Electronic Supplementary Information

Low-Bandgap Thieno[3,4-c]pyrrole-4,6-dione-Polymers for High-performance Solar Cells with Significantly Enhanced Photocurrents

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Contents

Part 1. General information S2
Part 2. Synthesis S4
Part 3. Physical properties and thin-film morphology S5
Part 4. Semiconducting properties S10
Part 5. Solid-state 2D $^{13}$C-$^1$H HETCOR NMR spectra S12
Part 1. General information

Materials: All the reactions dealing with air- or moisture-sensitive compounds were carried out in a dry reaction vessel under a positive pressure of nitrogen. Unless stated otherwise, starting materials were obtained from Adamas, Aldrich and J&K and were used without any further purification. Anhydrous toluene was distilled over Na/benzophenone prior to use. Anhydrous DMF was distilled over CaH$_2$ prior to use. 1,3-bis(4-bromo-2-hexylthieno[3,4-b]thiophen-6-yl)-5-(2-ethylhexyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (TBTT$_{EH}$-$i$)$^1$, 1,3-bis(6-bromo-2-hexylthieno[3,4-b]thiophen-4-yl)-5-(2-ethylhexyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (TBTT$_{EH}$-$o$)$^1$, 1,3-bis(4-bromo-2-hexylthieno[3,4-b]thiophen-6-yl)-5-(2-hexyldecyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (TBTT$_{HD}$-$i$)$^1$ and (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b’]dithiophene-2,6-diyl)bis(trimethylstannane) (BDT-Sn)$^2$ were synthesized according to the procedure reported in the literatures.

General Methods: Elemental analyses were measured on a Carlo Erba 1106 elemental analyzer. Gel permeation chromatography (GPC) was performed on Polymer Laboratories PL-GPC220 at 150 °C using 1, 2, 4-trichlorobenzene (TCB) as eluent. UV-vis spectra were recorded on a JASCO V-570 spectrometer. Cyclic voltammetry (CV) measurements were carried out on a CHI640C analyzer in a conventional three-electrode cell setup with glassy-carbon electrode as the working electrode, a platinum wire as the counter electrode, Ag/Ag$^{+}$ as the reference electrode and calibrated with ferrocene/ferrocenium (Fc/Fc$^{+}$) as an external potential marker in anhydrous acetonitrile solution containing 0.1 M tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte under a nitrogen atmosphere at room temperature. All potentials were corrected against Fc/Fc$^{+}$. CV was measured with a scan rate of 100 mV/ s. Ultraviolet photoemission spectroscopy (UPS) was performed by on an AXIS ULTRA DLD with a He I (21.2 eV) source. Thermogravimetric analysis (TGA) was performed on a Shimadzu DTG 60 instrument at a heating rate of 10 °C min$^{-1}$ under a N$_2$ atmosphere with runs recorded from room temperature to 550 °C. DSC analyses were recorded on a Perkin Elmer Pyris 1 instrument under a dry N$_2$ flow at a heating rate of 10 °C min$^{-1}$, heating from room temperature to 300°C. X-Ray diffraction (XRD) measurements of thin films were performed in reflection mode at 40 kV and 200 mA with Cu Kα radiation using a 2 kW Rigaku X-ray diffractometer. Atomic force microscopy (AFM) images of the thin films were obtained on a NanoscopeIIIa AFM (Digital Instruments) operating in tapping mode. Transmission electron microscopy (TEM) was performed using a JEOL 2200FS instrument at 160 kV accelerating voltage.

Computational Study: Density functional theory (DFT) (the B3LYP/6-31G** level of theory in vacuum) was utilized to model the structural and electronic properties of relevant molecular structures. The alkyl chains were replaced by methyl groups to keep the computational time within a reasonable range.
Fabrication of polymer solar cells: Polymer solar cell devices were fabricated using ITO-coated glass substrates (15 Ω sq⁻¹), which were cleaned with de-ionized water, acetone, and isopropyl alcohol in successive 25 min sonication steps applying a final 6 min oxygen plasma treatment to eliminate any remaining organic component. In the conventional structure devices, a thin layer (ca. 30 nm) of PEDOT:PSS (Bayer Baytron 4083) was first spin-coated on the pre-cleaned ITO-coated glass substrates at 2000 rpm and baked at 150°C for 15 min under ambient conditions. The substrates were then transferred into a nitrogen-filled glove box. Subsequently, the active layer was spin-coated on the PEDOT:PSS layer by spin-coating from a 10 mg/ml o-dichlorobenzene solution of polymer and PC$_{71}$BM. Solvent additive, 1,8-diiodooctane (DIO), and annealing were used to improve the BHJ morphology. At the final stage, the substrates were pumped down in high vacuum, and calcium (20 nm) topped with aluminium (80 nm) was thermally evaporated onto the active layer. For inverted device fabrication, a thin layer of sol-gel ZnO (ca. 30 nm) was spin-coated onto pre-cleaned ITO-coated glass substrates at 2000 rpm and then annealed at 200 °C for 1h in air. The ZnO precursor solution was prepared by dissolving zinc acetate dehydrate C$_4$H$_{10}$O$_4$Zn·2(H$_2$O) (99.5%, Merck 1 g) and monoethanolamine (HOCH$_2$CH$_2$NH$_2$, 98% Acros, 0.28 g) in 2-methoxyethanol (CH$_3$OCH$_2$CH$_2$OH, Aldrich, 98%, 10 mL) under stirring for 8 h for hydrolysis reaction and aging. The same process used for active layer in the conventional structure devices was also used for the inverted devices. After that, a 3 nm thick MoO$_3$ film and 80 nm Ag were deposited to complete the inverted device structure. Shadow masks were used to define the OSC active area (0.044 cm$^2$) of the devices.

Device Characterization: The current density–voltage (J–V) characteristics of unencapsulated photovoltaic devices were measured under N$_2$ using a Keithley 2400 source meter. A 300 W xenon arc solar simulator (Oriel) with an AM 1.5 global filter operated at 100 mW cm$^{-2}$ was used to simulate the AM 1.5G solar irradiation. The illumination intensity was corrected by using a silicon photodiode with a protective KG5 filter calibrated by the National Renewable Energy Laboratory (NREL). The external quantum efficiency (EQE) was performed using certified IPCE equipment (Zolix Instruments, Inc, SolarCellScan100).

OTFT Device fabrication and measurements: A heavily doped Si wafer with a 300 nm SiO$_2$ served as the gate electrode and dielectric layer, respectively. 30 nm Au electrodes were deposited and patterned by a typical lift-off technique with channel length ranging from 5–50 µm and channel width of 1.4 mm. The OTS modification was carried out in a vacuum oven at a temperature of 120 °C for 3 hours. The treated substrates were rinsed successively with hexane, ethanol and chloroform, respectively. The organic active layer was deposited on the OTS-treated substrates by a spin-coating process of their o-dichlorobenzene solutions, which followed by the annealing treatments at varied temperatures.

SCLC Mobility Measurements: Space charge-limited currents were tested in electron-only devices with a configuration of glass/Al/polymer:PC$_{71}$BM/Al and hole-only devices with a configuration of
ITO/PEDOT:PSS/polymer:PC\(_{71}\)BM/Au. The devices were prepared following the same procedure described in the experimental section for photovoltaic devices, except for the metal electrode. The mobilities were determined by fitting the dark current to the model of a single carrier SCLC current with field dependent mobility, which is described as

\[
J = \frac{9\varepsilon_0\varepsilon_r\mu_0V^2}{8L^3}
\]  

(1)

Where \(J\) is the current, \(\mu_0\) is the zero-field mobility, \(\varepsilon_0\) is the permittivity of free space, \(\varepsilon_r\) is the relative permittivity of the material, \(V\) is the effective voltage, and \(L\) is the thickness of the active layer.

Solid-state 2D \(^{13}\text{C}\{^1\text{H}\}\) HETCOR NMR experiments were performed on 600MHz Bruker Avance III spectrometer operating at a resonance frequency of 600.48 MHz for \(^1\text{H}\) and 151.00 MHz for \(^{13}\text{C}\). The experiments were conducted on a Bruker 4-mm double-resonance MAS probe at room temperature with the MAS speed at 10 kHz. Cross-polarization (CP) was used to transfer magnetization from \(^1\text{H}\) to \(^{13}\text{C}\) nuclei according to the Hartmann-Hahn condition. The 1D \(^{13}\text{C}\) CP-MAS experiments utilized a contact time of 2 ms. The 1D CP pulse sequence implemented a ramped (50 to 100 %) spin-lock pulse on the \(^1\text{H}\) channel and a square contact pulse on the \(^{13}\text{C}\) channel. Heteronuclear \(^1\text{H}\) decoupling was applied during signal acquisition using the SPINAL-64 pulse sequence at a \(^1\text{H}\) decoupling field of 80 kHz. The HETCOR experiments performed with CP contact times of 0.4 ms. A total of 256 t1 increments with 384 scans were collected. The chemical shift of \(^1\text{H}\) was referenced to tetramethylsilane (TMS, 0 ppm) and \(^{13}\text{C}\) was referenced to methylene carbon of adamantane at 38.48 ppm.

Part 2. Synthesis

Polymerization for PBDT-TBTTs

\[
\text{TBTT}_{	ext{EIH}} + \text{BDT-Sn} \rightarrow \text{PBDT}_{	ext{TEH}}\text{-TBTT}_{	ext{EIH}}\text{-i}(P1)
\]

\(\text{PBDT}_{	ext{TEH}}\text{-TBTT}_{	ext{EIH}}\text{-i}(P1)\)

\(\text{TBTT}_{	ext{EIH}}\text{-i}\) (102 mg, 0.117 mmol) and \(\text{BDT-Sn}\) (115 mg, 0.127 mmol) were dissolved with toluene (2 ml) and DMF (1 ml) in a pressure-proof tube. The reaction container was purged with argon for 10 min, and then Pd(PPh\(_3\))\(_4\) (10 mg, 0.008 mmol) was added. After another flushing with argon for 15 min, the reactant was heated to 100 °C for 36 h in dark. The reaction mixture was cooled to room temperature and poured into MeOH (80 mL), and filtered, which was then subjected to Soxhlet extraction with methanol, hexane, and chloroform successively. The polymer was recovered from the chloroform
fraction by precipitation with methanol. The dark red solid was dried under vacuum to give 120 mg of P1 in 80% yield. GPC: $M_w = 33.3$ K; $M_n = 7.9$ K; PDI = 4.21. Anal. Calcd for C$_{72}$H$_{87}$NO$_2$S$_9$ (%): C, 67.19; H, 6.81; N, 1.09; Found (%): C, 66.56; H, 6.72; N, 1.10.

**PBDT$_{\text{TEH}}$-TBTT$_{\text{EH-o}}$ (P2)**

P2 was synthesized following the same procedure as P1 starting from TBTT$_{\text{EH-o}}$ (150 mg, 0.17 mmol), BDT-Sn (169 mg, 0.187 mmol) and Pd(PPh$_3$)$_4$ (14 mg, 0.012 mmol). P2 was recovered from the chloroform fraction by precipitation with methanol. The dark red solid was dried under vacuum to give 142 mg of P2 in 64% yield. GPC: $M_w = 22.0$ K; $M_n = 5.5$ K; PDI = 3.98. Anal. Calcd for C$_{72}$H$_{87}$NO$_2$S$_9$ (%): C, 67.19; H, 6.81; N, 1.09; Found (%): C, 66.24; H, 6.71; N, 1.13.

**PBDT$_{\text{TEH}}$-TBTT$_{\text{HD-i}}$ (P3)**

P3 was synthesized following the same procedure as P1 starting from TBTT$_{\text{HD-i}}$ (100 mg, 0.102 mmol), BDT-Sn (100 mg, 0.110 mmol) and Pd(PPh$_3$)$_4$ (8 mg, 0.007 mmol). The polymer was recovered from the chlorobenzene fraction by precipitation with methanol. The dark red solid was dried under vacuum to get 125 mg of P3 in 88% yield. GPC: $M_w = 22.9$ K; $M_n = 6.1$ K; PDI = 3.77. Anal. Calcd for C$_{80}$H$_{103}$NO$_2$S$_9$ (%): C, 68.67; H, 7.42; N, 1.00; Found (%): C, 68.95; H, 7.15; N, 0.98.

**Part 3. Physical properties**

**Figure S1.** UV-Vis absorption spectra (a) and fluorescence spectra (b) of TBT, TBTT$_{-i}$ and TBTT$_{-o}$ in diluted CH$_2$Cl$_2$ solution ($1 \times 10^{-5}$ M).

**Table S1.** Photophysical properties of TBT, TBTT$_{-i}$ and TBTT$_{-o}$ in dilute CH$_2$Cl$_2$ solution.

<table>
<thead>
<tr>
<th>Cpd.</th>
<th>$\lambda_{\text{abs}}^{\max}$ (nm)</th>
<th>$\varepsilon_{\text{max}}$ (L mol$^{-1}$ cm$^{-1}$)</th>
<th>$\lambda_{\text{max}}^{\text{em}}$ (nm)</th>
<th>Stokes shift (cm$^{-1}$)</th>
<th>$E_{\text{g opt}}$ (eV)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBT</td>
<td>384</td>
<td>27100</td>
<td>457</td>
<td>4160</td>
<td>2.88</td>
</tr>
<tr>
<td>TBTT$_{-i}$</td>
<td>440, 460</td>
<td>31700</td>
<td>506</td>
<td>1976</td>
<td>2.48</td>
</tr>
</tbody>
</table>
a) The optical bandgap was calculated according to \( E_{\text{g,opt}} = \frac{1240}{\lambda_{\text{onset}}} \), where \( \lambda_{\text{onset}} \) is the onset value of the absorption spectrum in the long wavelength region.

Figure S2. (up) Calculated HOMO and LUMO orbitals of TBT, TBTT-\( i \), and TBTT-\( o \). Alkyl substituents are replaced by methyl groups to simplify the calculations. (down) Projected view of TBTT-\( i \) and TBTT-\( o \) from the short-axis direction.

Figure S3. The UV-vis spectra of P1 and P2 in chloroform (left) and thin film (middle) and P3 in chlorobenzene and thin film (right).
Figure S4. Cyclic voltammogram of (a) P1, (b) P2 and (c) P3 films on the glassy-carbon electrode with scan rate of 100 mV s$^{-1}$.

Figure S5. Ultraviolet photoelectron spectroscopy (UPS) of P1-P3 films on Si substrate.
Table S2. Photo physical and electrochemical properties of P1, P2 and P3 in solution and films

<table>
<thead>
<tr>
<th>Polymers</th>
<th>$\lambda_{\text{max}}^{\text{soln}}$ (nm)</th>
<th>$\lambda_{\text{max}}^{\text{film}}$ (nm)</th>
<th>$E_{\text{g}}^{\text{film}}$ (eV)</th>
<th>HOMO$^{\text{CV}}$ (eV)</th>
<th>LUMO$^{\text{CV}}$ (eV)</th>
<th>HOMO$^{\text{UPS}}$ (eV)</th>
<th>LUMO$^{\text{UPS}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>686</td>
<td>672,726</td>
<td>1.54</td>
<td>−5.12</td>
<td>−3.58</td>
<td>−4.64</td>
<td>−3.10</td>
</tr>
<tr>
<td>P2</td>
<td>704</td>
<td>706</td>
<td>1.46</td>
<td>−5.12</td>
<td>−3.66</td>
<td>−4.63</td>
<td>−3.17</td>
</tr>
<tr>
<td>P3</td>
<td>688</td>
<td>678,724</td>
<td>1.56</td>
<td>−5.12</td>
<td>−3.56</td>
<td>−4.78</td>
<td>−3.22</td>
</tr>
</tbody>
</table>

a) The optical bandgap was calculated according to $E_{\text{g}}^{\text{film}} = 1240/\lambda_{\text{onset}}$ (eV), where $\lambda_{\text{onset}}$ is the onset value of the absorption spectrum in the long wavelength region; b) Estimated from the empirical equation HOMO$^{\text{CV}} = -(5.10 + E_{\text{onset}})$ (eV); c) Determined from the empirical equation LUMO$^{\text{CV/UPS}} = $HOMO$^{\text{CV/UPS}} + E_{\text{g}}^{\text{film}}$ (eV); d) Estimated from the empirical equation HOMO$^{\text{UPS}} = $WF + $E_{\text{b}}$ (eV), where WF is the d-value between 21.22 and the onset value of the high binding energy, $E_{\text{b}}$ is the onset value of the low binding energy.

Figure S6. Thermal gravimetric analysis (TGA) curves of polymers (a) P1, (b) P2, and (c) P3.
Figure S7. Differential scanning calorimetry (DSC) curves of powders of P1 and P2. Upward peaks indicate exothermic processes, while downward peaks indicate endothermic processes.

Figure S8. X-ray diffraction (XRD) patterns of polymer:PC$_{71}$BM optimized blend films.

Figure S9. AFM height images (a, d), AFM phase images (b, e), and TEM images of optimized blend films (c, f) based on P1:PC$_{71}$BM (a–c) and P2:PC$_{71}$BM (d–e) blend films. The scan size of the AFM images is 5 × 5 μm.
Figure S10. TEM images of (a) P1:PC$_71$BM, (b) P2:PC$_71$BM, and (c) P3:PC$_71$BM optimized blend films.

Part 4. Semiconducting properties
**Figure S11.** The hole mobility (a) and electron mobility (b) of P1:PC$_{71}$BM, the hole mobility (c) and electron mobility (d) of P2:PC$_{71}$BM blend films, the hole mobility (e) and electron mobility (f) of P3:PC$_{71}$BM blend films at their best OSC device characters measured by SCLC method.

![Graph showing mobility vs. temperature for P1 and P2](image)

**Figure S12.** Comparison of the hole mobilities (OFET) of P1 and P2 at different annealing temperatures.
Part 5. Solid-state 2D $^{13}\text{C}[^1\text{H}]$ HETCOR NMR spectra

(a)

(b)

(c)
**Figure S13.** Solid-state 2D $^{13}$C{$^1$H} dipolar-mediated heteronuclear correlation (HETCOR) NMR spectra acquired at room temperature for neat P1 (a) and PC$_{61}$BM (b). Solid-state 2D $^{13}$C{$^1$H} dipolar-mediated heteronuclear correlation (HETCOR) NMR spectra acquired at room temperature for mixture contains 8 wt.% P1 and 92 wt% PC$_{61}$BM. (c) Diagrammatic sketch that indicate the most probable arrangement of P1 and PC$_{61}$BM according to the intermolecular interactions between them from the 2D NMR intensity correlations.

As shown in Figure S13, the mixture sample (Figure S13(c)), 8% polymer:92% PC$_{61}$BM by wt., were prepared by stirring approximately 150 mg of the material blend in o-DCB (20 mg/mL) overnight at room temperature. The solvent was removed under reduced pressure before being loaded into 4 mm zirconia rotors for measurement, while neat chemicals were loaded without processing. Because of the aggregation, the peaks in the polymer NMR spectrum (Figure S13(a)) are broadened, which are different from the relative sharp signals in the PC$_{61}$BM NMR spectrum (Figure S13(b)). Compared to the 2D $^{13}$C{$^1$H} HETCOR NMR of PC$_{61}$BM and P1, additional 2D intensity correlations are observed in Figure S13(c) that directly establishes intermolecular interactions between the PC$_{61}$BM and P1. The $^{13}$C signals at 24 and 34 ppm that are associated with C3’ and C2’ of the PC$_{61}$BM moiety are strongly correlated with the $^1$H signals at ~7.5 ppm from H2 (BDT moiety) of P1. Meanwhile, the $^{13}$C signal at 31 ppm and 51 ppm that are associated with C4’ and C6’ of the PC$_{61}$BM moiety are both correlated with the $^1$H signals at ~7.5 ppm from H2 (BDT moiety) of P1, too. Moreover, $^{13}$C signals associated with the C$_{60}$ fullerene group at 145–148 ppm are strongly correlated with the $^1$H signals at 3.0–3.5 ppm associated with the alkyl chain of TPD. These results are also in good agreement with a recently published paper, in which the alkoxy units on BDT have steric hindrance to push the PC$_{61}$BM to the TPDs. Thus, the thiophene substituents on BDT in P1–P3 should have greater steric hindrance.

**Reference**