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

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The open-circuit voltage ($V_{oc}$) of bulk heterojunction solar cells based on polymers and fullerene derivatives is limited to $\sim 1.15$ V by the optical band gap of the fullerene of $\sim 1.75$ 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. 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.

Higher PCEs can be obtained with multi-junction devices such as tandem cells that employ sub cells with $V_{ocs}$ that are more closely matched to $E_g$ of the active layer to minimize photon energy losses. 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 $eV_{oc}=E_g-0.6$ eV. 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. Commonly used acceptor materials in bulk heterojunction solar cells such as the fullerene derivatives [6,6]-phenyl-C$_{61}$-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 $V_{oc}=1.15$ V. So far the highest reported $V_{oc}$ for PCBM-based cells are <1.05 V, 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. The changes in work function are reported to be 0.13 to 0.25 eV for UV-ozone treated films, up to 0.65 eV for the films with Nafion.

Here we present poly[3,6-di(4′-ethyloctyldithieno[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 is approaching the limit of what seems possible in PCBM-based solar cells.

PTTBT was synthesized via a palladium catalyzed Suzuki reaction using 2,5-dibromo-3,6-di(4′-ethyloctyldithieno[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.

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 thienothiophene.

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. 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. Applying this rule

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

Solar cells were made by spin casting PEDOT:PSS (Clevios P, VP Al4083) 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 (PCE < 0.1%) and a significant dark current at reverse bias. The operation was limited by a low photocurrent and low \(V_{\text{oc}}\) 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 \(V_{\text{oc}}\) obtained as a function of UV-ozone exposure. The optimal exposure time of 3 min. results in a \(V_{\text{oc}}\) 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 \(V_{\text{oc}}\). The short-circuit current density \(J_{\text{sc}}\) also showed a dramatic increase, from \(<1\) to over 2.5 mA/cm². The treatment mainly affects the surface of the PEDOT:PSS and lowers the work function to 5.4 eV (Ref. 15) but also 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 (CHCl₃) 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 15–20 vol % CHCl₃ in CB, solar cells with an estimated efficiency of just over 1% were obtained. The \(V_{\text{oc}}\) does not vary significantly with CHCl₃: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 CHCl₃, we assume that the 15–20 vol % CHCl₃ serves to reduce the extent of phase separation obtained with pure CB. This view is consistent with the fact that layers obtained from pure CHCl₃ have the overall lowest rms-roughness. The lower performance for films made from pure CHCl₃ 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 350–500 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 \(J_{\text{sc}}\) of 2.81 mA/cm² is obtained. Combined with FF = 0.32 and \(V_{\text{oc}} = 1.15 \text{ V}\) this results in PCE = 1.0%. Under reverse bias the photocurrent is strongly enhanced, which suggests
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.\(^7\)

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17. See supplementary material at http://dx.doi.org/10.1063/1.3480598 for the experimental procedures used.