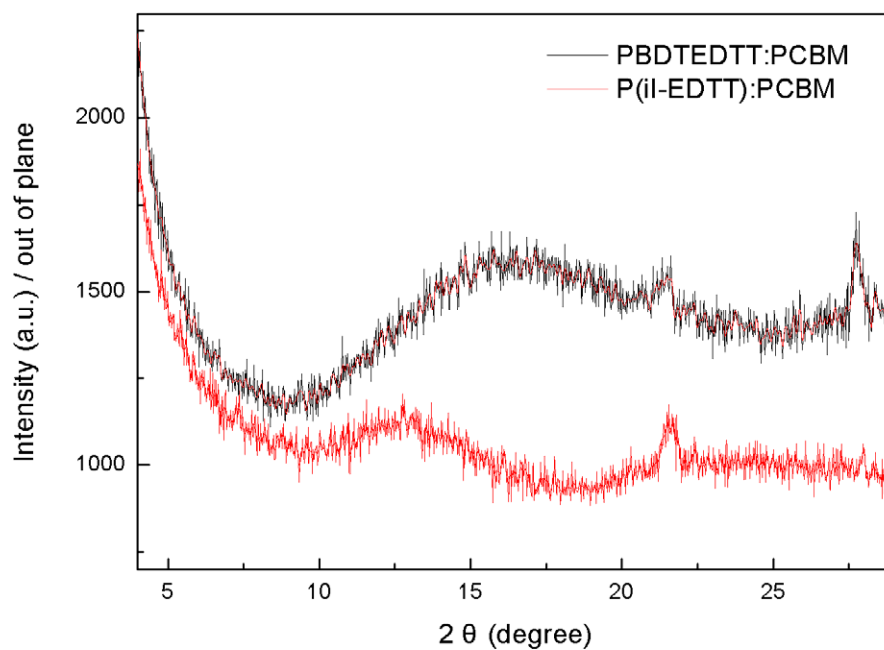


Figure S9 Out-of-plane XRD patterns of PBDTEDTT:PC₆₀BM (2:1) film and P(iI-EDTT):PC₆₀BM (1:1) film.

Current density-voltage measurements

Device characterization was performed in an ambient environment without any encapsulation

under 100 mW m^{-2} AM 1.5G illumination conditions. The incident photon to current efficiency (IPCE) was measured using a Newport 2931-C coupled with a 300 W Xenon lamp.

Table S1 Photovoltaic performance of the PSCs based on PBDTEDTT:PC₆₀BM (2:1 w/w) with thermal annealing, under the illumination of AM 1.5G, 100 mW cm^{-2}

Thermal annealing	V _{oc}	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
120 °C for 5 min	0.687	6.616	52.79	2.399
120 °C for 10 min	0.683	5.680	52.87	2.051
120 °C for 20 min	0.685	5.631	52.31	2.018
120 °C for 30 min	0.632	3.476	35.66	0.784

Table S2 Device performance of the cells with and without diiodooctane

copolymer	ratio	solvent	V _{oc}	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
PBDTEDTT: PC ₆₀ BM*	2:1	CB	0.68	4.95	46	1.55
PBDTEDTT: PC ₆₀ BM*	2:1	CB+2.5% DIO	0.69	4.04	38	1.06
PBDTEDTT: PC ₆₀ BM	2:1	CB+4% DIO	0.68	3.50	44	1.05
PBDTEDTT: PC ₆₀ BM*	2:1	CB+4% DIO	0.68	4.11	34	0.94
PBDTEDTT: PC ₆₀ BM*	1:1	CB+4% DIO	0.61	2.94	36	0.65
PBDTEDTT: PC ₆₀ BM	1:3	CB	0.12	0.009	24	0.0003

* Inverted cells

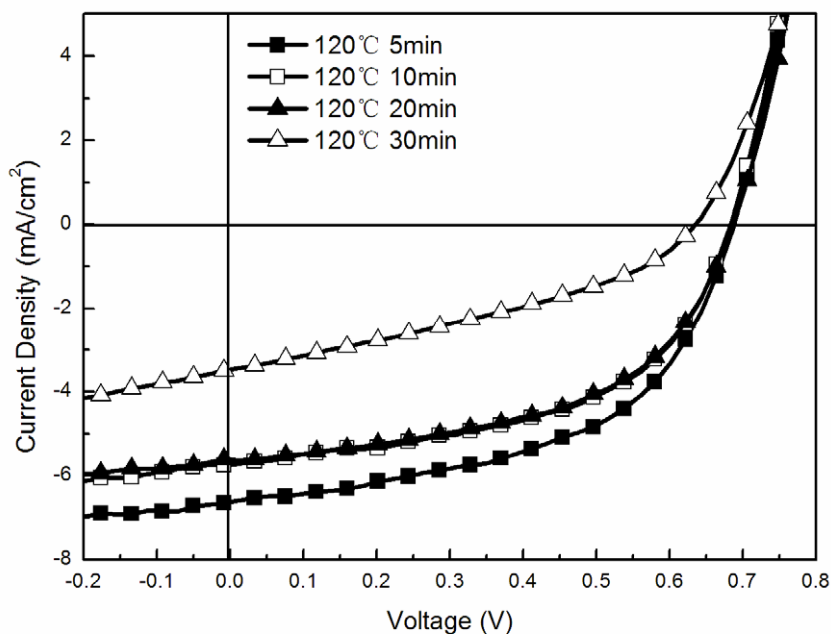


Figure S10 J-V curves of the PSCs based on PBDTEDTT:PC₆₀BM (2:1 w/w) with thermal annealing, under the illumination of AM 1.5G, 100 mW cm^{-2} .

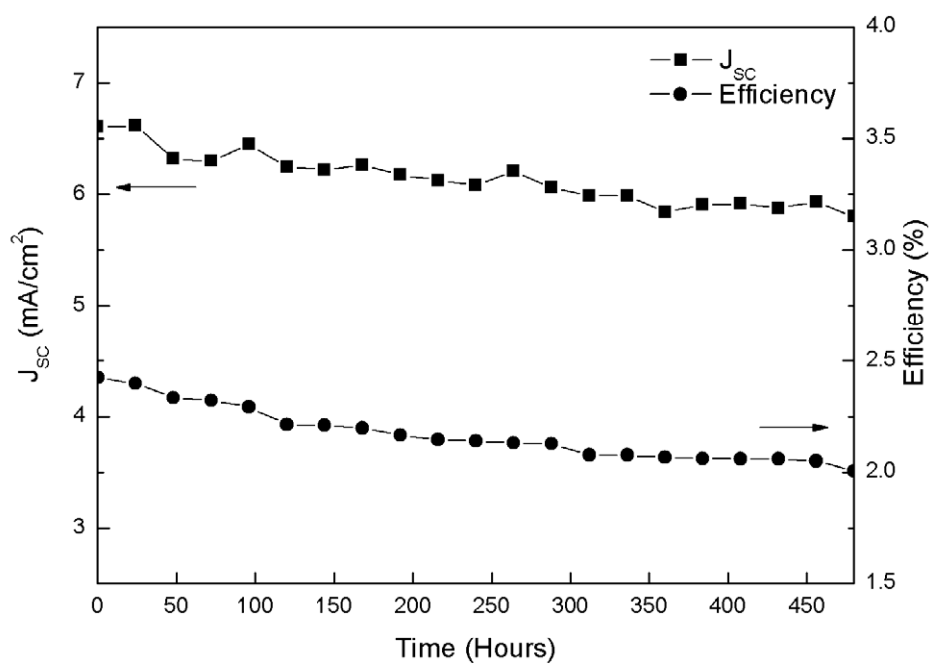


Figure S11 Extract of the J_{sc} and efficiency data up to 480 h ageing for PBDTEDTT:PC₆₀BM (2:1) solar cells.

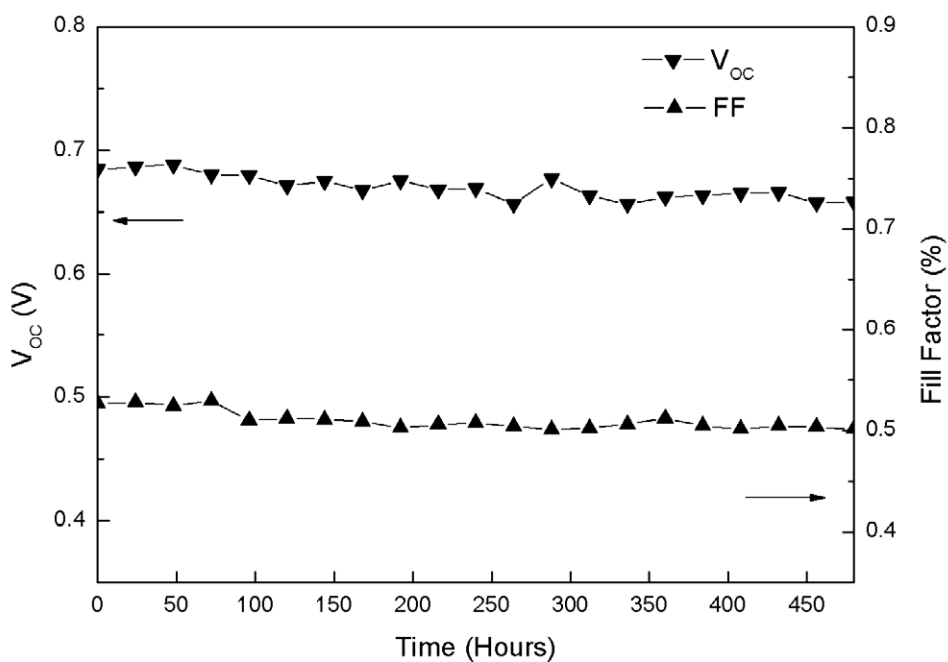


Figure S12 Extract of the V_{oc} and fill factor data up to 480 h ageing for PBDTEDTT:PC₆₀BM (2:1) solar cells.

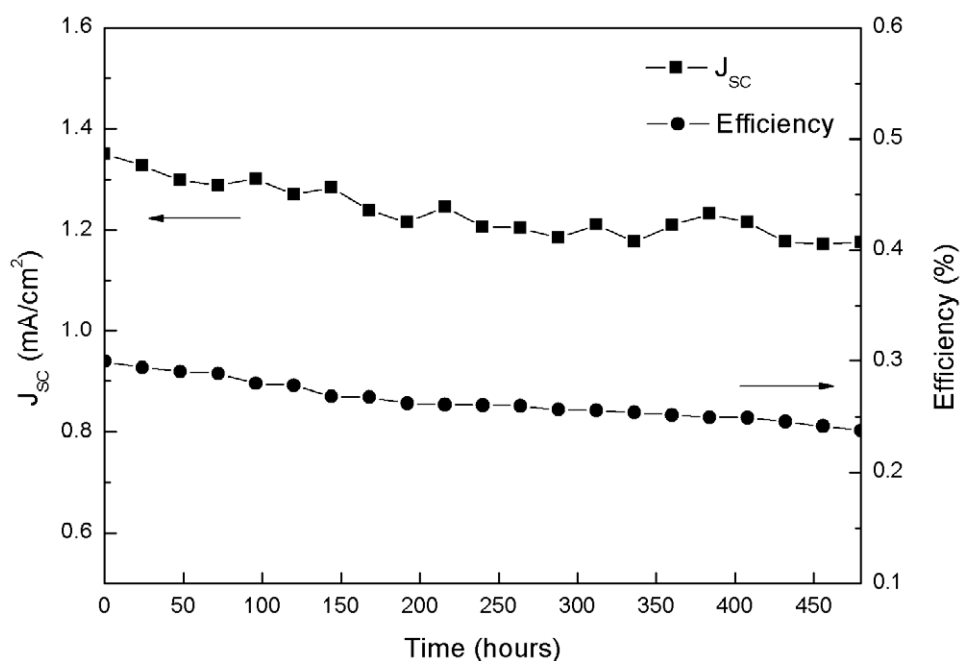


Figure S13 Extract of the J_{sc} and efficiency data up to 480 h ageing for P(iI-EDTT): PC₆₀BM (1:1) solar cells.

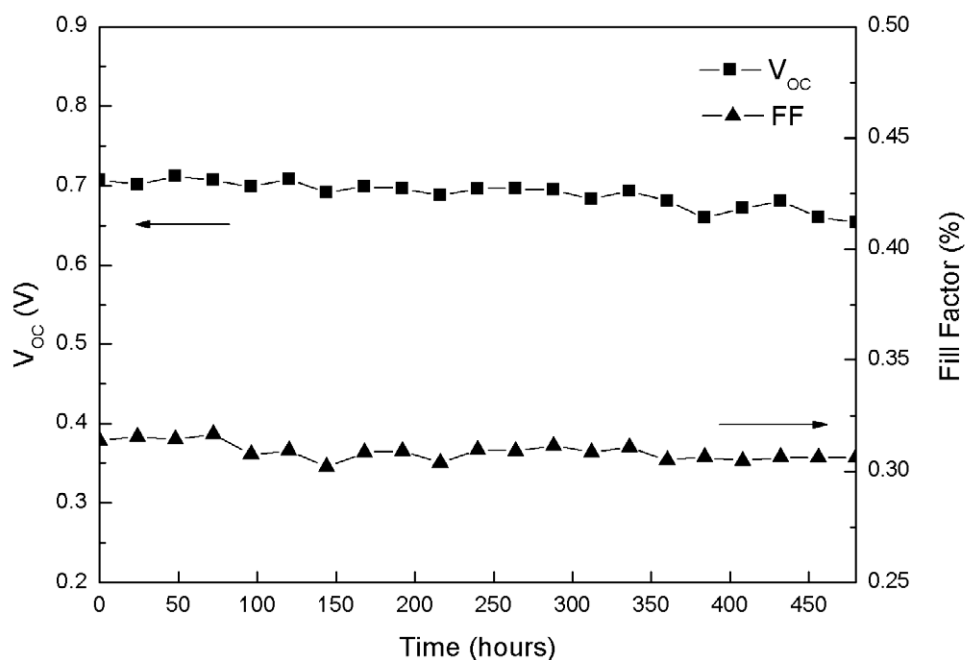


Figure S14 Extract of the V_{oc} and fill factor data up to 480 h ageing for P(iI-EDTT): PC₆₀BM (1:1) solar cells.

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