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Low-band gap poly(di-2-thienylthienopyrazine): fullerene solar cells

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Two side-chain substituted poly(di-2-thienylthienopyrazine) (PBEHTT and PTBEHT) are used as electron donor together with phenyl-C_{61} butyric acid methyl ester (PCBM) as an electron acceptor in low-band gap bulk heterojunction polymer solar cells. These low-band gap polymers absorb light up to ∼1 μm. Under simulated AM1.5 conditions PTBEHT:PCBM devices provide a short circuit current of $J_{sc}=3.5$ mA/cm$^2$, an open circuit voltage of $V_{oc}=0.56$ V, and a power conversion efficiency of $η=1.1\%$. Photoresponse up to 1 μm has been observed with external quantum efficiencies exceeding 15% in the 700–900 nm region. © 2006 American Institute of Physics.

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Presently, one of the limiting parameters for photovoltaic energy conversion in polymer solar cells is the mismatch of the absorption spectrum of the active layer and the solar emission. The optical band gap of poly(p-phenylene vinylene)s and polythiophenes typically used in bulk-heterojunction cells is not optimized with respect to the solar spectrum, and light with photon energies below 1.9 eV is not absorbed. Low-band gap polymers allow for absorbing more photons from the solar photon flux that peaks around 700 nm (1.77 eV) and improve the energy conversion efficiency of the solar cells. Reports on low-band gap polymers are emerging recently.

In designing low-band gap polymers for bulk heterojunction solar cells various aspects need to be considered. For a conventional p-n junction solar cell with a single band gap ($E_g$), a reduction of $E_g$ results in an increased absorption of light but decreased open circuit voltage ($V_{oc}$). As a consequence, the optimum band gap of such devices is at ∼1.35 eV. In polymer solar cells $V_{oc}$ is related to the energy difference between the oxidation potential (or highest occupied molecular energy level) of the donor and the reduction potential (or lowest unoccupied molecular energy level) of the acceptor. Reducing the band gap of the donor by decreasing the oxidation potential may therefore reduce the open circuit voltage. On the other hand, a lowering of the band gap by decreasing the reduction potential of the donor will leave $V_{oc}$ unaffected but decreases the driving force of the donor to transfer an electron in the excited state to the acceptor.

A reduction of the band gap of conjugated polymers can be accomplished, by minimizing the bond length alternation or by reducing the energy difference between aromatic and quinoid canonical resonance structures. One versatile strategy to achieve low-band gap conjugated polymers involves the alternation of electron-rich and electron-deficient units in a conjugated polymer chain. In this letter, we report two low-band gap polymers [Fig. 1(a)] that utilize this principle to achieve absorption in the 600–1000 nm region. We use 2,3-diphenyl-5,7-di-2-thienyl-thieno[3,4-b]pyrazine monomers that carry four 2-ethylhexyloxy side chains to ensure solubility, either on the main chain in PBEHTT or on the outer phenyl rings in PTBEHT. In thin films the optical band gap of PBEHTT and PTBEHT is 1.28 and 1.20 eV, respectively. When used as an electron donor in combination with phenyl-C_{61} butyric acid methyl ester (PCBM) as an acceptor, bulk heterojunction solar cells based on PBEHTT and PTBEHT exhibit a photovoltaic response up to 1 μm.

PBEHTT and PTBEHT were synthesized from the corresponding dibrominated monomers via a condensation polymerization using bis(1,5-cyclooctadiene)nickel(0) [Ni(COD)$_2$]. Both polymers were extensively purified by removing Ni with EDTA disodium salt, Soxhlet extraction using different solvents, and finally a BioBeads GPC column to remove the low molecular weight fraction. The molecular weights as determined with size exclusion chromatography

![Fig. 1. (a) Chemical structures of poly[5,7-bis[3,4-di(2-ethylhexyloxy)-2-thienyl]-2,3-diphenyl-thieno[3,4-b]pyrazine] (PBEHTT) and poly[5,7-di-2-thienyl-2,3-bis(3,5-di(2-ethylhexyloxy)phenyl)-thieno[3,4-b]pyrazine] (PTBEHT). (b) Optical absorption spectra of PBEHTT and PTBEHT in solution and as thin films on glass.](image-url)
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Polymers are soluble in most common organic solvents (e.g., THF, chloroform, toluene, chlorobenzene) and can be easily processed into thin films.

The UV/vis spectra of PBEHTT and PTBEHT in solution reveal an optical absorption extending into the near-infrared [Fig. 1(b)] with onsets at 915 and 960 nm, respectively. In the solid state the spectra exhibit an additional red shift, resulting in onsets at 965 nm (1.28 eV) and 1034 nm (1.20 eV) [Fig. 1(b)]. The slightly lower optical band gap of PTBEHT indicates improved conjugation and is most likely caused by a more coplanar structure of the main chain in PTBEHT due to the absence of bulky substituents compared to PBEHTT.

The oxidation and reduction potentials (Table I) were determined by cyclic voltammetry in solution with 0.1 M NBu4PF6 as supporting electrolyte, using an Ag/AgCl reference electrode and ferrocene as internal standard. The electron donating 2-ethylhexyloxy side chains attached to the polymer backbone decrease the oxidation potential of PBEHTT by 0.18 V compared to PTBEHT. The electrochemical band gap, taken as the difference between the onsets of oxidation and reduction potentials, amounts to 1.46 eV for both polymers and is slightly larger than the optical band gap. Despite their high molecular weights, both polymers are soluble in most common organic solvents (e.g., THF, chloroform, toluene, chlorobenzene) and can be easily processed into thin films.

**TABLE I.** Redox potentials\(^a\) and band gaps of PBEHTT, PTBEHT, and PCBM.

<table>
<thead>
<tr>
<th></th>
<th>(E_{\text{ox}}) (V)</th>
<th>(E_{\text{red}}) (V)</th>
<th>(E_i) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBEHTT</td>
<td>-0.19</td>
<td>-1.65</td>
<td>1.28</td>
</tr>
<tr>
<td>PTBEHT</td>
<td>-0.01</td>
<td>-1.47</td>
<td>1.20</td>
</tr>
<tr>
<td>PCBM</td>
<td>n.d.</td>
<td>-1.02</td>
<td>1.76</td>
</tr>
</tbody>
</table>

\(^a\) Recorded in THF for PBEHTT and PCBM; and in DCM/ODCB for PTBEHT.

Polymer:PCBM gave the best performance in terms of power conversion efficiency.

ITO/PEDOT:PSS/PBEHTT:PCBM/LiF/AI devices exhibit a good diode behavior in the dark with a rectification ratio of 1000 (at ±2 V). Under 75 mW/cm\(^2\) white light illumination, the cells give \(V_{\text{oc}}=0.39\) V, \(J_{\text{sc}}=1.5\) mA/cm\(^2\) \([J_{\text{sc}}(AM1.5)=1.3\) mA/cm\(^2\)]\(^\text{15}\) and a fill factor FF=0.57, providing an estimated energy conversion efficiency of \(\eta=0.29\%\) (Ref. 18) [Fig. 3(a)]. The rather low voltage of the PBEHTT:PCBM devices can be attributed to the low oxidation potential of the polymer. If the difference between oxidation and reduction potentials of PBEHTT and PCBM (0.83 V) is corrected for an expected voltage loss of 0.2 V at each electrode to account for band bending,\(^\text{12}\) the result (0.43 V) is in accordance with the observed \(V_{\text{oc}}=0.39\) V.

ITO/PEDOT:PSS/PTBEHT:PCBM/LiF/AI devices with 80 nm thick active layers spin coated from chlorobenzene. ITO/PEDOT:PSS/PBEHTT:PCBM/LiF/AI devices exhibit a good diode behavior in the dark with a rectification ratio of 1000 (at ±2 V). Under 75 mW/cm\(^2\) white light illumination, the cells give \(V_{\text{oc}}=0.56\) V, \(J_{\text{sc}}=3.1\) mA/cm\(^2\) \([J_{\text{sc}}(AM1.5)=3.5\) mA/cm\(^2\)]\(^\text{17}\) and FF=0.58 under white light illumination (75 mW/cm\(^2\)) [Fig. 3(a)]. The improved \(V_{\text{oc}}\) arises from to the higher oxidation potential of PTBEHT and \(V_{\text{oc}}\) is close to value that can be derived from the redox levels after correction for contact losses (0.61 V). Interestingly, \(V_{\text{oc}}=0.56\) V of PTBEHT:PCBM cells is close to the value observed in state-of-the-art poly(3-hexylthiophene):PCBM solar cells (\(V_{\text{oc}}=0.61–0.63\) V).\(^\text{4,5}\)

This demonstrates that the 0.7 eV reduction in optical band gap (i.e., from 1.9 eV for P3HT to 1.2 eV for PTBEHT) results in very minor (<0.1 V) loss in open circuit voltage. The improved \(J_{\text{sc}}\) of PTBEHT:PCBM compared to PBEHT-T:PCBM is somewhat surprising because the driving force for photoinduced electron transfer to PCBM is small [the energy of the charge separated state (~1.01 eV) is close to the band gap energy (1.20 eV)]. Tapping mode atomic force microscopy (AFM) on both blends [Fig. 3(b)] revealed a rough surface and coarse phase separation for PBEHT-T:PCBM layers compared to a rather smooth surface and more intimate mixing for PTBEHT:PCBM. The improved miscibility of PTBEHT and PCBM compared to PBEHT-T:PCBM gave the best performance in terms of power conversion efficiency.
photocurrent $J_{sc} = 3.5$ mA/cm$^2$ [12]. However, reduced fill factor FF = 0.41, resulting in a similar overall efficiency ($\eta = 1.1\%$). Although the active layer of these double-layer devices (140 nm) is thicker, layer thickness itself seems not the primary cause of the enhanced photocurrent because films with thicknesses varying from 60 to 140 nm made in a single step all gave rather similar $J_{sc}$, $V_{oc}$, and FF. We are presently studying this remarkable effect in more detail.

In conclusion, two high molecular weight low-band gap polymers, PBEHTT and PTBEHT, have been synthesized that show near infrared photovoltaic response in bulk heterojunction solar cells with PCBM as acceptor. For PTBEHT:PCBM blends the spectral response extents to 1 $\mu$m, with EQEs exceeding 15% in the 700–900 nm region. The best devices have an estimated conversion efficiency of 1.1% under simulated solar light, which is presently unsurpassed for low-band gap polymer solar cells. Although the overall performance is less than those of state-of-the-art P3HT:PCBM devices ($\eta = 4–5\%$), the lower performance is not due to a loss in $V_{oc}$. This suggests that further improvements for low-band gap polymers must be found in materials with high absorption coefficients and with improved charge generation and transport properties.

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17. Short circuit current densities $J_{sc}$ (AM1.5) were determined by convoluting the spectral response with the AM1.5 spectrum (100 mW/cm$^2$).
18. Efficiencies were calculated using the $V_{oc}$ and FF from the $J-V$ measurements and $J_{sc}(AM1.5)$.  

FIG. 3. (Color online) (a) $J-V$ measurement of PBEHTT:PCBM (1:4 weight) (squares) and PTBEHT:PCBM (1:4 weight) (circles) solar cells measured in the dark (closed symbols) and under illumination (75 mW/cm$^2$) with a tungsten halogen lamp (open circles). (b) Tapping mode AFM height images of films of PBEHTT:PCBM from chlorobenzene (left, $z$ scale 50 nm) and of PTBEHT:PCBM (right, $z$ scale 8 nm) from chloroform. (c) EQE of the devices (open symbols) shown in panel (a) and of a doubled layer PTBEHT:PCBM (solid circles) device.

and PCBM explains, at least in part, the increased photocurrent seen in Fig. 3(a) taking into account the nanometer range exciton diffusion lengths in conjugated polymers.

The spectrally resolved external quantum efficiency (EQE) reveals a photoresponse extending from the UV throughout the visible region into the near infrared [Fig. 3(c)]. For both polymers a maximum in the EQE occurs at 460 nm and broad plateau exists between 700 and 900 nm. The increased photocurrent for PTBEHT based devices is also reflected in a higher EQE over the entire wavelength region. Interestingly, devices with active layers prepared by depositing an additional quantity of the mixed PTBEHT:PCBM solution during spin coating on top of the drying layer exhibited a much higher EQE in the near-infrared (NIR) region. The EQE of these “doubled layer” devices exceeds 15% in the 700–900 nm region. The $J-V$ characteristics of the doubled layer devices gave a higher