**Supplementary Material**

Impact of Linker Positions for Thieno[3,2-*b*]thiophene in Wide Bandgap benzo[1,2-*b*:4,5-*b′*]dithiophene-based Photovoltaic Polymers

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Instruments and measurements

1H NMR spectra were recorded on a Bruker DRX 400 spectrometer operating at 400 MHz and were referred to tetramethylsilane (TMS). Analytical gel permeation chromatography (GPC) was performed using a Waters GPC 2410 in THF relative to polystyrene standards. Thermal gravimetric analysis (TGA) was conducted on a TGA 2050 (TA instruments) thermal analyses system under a heating rate of 10°C/min and a nitrogen flow rate of 20 mL/min. UV-visible absorption spectra were measured on a UV-1800 spectrophotometer (Shimadzu. Co.). The X-ray diffraction (XRD) was carried out on a PANalytical X’Pert PRO diffractometer equipped with a rotating anode (Cu Kα radiation, λ = 1.54 Å). The cyclic voltammetry (CV) was measured on CHI600D electrochemical workstations (Shanghai Chenhua Co.) at a scan rate of 50 mV/s with a nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu4NPF6) in acetonitrile (CH3CN) with glass carbon and Ag/AgNO3 electrode as the working and reference electrode, respectively. Tapping-mode atomic force microscopy (AFM) images were obtained on a NanoScope NS3A system (Digital Instrument).

Preparation and characterization of the photovoltaic solar cells

A patterned indium tin oxide (ITO) coated glass with a sheet resistance of 10–15 Ω/square, was cleaned by a surfactant scrub, followed by a wet-cleaning process inside an ultrasonic bath, beginning with de-ionized water, followed by acetone and*iso*-propanol (*i*-PrOH). After oxygen plasma cleaning for 5 min, a 5 nm thick PFN layers were spin-casted onto the ITO. The active layers with a thickness ranging in the 100−110 nm, were then deposited on the top of the PFN-modified ITO by spin-casting from the chlorobenzene (CB) solution containing PBDT-25TT/PC61BM, PBDT-36TT/PC61BM, with and without DIO as solvent additive. Then a 8 nm MoO3 and 100 nm silver layer were evaporated with a shadow mask under vacuum of (1–5)×10−5 Pa. The overlapping area between the cathode and anode defined a pixel size of device of 0.1 cm2. The thickness of the active layers was determined by a Profile system (BRUKER VDS-9400 QS). The thickness of the evaporated cathode was monitored by a quartz crystal thickness/ratio monitor (SI-TM206, Shenyang Sciens Co.). Except for the deposition of the PFN layers, all the fabrication processes were carried on inside a controlled atmosphere in a nitrogen drybox (Etelux Co.) containing less than 1 ppm oxygen and moisture. The PCEs of the resulting polymer solar cells were measured under 1 sun, AM 1.5G (Air mass 1.5 global) condition using a solar simulator (XEC-300M2, San-EI Electric Co.) with irradiation of 100 mW·cm-2. The current density-voltage (*J-V*) characteristics were recorded with a Keithley 2400 source-measurement unit. The spectral responses of the devices were measured with a commercial EQE/incident photon to charge carrier efficiency (IPCE) setup (7-SCSpecIII, Beijing 7-star Opt. In. Co.). A calibrated silicon detector was used to determine the absolute photosensitivity.

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**FIG. S1** 1H NMR spectrum of 2,5-dibromothieno[3,2-*b*]thiophene in CDCl3

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**FIG. S2** 1H NMR spectrum of 3,6-dibromothieno[3,2-*b*]thiophene in CDCl3

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**FIG. S3** TGA plots of PBDT-TT25 and PBDT-TT36 with a heating rate of 10 °C/min under an inert atmosphere.

**TABLE SⅠ.** Yields, GPC date, thermal properties for the copolymers

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Copolymer | Yield (%) | *M*n  kg/mol | *M*w  kg/mol | PDI | *T*d (°C) |
| PBDT-TT25 | 80 | 19.8 | 40.6 | 2.05 | 445 |
| PBDT-TT36 | 75 | 20.8 | 55.4 | 2.67 | 457 |

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**FIG. S4** UV-vis absorption spectra of PBDT-TT25 (a) and PBDT-TT36 (b) dissolved in *o*-DCB at various concentration and calculation of molar absorption coefficient (c).

**TABLE SⅡ.** Dihedral angles for the trimer models of BDT-TT25 and BDT-TT36 by DFT at the B3LYP/6-31G\*

|  |  |  |
| --- | --- | --- |
| Copolymer | Structure | Dihedral angles (deg) |
| PBDT-TT25 |  | ɸ1=10.89° ɸ2=11.19° |
| PBDT-TT36 |  | ɸ1=24.27° ɸ2=24.55° |



**FIG. S5** Calculated absorption spectra of (BDT-TT25)3 and (BDT-TT36)3 model compounds at B3LYP/6-311g (d,p) level.

 



**FIG. S6** The *J-V* curves of the studied copolymers with different weight ration to PC61BM (a, c) and EQE (b, d) spectra of corresponding PSCs.

**TABLE SⅢ.** Parameters of *i*- PSCs from the copolymers and PC61BM with different weight ratio

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Active Layer | D:A ratios | Additives | *V*OC (V) | *J*SC (mA/cm2) | *FF* (%) | PCE (%) |
| PBDT-TT25/PC61BM | 1:1 | / | 0.76 | 4.48 | 38.56 | 1.31 |
| 1:1.5 | / | 0.77 | 4.69 | 40.43 | 1.46 |
| 1:1.5 | 3%DIO | 0.75 | 4.73 | 49.25 | 1.75 |
|  | 1:2 | / | 0.77 | 4.53 | 37.19 | 1.30 |
| PBDT-TT36/PC61BM | 1:1 | / | 0.73 | 0.70 | 31.30 | 0.16 |
| 1:1.5 | / | 0.76 | 1.55 | 37.84 | 0.45 |
| 1:1.5 | 3%DIO | 0.79 | 1.73 | 44.37 | 0.61 |
|  | 1:2 | / | 0.79 | 0.91 | 27.23 | 0.20 |

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**FIG. S7** Tapping AFM height images of the active layers PBDT-TT25/PC61BM (a, b) and PBDT-TT36/ PC61BM (c, d): without 3% DIO (a, c) and with 3% DIO (b, d). Image size: 5 × 5 μm.

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**FIG. S8** Tapping AFM phase images of the active layers PBDT-TT25/PC61BM (a, b) and PBDT– TT36/ PC61BM (c, d): without 3% DIO (a, c) and with 3% DIO (b, d). Image size: 5 × 5 μm.