Supplementary Materials: Effect of Flanks Rotation on the Photovoltaic Properties of Dithieno[2,3-d:2’,3’-d’]benzo[1,2-b:4,5-b’]dithiophene-based Narrow Band Gap Copolymers

Mingjing Zhang, Liangjian Zhu, Pengzhi Guo, Xunchang Wang, Junfeng Tong, Xiaofang Zhang, Yongjian Jia, Renqiang Yang, Yangjun Xia and Chenglong Wang

1. Instruments and measurements

$^1$H NMR and $^1$C NMR spectra were recorded on a Bruker DRX 500 spectrometer operating at 500 MHz and 125 MHz 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 was 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, $\lambda = 1.54$ 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 (Bu$_4$NPF$_6$) in acetonitrile (CH$_3$CN) with glass carbon and Ag/AgNO$_3$ electrode as the working and reference electrode, respectively. Tapping-mode atomic force microscopy (AFM) images were obtained on a NanoScope NS3A system (Digital Instrument). Transmission electron microscopy (TEM) images were acquired with a Tecnai G2 F20 (FEI, Hillsboro, OR, USA) transmission electron microscope at an accelerating voltage of 200 kV.

2. Preparation and characterization of the photovoltaic solar cells

A patterned indium tin oxide (ITO) coated glass with a sheet resistance of 10-15 $\Omega$/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 $i$-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 PDTBDT-TE-DTNT/PC$_7$BM, PDTBDT-T-DTNT/PC$_7$BM, with and without DIO as solvent additive. Then a 8 nm MoO$_3$ and 100
nm silver layer were evaporated with a shadow mask under vacuum of \((1-5) \times 10^{-5}\) 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/cm². 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.

3. \(^1\text{H NMR and }^{13}\text{C NMR Spectra}

![Figure S1. \(^1\text{H NMR spectrum of DTBDT-TESn in CDCl}_3\)](image-url)
Figure S2. $^{13}$C NMR spectrum of DTBDT-TESn in CDCl₃

4. TGA Plots

Figure S3. TGA plots of PDTBDT-TE-DTNT and PDTBDT-T-DTNT with a heating rate of 10 °C/min under an inert atmosphere.

5. Absorption spectra

Figure S4. Normalized UV-Vis spectra of PDTBDT-T-DTNT in dilute chlorobenzene solution and solid thin film
6. Photovoltaic characteristics

Table S1. Parameters of \(i\)-PVCs from PDTBDT-TE-DTNT and PC\(_{61}\)BM with different ratio

<table>
<thead>
<tr>
<th>Additives (DIO)</th>
<th>(V_{OC}) (V)</th>
<th>(J_{SC}) (mA/cm(^2))</th>
<th>(FF) (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDTBDT-TE-DTNT:PC(_{71})BM (W : W = 1:1)</td>
<td>3%</td>
<td>0.64</td>
<td>8.67 (8.85)(^{a})</td>
<td>55.09</td>
</tr>
<tr>
<td>PDTBDT-TE-DTNT:PC(_{71})BM (W : W = 1:2)</td>
<td>3%</td>
<td>0.64</td>
<td>7.29 (7.02)(^{a})</td>
<td>45.58</td>
</tr>
<tr>
<td>PDTBDT-TE-DTNT:PC(_{71})BM (W : W = 1:3)</td>
<td>3%</td>
<td>0.64</td>
<td>5.84 (5.67)(^{a})</td>
<td>43.38</td>
</tr>
</tbody>
</table>

\(^{a}\)The value in the parentheses is integrated current get from the IPCE testing system.

Figure S5. The \(J-V\) curves of PDTBDT-TE-DTNT with different weight rations to PC\(_{61}\)BM (a) and the IPCE spectra (b) of corresponding \(i\)-PVCs.

7. Absorption spectra of blend films

Figure S6. Absorption spectra of the copolymer/PC\(_{61}\)BM blend films

8. Film morphology
Figure S7. Tapping AFM height images (a, b) and phase image (c, d) (5 μm × 5 μm) for the blend films of PDTBDT-T-DTNT/PC71BM (1:1, 3% DIO, a, c) and PDTBDT-TE-DTNT/PC71BM (1:1, 3% DIO, b, d).

Figure S8. TEM topography images for the blend films of PDTBDT-T-DTNT/PC71BM (1:1, 3% DIO, a) and the blend films of PDTBDT-TE-DTNT/PC71BM (1:1, 3% DIO, b).