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基于一种新型聚噻吩衍生物为给体的非富勒烯聚合物太阳能电池

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Non-Fullerene Polymer Solar Cells Based on a New Polythiophene Derivative as Donor

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Experimental Section

***Measurements**:* ^{1}H nuclear magnetic resonance (^{1}H NMR) spectra were measured on an Agilent arx-400 spectrometer. Elemental analysis was carried out on a flash EA1112 analyzer. Gel permeation chromatography (GPC) was performed on Agilent Technologies PL-GPC 220 High Temperature Chromatograph at 160 °C using 1,2,4-tricholorobenzene (TCB) as eluent and polystyrene as the standard. UV-Vis absorption spectra were measured by using an Agilent Carry-5000 UV-Vis spectrophotometer. Thermogravimetric analysis (TGA) was measured on TGA/DSC 3$^+$ from METTLER TOLEDO using STARe Software at a heating rate of 10 °C·min^{-1} under a nitrogen atmosphere. The electrochemical cyclic voltammetry (CV) was performed on a CHI660E A16139 Electrochemical Workstation with glassy carbon disk, Pt wire, and Ag/Ag$^+$ electrode as working electrode, counter electrode, and reference electrode respectively, in a 0.1 mol·L^{-1} tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile solution. The current density-voltage (*J–V*) characteristics were recorded with a Keithley 2450. The power conversion efficiencies of the resulting polymer solar cells were measured under 1 sun, AM 1.5G (air mass 1.5 global) (100 mW·cm^{-2}) using a SS-F5-3A (Enli Technology CO., Ltd.) solar simulator (AAA grade, 50 mm × 50 mm photo-beam size). 2 cm × 2 cm Monocrystalline silicon reference cell (SRC-00019) was purchased from Enli Technology CO., Ltd. The EQE was measured by Solar Cell Spectral Response Measurement System QE-R3011 (Enli Technology CO., Ltd.). The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell. TEM was surveyed on a Tecnai G2 F20 S-TWIN under the condition of 200 kV accelerating voltage. X-ray diffraction (XRD) measurement was executed by Bruker D8 Advance Instrument.

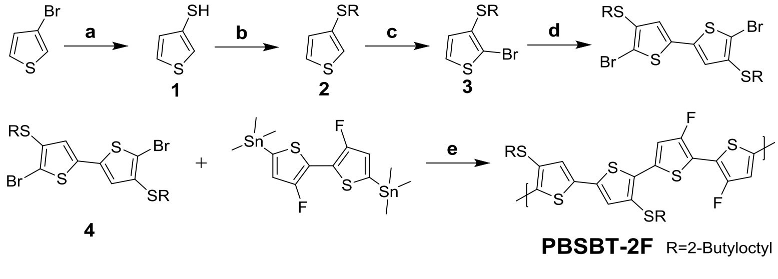
Fabrication of polymer solar cells

Polymer solar cells were fabricated by routine methods, the details of the devices as described in the following:

Polymer solar cells with the structure of ITO/ZnO/PBSBT-2F:ITIC/MoO_3/Al were fabricated under the conditions as follows: patterned indium tin oxide (ITO)-coated glass with a sheet resistance of 10–15 ohm/square was cleaned by a surfactant scrub and then underwent a wet-cleaning process inside an ultrasonic bath, beginning with deionized water followed by acetone and isopropanol. After UVO for 10 min, ZnO electron transport layers were prepared onto the cleaned ITO glass through spin coating at 5000 r·min^{-1} from a ZnO precursor solution. Then the ZnO substrates were immediately baked in air at 200 °C for 1 h. The active layer was then deposited on top of the ZnO layer by spin-coating the chlorobenzene solution of PBSBT-2F (8 mg·mL^{-1}) and ITIC with or without NMP. The thickness of the active layer was controlled by changing the spin speed during the spin-coating process and measured on a KLA-Tencor D-100 (KLA-Tencor Inc.). Except for the ZnO layers, all the fabrication processes were carried out inside a dry box containing less than 5×10^{-6} oxygen and moisture. Finally, 10 nm MoO_3 and 80 nm Al were sequentially deposited on top of the active layers through a shadow mask in a vacuum of ca. 2.5×10^{-4} Pa. The active area of the devices was 0.04 cm^2.

Materials

The chemical raw materials were purchased from Aldrich, TCI Chemical, J&K and Alfa Aesar, respectively, which were of reagent grade and used without further purification. ITIC was purchased from Solarmer Materials Inc. The monomer (TT) was purchased from Suna Tech Inc. (3,3'-difluoro-[2,2'-bithiophene]-5,5'-diyl)bis(trimethylstannane) was purchased from Derthon Optoelectronic Materials Science Technology Co LTD.



Scheme S1 Synthetic route and molecular structure of PBSBT-2F

3-Mercapto-thiophene (1). To a 2.5 mol·L^{-1} solution of *n*-butyllithium in hexane (25 mmol, 20 mL), a solution of 3-bromothiophene (50 mmol, 4.68 mL) in anhydrous tetrahydrofuran (50 mL) was added at −70 °C under an argon atmosphere and the mixture was stirred for 2.5 h at −70 °C. Then sublimed sulfur (50 mmol, 1.608 g) was added to the solution and stirred at −70 °C for 2 h before quenching with 100 mL of water. The resulting mixture was extracted with (3 × 50 mL) NaOH 1 mol·L^{-1}. The combined aqueous layers were cooled with ice and added 10% hydrochloric acid to pH < 7. The product was extracted with diethyl ether. The organic layers were dried over anhydrous sodium sulphate and the solvent was removed under reduced pressure and get 4.8 g Clear yellow oil.

3-(2-butyloctylsulphanyl)thiophene (2). A solution of potassium tert-butoxide (50 mmol, 5.6 g) in anhydrous ethanol (20 mL), was added at 0 °C to 3-mercapto-thiophene (41.3 mmol, 4.8 g) under an argon atmosphere and mixture was stirred for 30 min at 0 °C. 5-

(bromomethyl)undecane (34.4 mmol, 8.5 g) was slowly added to the solution and refluxed for 2 h before quenching with 100 mL of water. The product was extracted with diethyl ether (3 × 30 mL). The combined organic layers were dried over anhydrous sodium sulphate and the solvent was removed under reduced pressure. The residue was isolated by flash chromatography using hexane to give 8.0 g of product. Yield 82%. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$), *δ*: 7.32 (d, 1H), 7.08 (d, 1H), 7.02 (d, 1H), 2.84 (t, 2H), 1.61 (m, 1H), 1.30 (m, 16H), 0.88 (t, 6H); ^{13}C NMR (400 MHz, $CDCl_3$) , *δ*: 133.0, 129.5, 125.9 122.1, 40.2, 37.6, 31.8, 29.5, 28.7, 26.5, 23.0, 22.6, 14.1.

2-Bromo-3-(2-butyloctylsulphanyl)thiophene (3). Compound 2 (8.0 g, 28 mmol) was dissolved in a mixture of chloroform (100 mL) and acetic acid (20 mL). NBS (4.9 g, 28 mmol) was then added to the solution and stirred for 3h in the dark. The mixture was extracted with chloroform several times and the organic was combined. The solvent was removed and purified with a flash column chromatography using hexane as eluent and get the colorless oil product (8.2 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$), *δ*: 7.23 (d, 1H), 6.91 (d, 1H), 2.81 (t, 2H), 1.61 (m, 1H), 1.28 (m, 16H), 0.88 (t, 6H); ^{13}C NMR (400 MHz, $CDCl_3$) , *δ*: 133.7, 130.0, 125.8, 113.5, 40.0, 37.9, 32.9, 29.5, 28.7, 26.5, 22.9, 22.6, 14.1.

5,5’-dibromo-4,4’-bis(2-butyloctylsulphanyl)-2,2’-bithiophene (4). A solution of Compound 3 (8 g, 22.0 mmol) in DMSO (100 mL) with KF (1.28 g, 44.0 mmol) and $PdCl_2(PhCN)_2$ (0.17 g, 0.5 mmol) was stirred at 60 °C for 1 h under an argon atmosphere. Then $AgNO_3$ (7.48 g, 44.0 mmol) was divided into four parts to add to the mixture every one hour. The mixture was stirred at 60 °C for 17 h. The mixture was filtered (Celite®) after cooling to room temperature, and washed with dichloromethane. Then organic phases were washed with water (2 × 200 mL), dried with $MgSO_4$. The solvent was removed under reduced pressure and purified with a flash column chromatography using hexane as eluent and get the clean oil product (4 g, 50%).^{1}H NMR (400 MHz, CD_2Cl_2), *δ*: 6.95 (s, 2H), 2.87 (d, 4H), 1.61 (m, 2H), 1.29 (m, 32H), 0.88 (t, 12H);^{13}C NMR (400 MHz, $CDCl_3$) , *δ*: 136.0, 135.2, 126.3, 112.1, 39.8, 37.9, 32.9, 32.6, 31.8, 29.5, 28.7, 26.4, 22.9, 22.6, 14.1.

Synthesis of the polymer PBSBT-2F

In a 50 mL round bottom flask, monomers (0.5 mmol) were dissolved in 10 mL toluene. After being flushed with argon for 20 min, 30 mg of $Pd(PPh_3)_4$ was added into the flask as the catalyst, and then the mixture was flushed with argon for another 30 min. The solution was stirred at 110 °C for 13 h under an argon atmosphere and the reactant was cooled down to room temperature, and the polymer was precipitated into 100 mL of methanol. The polymer was collected by filtration and subjected to Soxhlet extraction with methanol, hexane and chloroform in the end. The solution was evaporated under reduced pressure and precipitated into 100 mL of methanol. The polymer was collected by filtration and dried under vacuum. Anal. calcd for $C_{40}H_{54}F_2S_6$ (%): C, 62.62; H,7.36; found (%): C, 62.08; H, 7.09.

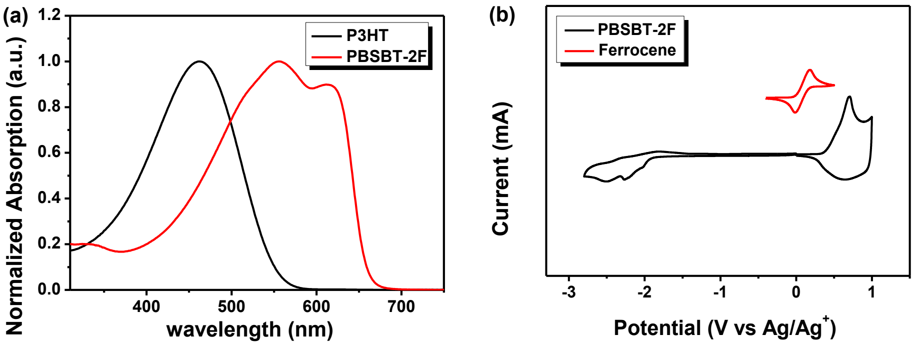


Fig. S1 (a) The absorption spectra of PBSBT-2F and P3HT films; (b) cyclic voltammograms of PBSBT-2F film on a platinum electrode measured in 0.1 mol·L^{-1} Bu_4NPF_6 acetonitrile solutions at a scan rate of 50 mV·s^{-1}.

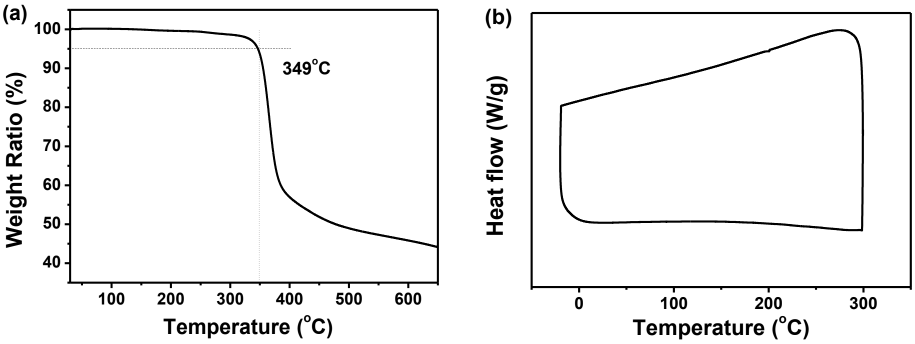


Fig. S2 (a) TGA curve of PBSBT-2F at a scan rate of 10 °C·min^{-1} under nitrogen atmosphere; (b) DSC thermogram of PBSBT-2F under inert atmosphere (nitrogen) at a scan rate of 10 °C·min^{-1} from −20 to 300 °C

Table S1 Photovoltaic properties of PBSBT-2F:ITIC devices treated with different content additives. (under AM 1.5G illumination, 100 mW·cm^{-2}).

Active layer	Additives [volume fraction]	V_{oc}/V	J_{sc}^{a}/(mA·cm^{-2})	FF/(%)	PCE ^{b}/(%)
PBSBT-2F：ITIC	W/O	0.75	13.0/12.4	46.2	4.5(4.3)
	0.5%NMP	0.74	13.4/12.7	48.7	4.8(4.6)
	1%NMP	0.73	13.1/12.4	52.3	5.0(4.8)
	2%NMP	0.73	13.8/13.1	47.5	4.8(4.6)
	3%NMP	0.74	13.0/12.4	51.0	4.9(4.6)

^{a} Values calculated from EQE in brackets. ^{b} Average PCEs in brackets for ten devices.

Table S2 Photovoltaic properties of PBSBT-2F:ITIC devices with different thermal annealing temperature for 10 min. (under AM 1.5G illumination, 100 mW·cm^{-2}).

Active layer	Temperature	V_{oc}/V	J_{sc}^{a}/(mA·cm^{-2})	FF/%	PCE ^{b}/%
PBSBT-2F：ITIC	Without	0.73	13.1/12.4	52.3	5.0(4.8)
	120 °C	0.75	13.2/12.5	65.8	6.5(6.3)
	140 °C	0.75	13.5/12.8	66.6	6.7(6.5)
	160 °C	0.75	12.9/12.3	66.2	6.4(6.2)

^{a} Values calculated from EQE in brackets. ^{b} Average PCEs in brackets for ten devices.

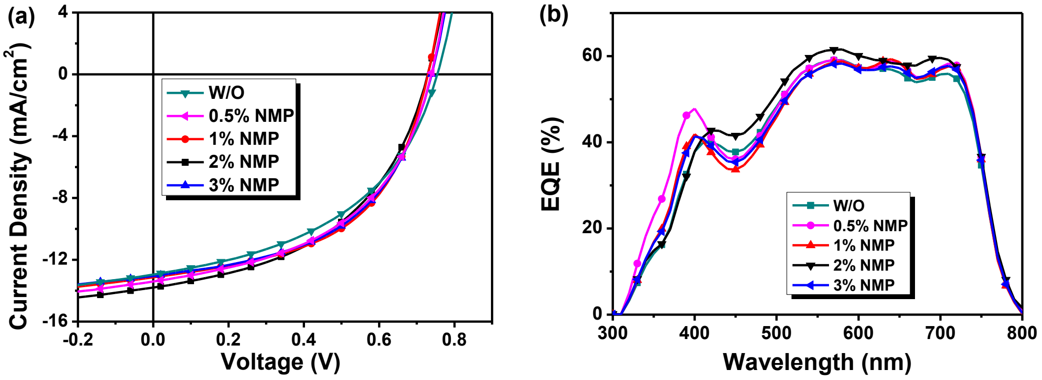


Fig. S3 The J–V curves and the corresponding EQE curves of PBSBT-2F:ITIC devices treated with different content additives. (under AM 1.5G illumination, 100 mW·cm^{-2}).

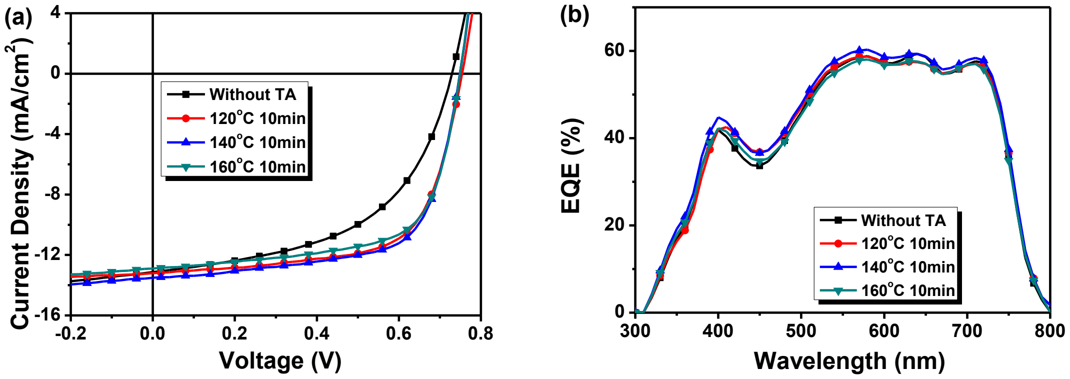


Fig. S4 The J–V curves and the corresponding EQE curves of PBSBT-2F:ITIC devices with different thermal annealing temperature. (under AM 1.5G illumination, 100 m W·cm^{-2}).