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Effect of Temperature and Illumination on the Electrical Characteristics of Polymer–Fullerene Bulk-Heterojunction Solar Cells**

By *Ingo Riedel, Jürgen Parisi, Vladimir Dyakonov,* *Laurence Lutsen, Dirk Vanderzande,* and *Jan C. Hummelen*

The current–voltage characteristics of ITO/PEDOT:PSS/OC_1C_{10}-PPV:PCBM/Al solar cells were measured in the temperature range 125–320 K under variable illumination, between 0.03 and 100 mW cm^{-2} (white light), with the aim of determining the efficiency-limiting mechanism(s) in these devices, and the temperature and/or illumination range(s) in which these devices demonstrate optimal performance. (ITO: indium tin oxide; PEDOT:PSS: poly(styrene sulfonate)-doped poly(ethylene dioxythiophene); OC_1C_{10}-PPV: poly[2-methoxy-5-(3,7-dimethyl octyloxy)-1,4-phenylene vinylene]; PCBM: phenyl-C_{61} butyric acid methyl ester.) The short-circuit current density and the fill factor grow monotonically with temperature until 320 K. This is indicative of a thermally activated transport of photogenerated charge carriers, influenced by recombination with shallow traps. A gradual increase of the open-circuit voltage to 0.91 V was observed upon cooling the devices down to 125 K. This fits the picture in which the open-circuit voltage is not limited by the work-function difference of electrode materials used. The overall effect of temperature on solar-cell parameters results in a positive temperature coefficient of the power conversion efficiency, which is 1.9 % at $T = 320$ K and 100 mW cm^{-2} (2.5 % at 0.7 mW cm^{-2}). The almost-linear variation of the short-circuit current density with light intensity confirms that the internal recombination losses are predominantly of monomolecular type under short-circuit conditions. We present evidence that the efficiency of this type of solar cell is limited by a light-dependent shunt resistance. Furthermore, the electronic transport properties of the absorber materials, e.g., low effective charge-carrier mobility with a strong temperature dependence, limit the photogenerated current due to a high series resistance, therefore the active layer thickness must be kept low, which results in low absorption for this particular composite absorber.

1. Introduction

The use of conjugated polymers and molecules exhibits a high potential for production of efficient and, at the same time, low-cost, flexible optoelectronic devices with the option for large-area applications.[1] One of the most important advan-

tages of polymer semiconductors over their inorganic counterparts is their ability to be processed in solution, which enables the use of effective deposition techniques, such as spin-coating, doctor-blading, and screen-printing. The efficiency of polymer light-emitting diodes is considered competitive on the display market.[2,3] For photovoltaic applications, however, the photogeneration yield (generation of electrons and holes due to light absorption) in pure polymers is insufficient.[4] One approach to achieve an efficient charge-carrier generation in polymer light absorbers is to blend them with suitable acceptors. For example, in polymer–fullerene composites, the conjugated polymer acts as a donor, and the fullerene molecule as an acceptor. Upon photoexcitation, the ultrafast electron transfer between donor and proximate acceptor takes place.[5,6] This ensures an efficient charge-carrier generation with a quantum efficiency close to unity. This value was experimentally confirmed recently, whereby an internal quantum yield of photocurrent of 90 % in a poly(3-hexylthiophene)–fullerene solar cell was demonstrated.[7] The charge-separated state is metastable, i.e., the hole remains on the polymer backbone and the electron is localized on the acceptor for microseconds at room temperature.[8] One of the most effective and therefore extensively studied device concepts, so far, is based on the bulk-heterojunction approach.[9,10] In this, the fullerene molecules are dispersed in a polymer or in a low-molecular-weight organic matrix. The thin photoactive film is then sandwiched between two electrodes with asymmetric work functions. In this configura-

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tion, each electrode is expected to form an ohmic contact with the respective p- or n-type semiconductor, while simultaneously blocking the minority charge carriers. For single-junction solar cells based on the polymer bulk-heterojunction concept, a power conversion efficiency of 2.5 % has been achieved under 1 sun AM 1.5 illumination conditions without light trapping.[11] Though this is the highest reported confirmed value for a polymer photovoltaic device, it is still quite modest for applications. On the other hand, much higher development potential can be anticipated taking the high quantum yield of charge-carrier generation in these composites into account. In spite of significant advances in the understanding of the qualitative behavior of organic solar cells, a fully quantitative description of charge injection at the electrodes, charge transport in the bulk, and electron–hole recombination has yet to emerge. The improvement of the purity of materials used in the absorber layer is clearly one important aspect to be addressed. The presence of defects and impurities in the bulk negatively influences the principal parameters of polymer solar cells.[12] The proper choice of electrodes is a powerful tool to improve the performance of polymer solar cells.[13] By special treatment of fabricated devices, efficiencies of around 3.5 % under "white light" were recently reported.[14] This indicates the importance of the electrical transport properties of the absorber material and the interfaces. In order to further develop the bulk-heterojunction concept, as well as to identify factors limiting a solar cell's performance, a detailed understanding of the underlying device physics is imperative.

We studied the influence of temperature and illumination intensity on the principal parameters of the polymer–fullerene bulk-heterojunction solar cells, such as short-circuit current, open-ciruit voltage, fill factor, and power conversion efficiency. The outdoor studies reported in a previous study[15] covered a temperature range between 25–60 °C and are complementary to ours (125–320 K), as they were done on similar device structures. They are important in the perspective of drawing generalized conclusions. In Figure 1, the configuration of the device under tests a) is shown together with the chemical structures of the photoactive materials used for the absorber b) (see Experimental for details). The investigations were performed on several tens of devices to ensure the reproducibility of the behavior under discussion. Moreover, the general trend of all characteristics was found to be the same after repeating the measurement procedure on the same device, whereas the absolute values were found to degrade slightly.

2. Results and Discussion

Current-density–voltage (J–V) measurements were performed in the temperature range $T = 125$–320 K in the dark and under illumination for incident light intensities P_{Light} from 0.03 to 100 mW cm^{-2}. The solar-cell parameters, i.e., the open-ciruit voltage V_{OC}, the short-circuit current density J_{SC}, the fill factor FF, and the power conversion efficiency η were determined. Also, the parallel (shunt) resistance R_{P} and series resistance R_{S} of the solar cells were deduced.
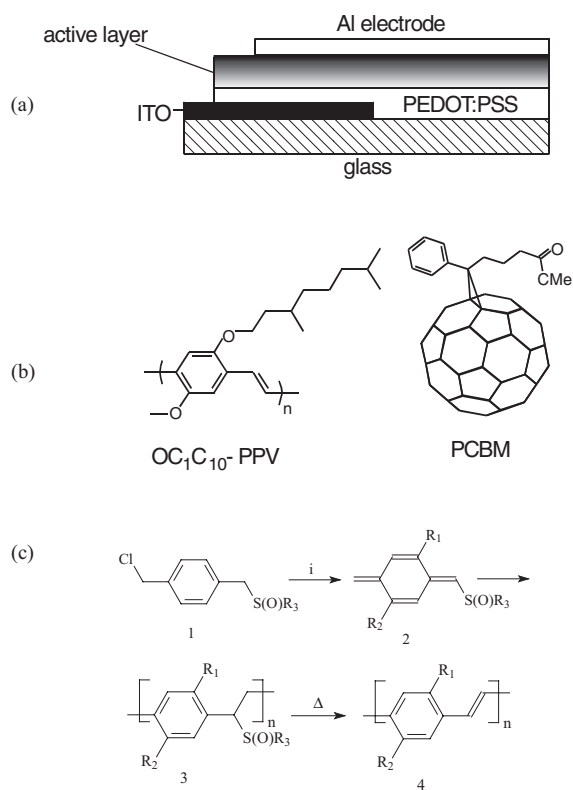
Figure 1. a) Configuration of the ITO/PEDOT:PSS/OC$_1$C$_{10}$-PPV:PCBM/Al solar cell. (ITO: indium tin oxide; PEDOT:PSS: poly(styrene sulfonate)-doped poly(ethylenedioxythiophene); OC$_1$C$_{10}$-PPV: poly[2-methoxy-5-(3,7-dimethyl octyloxy)-1,4-phenylene vinylene]; PCBM: phenyl-C$_{61}$ butyric acid methyl ester.) The thickness of the PEDOT:PSS film and the active layer are 80 nm and 100 nm, respectively. b) Chemical structures of OC$_1$C$_{10}$-PPV and PCBM. c) Formation of the *p*-quinodimethane **2** monomer in a sulfinyl synthesis route.

2.1. Temperature Dependence

2.1.1. Short-Circuit Current

Figure 2 shows the short-circuit current density J_{SC} versus temperature under different illumination intensities. The J_{SC} of the studied samples increases with temperature. Such a strong temperature dependence of the photocurrent is atypical for inorganic solar cells. In these devices, the main contribution to a positive temperature coefficient of the J_{SC} is due to thermally excited intrinsic charge carriers along with the narrowing of the semiconductor's bandgap with increasing temperature, resulting in a red-shift in the optical absorption. The strong temperature effect we observed is due to the electronic transport properties of the absorber material. Charge-carrier transport in disordered conjugated polymers and methanofullerenes is typi-
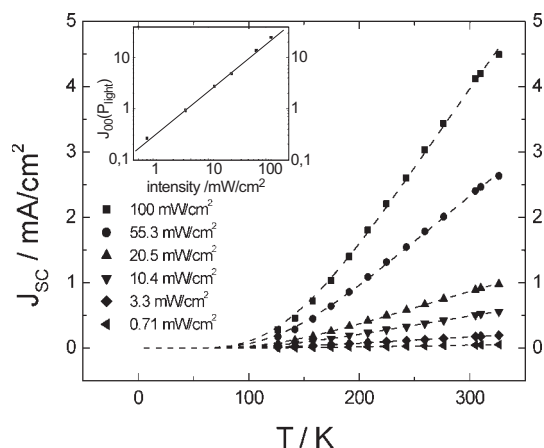
Figure 2. Short-circuit current density J_{SC} as a function of temperature at light intensities indicated in the legend. Dashed lines represent calculated values of $J_{SC}(T, P_{Light}) = J_{00}(P_{Light}) \exp(-\Delta/kT)$. For all light intensities, the best fit was obtained for $\Delta = 44.7 (\pm 1.5)$ meV. The inset shows $J_{00}(P_{Light})$ as a function of P_{Light}.

cally of hopping type and therefore thermally assisted.[16,17] There, the mobility is temperature-dependent and governs the charge-carrier transport. On the other hand, the current will be negatively influenced by the recombination of charge carriers on traps.[18] In both cases, one expects that an increase in temperature will promote the current through the device. In the absence of mono- or bimolecular recombination, the J_{SC} is expected to be weakly temperature-dependent, mainly due to thermal generation of charge carriers across the semiconductor bandgap and/or due to more efficient dissociation of precursor states for free electrons and holes, e.g., Coulomb bound polaron pairs. In this case, the thermally activated variation of mobility should not influence the photocurrent under, we emphasize, steady-state conditions. Independent of mobility, the total amount of extracted charges will remain the same. Instead, the capture of charge carriers by traps with subsequent recombination with opposite charges may lead to a variation of the current with temperature. Recombination of this type is denoted as monomolecular recombination. The capture itself is not necessarily a thermally activated process in contrast to the reemission. The probability to recombine will therefore depend on the dwell time on trap and will be higher at low temperatures. To prove this, the experimental data in Figure 2 were fitted with the expression

$$J_{SC}(T, P_{Light}) = J_{00}(P_{Light}) \exp\left(-\frac{\Delta}{kT}\right) \qquad (1)$$

where $J_{00}(P_{Light})$ is a pre-exponential factor which is comprised of the photogenerated charge-carrier density, their mobility, and the electric field. Finally, Δ is the trap depth with respect to the corresponding band, k the Boltzmann constant, and T the temperature. From the fits (dashed lines in Fig. 2) we obtained the activation energy $\Delta = 44.7 \pm 1.5$ meV for all the light intensities applied, and a strictly linear dependence for $J_{00}(P_{Light})$ with light intensity (see inset to Fig. 2). All $J_{SC}(T)$ curves have the same origin at $T = 0$ K. A saturation of J_{SC} with

temperature was not observed in the temperature range used. This is the material property of the absorber composites. We also note that the total photocurrent is determined by the interplay between the generation, drift, trapping/detrapping (i.e., scattering) and by the partial recombination on traps, therefore, the exact analysis of the system of rate equations that includes all those terms is necessary.[19]

We emphasize that this interpretation, i.e., the variation of short-circuit current due to the temperature variation of the charge carrier density, is only valid in case of monomolecular recombination of photogenerated charges. However, a low charge-carrier mobility of the absorber material (as well as the non-ohmic contacts) can favor the formation of space charge giving rise to a mutual recombination of electrons and holes, especially at high illumination intensity. In this case the temperature dependence of the mobility may be responsible for the variation of short-circuit current. The occurrence of bimolecular recombination in this case should be seen in a square-root current-density–intensity relationship. This aspect will be further discussed in Section 2.2.

2.1.2. Open-Circuit Voltage

The origin of the open-circuit voltage in bulk-heterojunction solar cells is a matter of debate. Physically the V_{OC} is controlled by the splitting of quasi-Fermi levels in the absorber. It was found to correlate directly with the acceptor strength, i.e., it is determined by the HOMO–LUMO (highest occupied molecular orbital–lowest unoccupied molecular orbital) energy gap of donor and acceptor, respectively, being nearly independent of electrode materials in the investigated range of work functions.[20] In a metal–insulator–metal (MIM) picture,[21] the V_{OC} is limited by the work-function difference between electrodes, i.e., is equal to the built-in field. According to the literature,[22] the V_{OC} is expected to be determined by both the built-in field and the photoinduced contribution, i.e., by the electrochemical potential gradient across the absorber layer.

The open-circuit voltage was measured as function of temperature at different illumination intensities and is shown in Figure 3. At $T = 320$ K and the highest illumination intensity used, $P_{Light} = 100$ mW cm^{-2}, the V_{OC} is 0.82 V. Upon cooling the sample to $T = 125$ K, the V_{OC} increases to 0.91 V. For conventional inorganic solar cells an increase in V_{OC} over a whole temperature range is expected.[23,24] In limit $T \to 0$ K, the V_{OC} approaches E_g/q, where E_g is the bandgap energy of the absorber material and q is the elementary charge. The applicability of such an approach to polymer solar cells is questionable, as the temperature dependence of several important parameters i.e., of diffusion length and acceptor density, is unknown.[23] The maximum value of 0.91 V measured is higher than the value expected in the MIM picture given by the difference in the work function of the electrode materials. The latter is expected to be in the range of 0.7 eV for PEDOT:PSS and Al. This feature of polymer solar cells was observed for many different composites used in the absorber, in some cases show-
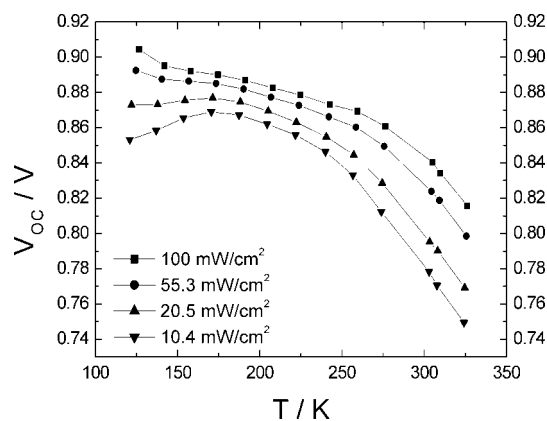
Figure 3. Open-circuit voltage V_{OC} as a function of temperature under different illumination intensities (white light) as indicated in the legend.

ing V_{OC} well above the difference in the work functions of the electrodes, already at room temperature.[25,26]

2.1.3. Fill Factor and the Power Conversion Efficiency

From the *J–V* curves of the illuminated sample, the series R_S and the parallel R_P resistances were deduced and are shown in Figure 4. R_S in the investigated OC$_1$C$_{10}$-PPV:PCBM-based so-
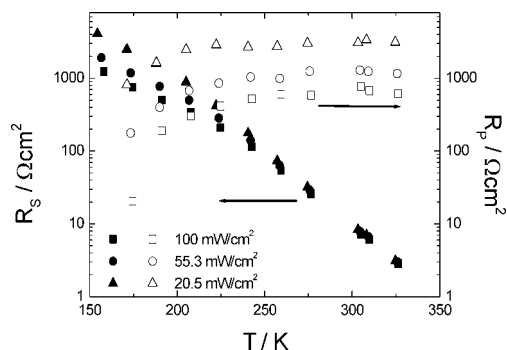

Figure 4. Temperature dependence of series (full symbols) and parallel resistance (open symbols) at light intensities as indicated by the legend.

lar cells decreases by three orders of magnitude in the temperature range 125–320 K, whereas R_P remains almost constant. R_S is primarily governed by the ohmic resistance of the absorber material. These two parameters determine the overall *J–V* shape, and show up themselves in the fill factor (*FF*). *FF* is a measure of the maximum electrical power P_{max} that can be extracted from a solar cell and is calculated using Equation 2.

$$FF[\%] = 100 \cdot \frac{P_{max}}{V_{OC} \cdot J_{SC}} \qquad (2)$$

The fill factor increases with temperature as is shown in Figure 5. At $T = 320$ K and 100 mW cm^{-2}, the value of $FF = 51$ % was obtained.
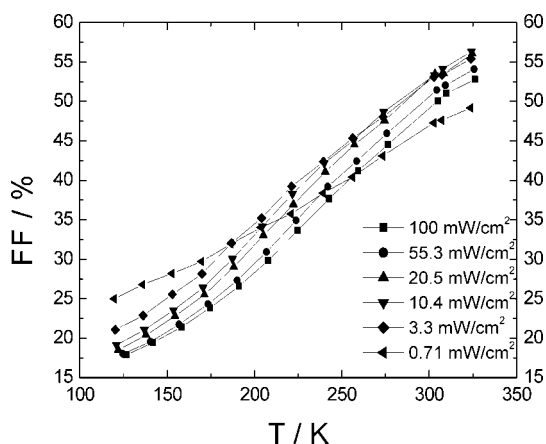

Figure 5. Fill factor *FF* of ITO/PEDOT: PSS/OC$_1$C$_{10}$-PPV:PCBM/Al device as a function of temperature for light intensities as indicated in the legend.

A strongly temperature-dependent short-circuit current and fill factor overwhelm a weakly temperature-dependent open-circuit voltage and result in a positive temperature coefficient of the power conversion efficiency defined as

$$\eta = \frac{J_{SC} \cdot V_{OC}}{P_{Light}} \cdot FF \qquad (3)$$

Figure 6 shows the temperature behavior of the power conversion efficiency for different illumination intensities. In contrast to our expectations, the highest value of $\eta = 2.5$ % was obtained not for the highest illumination intensity of 100 mW cm^{-2}, but for lowest light intensities in the range of 0.7 mW cm^{-2}. This fact will be discussed in the next section in terms of the light-dependent parallel resistance.
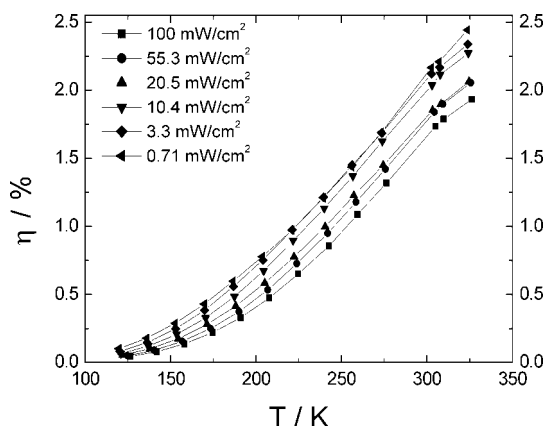

Figure 6. Calculated power conversion efficiency η as a function of temperature under white-light illumination. The legend indicates the corresponding light intensities in mW cm^{-2}.

2.2. Illumination Intensity Dependence

The charge carriers in the solar cells under investigation are efficiently photogenerated via ultrafast electron transfer between donor and acceptor counterparts of the composite, usually having a very low charge-carrier concentration in the dark. The fate of the photogenerated electrons and holes is crucial for the device efficiency, therefore, the influence of light intensity on the *J–V* characteristics is important.

2.2.1. Short-Circuit Current and Open-Circuit Voltage

Figure 7 displays the short-circuit current density as function of light intensity P_{Light} in a double-logarithmic scale. The J_{SC} follows the power-law dependence $J_{SC} = P_{Light}^{\alpha}$ with scaling ex-
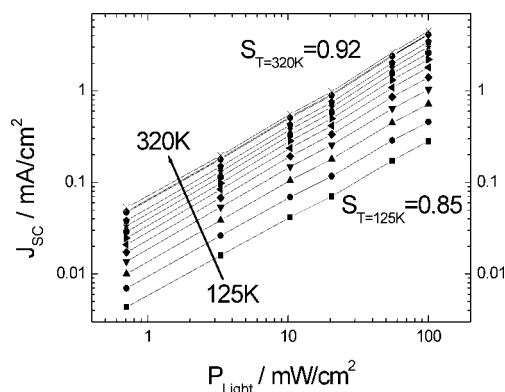
Figure 7. Double-logarithmic representation of the short-circuit current density as a function of light intensity for different temperatures. The scaling exponents between 0.85 and 0.92 are obtained for $T = 125$ K and $T = 320$ K, respectively.

ponents $\eta = 0.92$ and 0.85 for $T = 320$ K and $T = 125$ K, respectively. The nearly linear dependence of the J_{SC} indicates that charge-carrier losses in the absorber bulk are dominated by monomolecular recombination. Pure bimolecular recombination, e.g., the J_{SC} follows a square-root dependence on P_{Light} with $\alpha = 0.5$, was not observed even at highest illumination intensity. This is in agreement with the picture of photogeneration and transport of charge carriers in a donor–acceptor bulk heterojunction: an ultrafast electron–hole separation is followed by the transport of negatively and positively charged carriers within spatially separated networks: electrons along percolated fullerenes travel towards the Al contact, holes within the polymer matrix travel towards the PEDOT:PSS contact. As both contacts may be considered ohmic for the respective charge carriers (i.e., the potential barriers are below 0.5 eV), no space charge is formed at room temperature under short-circuit conditions, even at highest generation rates. The contribution of the bimolecular recombination resulting in a deviation of from 1 at $T = 125$ K may be, however, an indication of such a space charge effect and is due to low mobility. The predominance of monomolecular recombination together with a strong temperature dependence of the short-circuit current

confirms our assumption that the efficiency of devices is mainly limited by the charge-transport properties of the absorber materials, i.e., by trapping of charge carriers with subsequent recombination with charges of opposite sign. We note that this is valid by assuming a temperature-independent charge-carrier generation rate. In a solar cell, the steady-state current measured under short-circuit conditions is determined by the density of photogenerated charges driven to the outer circuit by the built-in electric field. In an ideal, recombination-free solar cell, the mobility alone is of no importance. In real devices, the product of mobility and the lifetime before recombination must be taken into account.[27]

Provided the short-circuit current density is proportional to the light intensity (see Fig. 7) and the saturation current density J_0 is independent of the illumination level, the V_{OC} is expected to be proportional to $\ln(J_{SC})$. This behavior (Fig. 8) was found only in the high temperature range $T = 280$–320 K.
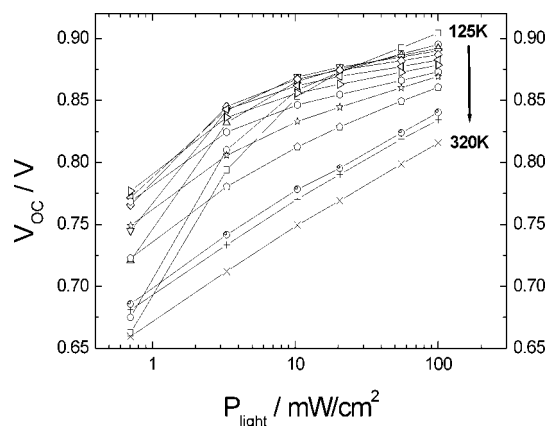
Figure 8. Open-circuit voltage as a function of light intensity in a semi-logarithmic scale at temperatures between 125 K and 320 K.

2.2.2. Fill Factor, Parallel Resistance, and Power Conversion Efficiency

Figure 9 shows *FF* as a function of illumination intensity. Above $T = 125$–140 K, *FF* depends on the light intensity only very weakly, i.e., it varies within 6 %, as compared to 28 % at $T = 125$ K. As expected, the highest *FF* of 51 % is measured at the highest temperature applied $T = 320$ K. As it was mentioned above, *FF* depends of both R_S and R_P in a complex way. Mostly dramatic is the variation of R_P with light intensity, as shown in Figure 10. The R_P, which is in the order of 100 kΩ cm² at a light intensity of 0.03 mW cm⁻², decreases by nearly three orders of magnitude at 100 mW cm⁻². This is qualitatively in agreement with the degradation of *FF* at higher illumination levels. In contrast, the R_S (not shown) varies very little, from 3 Ω cm² at $P_{Light} = 0.03$ mW cm⁻² to 2.8 Ω cm² at 100 mW cm⁻², both at $T = 320$ K.

The solar-cell efficiency decreases slightly with the light intensity. This is depicted in Figure 11, where η versus P_{Light} is
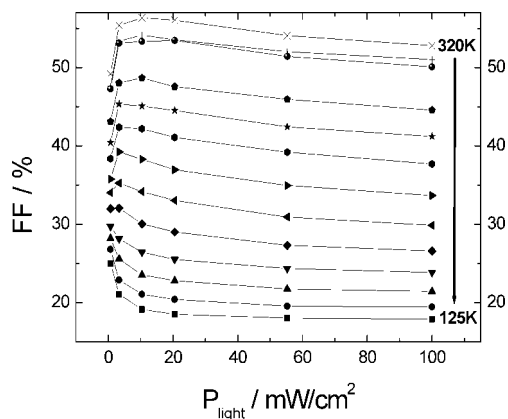
Figure 9. Fill factor *FF* of ITO/PEDOT:PSS/OC$_1$C$_{10}$-PPV:PCBM/Al device as a function of light intensity at temperatures between 125 K and 320 K.
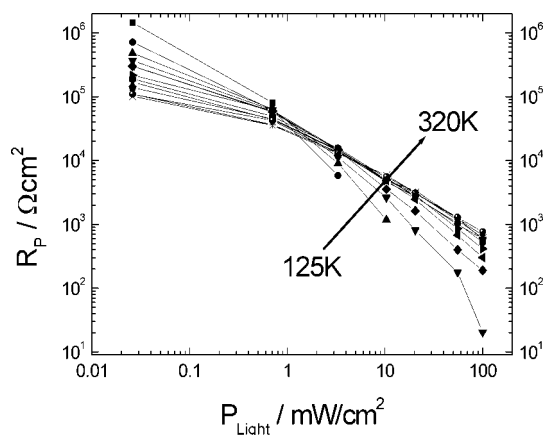

Figure 10. Parallel resistance R_P as a function of light intensity in double-logarithmic scale at temperatures between 125 K and 320 K.
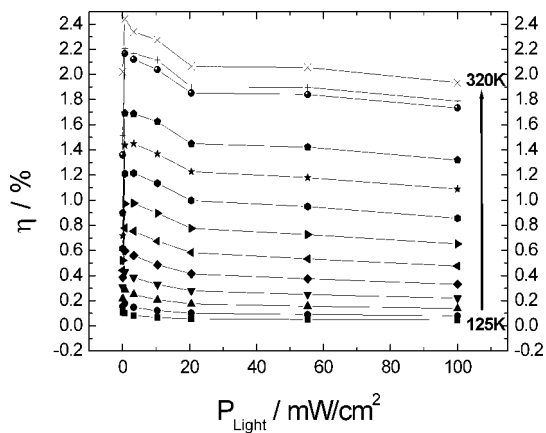

Figure 11. Calculated power conversion efficiency η as a function of illumination intensity at temperatures between 125 K and 320 K.

plotted for different temperatures. For all temperatures, the efficiency reaches its highest value at lowest excitation and decreases slightly when the illumination becomes more intense. We may conclude that the light-dependent R_P negatively influences the efficiency of our devices.

3. Conclusions

The parameters of ITO/PEDOT:PSS/OC$_1$C$_{10}$-PPV:PCBM/Al solar cells exhibit a strong dependence on light intensity as well as on temperature. Even at room temperature, the open-circuit voltage exceeds the value expected from the work function difference of the electrode materials used. The V_{OC} increases further upon cooling the device. The maximum value of 0.91 V exceeds the electrode's contact potential difference by 200 mV. The V_{OC} increases logarithmically with light intensity. However at low temperatures, a saturation of the V_{OC} at higher intensities is observed and remains to be clarified.

The short-circuit photocurrent is strongly temperature-dependent and has a value of 4.5 mA cm^{-2} at $T = 320$ K. It is thermally activated with an activation energy (trap depth) of 44.7 meV, which is independent of light intensity. The dominant contribution of shallow defects to the temperature dependence of J_{SC} rather than that of the mobility is supported by the monomolecular recombination of photogenerated charges observed, whereby the short-circuit current varies linearly with light intensity in a broad temperature range.

The overall solar-cell efficiency strongly increases with the temperature and is only weakly dependent on the light intensity, reaching the maximum value of 1.9 % at $T = 320$ K and 100 mW cm^{-2} and 2.5 % at 0.7 mW cm^{-2} (white-light) illumination.

The absence of bimolecular recombination, being the intrinsic feature of polymer–fullerene networks, together with a strong temperature dependence of the short-circuit current, confirms that the efficiency of ITO/PEDOT:PSS/OC$_1$C$_{10}$-PPV:PCBM/Al devices is limited by transport properties of the absorber. As a result, the active layer thickness must be kept low at the expense of the photogeneration of charge carriers.

4. Experimental

The devices studied in this work were made in a ITO/PEDOT:PSS/OC$_1$C$_{10}$-PPV:PCBM/Al configuration. The active layer was made by spin-coating a 1:4 chlorobenzene solution of poly[2-methoxy-5-(3,7-dimethyl octyloxy)-1,4-phenylene vinylene] (OC$_1$C$_{10}$-PPV) and phenyl-C$_{61}$ butyric acid methyl ester (PCBM) onto a glass substrate.

The OC$_1$C$_{10}$-PPV was synthesized via the sulfinyl route as described elsewhere [28]. This novel route is particularly attractive because it produces polymeric intermediates soluble in organic solvents avoiding the ionic precursors. The formation of the *p*-quinodimethane **2** (the "real" monomer) is represented in Figure 1c for OC$_1$C$_{10}$-PPV.

As a hole-extracting electrode, the 80 nm layer of poly(ethylene-dioxythiophene) doped with poly(styrene sulfonate) (PEDOT: PSS), BAYTRON P, (Bayer AG, Germany) was spin-coated on a glass substrate, coated with patterned indium tin oxide (ITO). The aluminum counter electrode was thermally evaporated in a vacuum chamber at rate 2 Å s^{-1}. The device active area was 1.3 mm^2.

The current–voltage measurements were carried out in a variable-temperature cryostat equipped with a liquid-nitrogen supply and a temperature controller (Lakeshore 330). The devices were illuminated through a sapphire window by white light from a xenon arc lamp whose intensity is controlled by a set of neutral density filters with transmission coefficients from 10^{-4} to 1. The spectral emission was corrected for the intense IR output by a water filter. The maximum intensity was calibrated to 100 mW cm^{-2} inside the cryostat. The current–voltage profil-

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ing was automatically carried out with a source-meter unit (Avantest TR-6143).

The R_S and R_P in Figures 4,10 were deduced from the slopes $(\delta I/\delta V)$ at $V = +1.5$ V and $V = 0$ V, respectively, from J–V characteristics under illumination.

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