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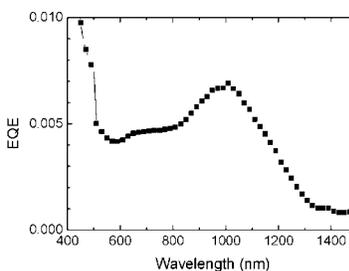
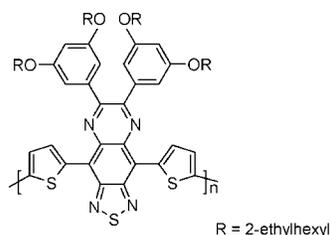
Photovoltaic Performance of an Ultrasmall Band Gap Polymer

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ABSTRACT



A conjugated polymer (PBTTQ) that consists of alternating electron-rich bithiophene and electron-deficient thiadiazoloquinoxaline units was synthesized via Yamamoto polymerization with $\text{Ni}(\text{cod})_2$ and provides a band gap of 0.94 eV. This represents one of the smallest band gaps obtained for a soluble conjugated polymer. When applied in a bulk heterojunction solar cell together with [84]PCBM as the electron acceptor, the polymer affords a response up to 1.3 μm .

Recently various small band gap polymers have been synthesized for application in polymer solar cells.^{1–10} The motivation for developing polymers with an optical absorption that extends into the near-infrared is to exploit the low

energy photons available in the solar spectrum. Traditionally polymers like poly(*p*-phenylene vinylene) and poly(3-hexylthiophene) (P3HT) have been used in organic solar cells^{11,12} but their optical band gaps close to 2 eV significantly limit the fraction of photons that can be absorbed from sunlight. A proven strategy to reduce the band gap of these π -conjugated materials and possibly enhance the photocurrent is to incorporate electron-rich and electron-deficient units in an alternating fashion in a polymer chain.^{13–15} Virtually all

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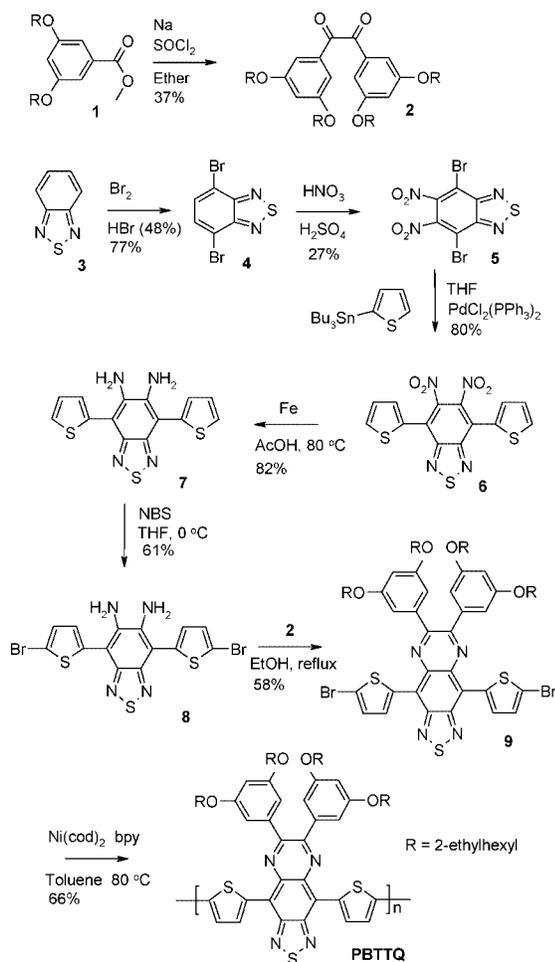
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small band gap polymers for use in solar cells employ this strategy to reach band gaps in the 1.2–1.6 eV range.^{1–10} For a copolymer of cyclopentadithiophene and benzothiadiazole (PCPDTBT) that has $E_g = 1.4$ eV, the energy conversion efficiency of 5.5% is among the highest reported for polymer solar cells.^{6,8} A further attractive approach to improve overall efficiencies involves stacking multiple solar cells that cover different parts of the solar spectrum.^{16–18} Hadipour et al. were able to cover a large part of the solar spectrum by using high and low band gap solution processable polymers.¹⁸ An efficiency of 6.5% was reported by Kim et al. when PCPDTBT was applied in tandem solar cells together with P3HT.¹⁹ Especially for multijunction polymer solar cells it is interesting to develop polymers that absorb near-infrared (NIR) light.^{5,10}

In our search for such attractive NIR materials we report here the synthesis of an ultrasmall band gap polymer (PBTTQ, Scheme 1) via Yamamoto coupling using $\text{Ni}(\text{cod})_2$. The polymer is based on alternating electron-rich bithiophene and electron-deficient thiadiazoloquinoxaline units. The optical and electrochemical properties of PBTTQ are described and the performance in solar cells is evaluated.

Scheme 1. Synthesis of PBTTQ



The synthesis of the PBTTQ is depicted in Scheme 1. A Williamson ether synthesis of methyl-3,5-dihydroxybenzoate and 1-bromo-2-ethylhexane afforded **1** in 92% yield, which was reacted in a sodium-induced acyloin coupling to α -diketone **2** in moderate yield. Next, bromination of 2,1,3-benzothiadiazole (**3**), with bromine in aqueous HBr, gave **4** as white needles after recrystallization from methanol. Nitration of **4** in fuming nitric acid and concentrated sulfuric acid resulted in **5** that was reacted with 2-tributylstannylthiophene to **6** in a Stille coupling with $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ as a catalyst. Reduction of **6** by iron dust in acetic acid resulted in diamine **7**. At this point in the route, the bromine atoms must be incorporated to allow a polymerization of **9** via Yamamoto coupling. We found that, after condensation coupling of **7** with **2**, the α -position of the thiophene rings became considerably less susceptible toward electrophilic aromatic substitution. The thiadiazoloquinoxaline unit is strongly electron deficient and reduces the reactivity of the thiophenes with respect to bromination. Diamine **7** could easily be halogenated by applying *N*-bromosuccinimide (NBS) in THF and afforded **8** in 61% yield. The electron-donating character of the amine groups compensates the electron-withdrawing nature of the thiadiazole ring and facilitates the electrophilic substitution. The condensation coupling of **8** with α -diketone **2** did result in some Br-cleavage, but purification by column chromatography gave pure **9**. Polymerization through Yamamoto coupling with bis(1,5-cyclooctadiene)nickel(0) ($\text{Ni}(\text{cod})_2$) resulted in a green/yellow polymer PBTTQ with $M_w = 58500$ g/mol and $M_n = 9300$ g/mol.

Incorporating the electron-deficient thiadiazoloquinoxaline unit in an alternating fashion with bithiophene results in a strong absorption in the near-infrared (Figure 1a). Dissolved in *o*-dichlorobenzene, the wavelength of maximum absorption (λ_{max}) is 1165 nm with a shoulder at about 1020 nm. In solution, the optical band gap is 0.94 eV as determined from the onset of absorption. This represents one of the smallest band gaps obtained for soluble conjugated polymers,^{5,10} although for electrochemically prepared conjugated polymer films gaps as small as 0.36 eV have been established.^{13f}

The small band gap of PBTTQ is also evidenced by the redox potentials determined by cyclic voltammetry. The onsets of the oxidation and reduction waves of PBTTQ in *o*-dichlorobenzene are at -0.09 and -1.06 V vs Fc/Fc^+ ,

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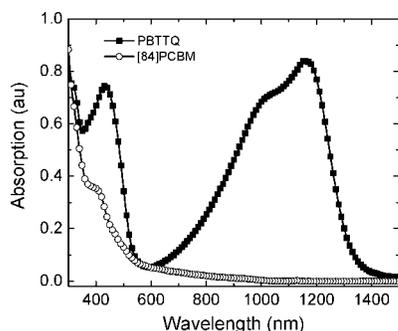


Figure 1. Absorption spectra of PBTTQ and [84]PCBM in *o*-dichlorobenzene.

respectively, and provide an electrochemical band gap of 0.97 eV, in excellent agreement with the band gap determined from optical absorption.

By incorporating the thiadiazoloquinoxaline unit the electron affinity increases and the reduction potential of PBTTQ is very close to the value of -1.07 V for [6,6]-phenyl- C_{61} -butyric acid methyl ester ([60]PCBM), which is commonly used as *n*-type material in bulk-heterojunction polymer solar cells. The negligible offset between the LUMO levels of PBTTQ and [60]PCBM likely precludes electron transfer between the two compounds in the excited state of PBTTQ because it is generally considered that a minimum offset of ~ 0.4 eV between the LUMO levels of electron donor and acceptor is required for efficient photoinduced charge transfer.^{20,21} The offset between HOMO levels is much larger: 0.7–0.8 eV when estimating the HOMO level of [60]PCBM at -1.07 eV plus its optical band gap of 1.75 eV.

Bulk heterojunction solar cells with a PBTTQ:[60]PCBM blend in a 1:4 ratio (by weight) as active layer (thickness 72 nm) were fabricated by spin coating the mixture from chlorobenzene (total concentration 25 mg/mL) on a ITO/PEDOT:PSS bottom electrode on a glass substrate and subsequently evaporating a LiF/Al top electrode. The current density–voltage (J – V) characteristics of this device under white light illumination are shown in Figure 2a and the relevant parameters are collected in Table 1. Both the open-circuit voltage ($V_{oc} = 0.37$ V) and short-circuit current ($J_{sc}(SR) = 0.45$ mA/cm²)²² are relatively low. The monochromatic external quantum efficiency (EQE) of the cell based on PBTTQ and [60]PCBM is virtually zero above 700 nm, which shows that only [60]PCBM contributes to the photocurrent. The selective photoresponse of [60]PCBM is tentatively explained by considering that charges can be

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(22) $J_{sc}(SR)$ represents the short circuit current estimated by convoluting the spectral response (SR) of the cell with the AM1.5G spectrum and generally provides a more accurate estimate of the performance of the cell under solar light than the $J_{sc}(WL)$ measured under white light conditions. The differences between the two are due to spectral mismatch of the white light source and the AM1.5 spectrum.

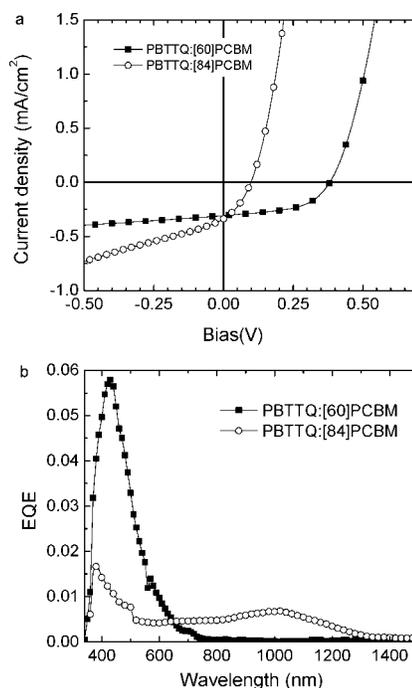


Figure 2. Performance of PBTTQ:[60]PCBM and PBTTQ:[84]PCBM solar cells: (a) J – V characteristics under 75 mW/cm² white light illumination and (b) monochromatic EQE. Device configuration: glass/ITO/PEDOT:PSS/PBTTQ:PCBM/LiF/Al.

generated by hole transfer from [60]PCBM to PBTTQ if this process is faster than the competing energy transfer to the small band gap polymer but not from photoexcited PBTTQ because of the negligible offset of its LUMO level with that of [60]PCBM.

[84]PCBM,²³ the C_{84} analogue of [60]PCBM, was used to increase the offsets between the LUMO levels of donor and acceptor and create more favorable conditions for photoinduced charge transfer from PBTTQ in the excited state. [84]PCBM has a reduction potential of -0.73 V vs Fc/Fc^+ and, hence, the electron affinity is 0.35 V larger than that of [60]PCBM.²³ This creates a driving force for photoinduced charge separation when combined with PBTTQ. The optical gap of [84]PCBM is at ~ 1.2 eV as determined from the onset of the spectrum in ODCB.

The photovoltaic performance of the cells based on PBTTQ:[84]PCBM as the active layer is shown in Figure 2a. The blend was spin coated from *o*-dichlorobenzene in a 1:4 ratio (by weight) at a total concentration of 36 mg/mL. The EQE (Figure 2b) shows that PBTTQ combined with

Table 1. Photovoltaic Performance of PBTTQ with PCBM Derivatives

	<i>d</i> (nm)	V_{oc} (V)	$J_{sc}(WL)$ (mA/cm ²)	$J_{sc}(SR)$ (mA/cm ²)	FF	η (%)
[60]PCBM	72	0.37	0.31	0.45	0.46	0.08
[84]PCBM	90	0.10	0.34	0.28	0.35	0.01

[84]PCBM gives rise to charge separation. The cell shows a photoresponse up to about 1.3 μm . This is one of the furthest red-shifted responses reported for polymer bulk heterojunction solar cells.^{5,10} The overall performance of the cell, however, is very modest and the EQE in the 800–1400 nm region does not exceed 0.01. Compared to the cell with [60]PCBM, the response in the visible region is reduced, possibly because hole transfer from [84]PCBM to PBTTQ is slower because of the reduced offsets of the HOMO levels. The low V_{oc} of 0.10 V is not unexpected. V_{oc} is often found to be ~ 0.4 eV less than the difference between the HOMO and LUMO levels of donor and acceptor, respectively and is expected at 0.24 V considering the levels of PBTTQ and [84]PCBM. The extra loss is due to the limited number of photogenerated charges that causes an incomplete quasi-Fermi level splitting.²⁴ The low charge density further reduces the energy difference (and hence V_{oc}) between the occupied hole and electron levels via the energetic disorder associated with these materials.

The morphology of the active layer in a bulk heterojunction solar cell is also important to the overall photovoltaic performance.²⁵ Spin coating from different solvents and thermal or solvent annealing affect charge separation efficiency and charge carrier mobility. For the present study, the use of chlorobenzene with [60]PCBM and *o*-dichlorobenzene with [84]PCBM proved to give the best results, consistent with earlier observations with [60]PCBM and [70]PCBM.²⁶

The morphology of the active layers was investigated by atomic force microscopy (AFM) (Figure 3). Both blends formed smooth and uniform films when spin coated from chlorobenzene and *o*-dichlorobenzene, respectively, which suggests that a relative intimate mixing of the two components exists that itself would not inhibit charge generation.

Several other causes, however, may contribute to the low photocurrent densities. Because of optical interference the absorption of light with wavelengths above 1 μm is limited in an active layer of about 100 nm thickness. Moreover at these long wavelengths the absorption by ITO and PEDOT:

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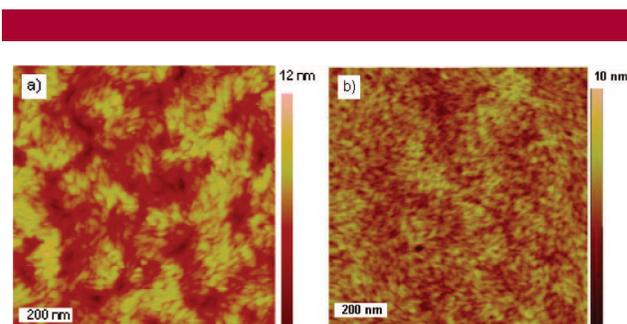


Figure 3. AFM height images of (a) PBTTQ:[60]PCBM spin coated from chlorobenzene and (b) PBTTQ:[84]PCBM spin coated from *o*-dichlorobenzene.

PSS is substantial. Nevertheless, for a similar NIR absorbing device Perzon et al. and Wen et al. have obtained higher EQEs up to 0.12 and 0.03 at ~ 950 nm, respectively.^{5,10} Therefore, specific properties of PBTTQ are expected to play an important role as well. Two factors can be noticed. First, the LUMO offset of ~ 0.33 eV might be just sufficient for photoinduced charge separation but does not ensure a quantitative formation of free charge carriers. Second, the low hole mobility ($\mu_{\text{hole}} = 1.7 \times 10^{-6}$ cm²/Vs in a FET) will reduce charge separation efficiency and enhance charge recombination.

In conclusion, by alternating bithiophene and thiadiazoloquinoline units along the chain PBTTQ has been obtained as a soluble polymer that exhibits an ultrasubtle band gap of ~ 0.94 eV. Together with a new fullerene derivative, [84]PCBM, as electron acceptor, the PBTTQ electron donor provides a photoresponse in bulk heterojunction solar cells up to 1.3 μm , one of the most red-shifted responses for this type of photovoltaic devices at present. The overall limited photocurrent, however, illustrates that creating NIR absorbing organic photoactive layers that provide efficient charge generation and collection remains a challenging task.

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Supporting Information Available: Detailed synthetic procedures and characterization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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