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A regioregular terpolymer comprising two electron-deficient and one electron-rich unit for ultra small band gap solar cells†

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A regioregular terpolymer that combines electron-deficient diketopyrrolopyrole and benzothiadiazole units with an electron-rich dithienopyrrole unit is presented. In solar cells, the terpolymer affords an open circuit voltage of 0.52 V and a power conversion efficiency of 3.7% with a spectral response up to 1050 nm.

Bulk heterojunction polymer solar cells (PSCs) with conjugated polymers as electron donor and fullerene derivatives such as [6,6]-phenyl-C61-butyric acid methyl ester ([70]PCBM) as electron acceptor have significantly progressed in the last decade and now reach power conversion efficiencies (PCEs) above 10% in single junction solar cells.1,3 The efficiencies have been further increased to 11-12% via tandem and triple junction device architectures, in which two or three photoactive layers with complementary absorption spectra are stacked and connected in series. By applying different conjugated polymers that absorb light from the visible light to the near-infrared region above 1000 nm, the conversion efficiencies of triple junction solar cells may achieve 15-20%.6 To reach this ambitious goal, it will be important to develop efficient conjugated polymers that absorb up to 1000 nm and beyond.

Conjugated polymers with tailored optical band gaps (E_g) can be obtained using electron donating and electron deficient units alternating along the main chain. In general stronger electron donors and stronger acceptors reduce the optical band gap. Using this design motif and by employing suitable side chains, the energy levels, solubility, aggregation and crystallinity of the polymers can be tuned. Alternating conjugated polymers have already reached high performance in polymer solar cells, especially for wide (E_g > 1.7 eV) and medium (1.7 eV > E_g > 1.4 eV) optical band gaps with PCEs above 9%.13 A few small band gap conjugated polymers with E_g close to 1.4 eV provide ≥8% PCE.7,9 For E_g below 1.25 eV the most efficient cells reach 5.3% PCE.10 In many of the successful materials a significant photon energy loss between E_g and open circuit voltage (Voc) is incurred, E_loss = E_g - qVoc. E_loss provides a driving force for photoinduced charge generation and often shortens the circuit current density (J_sc). When the optical band gap is reduced, charge generation is usually becomes negligible when E_loss becomes less than 0.6 eV.11 This problem becomes especially important when the absorption of conjugated polymers extends above 1000 nm where the optical band gap becomes less than 1.2 eV. To maintain a high quantum efficiency for charge generation, the Voc, which is controlled by the energy difference between the HOMO of the donor and the LUMO of the acceptor, must be designed to be less than 0.6 V. However, a too low Voc would quickly lead to an insignificant PCE. Hence, conjugated polymers with a very small band gap require a judicious design in terms of energy levels to be applicable in PSCs.

Several conjugated polymers with absorption beyond 1000 nm have been reported, often using strong electron deficient units such as thienoisoindigo, thiadiazoloquinoxaline, bisbenzothiadiazole, pyrazinoquinoxaline or diketopyrrolopyrole (DPP).16,17 When applied in polymer solar cells PCEs up to 5.3% have been obtained.10 Especially, PDPP2T-DTP (Fig. 1a) with DPP as electron acceptor and dithienopyrrole (DTP) as strong electron donor affords E_g = 1.23 eV19 and provides J_sc > 20 mA/cm².10 The Voc of cells based on this polymer is, however, relatively low with 0.43 V, resulting in E_loss = 0.80 eV. In order to reduce E_loss and enhance Voc, we introduce the use of two electron deficient units, DPP and benzothiadiazole (BT), in combination with DTP as electron donor. The new ultra low band gap polymer, PDPP2T-BT-co-DTP (Fig. 1c) provides a significantly higher Voc of 0.52 eV and PCE of 3.7% with a reduced optical band gap of 1.19 eV in polymer solar cells.

Fig. 1 The DPP polymers with (a) dithienopyrrole (DTP), (b) benzothiadiazole (BT) and (c) both DTP and BT.

PDPP2T-DTP10 and PDPP2T-BT-co-DTP were synthesized following previously reported procedures. The regioregular alternating copolymer PDPP2T-BT-co-DTP was synthesized using the
dibromo-monomer of T-DPP-BT-T-DPP-T and the bisstannyl-DTP monomer via Stille polymerization (Scheme S1, ESIf). The conditions applied in the polymerization reaction, toluene/DMF 10:1 (v/v) as solvent and Pd(dba)2/PPh3, 1:4 (mol/mol) as catalyst, were chosen to reduce homo coupling defects and achieve a high molecular weight.21 The viscous gel formed during polymerization indicates a high molecular weight and required that the work-up required the use of 1,1,2,2-tetrachloroethane at 140 °C. It was not possible to measure the molecular weight by gel permeation chromatography (GPC) in o-dichlorobenzene (o-DCB) because the polymer seems to adhere or decompose on the column. The same problem was previously encountered for PDDP2T-DTP.20 The thermal stability of PDDP2T-BT-co-DTP is somewhat less than that of PDDP2T-BT and PDDP2T-DTP (Fig. S1, ESIf). The strong electron donating DTP unit makes polymers based on DTP susceptible to oxidation in air, and processing of devices was performed under inert atmosphere.10 All three polymers absorb in the near-infrared region with onsets above 1000 nm (Fig. 2a). The absorption in thin films is slightly red-shifted compared to chloroform solution (Fig. S2, ESIf). PDDP2T-BT has a lower band gap (1.19 eV) than PDDP2T-DTP (Eg = 1.23 eV). While we anticipated that the combination of two acceptors (DPP and BT) would increase the electron withdrawing character and could further reduce the band gap, the terpolymer PDDP2T-BT-co-DTP, that combines DPP, BT, and DTP also has Eg = 1.19 eV.

Fig. 2 (a) Optical absorption spectra of the polymers in solid state films and (b) Cyclic voltammograms of the polymers thin films on ITO substrates.

Table 1 Optical and electrochemical properties of the polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>ECHA (eV)</th>
<th>Eg (eV)</th>
<th>ELUMO (eV)</th>
<th>EHOMO (eV)</th>
<th>Eg (V)</th>
<th>ΔEHL (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDDP2T-BT</td>
<td>2.12</td>
<td>1.19</td>
<td>-0.01</td>
<td>-5.55</td>
<td>1.54</td>
<td>0.15</td>
</tr>
<tr>
<td>PDDP2T-DTP</td>
<td>2.12</td>
<td>1.23</td>
<td>-3.68</td>
<td>-5.26</td>
<td>1.58</td>
<td>0.48</td>
</tr>
<tr>
<td>PDDP2T-BT-co-DTP</td>
<td>2.12</td>
<td>1.23</td>
<td>-3.92</td>
<td>-5.35</td>
<td>1.43</td>
<td>0.24</td>
</tr>
</tbody>
</table>

* Determined using a work function value of –5.23 eV for Fe/Fe+.

Importantly, however, the introduction of two acceptors allows to effectively tune the frontier orbital energy levels.22,23 Cyclic voltammetry (Fig. 2b and Table 1) reveals that as a consequence of incorporating two electron deficient units (DPP and BT), the PDDP2T-BT copolymer has deep HOMO and LUMO levels (–5.55 eV and –4.01 eV). Hence, the LUMO-LUMO offset (∆EHL) between PDDP2T-BT and [70]PCBM is only 0.15 eV and significantly less than the ~0.3 eV threshold for charge separation. This problem often occurs in very small band gap conjugated polymers.24,25 With one electron deficient (DPP) and one electron rich unit (DTP), the PDDP2T-DTP copolymer exhibits significantly less negative HOMO and LUMO levels (–5.26 eV and –3.68 eV) to give ∆EHL = 0.48 eV. The new terpolymer PDDP2T-BT-co-DTP has the HOMO and LUMO in between those of the two copolymers PDDP2T-BT and PDDP2T-DTP, so that ∆EHL = 0.24 eV. The low lying HOMO level will help to achieve a higher Voc than that of PDDP2T-DTP, while the higher Voc that of PDDP2T-BT is beneficial for the efficiency of photoinduced charge separation.

The three polymers were applied in polymer solar cells with a transparent ITO/poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS) bottom contact for hole collection and LiF/Al top contact for electron collection. The photoactive layers, in which the polymers were blended with [70]PCBM, were carefully optimized for the donor to acceptor weight ratio, solvent, co-solvent, and thickness. In general, the optimized donor-acceptor ratio is 1:2 (w/w) and the optimal thickness was around 110 nm, when spin coating from chloroform solution. For PDDP2T-BT 10% o-DCB as co-solvent gave the best performance. For PDDP2T-DTP and PDDP2T-BT-co-DTP the best co-solvents concentrations are 5% o-DCB and 3% 1-chloronaphthalene (1-CN), respectively. The J-V characteristics and external quantum efficiencies (EQEs) of the optimized devices are depicted in Fig. 3 and the device parameters are summarized in Table 2.

Fig. 3 (a) J-V characteristics in dark (dashed lines) and under white light illumination (solid lines) of optimized solar cells of the polymers with [70]PCBM. (b) EQE of the same devices.

Table 2 Solar cell parameters of optimized solar cells of the DPP polymers with [70]PCBM.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Jsc (mA cm−2)</th>
<th>Voc (V)</th>
<th>FF</th>
<th>PCE (%)</th>
<th>Eloss (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDDP2T-BT</td>
<td>2.8</td>
<td>0.66</td>
<td>0.66</td>
<td>1.2</td>
<td>0.53</td>
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<tr>
<td>PDDP2T-DTP</td>
<td>16.6</td>
<td>0.43</td>
<td>0.54</td>
<td>3.9</td>
<td>0.80</td>
</tr>
<tr>
<td>PDDP2T-BT-co-DTP</td>
<td>12.2</td>
<td>0.52</td>
<td>0.58</td>
<td>3.7</td>
<td>0.67</td>
</tr>
</tbody>
</table>

As expected from the low ∆EHL the PDDP2T-BT copolymer gives a low PCE of 1.2%, mainly due to a low short circuit current density (Jsc = 2.8 mA cm−2). The cells have a high Voc of 0.66 V at this low band gap (1.19 eV). The photon energy loss Eloss equals 0.53 eV and is below the threshold of 0.6 eV for efficient charge transfer,13 rationalizing the low Jsc. In contrast, photovoltaic devices based on the copolymer PDDP2T-DTP give a high Jsc of 16.6 mA cm−2 and PCE of 3.9%, but a relatively low Voc of 0.43 V as consequence of the higher lying HOMO. The low Voc increases the photon energy loss to Eloss = 0.80 eV. The new terpolymer PDDP2T-BT-co-DTP gives Voc = 0.52 V, i.e. in between the Voc’s obtained with the two copolymers, but a somewhat lower Jsc (12.2 mA cm−2) and PCE of 3.7%. Here Eloss is 0.67 eV. The differences in photocurrent are also reflected in the EQE spectra (Fig. 3b). In PDDP2T-BT-[70]PCBM cells the contribution of light absorbed by the polymer in the 700–1050 nm range is 24% and in PDDP2T-DTP-[70]PCBM cells this contribution is 40%.

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nm region is negligible and photocurrent is only created via excitation of [70]PCBM. In contrast, a broad spectral response from 350 to 1050 nm, covering the absorption spectra of fullerene and polymer is found for PDPP2T-BT-co-DTP-[70]PCBM blends. Unfortunately, the PDPP2T-BT-co-DTP terpolymer provides a relatively low EQE (maximizing at 0.32) compared to that of the PDPP2T-DTP copolymer (maximizing at 0.53).

As previously reported, a lower energy loss decreases the driving force for electron transfer and correlates with a lower EQE.7 Hence, the lower EQE of the terpolymer PDPP2T-BT-co-DTP is possibly related to the reduced $\Delta E_{LL}$ and $E_{loss}$. However, the energy loss of the terpolymer is 0.67 eV, i.e. above the threshold of 0.6 eV.11 Actually, another DPP-polymer, PDPP3T, where $E_{loss} = 0.65$ eV gave a maximum EQE of 0.50,7 which is significantly higher than the 0.32 of the terpolymer. Therefore other effects than $E_{loss}$ likely contribute to the low EQE.

First, TEM reveals that the morphology of the PDPP2T-BT-co-DTP-[70]PCBM blends consists of semicrystalline polymer fibrils (Fig. 4). The crystallinity can be readily seen from the lattice fringes in Fig. 4b. The width of these semicrystalline fibrils exceeds 10 nm, commonly considered as the maximum exciton diffusion length. We have shown recently for a range of DPP-polymer that the fibril width anti-correlates with the EQE and that exciton loss via intrinsic decay may contribute to a low EQE.23

Second, localization of excitons on the T-DPP-T-BT-T-DPP-T segments may occur. Because PDPP2T-BT has a smaller band gap than PDPP2T-DTP, excitons may prefer T-DPP-T-BT-T-DPP-T segments. Excitons on such segments may have a lower tendency to transfer an electron to the fullerene, as suggested by the fact that the PDPP2T-BT copolymer is unable to create charges efficiently. This explanation is supported by our recent work on the detrimental effect of low-LUMO chain segments on the charge generation efficiency.21

![Fig. 4 Bright field TEM images of the optimized PDPP2T-BTD-co-DTP-[70]PCBM blend films. Scale bars: (a) 200 nm and (b) 50 nm.](image)

In conclusion, a new conjugated terpolymer with an ultra small band gap, $E_g = 1.19$ eV, was designed and applied in polymer solar cells. By incorporating two electron-deficient and one electron-rich unit into the conjugated backbone the frontier energy levels were tailored to maximize $V_{oc}$ and $J_{sc}$. The terpolymer provided a relatively high $V_{oc}$ (0.52 V) and PCE (3.7%) with a photoresponse up to 1050 nm, despite a moderate EQE. The study shows that by extending the push-pull approach and incorporating more units than single electron rich and electron poor units is viable way to create semiconducting polymers with finely tuned energy levels.

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Notes and references


