

Maximizing the open-circuit voltage of polymer : fullerene solar cells

Citation for published version (APA):

Bijleveld, J. C., Verstrijden, R. A. M., Wienk, M. M., & Janssen, R. A. J. (2010). Maximizing the open-circuit voltage of polymer : fullerene solar cells. *Applied Physics Letters*, 97(7), 073304-1/3. Article 073304. <https://doi.org/10.1063/1.3480598>

DOI:

[10.1063/1.3480598](https://doi.org/10.1063/1.3480598)

Document status and date:

Published: 01/01/2010

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Maximizing the open-circuit voltage of polymer: Fullerene solar cells

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(Received 23 May 2010; accepted 29 July 2010; published online 20 August 2010)

The open-circuit voltage (V_{oc}) of bulk heterojunction solar cells based on polymers and fullerene derivatives is limited to ~ 1.15 V by the optical band gap of the fullerene of ~ 1.75 eV and the required 0.6 eV offset for efficient charge generation. In practice this limit has not yet been reached. We present a semiconducting polymer that gives $V_{oc}=1.15$ V. To reach this value the surface of the hole collecting electrode is modified by UV-ozone, which increases the work function and creates an Ohmic contact. Under simulated AM1.5 conditions optimized cells provide a power conversion efficiency of $\sim 1\%$. © 2010 American Institute of Physics. [doi:10.1063/1.3480598]

Organic photovoltaic cells based on polymers hold the promise of low cost large area energy production. In recent years the focus in this area shifted toward designing and creating materials with decreased optical band gap energy (E_g) to enhance optical absorption in sunlight.¹ As a result of these efforts power conversion efficiencies (PCEs), up to 7.4% have been reported for bulk heterojunction solar cells comprising blends of a conjugated polymer and a fullerene derivative.²

Higher PCEs can be obtained with multi-junction devices such as tandem cells that employ sub cells with V_{oc} s that are more closely matched to E_g of the active layer to minimize photon energy losses.^{3–6} We have shown recently that in practice (295 K, solar light) the maximum attainable V_{oc} for single junction cells is limited by the optical gap energy via $eV_{oc} \leq E_g - 0.6$ eV.⁷ This limit is controlled by the free energy needed for efficient charge transfer and by a loss in V_{oc} relative to the energy of the charge separated state.⁷ Commonly used acceptor materials in bulk heterojunction solar cells such as the fullerene derivatives [6,6]-phenyl- C_{60} -butyric acid methyl esters ([60]PCBM and [70]PCBM, for $n=61$ and 71) feature a high electron mobility and have $E_g=1.75$ eV. This limits the V_{oc} of any polymer:PCBM solar cell to $V_{oc} \leq 1.15$ V. So far the highest reported V_{oc} s for PCBM-based cells are < 1.05 V,^{8–12} which leaves room for further optimization.

Increasing the V_{oc} for PCBM-based solar cells requires a lowering of the highest occupied molecular orbital (HOMO) energy of the polymer with respect to the vacuum level. This can be effective as long as the polymer semiconductor can form an Ohmic contact with the hole collecting electrode by aligning its HOMO level with the Fermi level of the electrode. Hence, for the commonly used poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) electrode the work function of 5.1 ± 0.2 eV (Ref. 13) will limit the V_{oc} , when the HOMO level of the semiconducting polymer becomes less than -5.3 eV versus vacuum. Fortunately, the work function of PEDOT:PSS can be increased via treatment with UV-ozone or by mixing or covering with Nafion[®].^{14–18} The changes in work function are reported to be 0.13 to 0.25 eV for UV-ozone treated films,^{14–16} up to 0.65 eV for the films with Nafion[®].^{17,18}

Here we present poly[3,6-di(4'-ethyloctyl)thieno[3,2-*b*]thiophene-2,5-diyl-2,1,3-benzothiadiazole-4,7-diyl] (PTTBT) (Fig. 1), a polymer with a low HOMO energy that provides $V_{oc}=1.15$ V in solar cells when combined with [70]PCBM and using an UV-ozone treated PEDOT:PSS electrode. This V_{oc} is approaching the limit of what seems possible in PCBM-based solar cells.⁷

PTTBT was synthesized via a palladium catalyzed Suzuki reaction using 2,5-dibromo-3,6-di(4'-ethyloctyl)thieno[3,2-*b*]thiophene and 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester). PTTBT is an orange powder with a number average molecular weight $M_n=15$ kg/mol and a polydispersity of 3.2 as determined by gel permeation chromatography in *o*-dichlorobenzene (ODCB) at 80 °C. Detailed experimental procedures for the synthesis are described in the supplemental material.¹⁹

UV/visible absorption (Fig. 2) reveals that PTTBT has an optical band gap of 2.31 eV in solution and of 2.20 eV in thin films. This relatively wide band gap is most probably due to a non planar configuration of the chain caused by steric hindrance between the 4'-ethyloctyl side chains and the benzothiadiazole unit. The absorption of PTTBT is slightly blue shifted compared to the related poly[4,7-bis(3-octyl-2-thienyl)-2,1,3-benzothiadiazole] that incorporates a bithiophene unit instead of a thienothienophene.²⁰

The HOMO and lowest unoccupied molecular orbital (LUMO) levels of PTTBT were estimated using cyclic voltammetry in ODCB to be +0.54 and -1.80 V versus ferrocene/ferrocinium (Fc/Fc⁺) or -5.64 and -3.3 eV versus vacuum.¹⁹ The difference, matches with the optical band gap in solution. The V_{oc} for donor (D)—acceptor (A) bulk heterojunction cells can be estimated from $eV_{oc} = |E_{HOMO}(D) - E_{LUMO}(A)| - 0.4$ eV.²¹ Applying this rule

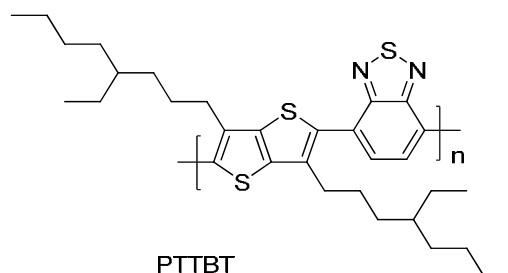


FIG. 1. Chemical structure of PTTBT.

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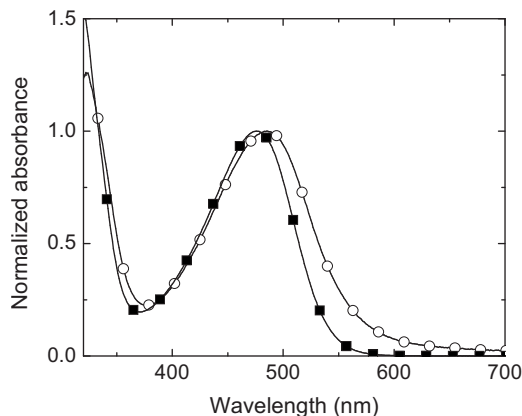


FIG. 2. Absorption spectrum of PTTBT in CHCl_3 ($20 \mu\text{g}/\text{mg}$) (solid squares) and as thin film (open circles).

to PTTBT and [70]PCBM [$E_{\text{LUMO}}(\text{A}) = -1.07 \text{ V}$ versus Fc/Fc^+ ,²² -4.03 eV versus vacuum] provides 1.2 V as the estimate V_{oc} for a PTTBT:[70]PCBM solar cell.

Solar cells were made by spin casting PEDOT:PSS (Clevios P, VP A14083) directly followed by a mixture of PTTBT and [70]PCBM from chlorobenzene (CB) onto a pre-cleaned glass slide with a pattern of indium tin oxide (ITO). The devices were completed by evaporating 1 nm LiF and 100 nm Al onto the active layer in vacuum which is known to form an Ohmic contact with PCBM.²¹ The use of pristine PEDOT:PSS resulted in rather irreproducible and poor performance ($\text{PCE} < 0.1\%$) and a significant dark current at reverse bias. The operation was limited by a low photocurrent and low V_{oc} of 0.4 V on average (Fig. 3). We found that a short treatment of the freshly spin coated PEDOT:PSS layer in a UV-ozone reactor before deposition of the active layer results in a dramatic increase in performance. Figure 3 shows the V_{oc} obtained as a function of UV-ozone exposure. The optimal exposure time of 3 min. results in a V_{oc} of 1.15 V , with little variation. The effect is already very strong after 30 s and longer treatment times than 3 min. do not further improve V_{oc} . The short-circuit current density (J_{sc}) also showed a dramatic increase, from $\ll 1$ to over $2.5 \text{ mA}/\text{cm}^2$. The treatment mainly affects the surface of the PEDOT:PSS and lowers the work function to 5.4 eV (Ref. 15) but also

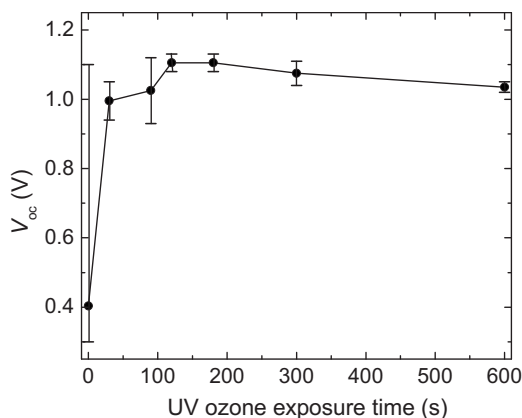


FIG. 3. Open circuit voltage of an ITO|PEDOT:PSS|PTTBT:[70]PCBM|LiF|Al solar cell vs UV-ozone exposure time of the PEDOT:PSS layer. Closed circles represent average values, bars represent highest and lowest values found. For $t=0$, data from five cells were used for averaging, for $t>0$ two cells were used.

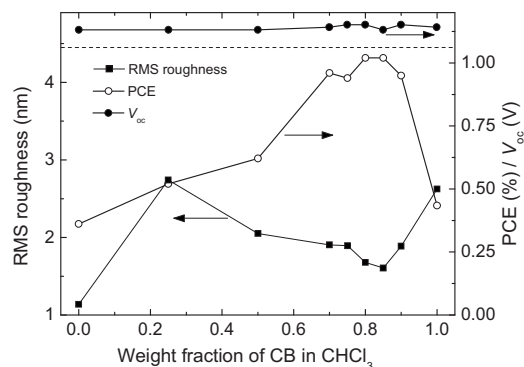


FIG. 4. Efficiency and layer rms-roughness of PTTBT:[70]PCBM solar cells vs the solvent composition used for spin coating.

seems to influence the photoactive layer, increasing the photocurrent. The fill factor, however, remained low, possibly due to the low hole mobility of PTTBT, which was $\sim 10^{-6} \text{ cm}^2/\text{V s}$ as measured in a FET bottom gate bottom contact structure.

The ideal blend layer for an organic solar cell has a large interface area between the two components to effectively split the excitons and at the same time comprises large enough phase-separated domains of PCBM or polymer to form effective percolating pathways for collecting the charges at the electrodes. To optimize the performance the PTTBT:[70]PCBM blend was spin coated from different solvent mixtures onto UV-ozone treated PEDOT:PSS layers. The solvents tested consisted of mixtures of chloroform (CHCl_3) and CB. From either of the two pure solvents, the thin films featured low performance, whereas layers spin coated using a mixture of the two yielded improved solar cells. Figure 4 shows the efficiency versus composition of the solvent mixture. Using $15\text{--}20 \text{ vol } \%$ CHCl_3 in CB, solar cells with an estimated efficiency of just over 1% were obtained. The V_{oc} does not vary significantly with CHCl_3 :CB ratio (Fig. 4).

Atomic force microscopy (AFM) studies revealed that the composition of the solvent mixture affects the morphology of the active layer.¹⁹ Figure 4 shows that the efficiency of the cells inversely correlates with the rms-roughness of the films as measured with AFM over a $1 \times 1 \mu\text{m}^2$ area. At the optimal performance the rms-roughness is in a (local) minimum. Since films from pure CB appear more corrugated than films from pure CHCl_3 , we assume that the $15\text{--}20 \text{ vol } \%$ CHCl_3 serves to reduce the extent of phase separation obtained with pure CB. This view is consistent with the fact that layers obtained from pure CHCl_3 have the overall lowest rms-roughness. The lower performance for films made from pure CHCl_3 is then likely due to a lack of phase separation.

The J - V curve and external quantum efficiency (EQE) recorded with 1 sun light bias of an optimized cell (with layer thicknesses typically between 70 and 80 nm) and a PTTBT:[70]PCBM weight ratio of $1:4$ are shown in Fig. 5. In the spectral region from $350\text{--}500 \text{ nm}$, more than 20% of the photons are converted in electrons. From convolution of the EQE with the global air mass 1.5 (AM1.5G) spectrum a J_{sc} of $2.81 \text{ mA}/\text{cm}^2$ is obtained. Combined with $\text{FF}=0.32$ and $V_{\text{oc}}=1.15 \text{ V}$ this results in $\text{PCE} \approx 1.0\%$. Under reverse bias the photocurrent is strongly enhanced, which suggests

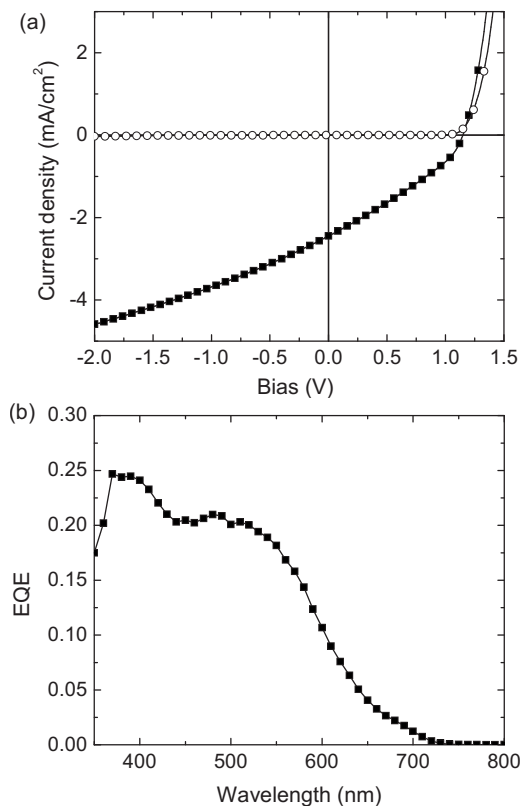


FIG. 5. J - V curve in dark (open circles) and under illumination (closed squares) of an optimized PTTBT:[70]PCBM solar cell. (b) EQE of the same cell.

that the generation of free charge carriers is assisted by the electric field.

In conclusion, PTTBT is a semiconducting polymer that exhibits a high oxidation potential and $V_{oc}=1.15$ V when combined with [70]PCBM in bulk heterojunction solar cells. To reach the high V_{oc} the PEDOT:PSS electrode was treated with UV-ozone to increase the work function and create an Ohmic contact with PTTBT. The overall power conversion efficiency of the optimized cells (1%) is moderate and limited by a low hole mobility and the incomplete generation of free carriers close in the maximum power point. With $V_{oc}=1.15$ the practical limit thought to be possible for PCBM-containing polymer solar cells has been reached.⁷

The authors thank Simon Mathijssen for mobility measurements. The research was supported by a TOP grant of the

Chemical Sciences (CW) division of the Netherlands Organization for Scientific Research (NWO) and is part of the Joint Solar Programme (JSP). The JSP is co-financed by the Foundation for Fundamental Research on Matter (FOM), Chemical Sciences of NWO, and the Foundation Shell Research.

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