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Enhanced dissociation of charge-transfer states in narrow band gap polymer:fullerene solar cells processed with 1,8-octanedithiol

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The improved photovoltaic performance of narrow band gap polymer:fullerene solar cells processed from solutions containing small amounts of 1,8-octanedithiol is analyzed by modeling of the experimental photocurrent. In contrast to devices that are spin coated from pristine chlorobenzene, these cells do not produce a recombination-limited photocurrent. Modeling of the experimental data reveals that a sixfold reduction in the decay rate of photogenerated bound electron-hole pairs can account for the marked increase in short-circuit current density and fill factor. At short-circuit conditions, the dissociation probability of bound pairs is found to increase from 48% to 70%.

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Conjugated polymers have a great potential for application in thin film photovoltaics. In contrast with inorganic materials, their chemical structure can be tuned in order to optimize solar cell performance. Engineering of the optical band gap is of particular interest, as narrow band gap materials enable harvesting of lower energy photons that are not absorbed by wide band gap materials. One of the most promising narrow band gap polymers to date is poly[2,6-(4,4-bis(2-ethylhexyl) - 4H-cyclopenta[2,1-b;3,4-b']dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT, see Fig. 1), which has been used as an electron donor to [6,6]-phenyl C₆₁ butyric acid methyl ester (PCBM) in bulk heterojunction solar cells with a power conversion efficiency of 2.7%.¹ Substitution of PCBM with PC₇₁BM resulted in an increase of the efficiency to 3.2% due to enhanced absorption in the visible. In both cases, however, device performance is limited by a low fill factor (FF). In a recent paper, geminate recombination of photogenerated electron-hole (e-h) pairs was identified as a plausible origin of this behavior.² Modeling of the field- and temperature-dependent photocurrent revealed a very short lifetime of bound e-h pairs, leading to a low probability of dissociation at the donor/acceptor interface. The inefficient dissociation mechanism in these cells is closely related to the nanoscale morphology, which is characterized by excessive intermixing of the polymer and fullerene phases.³

A dramatic improvement in photovoltaic performance has been reported for PCPDTBT:PC₇₁BM solar cells that were processed from chlorobenzene solutions containing small amounts of 1,8-octanedithiol (ODT).⁴ The observed increase in short-circuit current density (J_{sc}) and FF was ascribed to improved phase separation. Recently, transient absorption spectroscopy has revealed an increased photogeneration of charges in cells processed with ODT, which was assigned to a reduction in geminate recombination losses.⁵

Here, we present a direct investigation of the effects of processing with ODT on geminate recombination of e-h pairs in PCPDTBT:PCBM cells by modeling of the experimental photocurrent.

PCPDTBT (Konarka) and PCBM (Solenne) were dissolved in a 1:2.5 weight ratio in pristine chlorobenzene, or chlorobenzene containing 1.75 vol % ODT (Aldrich). The photoactive layers were spin coated under a nitrogen atmosphere on thoroughly cleaned glass substrates patterned with indium tin oxide on which a thin layer of poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (VP AI4083, H.C. Starck) was applied. After thermal deposition of a 1 nm LiF/100 nm Al cathode at 10⁻⁶ mbar, the samples were kept under nitrogen atmosphere for current-voltage (IV) and external quantum efficiency (EQE) measurements. IV measurements were performed in the dark and under illumination from a Steuernagel SolarConstant 1200 metal halide lamp set to 1 sun intensity using a silicon reference cell and correcting for spectral mismatch ($M=1.05$).⁶ EQE spectra were recorded versus a silicon reference, using a custom-built setup comprising a lock-in amplifier, a transimpedance amplifier, and a focused, chopped monochromatic beam from a quartz tungsten halogen lamp, and a range of narrow band pass filters.

The influence of processing with ODT on the spectral response of PCPDTBT:PCBM solar cells is shown in Fig. 2. The EQE maximum increases from 28% to 41% at 710 nm and the spectrum broadens to approximately 800 nm. A simi-

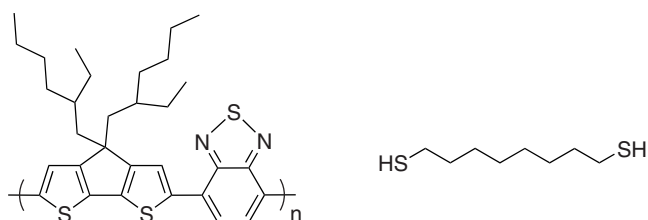


FIG. 1. Chemical structures of PCPDTBT and ODT.

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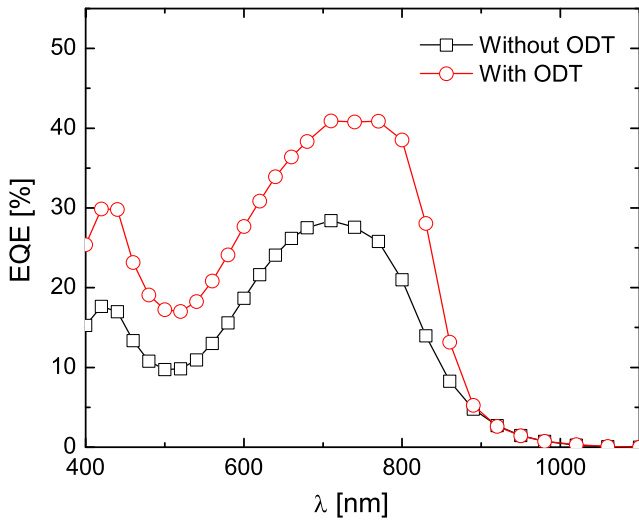


FIG. 2. (Color online) EQE spectra of PCPDTBT:PCBM solar cells spin coated with (circles) and without (squares) ODT. The lines serve as a guide to the eye.

lar effect has been observed with ultraviolet-visible absorption spectroscopy.⁴ Integration of the EQE spectra with the AM1.5 global reference spectrum gives short-circuit current densities of 61 A/m² for the device processed without ODT and 95 A/m² for the cell with ODT. A similar increase in J_{sc} was observed in IV measurements, which will be discussed below.

Figure 3 shows the influence of processing with ODT on the photocurrent of two cells with a layer thickness of approximately 100 nm. The photocurrent J_{ph} is obtained by subtracting the dark current J_D from the current under illumination J_L , and is plotted against the effective voltage over the device, which is defined as $V_0 - V$, with V_0 given by $J_{ph}(V_0) = 0$. As previously described in detail by Lenes *et al.*,² the recombination-limited photocurrent of the pristine PCPDTBT:PCBM solar cell (squares) is characterized by a

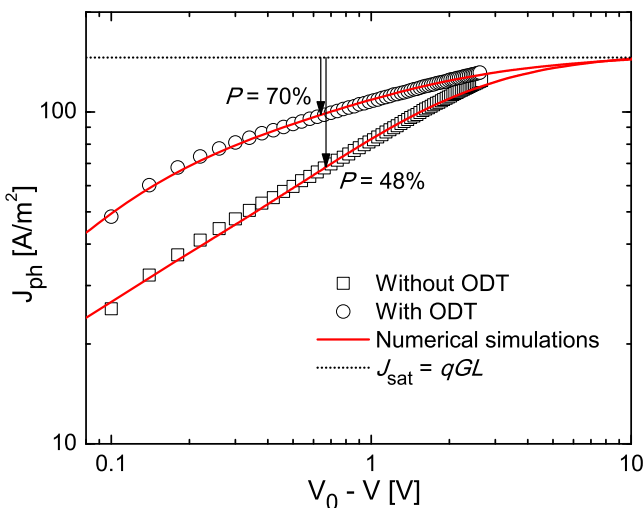


FIG. 3. (Color online) Symbols: experimental photocurrent of PCPDTBT:PCBM solar cells processed from pristine chlorobenzene (squares) and chlorobenzene containing 1.75 vol % ODT (circles). Please note that V_0 is slightly higher (approximately 30 mV) than V_{oc} . P denotes the average dissociation probability of bound pairs under short-circuit conditions. Solid lines: numerical simulations of the photocurrent in which only the value of k_f was changed (without ODT $k_f = 1.7 \times 10^7$ s⁻¹ and with ODT $k_f = 3 \times 10^6$ s⁻¹).

square-root dependence on voltage and a linear dependence on light intensity.⁷ The photocurrent of the cell processed with ODT, however, does not exhibit such a voltage dependence (circles). A clear enhancement of J_{ph} at moderate effective voltages is observed when processing is performed with the additive, indicating an increase in both short-circuit current and FF. It has been shown that without ODT hole transport in the PCPDTBT phase and electron transport in the PCBM phase are well-balanced with low-field hole and electron mobilities $\mu_h = 3 \times 10^{-8}$ m²/V s and $\mu_e = 8 \times 10^{-8}$ m²/V s, respectively.² The electron mobility in the fullerene phase of a polymer solar cell can be examined by considering the space-charge limited dark current under forward bias. This current is usually determined by the high electron mobility in PCBM. Dark current measurements on the device processed with ODT showed no signs of a change in charge transport parameters. Therefore, space-charge effects are insignificant in this system⁸ and the considerable improvement in J_{ph} is expected to be related to a change in recombination losses.²

The experimental photocurrents were simulated with our numerical device model,⁹ which includes Onsager–Braun theory to describe the field- and temperature-dependent dissociation of bound e–h pairs.¹⁰ In this model, a photogenerated bound e–h pair, initially separated by a distance a , can either decay to the ground state with a rate constant k_f , in which case the carriers are lost, or dissociate into free charge carriers to contribute to the photocurrent. Bimolecular recombination of free carriers results again in a charge-separated state across the donor/acceptor interface and is assumed to be Langevin-type,¹¹ dominated by the slowest charge carrier.¹² Since no change in charge transport upon addition of ODT was found, the simulations discussed below indicate only a small loss of free carriers ($\sim 5\%$) due to bimolecular recombination under short-circuit conditions, irrespective of any possible morphological changes upon addition of ODT.

Using the previously reported values of the mobilities and dissociation parameters,² i.e., $a = 2.1$ nm and $k_f = 1.7 \times 10^7$ s⁻¹, the calculated photocurrent (solid line in Fig. 3) is in excellent agreement with measurements on the pristine PCPDTBT:PCBM cell. Note that compared to other polymer:fullerene systems, for which k_f values ranging from 10^4 to 10^6 s⁻¹ have been found,^{13–15} PCPDTBT:PCBM heterojunctions have an extremely high bound pair decay rate. In order to fit the markedly different photocurrent of the solar cell processed with ODT, only k_f was reduced to 3×10^6 s⁻¹. The dramatic improvement of J_{ph} upon addition of ODT can thus be described with an almost sixfold reduction in the bound pair decay rate. At high reverse voltages, the photocurrent saturates as the dissociation probability P of bound pairs approaches unity and all photogenerated charges are extracted at the electrodes. In this regime, the saturated photocurrent density (dotted line in Fig. 3) is given by $J_{sat} = qGL$, where q is the elementary charge, G the amount of generated e–h pairs, and L the layer thickness. Since both cells have the same thickness and show saturation of the photocurrent at the same value of J_{sat} , it is evident that they produce the same amount of bound e–h pairs. The sole difference is the efficiency with which these are dissociated. Outside the saturation regime, $P < 1$ and the generation rate of free carriers is equal to PG . Figure 3 can therefore be used

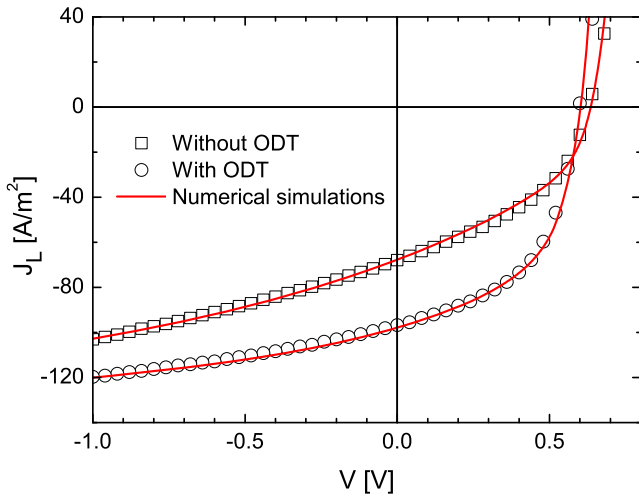


FIG. 4. (Color online) Experimental and simulated IV characteristics of the solar cells under illumination.

to directly assess P at short-circuit conditions, as indicated by the arrows, by comparison of J_{ph} with J_{sat} . It follows that the addition of ODT results in an increase in the dissociation probability from 48% to 70%.

Using the experimentally determined model parameters, we simulated the entire current-voltage characteristics of PCPDTBT:PCBM cells processed with and without ODT. This is shown in Fig. 4. As predicted,² the lower value of k_f accounts for both the enhanced short-circuit current and the increase in FF from 0.42 to 0.52.

In conclusion, we have shown that the photocurrent of PCPDTBT:PCBM solar cells loses its recombination-limited character when the polymer:fullerene layer is processed from chlorobenzene containing 1.75 vol % 1,8-octanedithiol. Numerical device modeling revealed a reduction in the decay rate of bound e-h pairs from 1.7×10^7 to 3×10^6 s⁻¹ due to the addition of ODT. The lower amount of geminate recom-

bination enables more efficient dissociation of bound pairs into free charge carriers, which results in a higher short-circuit current density and FF. The average dissociation probability at short-circuit was found to increase from 48% for the device processed from pristine chlorobenzene to 70% for the cell processed with ODT.

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