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Electrical and optical design and characterisation of regioregular poly(3-hexylthiophene-2,5diyl)/fullerene-based heterojunction polymer solar cells

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Abstract

Electrical and optical properties of poly(3-hexylthiophene-2,5diyl) (P3HT-2,5diyl) used as the main component in a bulk heterojunction polymer/fullerene solar cell were investigated. The HOMO level of the polymer was estimated at about 4.7–5.1 eV, from the observed space charge limited current (SCLC) studies in ITO/P3HT-2,5diyl/Au hole-only devices, which confirmed the formation of ohmic contacts between the polymer and the Au and ITO electrodes. The values calculated for hole mobility and density range from 1.4×10^{-6} cm^2/(V s) and 5.3×10^{14} cm^{-3} at 150 K to 8.5×10^{-5} cm^2/(V s) and 1.1×10^{15} cm^{-3} at 250 K, respectively. A HOMO–LUMO gap of 2.14 eV was estimated from an absorption spectrum of the polymer. Photoinduced charge transfer from polymer to PCBM was evidenced by strong photoluminiscence quenching, which was observed when the polymer was mixed with [6,6]-phenyl-C$_{61}$ butyric acid methyl ester (PCBM). Charge carrier transport properties of the polymer/fullerene solar cells were studied by analysing the dependence of *J–V* characteristics on temperature and illumination intensity. A linear decrease of the open-circuit voltage with increasing temperature, with a local maximum around 320 K, was observed. The short-circuit current density increased with temperature, having a maximum around 300 K and decreased thereafter. Efficiency and fill factor presented maxima around 3 mW/cm^2 white light intensity, and this was attributed to the poor bulk transport properties of the active layer. Typical values recorded for the solar cell at 300 K under white light of 100 mW/cm^2 intensity were: open-circuit voltage 0.48 V, and current density 1.28 mA/cm^2, with an efficiency of 0.2% and fill factor of 30.6%.
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Keywords: Polyhexylthiophene; Space charge limited current; Polymer solar cells

1. Introduction

In the context of technological applications, among many conjugated polymers, poly(3-alkylthiophenes) have been found to be a special class of polymers with good solubility, processability and environmental stability. Generally this class of materials exhibits an optical band gap in the range of 1.7–2.1 eV [6].

In this article, the development of a bulk heterojunction polymer/fullerene solar cell based on poly(3-hexylthiophene-2,5diyl) (P3HT-2,5diyl), as an electron donor, and a soluble fullerene derivative [6,6]-phenyl-C$_{61}$ butyric acid methyl ester (PCBM), as an electron acceptor, is reported.

Space charge limited current (SCLC) measurements have been performed in order to determine the choice of electrodes and the bulk transport properties of the polymer. Optical properties of the polymer, like photoinduced absorption and photoluminescence were studied experimentally to establish the possibility of making a functional solar cell using this polymer. Electrical properties of the developed polymer/fullerene heterojunction solar cell have been investigated by recording the variation of current density–voltage characteristics of the solar cell with light intensity and temperature.

2. Experimental

ITO/P3HT-2,5diyl/Au hole-only devices were prepared by spin coating P3HT-2,5diyl from a chloroform solution, on

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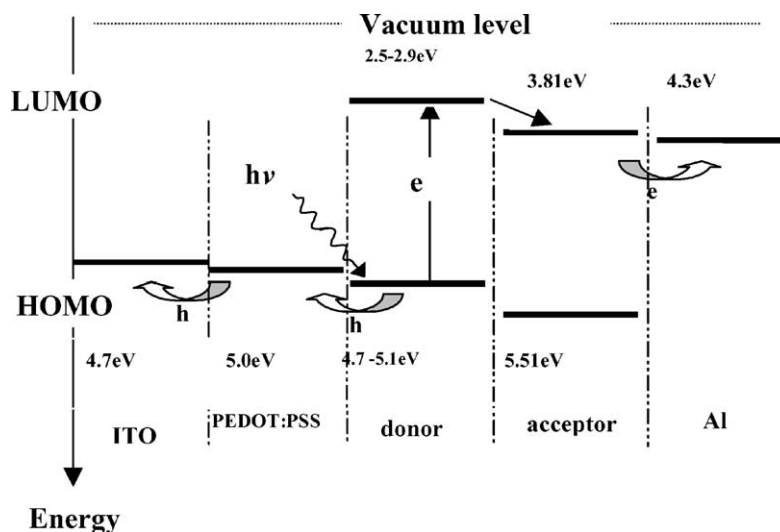
Fig. 1. Operation principle: photons with energy $hv = 2.14$ eV excite electrons from HOMO (P3HT-2,5diyl) ≈ 4.7–5.1 eV into LUMO (P3HT) ≈ 2.56–2.96 eV, which are then transferred to LUMO (PCBM) ≈ 3.81 eV, from which they can be collected by a $-$ve Al electrode with workfunction $\varphi \approx 4.3$ eV. Holes are collected, via PEDOT:PSS workfunction ≈ 5.0 eV, by $+$ve ITO electrode with workfunction ≈ 4.7 eV. (Possible recombination paths are not indicated in the diagram.)

clean ITO coated glass substrates, in a nitrogen atmosphere of a glove box, and depositing Au contacts by thermal evaporation at low rate in high vacuum (better than 10^{-6} mbar) in all cases. Four-point, temperature-dependent, dark current–voltage measurements were performed in a vacuum of about 5×10^{-5} mbar in a liquid-nitrogen-cooled cryostat, using a source measure unit (Advantest TR 6143). This step was necessary because the information concerning the HOMO–LUMO values of P3HT-2,5diyl was not available to our knowledge, even from Sigma–Aldrich Chemie GmbH (Germany) from where the polymer was commercially available on a large scale.

ITO/PEDOT:PSS/P3HT-2,5diyl:PCBM/Al heterojunction solar cells were prepared in a nitrogen atmosphere of a glove box and characterised. First, a thin layer of polyethylene-dioxythiophene doped with polystyrene-sulfonic acid (PEDOT:PSS) (Baytron P, Bayer AG, Germany) was spin coated (1500 rpm) on patterned clean ITO coated glass substrates. PEDOT:PSS is known as a p-type semiconductor, a good hole transport material, and assures a better hole collection from the active layer onto the ITO electrode. An active layer consisting of a mixture of P3HT-2,5diyl/PCBM at a 1:4 mass ratio dissolved in a chloroform–toluene solvent mixture at 0.25 wt.% was then spin coated (speed 4000 rpm) on top of the dry PEDOT:PSS film to give a thin film of about 100 nm. Finally, 100 nm Al contacts were deposited on the active layer by thermal evaporation. The structure of the device is indicated in Fig. 1. Temperature- and illumination-dependent current–voltage characteristics were obtained by utilising an Advantest TR 6143 source measure unit, with the solar cell placed in a liquid-nitrogen-cooled cryostat at better than 10^{-5} mbar vacuum. A 150 W xenon lamp (Osram XB0 150 W/XBR) was used as the illumination source with a water filter placed in the light path in order to

approximate the AM1.5 solar spectrum. The light intensity was varied by three orders of magnitude, i.e. from 0.1 to 100 mW/cm^2.

3. Results and discussion

3.1. Photoluminescence quenching in P3HT-2,5diyl: PCBM composite

It has been observed that P3HT-2,5diyl exhibits photoluminescence, which is strongly (almost completely) quenched when the polymer is mixed with PCBM. This is the evidence of the photoinduced charge transfer from the polymer to the fullerene (Fig. 2). The HOMO–LUMO energetic difference has been estimated to be about 2.14 eV from an absorption spectrum of a spin cast thin film (Fig. 2), which corresponds to the midpoint of the absorption edge, at a wavelength of about 580 nm.

3.2. I–V studies of ITO/P3HT-2,5diyl/Au devices

The choice of electrodes was done after the analysis of current injection into hole-only ITO/P3HT-2,5diyl/Au devices. Fig. 3a shows typical curves of $\log(J)$ against $\log(V)$ plots obtained when injecting holes through the gold contact (higher potential on Au) and Fig. 3b shows the same but for injection through the ITO contact (higher potential on ITO). It is noted that the current at 150 K is lower than that at 250 K.

The current density–voltage characteristics are nearly linear at low voltages and become super linear at high voltages. In Fig. 3a, the slope of the curve at low voltages is exactly 1 and at higher voltages it is exactly 2. The dotted lines have slopes 1 and 2, respectively. Superlinear J–V
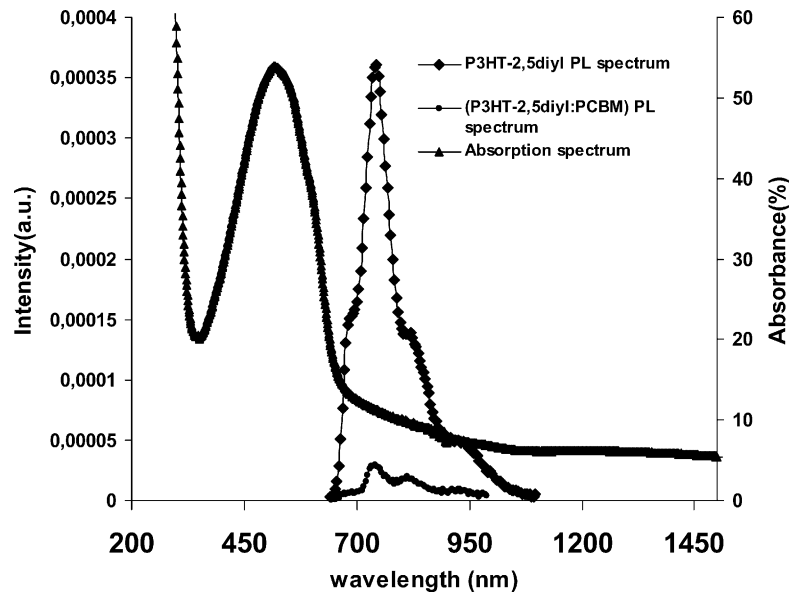
Fig. 2. Photoluminiscence quenching is evidence of photoinduced charge transfer from P3HT-2,5diyl to PCBM. The absorption spectrum of P3HT-2,5diyl indicates an absorption edge at about 580 nm corresponding to a HOMO–LUMO energetic difference of 2.14 eV.
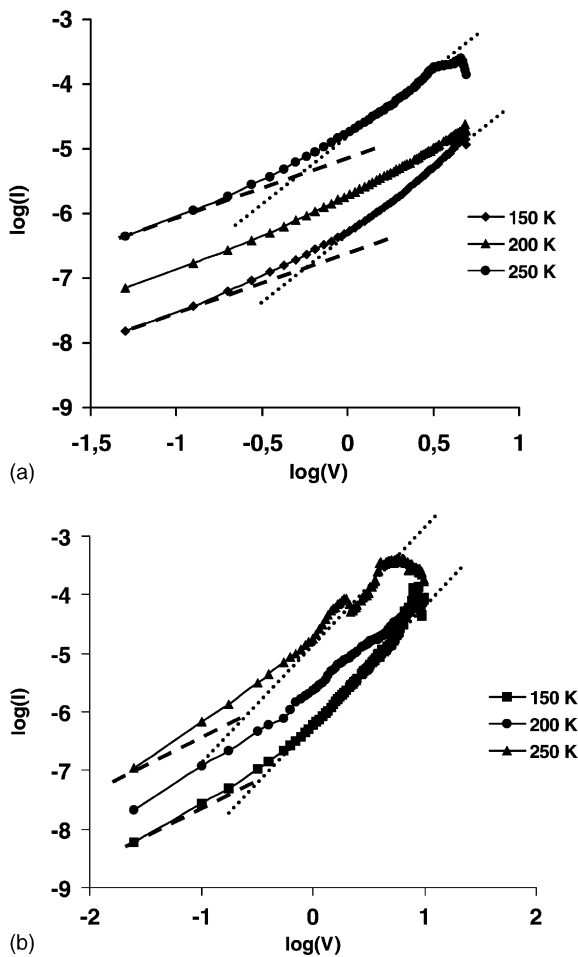

Fig. 3. Current–voltage curves for hole injection into P3HT-2,5diyl through (a) Au and (b) ITO. Dotted lines show slopes 1 and 2.

behaviour indicates the so-called space charge limited current, where the electrode injects more holes than what the material can transport.

Space charge limited currents in a device can occur if at least one contact [4] is able to inject locally higher carrier densities than the material has in thermal equilibrium without carrier injection. Such a contact is referred to as ohmic. With ohmic contacts, the current–voltage relation is often ohmic at low bias up to a certain value since the field due to the injected carriers is negligible compared to that due to the applied bias. This can be seen by a linear relation (slope 1 in log–log plot) between current I (or current density J), and voltage V at low voltages described by Eq. (1) [9]:

$$J_{\text{ohm}} = q n_{\text{p}} \mu \frac{V}{d} \qquad (1)$$

where q is the electronic charge, n_{p} the charge carrier density, μ the carrier mobility, V the applied voltage and d the thickness of sample. This condition breaks down at the space charge limit when the injected carrier density becomes so great that the field due to the carriers themselves dominates over that of the applied bias and then becomes space charge limited. At this point the J–V characteristics should switch to pure space charge limited current flow for higher voltages. In the absence of traps, the trap-free space charge limited currents (TFSCLC) situation can be observed, and the J–V follows Child's law (Eq. (2)). This behaviour is characterised by a strict quadratic dependence of voltage on current (slope 2) (note that this does not necessarily imply the absence of traps in the material, but rather that they are all filled):

$$J_{\text{SCL}} = \frac{9}{8} \varepsilon_0 \varepsilon_{\text{r}} \mu \frac{V^2}{d^3} \qquad (2)$$

If at higher applied bias the quasi-Fermi level intersects a trap distribution, e.g. exponential, then the characteristics will begin to follow Eq. (3):

$$J_{SCL} = \frac{9}{8}\varepsilon_0\varepsilon_r\theta\mu\frac{V^2}{d^3} \qquad (3)$$

where θ is the fraction of the total charges free to move, which depends on the trap density and the activation energy to thermally excite a charge from the trap to the conduction band.

Hole mobilities and densities were calculated by equating Ohm's (Eq. (1)) and Child's (Eq. (2)) laws at cross-over points indicated by the intersection of lines of slopes 1 and 2 in Fig. 3a. The calculated hole mobility and density range from 1.4×10^{-6} cm^2/(V s) and 5.34×10^{14} cm^{-3} at 150 K to 8.5×10^{-5} cm^2/(V s) and 1.09×10^{15} cm^{-3} at 250 K, respectively, for a 465 nm film, where dielectric permittivity has been assumed to be 3. The ITO contact does not show the slope 1 behaviour at low voltages, indicating that the carrier density is very great even at low applied bias. Unfortunately this behaviour cannot be used to estimate this density, i.e. suffice to say that Au is an ohmic contact and ITO provides an even better injection. Based on these results one can conclude that the HOMO of P3HT-2,5diyl must lie within 0.5 eV of the workfunction of Au, i.e. at about 5.1 ± 0.5 eV otherwise SCLC behaviour is less probable [1–4]. It is even argued that this is only possible within less than 0.3 eV workfunction difference [8]. Since ITO also provides ohmic injection, and this is only possible if its workfunction lies within 0.5 eV of that of the HOMO of the polymer, it may be concluded that the HOMO of the polymer lies between the workfunction of ITO and that of Au, i.e. between 4.7 and 5.1 eV. This estimated value compares well with the results of Yamamoto et al. [11], who used silver electrodes in cyclic voltammetry experiments and obtained a redox potential of 0.78 V for P3HT-2,5diyl in reference to the Ag|Ag$^+$ electrode. In this case the workfunction of the polymer would be equal to that of the reference electrode plus the obtained redox potential. The workfunction of silver is reported to be about 4.30 eV [3], implying that the HOMO of P3HT-2,5diyl would be about 5.08 eV.

3.3. Studies of ITO/PEDOT:PSS/P3HT-2,5diyl:PCBM/Al solar cell

Typical current density–voltage characteristic curves of an ITO/PEDOT:PSS/P3HT-2,5diyl:PCBM/Al solar cell have been plotted in a semi-logarithmic representation in Fig. 4 at different light intensities from 1 to 100 mW/cm^2 at $T = 300$ K. For this cell, values obtained for the main parameters such as power conversion efficiency, η, open-circuit voltage, V_{oc}, short-circuit current density, J_{sc}, and fill factor, FF, are shown in Table 1. An increase of short-circuit current density with temperature, which tends to saturate to some maximum value around 300 K, followed by a decrease at higher temperature values was observed, as shown in
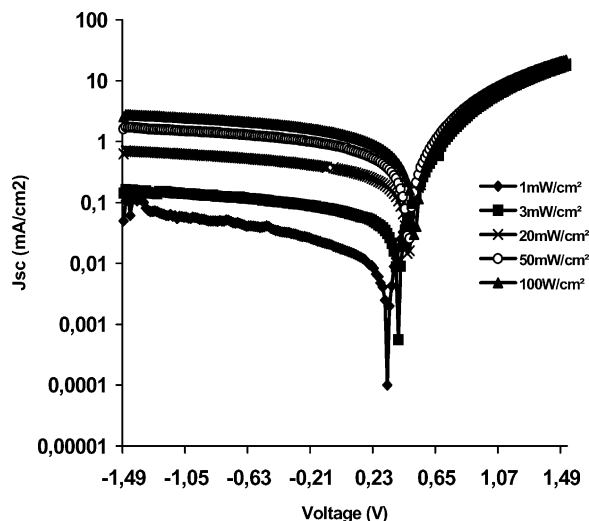

Fig. 4. Current density–voltage characteristics of an ITO/PEDOT:PSS/P3HT-2,5diyl:PCBM/Al solar cell.

Table 1
Typical output characteristics of an ITO/PEDOT:PSS/P3HT-2,5diyl:PCBM/Al solar cell

P_{light} (mW/cm^2)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	η (%)
100	1.280	0.480	30.6	0.188
50	0.807	0.450	33.9	0.246
20	0.335	0.420	37.0	0.260
10	0.189	0.405	38.0	0.291
3	0.070	0.360	39.7	0.332
1	0.016	0.300	33.7	0.166
0.1	0.012	0.045	20.0	0.108

Fig. 5. This can be understood by considering that the current output of a solar cell is proportional to the number of generated charge carriers and to their mobility. In most conventional inorganic semiconductors mobility varies with temperature according to the following law [13]:

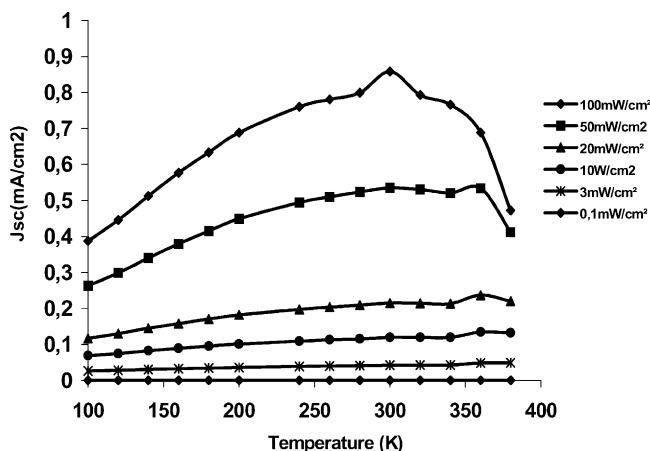$$\mu \propto T^n \qquad (4)$$

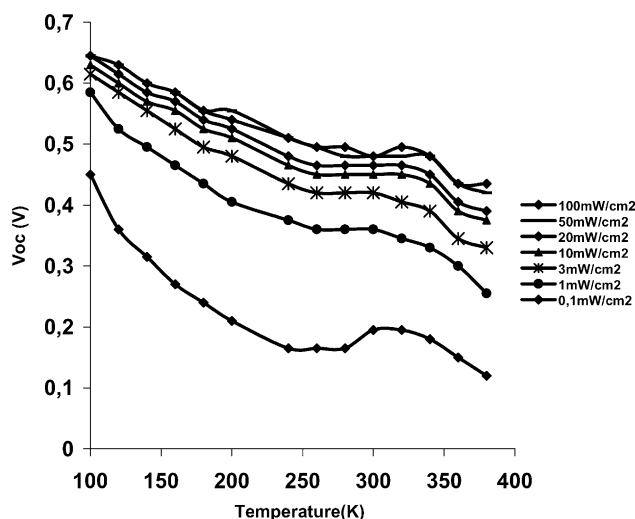Fig. 5. Variation of the short-circuit current density with temperature.

Fig. 6. Variation of open-circuit voltage with temperature.

where $n = 3/2$ for impurity scattering and $n = -3/2$ for lattice scattering. Due to the fact that the scattering events increase with temperature, the mobility is expected to decrease as the sample is heated.

In organic materials the mobility is thermally activated and charge carriers transport mechanism occurs via localised states through phonon activated hopping mechanism. This is justified by considering that for organic materials another law determines the conductivity [10]:

$$\sigma = \sigma_0 \exp\left(-\frac{\Delta E}{2kT}\right) \tag{5}$$

where σ is conductivity ($\Omega^{-1} \, cm^{-1}$), T the temperature and ΔE the activation energy (energy corresponding to the band gap + energy for delocalisation of charge carriers).

As a general conclusion for organic materials, at low temperatures few charge carriers are thermally generated and are not easily transported, therefore the current, without illumination, is low. On the other hand, the heating of the polymer above a certain temperature may have a negative influence upon the polymer chain conformation which determines a decrease in the conductivity [2].

The previously mentioned thermally activated hopping mechanism and the temperature-dependent morphology alteration of the polymer are opposing processes which appear to give maximum of charge carrier mobility around room temperature.

The open-circuit voltage of a ITO/PEDOT:PSS/P3HT-2,5diyl:PCBM/Al solar cell decreases almost linearly increasing the temperature from 80 to 300 K, as shown in Fig. 6. The model for conventional inorganic semiconductor solar cells could be used to explain the obtained behaviour of open-circuit voltage. For a p–n junction solar cell, the open-circuit voltage is given by

$$V_{oc} = \frac{kT}{e}\left(\ln\frac{I_{sc}}{I_0} + 1\right) \approx \frac{kT}{e}\left(\ln\frac{I_{sc}}{I_0}\right) \tag{6}$$

where I_{sc} is the short-circuit current, I_0 the reverse saturation current, k the Boltzmann's constant, T the absolute temperature and e the electronic charge. Considering that

$$I_0 = I_{0\,max} \exp\left(-\frac{E_g}{kT}\right) \tag{7}$$

where E_g is the energy gap of the material, and substituting it in (6), an expression for V_{oc} is obtained:

$$V_{oc} = \frac{E_g}{e} - \left(\frac{kT}{e} \ln\frac{I_{0\,max}}{I_{sc}}\right) \tag{8}$$

The open-circuit voltage manifests an almost linear decrease with increase in temperature, consistent with inorganic solar cell theory. However, around 320 K a local maximum was observed. The highest recorded open-circuit voltage value of 0.65 V was obtained at 100 K. Moreover, for all illumination intensities studied, the $V_{oc}(T)$ increases to a convergence point of 0.75 V that can be extrapolated for $T \to 0$ K. This voltage can be treated as an upper limit value for the device in question. The dependence can however not be completely linear, because the in previously mentioned model even inorganic materials does not take into account the variation of the band gap with temperature [12], which should follow Eq. (9):

$$E_g = E_{g0} - \frac{aT^2}{b + T} \tag{9}$$

where E_{g0} is the band gap at $T = 0$ K, and a and b are constants.

Katz and Faiman [7] have measured for PPV the same dependence of the V_{oc} with temperature. They proposed a straight-line equation to describe this dependence, where they considered the energy gap to be independent of temperature. The matching of their proposed equation with experimental data suggests that the variation of the band gap with temperature might be negligible when compared to that of the second term on the right-hand side of Eq. (8).

As stated earlier, it may be concluded that the open-circuit voltage for the studied solar cells is less than the contact potential difference of respective electrodes (ITO/PEDOT:PSS and Al), which is in the range 0.9–1.3 eV consistent with the estimated HOMO of the polymer at 4.7–5.1 eV. Therefore, it may be concluded that the V_{oc} might be determined by the energetic difference between the LUMO of the acceptor and the HOMO of the donor. This can be defined as a thermodynamic limit for the open-circuit voltage of a donor–acceptor solar cell. This is a possible reason why the curves in Fig. 5 come closer to each other as the light intensity increases. This fact demonstrates saturation behaviour and indicates that open-circuit voltage is an intrinsic property of the absorber material. The fill factor and energy conversion efficiency show maxima around 300 K, possibly due to an adding effect of short-circuit current and open-circuit voltage. The fact that the maximum value of solar cell power conversion efficiency has been
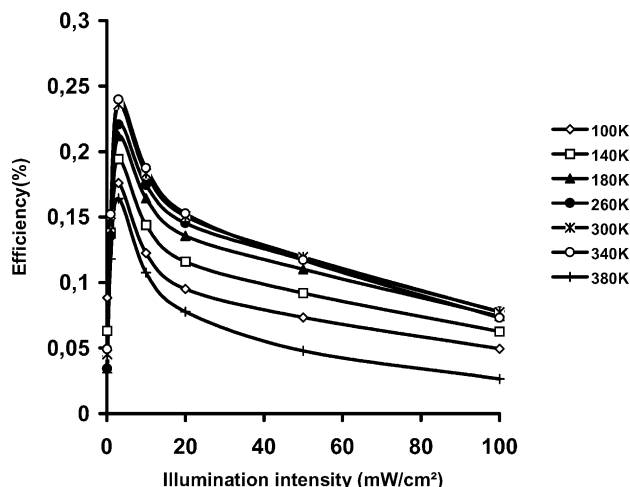
Fig. 7. Variation of efficiency with illumination intensity.

recorded at 3 mW/cm^2 (Fig. 7), may be attributed to the poor transport properties of the absorber, implying that although more charge carriers are photo-generated at higher light intensities, they cannot be easily transported to the electrodes. In the case of polythiophene this effect might be a contribution of the highly disordered structure and possible phase separation between donor and acceptor, both resulting in low mobility of charge carriers.

4. Conclusions

SCLC studies of a hole-only device were employed to estimate the HOMO level of a donor, and the resulting energy gap calculated from absorption spectroscopy, was used to estimate the LUMO. It is further proposed that the LUMO level of an acceptor may be estimated by SCLC analysis of an electron only device. A 0.2% efficient solar cell based on regioregular P3HT-2,5diyl, as donor, and PCBM, as acceptor, has been fabricated and characterised by means of temperature and illumination-dependent current density–voltage characteristics. It is necessary to stress the need to use high purity materials, to optimise the morphology and to avoid any contact with oxygen or other contaminants as the main conditions for a better efficiency of the solar cells based on P3HT-2,5diyl [5].

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