A Polythiophene Derivative with Superior Properties for Practical Application in Polymer Solar Cells

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Polymer solar cells (PSCs) have attracted much attention in recent years because of their advantages of low cost, easy fabrication, light weight, and the possibility of using them to fabricate flexible large-area devices. In the past decade, a great many conjugated polymers have been designed, synthesized, and applied as donor materials in PSCs. Among these polymers, polythiophene (PT) derivatives are one of the most important types of donor materials, the most prominent of which is regioregular poly(3-hexylthiophene) (P3HT), which is also a classic photovoltaic donor material. As is well known, P3HT has played a very important role in advancing the development of the field of PSCs. Under optimal device fabrication conditions, the PSCs based on P3HT/[6, 6]-phenyl C71 butyric acid methyl ester (P3HT:PC71BM) and P3HT:indene-C60 bisadduct (P3HT:IC61BA) typically show power conversion efficiencies (PCEs) of ca. 4% and ca. 7%, respectively, and these results are among the highest in the field.

Much effort has been devoted to designing PT derivatives to realize higher efficiency in PSCs, that is, to explore PT derivatives with better photovoltaic properties than P3HT. For example, the PT derivatives with two-dimensional (2D) conjugated structure showed enhanced light absorption properties compared to P3HT; the PT derivative P3HDTTT (shown in Figure 1) with fewer electron-donating groups showed a lower HOMO level and thus higher open circuit voltage (Voc) than P3HT in PSCs. More recently, a series of PT derivatives (named PT-C1, PT-C2, and PT-C3) containing carboxylate substituents were reported and the PSCs based on PT-C3 (Figure 1) showed improved Voc of 0.78 V in comparison with the P3HT-based PSCs. Besides the polymers mentioned above, there are many interesting examples of molecular structure optimization of PT derivatives. Hence, it is attractive to improve the photovoltaic performance of PT derivatives by molecular structure modification.

In the work reported here, a new PT derivative, poly[5,5’-bis(2-butyloctyl)-2,2’-bithiophene)-4,4’-dicarboxylate-alt-5,5’-2,2’-bithiophene] (PDCBT, shown in Scheme 1), was designed and synthesized. By attaching electron-withdrawing carboxylate substituents to the side chain, it is possible to reduce the HOMO level from -4.90 eV for P3HT to -5.26 eV for PDCBT with minor effect on the optical bandgap. PDCBT is highly crystalline and exhibits compact π–π stacking with a smaller separation than P3HT. The PSCs based on PDCBT/PC71BM (1:1, w/w) fabricated under optimal conditions exhibit a PCE of 7.2% with Voc = 0.91 V, short-circuit current density Jsc = 11.0 mA cm-2, and fill factor FF = 72.0%. In contrast, the PSCs based on P3HT/PC71BM (1:1, w/w) fabricated under the same conditions showed a PCE of only 1.8% with Voc = 0.63 V, Jsc = 4.5 mA cm-2, and FF = 62%. Furthermore, the performance of PSCs based on PDCBT is insensitive to variations of active layer thickness and processing conditions such as additives and thermal treatment. In addition, compared with other high-efficiency low-bandgap photovoltaic materials, this polymer exhibits a simpler structure and easier synthesis, which is beneficial for mass production. These results indicate that PDCBT has great potential in large-scale manufacturing of low-cost, high-performance PSCs and also will be a more suitable candidate than P3HT as the broad-bandgap material in tandem solar cells.

As shown in Scheme 1, the polymer PDCBT can be prepared by four steps, starting from commercially available chemicals, and it shows good solubility in common solvents such as chloroform (CF), chlorobenzene (CB), ortho-dichlorobenzene (o-DCB), and so on. Since the backbone of the polymer consists of thiophene units and the functional groups used to modulate its properties are carboxylates only, this polymer can be easily synthesized and also the synthetic method has great potential for optimization.

The absorption spectra of PDCBT and P3HT in solid films are shown in Figure 2a. In comparison with P3HT, PDCBT shows a similar absorption edge located at 650 nm, corresponding to a bandgap (Eg) of 1.9 eV. However, the main absorption peak of PDCBT is located at 551 nm, which is

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The absorption coefficient of the PDCBT film is $1.05 \times 10^5$ cm$^{-1}$, which is ca. 30% higher than that of P3HT film, implying that PDCBT film can utilize sunlight more efficiently than P3HT film of the same thickness.

 Interestingly, the absorption spectra of PDCBT and P3HT films are $37$ nm red-shifted compared to that of P3HT. Interestingly, the absorption coefficient of the PDCBT film is $1.05 \times 10^5$ cm$^{-1}$, which is ca. 30% higher than that of P3HT film, implying that PDCBT film can utilize sunlight more efficiently than P3HT film of the same thickness.  

Electrochemical cyclic voltammetry (CV) was performed to determine the HOMO and the lowest unoccupied molecular orbital (LUMO) levels of the conjugated polymers. Figure 2b shows the CV plots of PDCBT and P3HT films on a platinum electrode in 0.1 mol L$^{-1}$ Bu$_4$NPF$_6$ acetonitrile solution, respectively. The onset oxidation potentials ($\phi_{\text{ox}}$) are 0.19 and 0.55 V versus Ag/Ag$^+$. From $\phi_{\text{ox}}$ of the polymers, HOMO levels of the polymers, in electron volts, were calculated according to the equation $\phi_{\text{HOMO}} = \omega \phi_{\text{ox}} + 4.71$. The HOMO levels of PDCBT and P3HT are $-4.90$ and $-5.26$ eV, respectively. It is very clear that attaching the electron-withdrawing carboxylate substituent to the side chains made the HOMO level of PDCBT decrease by $0.36$ eV in comparison with P3HT, which is beneficial for achieving higher $V_{\text{oc}}$ in PSCs.

PSC devices were fabricated and characterized to investigate the photovoltaic properties of the polymer. The device structure used in this work was ITO/PEDOT:PSS (30 nm)/polymer:PC$_{61}$BM/Ca (20 nm)/Al (80 nm), where ITO is indium tin oxide, PEDOT is poly(3,4-ethylenedioxythiophene), and PSS is poly(styrene sulfonate). Initially, PSC devices with different donor/acceptor (D/A) ratios (PDCBT/PC$_{61}$BM, w/w) were fabricated. Figure 3a shows the current density–voltage ($J$–$V$) curves of the devices under AM 1.5G, that is, standard solar spectrum (100 mW cm$^{-2}$) illumination with different D/A ratios (1.5:1, 1:1, and 1:0.5); the corresponding photovoltaic parameters are summarized in Table 1. The PSCs based on PDCBT/PC$_{61}$BM (1:1, w/w) exhibited a PCE of 6.3% with a PDCBT-based device shows a significant improvement of EQE in the wavelength range 450–600 nm, which means more efficient photoelectron conversion in this range and hence
benefits for the improvement of $J_{SC}$. The variations between the integral values deduced from the EQE curves and the standard solar spectrum (AM 1.5G) and the measured values are below 5%. Furthermore, as shown in Figure 3c, the blend of PDCBT/PC$_{71}$BM (1:1, w/w) exhibits stronger absorption in the long-wavelength range 510–650 nm compared with that of the P3HT/PC$_{71}$BM blend. The enhancement of absorbance at long wavelengths will contribute to the improvement of $J_{SC}$.

Furthermore, in order to study the relationship between the photovoltaic performance of the PDCBT-based PSCs and the device fabrication conditions, the following investigations were carried out. First, the widely used solvent additive 1,8-diodooctane (DIO) was used to further improve photovoltaic performance of the devices. As shown in Figure 4a and Table 1, when 3% DIO was used as a solvent additive, the PCE of the PDCBT-based device was improved to 7.2%, which is slightly higher than the device processed using pure $o$-DCB. Then the effect of thermal annealing on photovoltaic performance was also investigated. Because the glass transition temperature of poly(ethylene terephthalate) (PET), the transparent substrate material that is widely used for making flexible PSCs, is ca. 80$^\circ$C, the blend film of PDCBT/PC$_{71}$BM was treated under 100$^\circ$C for 10 min. As shown in Figure 4a and Table 1, after the thermal annealing process, there is no change in photovoltaic properties, meaning that the blend of PDCBT/PC$_{71}$BM is robust enough to endure the thermal treatment process for making flexible devices. Finally, we also investigated the relationship between the thickness of the active layers and the photovoltaic performance. As shown in Figure 4a and Table 1, benefiting from the strong absorption coefficient, the PDCBT-based PSC with 70 nm thick active layer still exhibited a high $J_{SC}$ of 9.9 mA cm$^{-2}$. Interestingly, when the thickness increased from 70 nm to 230 nm gradually, the $FF$ values of the devices dropped slightly from over 70% to ca. 66%, while the $J_{SC}$ and $V_{OC}$ values of the devices remained virtually unchanged. As a

<table>
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<tr>
<th>Active layers</th>
<th>D/A [w/w]</th>
<th>Thickness [nm]</th>
<th>$V_{OC}$ [V]</th>
<th>$J_{SC}$ [mA cm$^{-2}$]</th>
<th>$FF$ [%]</th>
<th>PCE$<em>{max}$/PCE$</em>{ave}$ [%]</th>
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</thead>
<tbody>
<tr>
<td>PDCBT/PC$_{71}$BM</td>
<td>1.5:1</td>
<td>95</td>
<td>0.93</td>
<td>8.8</td>
<td>71</td>
<td>5.8 (5.6)</td>
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<td>PDCBT/PC$_{71}$BM</td>
<td>1:1</td>
<td>70</td>
<td>0.93</td>
<td>9.9</td>
<td>71</td>
<td>6.5 (6.3)</td>
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<td>PDCBT/PC$_{71}$BM</td>
<td>1:1</td>
<td>95</td>
<td>0.94</td>
<td>10.2</td>
<td>72</td>
<td>6.9 (6.7)</td>
</tr>
<tr>
<td>PDCBT/PC$_{71}$BM</td>
<td>1:1</td>
<td>94</td>
<td>0.91</td>
<td>10.0</td>
<td>72</td>
<td>7.2 (7.0)</td>
</tr>
<tr>
<td>PDCBT/PC$_{71}$BM</td>
<td>1:1</td>
<td>95</td>
<td>0.95</td>
<td>10.5</td>
<td>69</td>
<td>6.9 (6.7)</td>
</tr>
<tr>
<td>PDCBT/PC$_{71}$BM</td>
<td>1:1</td>
<td>110</td>
<td>0.92</td>
<td>10.3</td>
<td>70</td>
<td>6.6 (6.3)</td>
</tr>
<tr>
<td>PDCBT/PC$_{71}$BM</td>
<td>1:1</td>
<td>150</td>
<td>0.92</td>
<td>10.5</td>
<td>68</td>
<td>6.5 (6.2)</td>
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<tr>
<td>PDCBT/PC$_{71}$BM</td>
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<td>230</td>
<td>0.91</td>
<td>10.6</td>
<td>66</td>
<td>6.4 (6.1)</td>
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<tr>
<td>PDCBT/PC$_{71}$BM</td>
<td>1:1.5</td>
<td>95</td>
<td>0.92</td>
<td>8.8</td>
<td>66</td>
<td>5.3 (5.2)</td>
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<tr>
<td>PDCBT/PC$_{71}$BM</td>
<td>1:1</td>
<td>95</td>
<td>0.90</td>
<td>11.1</td>
<td>63</td>
<td>6.3 (6.1)</td>
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<td>9.7</td>
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<td>0.90</td>
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</table>

$^a$With 3% DIO; $^b$With thermal annealing at 100$^\circ$C for 10 min; $^c$The devices were fabricated under the same conditions as used for PDCBT/PC$_{71}$BM-based devices; $^d$The devices were fabricated with solvent annealing; $^e$The devices were fabricated under the optimal conditions from the literature. $^{[4a]}$The average PCE was obtained from over 20 devices.
result, when the active layer thickness changed from 70 nm to 230 nm, the variation of PCE was (6.6 ± 0.3)%. According to these above investigations, it can be concluded that the photovoltaic performance of the PDCBT/PC71BM-based device is insensitive to the device fabrication conditions.

Grazing incidence X-ray diffraction (GIXD) measurements were carried out to investigate molecular packing of the neat PDCBT film and the blend film of PDCBT and PC71BM. Figure 5a shows 2D GIXD images and the in-plane (IP) and out-of-plane (OOP) GIXD profiles of the samples, including thin films for pure PDCBT and the PDCBT/PC71BM (1:1, w/w) blend film cast from pure o-DCB. The OOP profile of the pure polymer film showed pronounced 100, 200, and 300 diffraction peaks at 0.31 Å\(^{-1}\), 0.62 Å\(^{-1}\) and 0.93 Å\(^{-1}\), respectively, arising from the alkyl chain packing with \(d\)-spacing of ca. 20 Å. This indicates a highly crystallized nature of the PDCBT. Impressively, in the IP profile, it showed one sharp and intensive peak at ca. 1.7 Å\(^{-1}\), which corresponds to (010) \(\pi-\pi\) stacking with the \(d\)-spacing of 3.7 Å. This suggests an edge-on dominated molecular orientation with respect to the substrate. Moreover, on going from the pure polymer film to the blend film, the crystalline structure of the polymer is well maintained. Compared with that of P3HT, PDCBT exhibited smaller \(\pi-\pi\) stacking spacing in the neat film, which means more compact inter-chain packing and benefits for \(\pi\)-electron hopping among the polymer chains.\(^{[18]}\)

The bulk morphology of the blend of PDCBT and PC71BM was investigated by resonant soft X-ray scattering (RSoXS).\(^{[19]}\) X-rays with photon energy of 283 eV were utilized to enhance the contrast between PDCBT and PC71BM and also to minimize the fluorescence background. The measurements were performed in transmission geometry with the diffraction vector being in the plane of the film. Figure 5b shows the RSoXS profiles for PDCBT/PC71BM (1:1, w/w) blends cast from o-DCB. As shown in Figure 5b, the median \(s_{\text{median}}\) of the spatial frequency distribution \(s = q/2\pi\) corresponds to the characteristic median length scale, \(\xi\), of the corresponding log-normal distribution in real space, with \(\xi = 1/s_{\text{median}}\) a model-independent statistical quantity. The \(\xi\) of the blend showed a multi-modal distribution that can be fitted very well with two log-normal distributions, that
is, two well-defined peaks with $\xi$ of ca. 20 nm and ca. 50 nm. Such multiple-length-scale phase separation is observed in other blends too and is considered to be favorable for charge separation and transport.\[20\] Furthermore, atomic force microscopy (AFM) and transmission electron microscopy (TEM) methods were used to give complementary, real-space morphological information about the PDCBT/PC$_{71}$BM (1:1, w/w) blend film (see Figure S2 in the Supporting Information). As shown in Figure S2a, the root-mean-square (RMS) value of the blend film is 0.86 nm, obtained by AFM. In the TEM images (see Figure S2b), dark and light domains can be clearly distinguished, indicating that a network of the polymer and PC$_{71}$BM is formed. These results are consistent with the RSoXS results.

In conclusion, a PT derivative with simple molecular structure, PDCBT, was easily synthesized for photovoltaic applications. PDCBT showed a lower HOMO level (~5.26 eV) and better light-harvesting ability (maximum absorption coefficient $1.05 \times 10^5$ cm$^{-1}$) than P3HT. The best device based on PDCBT/PC$_{71}$BM (1:1, w/w) exhibited a good PCE of 7.2% with a high FF of 72%. The EQE of the device reached 75% so that a $J_{SC}$ of 11 mA cm$^{-2}$ was obtained, which is a high value for a polymer with a bandgap of 1.9 eV. Furthermore, the device performance is not sensitive to variation of the device processing conditions, such as addition of solvent additives (e.g., DIO) and thermal treatment. In addition, when the active layer thickness was changed from 70 nm to 230 nm, the photo-voltaic performance of the PDCBT-based device changed little.

The PCE of 7.2% is an outstanding result for the polymers and blends too and is considered to be favorable for charge separation and transport. A PT derivative with simple molecular structure, PDCBT, was easily synthesized for photovoltaic applications. PDCBT showed a lower HOMO level (~5.26 eV) and better light-harvesting ability (maximum absorption coefficient $1.05 \times 10^5$ cm$^{-1}$) than P3HT. The best device based on PDCBT/PC$_{71}$BM (1:1, w/w) exhibited a good PCE of 7.2% with a high FF of 72%. The EQE of the device reached 75% so that a $J_{SC}$ of 11 mA cm$^{-2}$ was obtained, which is a high value for a polymer with a bandgap of 1.9 eV. Furthermore, the device performance is not sensitive to variation of the device processing conditions, such as addition of solvent additives (e.g., DIO) and thermal treatment. In addition, when the active layer thickness was changed from 70 nm to 230 nm, the photo-voltaic performance of the PDCBT-based device changed little.

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Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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