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Charge dissociation in polymer:fullerene bulk heterojunction solar cells with enhanced permittivity

M. Lenes,[1,2] F. B. Kooistra,[1] J. C. Hummelen,[1] I. Van Severen,[3] L. Lutsen,[4] D. Vanderzande,[3,4] T. J. Cleij,[3] and P. W. M. Blom[1,a]

[1]*Molecular Electronics, Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands*
[2]*Dutch Polymer Institute, P.O. Box 902, 5600 AX, Eindhoven, The Netherlands*
[3]*Institute for Materials Research (IMO), Hasselt University, Agoralaan, Building D, B-3590 Diepenbeek, Belgium*
[4]*IMEC, Division IMOMEC, Wetenschapspark 1, B-3590 Diepenbeek, Belgium*

The dissociation efficiency of bound electron-hole pairs at the donor-acceptor interface in bulk heterojunction solar cells is partly limited due to the low dielectric constant of the polymer:fullerene blend. We investigate the photocurrent generation in blends consisting of a fullerene derivative and an oligo(oxyethylene) substituted poly(*p*-phenylene vinylene) (PPV) derivative with an enhanced relative permittivity of 4. It is demonstrated that in spite of the relatively low hole mobility of the glycol substituted PPV the increase in the spatially averaged permittivity leads to an enhanced charge dissociation of 72% for these polymer:fullerene blends. © *2008 American Institute of Physics*. [DOI: 10.1063/1.3039191]

I. INTRODUCTION

An important difference between semiconductors used in inorganic and organic solar cells is the much lower permittivity of the latter. As a result, strongly bound excitons are created after absorption of light instead of free charge carriers. To overcome this problem, a donor-acceptor system is used in which the electron transfers from the donor to the acceptor material. However, electron-hole (e-h) pairs generated in this way are still strongly bound by Coulomb interaction and need to be dissociated into free carriers in order to be collected at the electrodes.[1,2] The occurrence of such an interfacial geminate charge pair has been spectroscopically observed for polymer:polymer systems[3,4] and recently also for polymer:fullerene blends.[5] In addition, a strong indication for the existence of a bound e-h pair in polymer:fullerene blends is the field and temperature dependence of the photocurrent at reverse bias. At sufficiently high reverse bias, all bound e-h pairs are dissociated, leading to a saturated photocurrent that is field and temperature independent.[2] As a result, the saturated photocurrent is a direct measure for the amount of photons absorbed in the blend.[6] Typically, the dissociation efficiency in poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-*p*-phenylene vinylene] (MDMO-PPV) and [6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM) bulk heterojunction (BHJ) solar cells is only 60% at short circuit conditions, representing a major loss mechanism in these devices.[2,7]

II. THEORY

The field and temperature dependent process of charge dissociation of the bound e-h pair in polymer:fullerene solar cells can be described using Onsager's theory[8] of ion pair dissociation. This e-h pair can dissociate into free carriers by a rate constant k_D given by

$$k_D(E) = k_R \frac{3}{4\pi a^3} e^{-E_B/kT} \left[1 + b + \frac{b^2}{3} + \frac{b^3}{18} + \frac{b^4}{180} + \dots \right] \tag{1}$$

with E_B being the e-h pair binding energy $b = q^3 E/(8\pi\varepsilon k_B^2 T^2)$, E is the field strength, and $\varepsilon = \varepsilon_0 \varepsilon_r$ is the permittivity.[1] Free carriers generated in this way can recombine back to the bound state by Langevin[9] recombination

$$k_R = \frac{q}{\varepsilon} \min(\mu_e, \mu_h), \tag{2}$$

where it was pointed out that the recombination strength is dominated by the slowest carrier mobility in BHJ solar cells.[10] Finally, the bound state can decay to the ground state with a rate k_F. The model now predicts the probability that free charge carriers will be produced at a particular field (E), temperature (T), and donor-acceptor separation radius (a),

$$P(a,T,E) = \frac{k_D(E)}{k_D(E) + k_F}. \tag{3}$$

From the abovementioned equations, it is clear that the charge dissociation is governed by four relevant parameters, viz., the charge carrier mobility μ, the permittivity of the blend ε, the initial separation distance a, and the decay rate k_F. For the MDMO-PPV:PCBM system, it has been shown to be vital to take into account the overall relative permittivity of the blend when describing the charge dissociation.[11] The relative permittivity ε_r of MDMO-PPV is 2.1,[12] whereas the ε_r of PCBM amounts to 4. As a result, when going from a 1:1 to a 1:4 polymer:fullerene weight ratio, the increase in photocurrent is shown to originate not only from an increase

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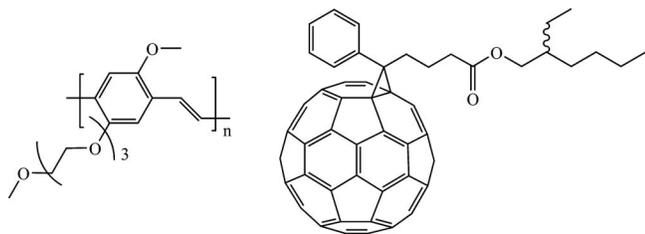
a)Electronic mail: p.w.blom@rug.nl.

FIG. 1. Chemical structure of PEO-PPV and PCB-EH.

in the hole mobility, but also from an increase in the average permittivity, due to the loading of more PCBM. An increase in the permittivity of the donor polymer is therefore expected to enhance the dissociation efficiency and thus the efficiency of the solar cells. In this study, an oligo(oxyethylene) substituted PPV derivative with $\varepsilon_r=4$ is used to study the effect of an enhanced permittivity of the blend on the photogeneration.

III. RESULTS AND DISCUSSION

A. Single carrier devices

Figure 1 shows the chemical structure of poly[2-methoxy-5-(triethoxymethoxy)-1,4-phenylene vinylene] (PEO-PPV), the donor material used in this study. The synthesis and characterization have been previously reported.[13] Furthermore, previous studies using impedance measurements have shown the relative permittivity of the material to be equal to 4.[14] The chemical structure of phenyl-C_{61} butyric acid 2-ethylhexyl ester (PCB-EH), which is the acceptor used here, is also shown in Fig. 1. PCB-EH is used instead of PCBM to provide a better mixing of donor and acceptor. The charge transport in pristine polymer films is investigated by sandwiching a layer of PEO-PPV between a layer of indium tin oxide (ITO) covered with ~70 nm of poly(3, 4ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT-:PSS) and a palladium (Pd, 20 nm)/gold (Au, 80 nm) top electrode. The high work function of Pd prevents electron injection and only holes flow through the device. Figure 2 shows the *J-V* characteristics of such a PEO-PPV hole only device, corrected for the built-in voltage (V_{bi}) and the series
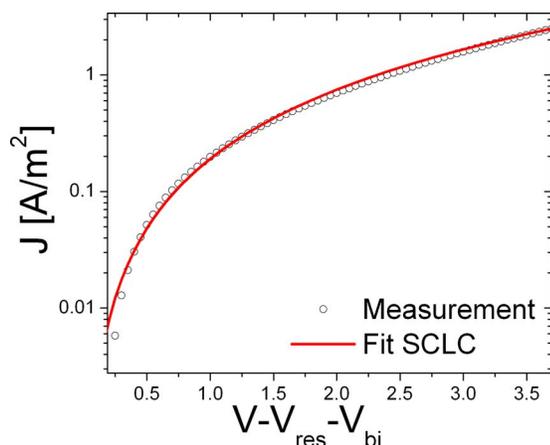

FIG. 2. (Color online) Current density vs voltage, corrected for built in voltage and series resistance, of PEO-PPV hole only device. Data (symbols) is fitted (solid line) using a SCLC.
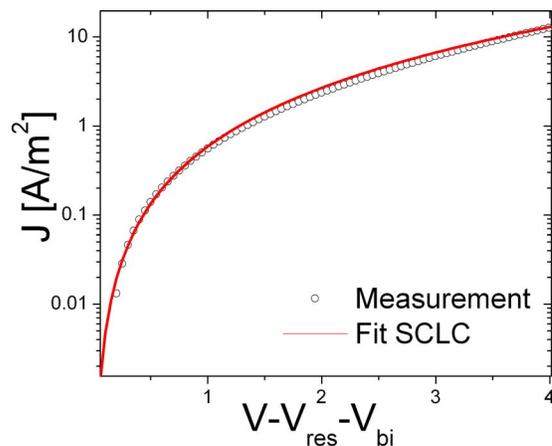

FIG. 3. (Color online) Current density vs voltage, corrected for built in voltage and series resistance, of a PEO-PPV:PCB-EH hole only device. Data (symbols) is fitted (solid line) using a SCLC.

resistance of the electrodes. The *J-V* curve is fitted to a space-charge limited current (SCLC), yielding a hole mobility of 1.8×10^{-10} m^2/V s. The observed hole mobility is comparable to hole mobilities reported for pristine MDMO-PPV films.[15] For MDMO-PPV, however, blending the polymer in a 1:4 weight ratio with PCBM results in a dramatic increase in hole mobility of more than two orders of magnitude,[16] which turns out to be essential for device operation.[2,7] As a next step the hole transport in a PEO-PPV:PCB-EH blend (1:4 weight ratio) is investigated, also using a Pd top electrode to prevent electron injection into the PCB-EH. In Fig. 3, the *J-V* characteristics of such a hole only device are shown. The determined hole mobility of 4×10^{-11} m^2/V s indicates that an enhancement of the hole mobility, as seen in blends of MDMO-PPV, does not occur for blends of PEO-PPV and PCB-EH. A low hole mobility will lead to the formation of space charges as well as a low dissociation efficiency and is expected to limit the performance of the PEO-PPV:PCB-EH solar cells. To separately illustrate the effect of a low charge carrier mobility on the charge dissociation efficiency, Fig. 4 shows calculations of the Braun model using the following parameters for the MDMO-PPV:PCBM system: $a=1.25\times10^{-9}$ m, $k_f=1\times10^5$ s^{-1}, $\varepsilon_r=3.4$, and $\mu_h=4\times10^{-8}$ m^2/V s, and identical parameters but now with the lower hole mobility of PEO-PPV 4×10^{-11} m^2/V s. The calculated charge dissociation at short circuit is reduced from 62% to only 22% by lowering the hole mobility to such a low value. Furthermore, the formation of space charges is expected to limit the fill factor.[17]

B. Solar cells

Polymer:fullerene BHJ solar cells were fabricated by spin coating a layer of PEO-PPV:PCB-EH in a 1:4 weight ratio from chlorobenzene on top of PEDOT:PSS covered ITO. As a cathode, 1 nm of lithium fluoride and 100 nm of aluminum are evaporated. Figure 5 shows the *J-V* characteristics of a PEO-PPV:PCB-EH solar cell measured under illumination of a white light halogen lamp set at 1000 W/m^2. Due to the low charge carrier mobility, the optimal device thickness is only 68 nm,[18] resulting in a low short circuit
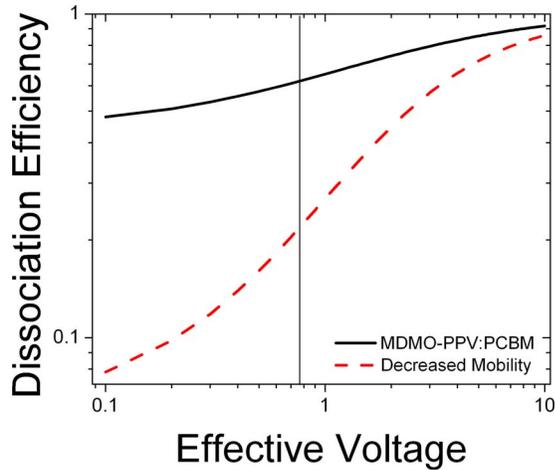
FIG. 4. (Color online) Dissociation efficiency for a MDMO-PPV:PCBM solar cell as determined in Ref. 2 (solid line), together with a calculated dissociation efficiency for a similar system but with a lower hole mobility of 4×10^{-11} m²/V s. The dissociation efficiency at short circuit conditions (as indicated by the vertical solid line) drops from 62% to 22% due to the lower hole mobility.

current of 13.8 A/m². Combined with a fill factor of 52% and an open circuit voltage of 0.67 V, the estimated overall power efficiency is 0.5%, which is considerably lower compared to the model system MDMO-PPV-PCBM. The main reason for this lower efficiency is the low short circuit current, which is likely to be caused by an unfavorable large domain formation of polymer and fullerene leading to a loss of excitons.

Even though the power conversion efficiency is much lower as compared to MDMO-PPV, the devices can still be used to study the effect of the raised permittivity on the charge dissociation. For this, the photocurrent density J_{ph} $=J_L-J_D$, where J_L and J_D are the current density under illumination and in dark, respectively, is plotted as a function of effective applied voltage V_0-V_A, as is shown in Fig. 6. Here V_0 is the compensation voltage defined as $J_{ph}(V_0)=0$ and V_A is the applied bias. The previously mentioned Braun model can only be applied to describe the photocurrent at relatively high effective voltages where the photocurrent is in the saturated regime and is governed by the dissociation of bound
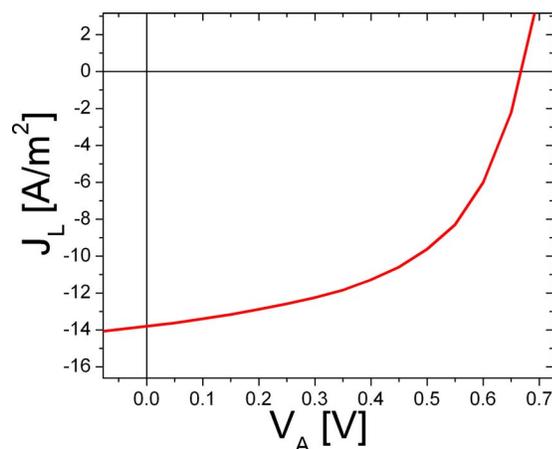

FIG. 5. (Color online) Current density vs voltage PEO-PPV:PCB-EH solar cell under illumination of a 1000 W/m² halogen lamp.

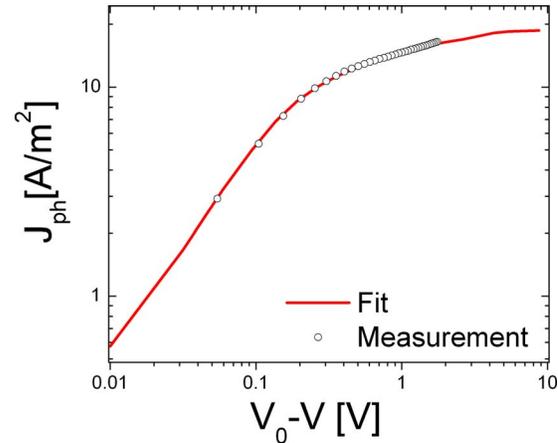FIG. 6. (Color online) Experimental photocurrent density J_{ph} as a function of effective applied voltage V_0-V_A under 1 kW/m² illumination. Circles indicate experimental data and solid line indicates fit of the photocurrent.

e-h pairs.[2] To fully describe the photocurrent, a numerical model, including drift and diffusion of charge carriers, the effect of space charge formation on the electric field, bimolecular recombination, and a field and temperature dependent generation rate of free charge carriers is used.[7] Input parameters for the numerical program are identical to the above described Braun model, i.e., the charge carrier mobilities including their field dependence, the average permittivity ε_r, separation distance a, and decay rate k_f. Since the charge carrier mobility has been determined using hole only diodes and the electron mobility of the fullerene is known,[19] only a and k_f are used as fitting parameters. Both separation distance a and decay rate k_f have different effects on the fits of the photocurrent. The distance a determines at which voltage the dissociation saturates, whereas the decay rate k^f determines how fast the dissociation drops when the field in the device is lower. Indicated in Fig. 6 is a fit to the experimental photocurrent using our numerical program with input parameters $\varepsilon_r=4$, $\mu_h=4 \times 10^{-11}$ m²/V s, $a=1.5 \times 10^{-9}$ m, μ_e $=2.5 \times 10^{-7}$ m²/V s, and $k_f=4 \times 10^4$ s⁻¹. In Fig. 7, using the same input parameters, a fit using the Braun model is shown. From these figures, one can see that for voltages V_0 $-V>0.3$ the photocurrent is dominated by the field dependent dissociation of bound e-h pairs and that bimolecular recombination and space charge effects do not play a role. This allows one to directly determine the dissociation efficiency by comparing the generated photocurrent at short circuit with the saturated photocurrent at a large reverse bias resulting in a dissociation efficiency of no less than 72%. Thus, we can conclude that even when the charge carrier mobility is significantly lower as compared to MDMO:PPV, the charge dissociation at short circuit is increased by using a high permittivity polymer. Above we calculated the dissociation efficiency for materials with a hole mobility of 4 $\times 10^{-11}$ m²/V s and normal permittivity to be only 22%. The origin of the observed enhanced dissociation efficiency in the PEO-PPV:PCB-EH blend is due to two effects, as shown in Fig. 7. First of all, the initial separation distance of charges is enlarged from 1.25×10^{-9} to 1.5×10^{-9} m and the decay rate k_f is lowered from 1×10^5 to 4×10^4 s⁻¹. Using
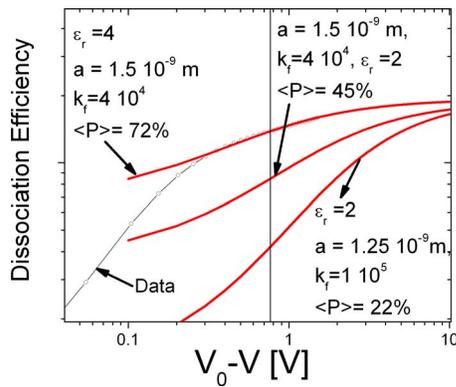
FIG. 7. (Color online) Dissociation efficiency as a function of effective voltage calculated for various values of permittivity of the polymer ε, initial separation distance a and e decay rate k_F. In all cases the hole mobility is taken to be the measured value of 4×10^{-11} m^2/V s. Starting from a low dissociation of 22% at short circuit conditions (indicated by the vertical solid line) the dissociation efficiency is increased first to 45% by an improved separation distance and decay rate and subsequently to the measured value of 72% by increasing the relative permittivity of the polymer from 2 to 4. The measured photocurrent is indicated as a reference (symbols).

these parameters, we predict the dissociation efficiency to be 45%. The second effect is the direct effect of the higher relative permittivity of PEO-PPV of 4, raising the dissociation efficiency even more to the measured 72%. With these parameters, but now combined with the MDMO:PPV hole mobility of $\mu_h = 4 \times 10^{-8}$ m^2/V s, the calculated dissociation is as high as 78%. Combined with an increase in fill factor, our numerical program predicts a power conversion efficiency of 3.5% to be possible for a PPV-type polymer with a relative permittivity of 4.

IV. CONCLUSIONS

To conclude, an oligo(oxyethylene) substituted PPV derivative is used to study the effect of an enhanced permittivity on the dissociation efficiency in polymer:fullerene BHJ solar cells. Besides the permittivity, also the charge carrier mobility, separation distance and decay rate are important factors determining the charge dissociation. Despite a low hole mobility of 4×10^{-11} m^2/V s in the blend of PEO-PPV and PCB-EH, a dissociation efficiency of 72% is observed. It is shown that the effect of a higher relative permittivity is twofold. Not only a direct enhancement of the charge dissociation is observed, but also the separation distance and de-

cay rate are improved upon increasing the relative permittivity. Therefore we conclude that enhancing the relative permittivity of the polymer can be very beneficial for the device operation of polymer:fullerene solar cells.

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