Supporting Information

Enhanced Performance for Organic Bulk Heterojunction Solar Cells by Cooperative Assembly of Ter(ethylene Oxide) Pendant

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Experimental section

Materials

4,6-dibromo-thieno[3,4-b]thiophene-2-carboxylic acid, 2-ethylhexyl 4,6-dibromo-thieno[3,4-b]thiophene-2-carboxylate (TT) and 2,6-bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl) thiophen-2-yl) benzo [1,2-b:4,5-b'] dithiophene (BDTT) were purchased from Solarmer Materials Inc.; Triglycol monomethyl ether (TEO), 4-(dimethylamino) pyridine (DMAP), N,N'-dicyclohexyl-carbodiimade (DCC), LiF(99.99%), Al (99.998%) and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM, >99%) were purchased from Alfa Aesar or Aldrich without any further purification; Other chemical reagents were obtained from Shanghai Reagent Co., Ltd. Dichloromethane (CH₂Cl₂), N, N-Dimethylformamide (DMF) and toluene were dried and freshly distilled under nitrogen before use. Indium tin oxide (ITO) glass was purchased from Delta Technologies Limited, whereas PEDOT:PSS (Baytron PAL4083) was obtained from Bayer Inc.

Instruments

The nuclear magnetic resonance (NMR) spectra were collected on a Bruker ARX 400 NMR spectrometer with deuterated chloroform as the solvent and with tetramethylsilane (δ=0) as the internal standard. The gel permeation chromatography (GPC) was conducted with a Breeze Waters system equipped with a Rheodyne
injector, a 1515 Isocratic pump and a Waters 2414 differential refractometer using polystyrenes as the standard and tetrahydrofuran (THF) as the eluent at a flow rate of 1.0 mL/min and 40 °C through a Styrigel column set, Styrigel HT3 and HT4 (19 mm×300 mm, 10³⁻¹⁰⁴ Å) to separate molecular weight (MW) ranging from 10² to 10⁶. Thermogravimetric analysis (TGA) was performed on a PerkinElmer TGA 7 for thermogravimetry at a heating rate of 10 °C/min under nitrogen with a sample size of 5-8 mg. The cyclic voltammetry (CV) was performed on a CHI660C potentiostat equipped with electrochemical analysis system software and standard three-electrode configuration under an argon atmosphere at RT and a scan rate of 50 mV/s. Platinum rod, platinum wire, and saturated calomel electrode were used as working electrode, counter electrode, and reference electrode in a 0.1 mol/L Bu₄NPF₆-acetonitrile solution, respectively. The ultraviolet-visible (UV) spectra of the samples were recorded on a PerkinElmer Lambda 750 spectrophotometer. Texture observations by polarizing optical microscopy (POM) were made with a Nikon E600POL polarizing optical microscope equipped with an Instec HS 400 heating and cooling stage. The X-ray diffraction (XRD) study of the samples was carried out on a Bruker D8 Focus X-ray diffractometer operating at 30 kV and 20 mA with a copper target (λ =1.54 Å) and at a scanning rate of 1°/min. AFM measurement was carried out using a Digital Instrumental Nanoscope 31 operated in the tapping mode. TEM images were recorded using a JEOL-2100F transmission electron microscope and an internal charge-coupled device (CCD) camera.

**Device Fabrication and Characterization**

The structure of the devices was ITO/PEDOT:PSS/polymer:fullerence/LiF/metal cathode. Prior to use, The ITO coated glass substrates were cleaned by sonication in detergent, deionized water, acetone, and isopropyl alcohol. The substrates were dried under a stream of nitrogen and subjected to the treatment of UV ozone over 20 min. A filtered dispersion of PEDOT:PSS in water (Baytron Al4083) was then spun-cast onto clean ITO substrates at 4000 rpm for 30 s and then baked at 140 °C for 15min. The donor/acceptor (1:2 w/w or 1:1.5 w/w) blend solution (10 mg/mL in 1,2-
dichlorobenzene) was spin-coated on the PEDOT:PSS layer, the active layer was obtained by spin-coating the blend solution at 1000 rpm for 30 s and the thickness of film was ~ 110 nm.

Synthesis Procedures

4,6-Dibromo-thieno[3,4-b]thiophene-2-carboxylic acid 2-[2-(2-methoxy-ethoxy)-ethoxy]-ethyl ester (TT-TEO)

Triglycol monomethyl (1.64 g, 10.0 mmol) ether was added to the mixture of 4,6-dibromo-thieno[3,4-b] thiophene-2-carboxylic acid (0.68 g, 2.0 mmol), DCC (0.50 g, 2.4 mmol), DMAP (84 mg, 0.69 mmol) in a 100 mL round-bottom flask with 10 mL CH2Cl2. The mixture was stirred for 20 h under N2 atmosphere, was poured into 50 mL water, and then extracted with CH2Cl2 three times. The organic phase was dried with anhydrous magnesium sulfate and the solvent was removed. The product was purified with column chromatography on silica gel using hexane/ethyl acetate) 4:1, yielding the pure compound as a light orange solid 0.58 g (60%). 1H NMR (CDCl3, 400 MHz), δ (ppm): 7.56 (s, 1H), 4.47 (t, 2H), 3.82 (t, 2H), 3.71-3.63 (t, 6H), 3.53 (t, 2H), 3.37 (s, 3H). 13C- NMR (CDCl3, 400 MHz), δ (ppm): 162.17, 145.53, 140.61, 140.37, 123.43, 102.39, 97.14, 71.90, 70.59, 68.89, 65.01, 58.96, 51.15, 49.36. MALDI-TOF MS [m/z (%)]: calcd for C14H16Br2O5S2, 488.23; found, 488.

Synthesis of Polymer PBDTT-TT-TEO

2,6-bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b’]dithiophene (BDTT 271 mg, 0.30 mmol) was weighed into a 100 mL round-bottom flask. TT-TEO (146mg, 0.30 mmol) and Pd(PPh3)4 (18 mg) were added. The mixture was then purged with N2 for 30 min. Then, anhydrous DMF (2 mL) and anhydrous toluene (8 mL) were added via a syringe. The reaction mixture was stirred and heated to reflux for 16 h. Then the reaction mixture was cooled to room temperature, and the polymer was precipitated by addition of methanol. The precipitate was then subjected to Soxhlet extraction with methanol, hexane, and chloroform. The polymer was recovered as solid from the chloroform fraction by precipitation from methanol. The solid was dried under vacuum. Yield 190mg, 70%.
Synthesis of Polymer PBDTT-TT
Prepared as for PBDTT-TT-TEO: BDTT (271 mg, 0.30 mmol), TT (146 mg, 0.30 mmol), Pd(PPh₃)₄ (18 mg). Yield 173 mg, 65%.

Synthesis of PCBA
To a solution of PCBM (50 mg, 5.5×10⁻² mmol) in chlorobenzene (20 mL) was refluxed under nitrogen atmosphere for 3 h. HCl (12 M, 2 mL) and acetic acid (5 mL) were introduced to the solution in one portion. The reaction mixture was refluxed for 16 h. The solvent was removed under reduced pressure to give a residue which was purified by precipitation from MeOH to obtain a brown solid PCBA (42 mg).

Synthesis of PCBM derivates PCB-TEO
PCBA (72 mg, 0.08 mmol), TEO (0.10 mmol) and chlorobenzene (10 ml) were mixed in a 50 mL round-bottom Schlenk flask under the atmosphere of N₂. The mixture was stirred in room temperature for 2 h, then cooled down to 0 °C in an ice/water bath. Then DMAP (24 mg, 0.20 mmol) and DCC (43 mg, 0.20 mmol) were added quickly to the reaction flask. The mixture was continuously stirred at 0 °C for 30 min, followed by warming to the room temperature and being continuously stirred overnight. Then, the solvent was removed under the reduced pressure; the residue was purified by silica gel chromatography using n-hexane then toluene as eluent gradients to give a brown solid. Finally, the sediment was washed with MeOH and dried in vacuum. Yield 50 mg (64%). ¹H NMR (CDCl₃, 600 MHz) δ (ppm): 7.96-7.90 (d, 2H), 7.58-7.52 (t, 2H), 7.43 (t, H), 4.24 (t, 2H), 3.71-3.68 (t, 2H), 3.67-3.63 (t, 6H), 3.57-3.53 (t, 2H), 3.38 (s, H), 2.93-2.89 (m, 2H), 2.57-2.53 (t, 2H), 2.22-2.19 (m, 2H). MALDI-TOF MS [m/z (%): calcd for C₁₄H₁₆Br₂O₅S₂, 1042.53; found, 1042.
Figure S1. $^1$H NMR spectra of the monomer TT-TEO.
Figure S2. $^1$H NMR spectra of the polymers PBDTT-TT-TEO and PBDTT-TT.

Figure S3. $^1$H NMR spectra of PCB-TEO.
**Figure S4.** TGA thermograms of the polymers with a heating rate of 10 °C/min under nitrogen.
Figure S5. Cyclic voltammograms of PBDTT-TT and PBDTT-TT-TEO drop-cast on a Pt electrode in 0.1 mol/L Bu$_4$NPF$_6$-acetonitrile solutions at a scan rate of 50 mV/s.
Figure S6. X-ray diffraction patterns of the polymers PBDTT-TT and PBDTT-TT-TEO.
Figure S7. AFM topography images (1 μm × 1 μm) of PBDTT-TT-TEO:PCB-TEO (1:2 w/w).
Table S1. Solar Cell Performance Parameters of PBDTT-TT:PCBM with different ratio of PCB-TEO

<table>
<thead>
<tr>
<th>PV Devices</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>$R_s$ ($\Omega \text{cm}^2$)</th>
<th>$R_{sh}$ ($\Omega \text{cm}^2$)</th>
<th>PCE (%) $^b$</th>
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<tbody>
<tr>
<td>3% PCB-TEO</td>
<td>0.724</td>
<td>9.16</td>
<td>49.0</td>
<td>24</td>
<td>197</td>
<td>3.2</td>
</tr>
<tr>
<td>5% PCB-TEO</td>
<td>0.720</td>
<td>10.19</td>
<td>37.4</td>
<td>9.0</td>
<td>113.8</td>
<td>2.7</td>
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$^a$ Weight ratio to the total amount of PCB-TEO and PCBM (blended with BDTT-TT);

$^b$ All values represent averages.
Figure S8. J-V curves of PBDTT-TT:PCBM with 3% PCB-TEO and PBDTT-TT:PCBM with 5% PCB-TEO.
Figure S9. AFM topography images (1 μm × 1 μm) of (A) PBDTT-TT:PCBM, (B) PBDTT-TT:PCBM with 3% PCB-TEO.