Poly[4,4-bis(2-ethylhexyl)cyclopenta[2,1-b;3,4-b#]dithiophene-2,6-
diyl-alt-2,1,3- benzoselenadiazole-4,7-diyl], a New
Low Band Gap Polymer in Polymer Solar Cells
Jianhui Hou, Teresa L. Chen, Shaoqing Zhang, Hsiang-Yu Chen, and Yang Yang


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A low band gap polymer named as poly[4,4-bis(2-ethylhexyl)cyclopenta[2,1-b;3,4-b′]dithiophene-2,6-diyl-alt-2,1,3-benzoselenadiazole-4,7-diyl], PCPDTBSe, was designed and synthesized. The band gap of PCPDTBSe is 1.35 eV, which is 0.1 eV lower than that of poly[4,4-bis(2-ethylhexyl)cyclopenta[2,1-b;3,4-b′]dithiophene-2,6-diyl-alt-2,1,3-benzothiadiazole-4,7-diyl], PCPDDBT. In the visible range, the PCPDTBSe film exhibits weaker absorption than that of PCPDDBT, making PCPDTBSe a promising candidate as a low band gap material for tandem cells. Polymer solar cell (PSC) devices using PCPDTBSe as the electron donor material and 6,6-phenyl-C71-butyric acid methyl ester (PC70BM) as the electron acceptor material were fabricated and characterized to investigate the photovoltaic properties of PCPDTBSe. The external quantum efficiency spectrum indicates that the response range reaches 1000 nm. Under AM 1.5 G, 100 mW/cm² illumination, a PCE of 0.89% was recorded, with a short circuit current of 5.0 mA/cm², an open circuit voltage of 0.52 V, and a fill factor of 34.3%. Based on the results from the absorption spectrum and the carrier mobility of the PCPDTBSe:PC70BM blend film, we found that the photovoltaic performance of the PCPDTBSe-based PSC device is limited by the weak absorbance and an imbalance in hole and electron transport of the active layer. In conclusion, based on preliminary results, PCPDTBSe is a promising low band gap material for applications in PSCs, especially for PSCs with tandem structures.

Introduction

Polymeric photovoltaic devices have attracted much attention as potential large-area, flexible, and low-cost solar cells.¹−⁶ Bulk heterojunction polymer solar cells (PSCs) have been proven to be the most successful device structure. The active layer of this kind of device consists of an interpenetrating network formed by an electron donor material blended with an electron acceptor material. Commonly, a derivative of fullerene, such as 6,6-phenyl-C60-butyric acid methyl ester (PCBM), is used as an electron acceptor material, along with a conjugated polymer as an electron donor material, to form the active layer of bulk heterojunction devices. In order to obtain a highly efficient PSC device, the absorption spectrum of the active layer of the PSC device should match the solar photon flux spectrum closely. The solar spectrum exhibits a maximum peak at around 670 nm,⁷ and hence low band gap conjugated polymers have been employed to achieve better harvesting of the sunlight.⁸,⁹ Low band gap conjugated polymer poly[4,4-bis(2-ethylhexyl)cyclopenta[2,1-b;3,4-b′]dithiophene-2,6-diyl-alt-2,1,3-benzothiadiazole-4,7-diyl], PCPDDBT,¹⁰,¹¹ has proven to be one of the most efficient low band gap photovoltaic materials with a spectral response that extends to 900 nm. As reported, for the PCPDDBT/PC70BM-based polymer solar cell, an efficiency of 3.2% was achieved.¹¹ The solar cell device efficiency was further increased to 5.4% by morphology control using octane-1,8-dithiol as an additive in the device fabrication process.¹¹ The response range of the solar cell based on PCPDDBT covers the whole visible light range, making this characteristic the main advantage of this material.¹¹,¹² In the cyclopenta[2,1-b;3,4-b′]dithiophene (CPDT) unit of PCPDDBT, the two thiophene units are confined to one plane, which prolongs the effective conjugated length of the polymer and effectively lowers the band gap. Additionally, the planar structure facilitates carrier transfer between two conjugated main chains, allowing the hole mobility of PCPDDBT to reach 1 × 10⁻² cm²/V s,¹² which is a fairly high value for conjugated polymers. Furthermore, the two alkyl side chains on the CPDT unit give the polymer its excellent solubility, which is important for the formation of uniform films by the spin-coating process. Based on these properties, CPDT is a very useful unit for photovoltaic materials.

Another important application of low band gap polymers is in tandem PSC devices, in which two solar cells with different absorption characteristics are linked together to make use of a wider range of the solar spectrum.¹³ In order to better harvest the sunlight, absorption spectra of the two cells should not overlap too much; typically one cell consisting of a broad band gap material and another cell with a low band gap material are employed in tandem PSC devices. Although PCPDDBT has been proven to be a useful material in tandem PSC devices,¹³ its absorption extends to 500 nm in the short-wavelength region, which overlaps partially with the spectrum of most broad band gap materials.¹²,¹³ Therefore, if the absorption of PCPDDBT can be further shifted to longer wavelengths, the overlapping of absorption spectra between the two cells of the tandem PSC will be reduced, giving rise to improved photon harvesting of the device at longer wavelengths. Hence, there is a need to further lower the band gap of PCPDDBT.

2,1,3-Benzoselenadiazole (BSe) has a similar chemical structure as 2,1,3-benzothiadiazole (BT), and the conjugated polymers with BSe exhibit interesting properties in conjugated polymeric materials of photovoltaic devices.¹⁴,¹⁵ Recently, we reported the use of BSe as a low band gap unit in benzo[1,2-b;4,5-b′]dithiophene (BDT)-based polymers.¹⁵ The molecular
structures of the two BDT-based polymers, BDT-BSe and BDT-BT, are shown in Scheme 1. As reported, the band gap of the two polymers, BDT-BT and BDT-BSe, are 1.70 and 1.52 eV, respectively. In comparison with BDT, it is apparent that BSe is more effective in lowering the band gap of the BDT-based polymers. As a result, BSe was selected to further reduce the band gap of the CPDT-based polymer, and hence poly[4,4-bis(2-ethylhexyl)cyclopenta[2,1-b:3,4-b']dithiophene-2,6-diyl-alt-2,1,3-benzoselenadiazole-4,7-diyl], PCPDTBSe, as shown in Scheme 1, was designed and synthesized.

Experimental Section

Characterization and Materials. $^1$H NMR and $^{13}$C NMR spectra were measured on a Bruker DMX-400 spectrometer. A TGA measurement was performed on a TA Instrument 2050 TGA with a heating rate of 10 °C/min under atmospheric pressure. Absorption spectra were taken using a Varian Cary 50 ultraviolet–visible spectrometer. The molecular weight of polymers was measured by the GPC method, where polystyrene was used as a standard. The electrochemical cyclic voltammetry was conducted with a Pt disk coated with the polymer film as the working electrode, a Pt wire as the counter electrode, and Ag as the reference electrode in a 0.1 mol/L tetrabutylammonium hexafluorophosphatium (Bu$_4$NPF$_6$) acetonitrile solution. Since the Ag wire is a semireference electrode, a trace amount of ferrocene was used as a standard material to determine the p- and n-doping potential of the polymers. The polymer PCPDTBT was used as a reference material and was synthesized and purified following the reported method.

Fabrication and Characterization of PSC Devices. PSC devices with the typical structure of ITO/PEDOT-PSS/polymer: PC$_{70}$BM:3,4-ethylenedioxythiophene-poly(styrenesulfonate):poly(3,4-ethylhexyl)cyclopenta[2,1-b:3,4-b']dithiophene-2,6-diyl-alt-2,1,3-benzoselenadiazole (PSC) were fabricated under similar conditions as follows: After spin-coating a 30 nm layer of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) onto a precleaned silicon diode (with KG5 visible filter) calibrated with assistance from the National Renewable Energy Laboratory (NREL). The two monomers, 4,4-bis(2-ethylhexyl)-2,6-bis(trimethylstannanyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene and 4,7-dibromo-2,1,3-benzoselenadiazole, along with the polymer PCPDTBT, which was used as a reference material to make clear comparisons, were synthesized following the reported methods. The polymer PCPDTBSe was synthesized by the Stille coupling reaction, as shown in Scheme 2, and the detailed procedure of the polymerization and purification step is described as follows.

In a 100 mL flask, two of the monomers (1 mmol of each) were dissolved by 40 mL of toluene and then flushed by argon for 10 min. Following that, 22 mg of Pd(PPh$_3$)$_4$ was added, and the reactant was purged by argon for another 20 min. The reactant was then heated to reflux for 24 h under the protection of argon. The sticky, deep green solution was cooled and poured into 100 mL of methanol, where the crude polymer was precipitated and collected as dark green powder, which was then subjected to Soxhlet extraction with methanol, hexane, and chloroform. The polymer was recovered from the chloroform fraction by rotary evaporation. The low molecular weight portion of the polymer was then removed by gel permeation chromatography (GPC) with THF as the eluent, and the high molecular weight portion was recovered from the THF solution as dark green solid (116 mg, yield 20%, Mn = 22 K, PDI = 1.6). $^1$H NMR (CDCl$_3$, 400 MHz): 8.20 (s, br, 2H), 7.87 (s, br, 2H), 2.09 (s, br, 2H), 1.22 (m, 20H), 0.89 (m, 12H). 1H NMR (CDCl$_3$, 400 MHz): 8.20 (s, br, 2H), 7.87 (s, br, 2H), 2.09 (s, br, 2H), 1.22–1.08 (m, 20H), 0.89–0.75 (m, 12H).

Results and Discussion

In order to make a clear comparison, thermogravimetric analysis (TGA) plots of PCPDTBSe and PCPDTBT are shown in Figure 1. The onset decomposition temperature of PCPDTBSe is at 260 °C without the protection of an inert atmosphere, which is slightly higher than that of PCPDTBT under the same conditions. The comparison indicates that the replacing of the sulfur atoms by the selenium atoms has little negative influence on the thermal stability of the polymers; furthermore, the
the range from 500 to 620 nm; however, the absorption spectrum of the PCPDTBT film overlaps with that of the P3HT film in plotted in Figure 3b. It can be seen that the absorption spectrum gap (in film the absorption peak shifts to 783 nm. The optical band absorption peak of PCPDTBSe in solution is 730 nm, whereas in films are shown in Figure 3a, b. As listed in Table 1, the optical band gap polymer commonly used in tandem cells,13 is also

Table 1: Optical and Electrochemical Properties of PCPDTBSe and PCPDTBT

<table>
<thead>
<tr>
<th>Polymer</th>
<th>λ_{max, abs} (nm)</th>
<th>E_{g, opt} (eV)</th>
<th>( \varphi_{\text{red}} ) (eV)/LUMO</th>
<th>( \varphi_{\text{ox}} ) (V)/HOMO</th>
<th>( E_{\text{g, e}} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCPDTBSe</td>
<td>730</td>
<td>1.35</td>
<td>-1.52/-3.28</td>
<td>0.10/-4.90</td>
<td>1.62</td>
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<tr>
<td>PCPDTBT</td>
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<td>1.45</td>
<td>-1.40/-3.40</td>
<td>0.20/-5.00</td>
<td>1.60</td>
</tr>
</tbody>
</table>

stability of PCPDTBSe is also adequate for both the fabrication processes for PSCs and other applications in optoelectronic devices.

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of PCPDTBSe were measured by electrochemical cyclic voltammetry (CV). Figure 2 shows the CV curves of PCPDTBSe and PCPDTBT films on a Pt electrode in 0.1 mol/L Bu4NPF6, CH3CN solution. From the value of the onset oxidation potential (\( \varphi_{\text{ox}} \)) and the onset reduction potential (\( \varphi_{\text{red}} \)) of the polymers, the HOMO and the LUMO levels, as well as the band gaps (\( E_{g, \text{e}} \)), were calculated and listed in Table 1. As reported, for BDT-based polymers, BDT–BSe exhibited lower HOMO and LUMO levels than BDT–BT; the same trend was observed in the two CPDTBSe-based polymers.16

The absorption spectra of the polymers in THF solution and in films are shown in Figure 3a, b. As listed in Table 1, the absorption peak of PCPDTBSe in solution is 730 nm, whereas in film the absorption peak shifts to 783 nm. The optical band gap (\( E_{g, \text{opt}} \)) of PCPDTBSe is calculated to be 1.35 eV, which is 0.1 eV lower than that of PCPDTBT. These results indicate that BSe is a more efficient low band gap unit as compared with BT. In order to make clear comparisons, the absorption spectrum of poly(3-hexylthiophene) (P3HT), which is a broad band gap polymer commonly used in tandem cells, is also plotted in Figure 3b. It can be seen that the absorption spectrum of the PCPDTBT film overlaps with that of the P3HT film in the range from 500 to 620 nm; however, the absorption spectrum

Since the motivation of this work is to explore new photovoltaic materials, PSC devices were fabricated and characterized to investigate the photovoltaic properties of PCPDTBSe. The power conversion efficiency (PCE) of 50 devices was in the range of 0.80 ± 0.1%, with a best PCE of 0.92%. Figure 4 shows the I–V curves of a typical PSC device in the dark and under illumination with AM 1.5 G, 100 mW/cm² conditions. The PCE of the device was calculated to be 0.89%, with a short circuit current (\( J_{sc} \)) of 5.0 mA/cm², an open circuit voltage (\( V_{oc} \)) of 0.52 V, and a fill factor (FF) of 34.3%. In comparison with PCPDTBT-based devices, the \( V_{oc} \) of the PCPDTBSe-based device is 0.1 V lower.11 It is known that in heterojunction PSC devices, \( V_{oc} \) is determined by the difference between the HOMO level of the electron donor material and the LUMO level of the electron acceptor material.7 As mentioned above, the HOMO level of PCPDTBSe is 0.1 V lower than that of PCPDTBT, which should be the main reason for the lower \( V_{oc} \) of the PCPDTBSe-based devices.

Photoluminescence (PL) quenching provides direct evidence for exciton dissociation, and thus efficient PL quenching is necessary to obtain efficient organic solar cells. PL emission spectra of the HSe film and HSe:PCBM blend film are shown in Figure 5. In order to make clear comparison, these two kinds of films in PL testing were prepared by the same conditions as in PSC device fabrications. It can be seen that the pure polymer film exhibited a PL emission peak at around 830 nm under excitation of 750 nm, but PL of the polymer was quenched thoroughly in the HSe:PCBM blend film, which indicated that efficient PL quenching took place in the blend film.

The absorption spectrum of the PCPDTBSe:PC70BM blend film prepared under the same conditions as those described in the device fabrication section is shown in Figure 6. The IPCE curve of the PSC device is also plotted in the figure for comparison. It is apparent that although the response range of the device is very broad, covering from 300 to 1000 nm, the external quantum efficiency (EQE) of the device is lower than 20% within the whole absorption range. The low EQE of the device should be due to the low absorbance value of the blend film. It is known that the absorption in the long-wavelength region is contributed by the polymer, and the absorption in the short-wavelength region is mainly from PC70BM; however, the peak value of the absorbance in the long-wavelength region is only 0.1, which means that only a small part of sunlight is

![Figure 2](image-url)  
Figure 2. Cyclic voltammograms of PCPDTBSe and PCPDTBT films on a platinum electrode in 0.1 mol/L Bu4NPF6, CH3CN solution.

![Figure 3](image-url)  
Figure 3. UV–vis absorption spectra of PCPDTBSe and PCPDTBT: (a) solution in THF and (b) film on quartz.
absorbed in the device. The relationship between the thickness of the active layer and the PCE was investigated by controlling the spin speed during the spin-coating process. We found that when the thickness is increased, the $J_{sc}$ decreased slightly, while the $V_{oc}$ and FF stayed about the same, and as a result, the PCE of the device decreased. This phenomenon indicates that photovoltaic performance of the PCPDTBSe:PC$_{70}$BM-based solar cell may be limited by the poor charge transport properties (hole mobility and electron mobility) of the blend film. Therefore, if the EQE of the device can be improved by increasing the thickness of the active layer without hampering charge separation and transport properties, the device performance could be improved significantly.

Carrier transport properties, including hole mobility and electron mobility, are important parameters for both material design and device fabrication. The space charge limited current (SCLC) method$^{18-20}$ was used to evaluate the hole and electron mobility of the PCPDTBSe:PC$_{70}$BM blend film. As measured by the SCLC method, the hole mobility and electron mobility of the blend film were calculated to be $2.5 \times 10^{-5}$ and $2.1 \times 10^{-4}$ cm$^2$/V s, respectively. Evidently, the electron mobility of the blend film is 1 order of magnitude higher than the hole mobility, resulting in an imbalance in the hole and electron transport in the blend film. This imbalance should be one of the reasons for the low FF value and limited performance of the device. For comparison, we also measured the charge-carrier mobility of the PCPDTBT:PC$_{70}$BM blend film fabricated with a solution of the same concentration and weight ratio as the PCPDTBSe-based blend. The SCLC hole and electron mobility were calculated to be $4.5 \times 10^{-4}$ and $7.0 \times 10^{-4}$ cm$^2$/V s, respectively. The more balanced hole and electron transport in the film and the higher hole mobility are likely factors for the higher efficiency achieved with the PCPDTBT-based device.

Hence, we have attempted to further increase the hole mobility of the PCPDTBSe-based blend to achieve charge-carrier balance by optimizing the weight ratio of the PCPDTBSe:PC$_{70}$BM. It was speculated that since the holes are conducted through the polymer phase, increasing the polymer content in the polymer/PC$_{70}$BM blend would improve the hole transport property. Unfortunately, we found that a change in the weight ratio did not directly affect the electron and hole mobility values significantly. Blend films with weight ratios of 1:2, 1:3, and 1:4, which are optimized to the best individual thicknesses, all show a hole mobility on the order of $10^{-5}$ cm$^2$/V s and an electron mobility on the order of $10^{-4}$ cm$^2$/V s. It should be noted that the optimal weight ratio for the PCPDTBSe:PC$_{70}$BM blend was determined to be 1:3, which is the same as that for the PCPDTBT:PC$_{70}$BM system. It is likely that the higher performance of the 1:3 weight ratio blend arises from a more optimal morphology. A summary of the device performance, as well as the charge-carrier mobility values for the optimized devices with different weight ratios, is listed in Table 2.

Evidently, other methods for optimizing the hole mobility need to be considered. One method that can be utilized to directly modify the hole mobility is through polymer structural side chain design and modification. It has also been shown that certain processing additives help in improving device performance in bulk heterojunction systems through morphology control and

<table>
<thead>
<tr>
<th>condition</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>PCE (%)</th>
<th>FF (%)</th>
<th>thickness (Å)</th>
<th>hole mobility (cm$^2$/V s)</th>
<th>electron mobility (cm$^2$/V s)</th>
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<tr>
<td>1:2</td>
<td>0.52</td>
<td>4.1</td>
<td>0.74</td>
<td>34.5</td>
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<td>0.52</td>
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<td>0.89</td>
<td>34.3</td>
<td>600</td>
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<td>$2.1 \times 10^{-4}$</td>
</tr>
<tr>
<td>1:4</td>
<td>0.50</td>
<td>4.0</td>
<td>0.64</td>
<td>32.2</td>
<td>700</td>
<td>$3.6 \times 10^{-5}$</td>
<td>$1.8 \times 10^{-4}$</td>
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Low Band Gap Polymer PCPDTBSe

Conclusion

A cyclopenta[2,1-b;3,4-b’]dithiophene-based low band gap polymer, PCPDTBSe, was designed and synthesized. The band gap of PCPDTBSe is 1.35 eV, which is 0.1 eV lower than that of PCPDTBT, and its HOMO level is calculated to be −4.0 eV. In the visible range, the PCPDTBSe film exhibits weaker absorption than that of PCPDTBT, making it a promising candidate as a low band gap material in tandem cells. PSC devices were fabricated and characterized to investigate the photovoltaic properties of PCPDTBSe. Under AM 1.5 G 100 mW/cm² illumination, a typical PCE of 0.89% was recorded, with an $J_{sc}$ of 5.0 mA/cm², a $V_{oc}$ of 0.52 V, and a FF of 34.3%. The IPCE spectrum indicates that the response range reaches wavelengths up to 1000 nm. Based on the results of the absorption spectrum and carrier mobility of the PCPDTBSe:PC$_{70}$BM blend, we found that the photovoltaic performance of the PCPDTBSe-based PSC device is limited by the weak absorbance of the active layer and an imbalance in the hole and electron transport of the active layer. Since the side chain of the polymer and the morphology of the PCPDTBSe:PC$_{70}$BM blend can be optimized further to yield even better performance, the polymer PCPDTBSe should be a promising low band gap material for applications in polymer solar cells.

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References and Notes