Advanced Energy Materials 2 (2012) 1100-1108
DOI: 10.1002/aenm.201200077
Article type: Full Paper

Thermodynamic efficiency limit of molecular donor-acceptor solar cells and its application to diindenoperylene / C_{60} based planar hetero-junction devices

*Mark Gruber, Julia Wagner, Konrad Klein, Ulrich Hörmann, Andreas Opitz, Martin Stutzmann, and Wolfgang Brütting**

[*] Prof. Wolfgang Brütting, M. Gruber, J. Wagner, U. Hörmann, A. Opitz
Institut für Physik
Universität Augsburg
Universitätsstr.1, 86135 Augsburg, Germany
E-mail: wolfgang.bruetting@physik.uni-augsburg.de

Konrad Klein, Martin Stutzmann
Walter Schottky Institut
Technische Universität München
Am Coulombwall 4, 85748 Garching, Germany

Keywords: diindenoperylene, open circuit voltage, organic solar cells

Abstract

In organic photovoltaic (PV) cells, the well-established donor-acceptor (D/A) concept enabling photo-induced charge transfer between two partners with suitable energy level alignment has proven extremely successful. Nevertheless, the introduction of such a hetero-junction is accompanied with additional energy losses as compared to an inorganic homo-junction cell, owing to the presence of a charge-transfer (CT) state at the D/A interface. Based on the principle of detailed balance we have developed a modified Shockley-Queisser theory, including the essential effects of interfacial CT states, that allows for a quantitative assessment of the thermodynamic efficiency limits of molecular D/A solar cells. Key parameters, apart from the optical gap of the absorber material, entering the model are the energy (E_{CT}) and relative absorption strength (α_{CT}) of the CT state. We demonstrate how the open-circuit voltage (V_{OC}) and thus the power conversion efficiency are affected by different parameter values.

Furthermore, we show that temperature dependent device characteristics can serve to determine the CT energy, and thus the upper limit of V_{OC} for a given D/A combination, as well as to quantify non-radiative recombination losses. The model is applied to

diindenoperylene (DIP)-based photovoltaic devices, where open-circuit voltages between 0.9 and 1.4 V, depending on the partner, have recently been reported.

1. Introduction

Harvesting solar energy can be established by several methods including natural processes, like photosynthesis, or artificial processes, like photovoltaics (PV) and solar thermal heat conversion. In the latter cases, the underlying basic principles are the solar thermal converter and the photochemical converter, respectively.[1.2] Solar thermal processes use the whole sun spectrum to convert photo-induced heat into extractable energy, whereas photochemical converters, like PV cells, only use sunlight exceeding a specific energy. Regarding this under thermodynamic aspects, the Carnot limit exhibits the best description for solar thermal processes being mainly classical heat engines, while photochemical converters have a more stringent limit first described by Shockley and Queisser in 1961, which is of course consistent with the Carnot theory.[3,4]

The Shockley-Queisser (SQ) limit for inorganic homo-junction cells, considers detailed balance between the absorbed and emitted photon flux in thermal equilibrium.[5] The calculations are almost independent of the details of the internal photovoltaic conversion processes and establish a correlation between band gap energy (E_g) and maximum attainable open circuit voltage (V_{OC}), short circuit current density (j_{SC}), fill factor (FF) and power conversion efficiency (η). One of the central assumptions made for the calculation is based on complete absorption of photons with energy exceeding the band gap of the semiconductor. It further assumes that generated electron-hole pairs are directly available as free charges and not as Coulombically bound excitons. In crystalline inorganic semiconductors this assumption is reasonable, as high dielectric constants and efficient carrier screening lead to low exciton binding energies, which can be overcome by the thermal energy at room temperature.

In contrast, the working mechanism of organic semiconductors is markedly different, most importantly due to the excitonic nature of photo-excitations. Using them in photovoltaic devices thus requires finding ways for an efficient dissociation of excitons with binding energies of the order of 0.5 eV, mainly resulting from weak electronic delocalisation and low dielectric constants.[6] In this context, the well-established donor-acceptor (D/A) concept enabling photo-induced charge transfer between two partners with suitable energy level alignment has proven extremely successful.[7,8] However, the hetero-junction concept entails

an intrinsic energy loss in the dissociation process of excitons given by the energy difference of the lowest unoccupied molecular orbitals (LUMO) and the highest occupied molecular orbitals (HOMO) of both partners (see **Figure 1**), leading to a reduction of the open-circuit voltage and thus of the overall device efficiency. Furthermore, charge generation and recombination are no more exclusively related to the optical gap of the absorbers (E_g), but additionally depend on the energy of the charge transfer (CT) state (E_{CT}), which is formed at the D/A interface and its relative absorption strength (α_{CT}).[9,10] While light absorption, and with that the generated photocurrent of the solar cell, is still dominated by E_g as long as α_{CT} is small, E_{CT} severely affects charge carrier recombination and, accordingly, the open circuit voltage of a solar cell, as will be discussed in detail in this paper.
Thus, for calculating the efficiency limits in organic D/A solar cells, the basic approach of the SQ theory has to be modified to account for the peculiarities of organic semiconductors and the energetic constellation determined by the D/A hetero-junction. Corresponding studies have recently been performed, suggesting that a modified SQ theory is applicable to calculate the radiative efficiency limits of organic hetero-junction solar cells.[11-13]

In the present work, we follow the approach put forward by Giebink *et al.*[13], however, we extend their treatment in two ways. First, we investigate the influence of different absorption strength α_{CT} of the CT state on the open-circuit voltage and the overall PV efficiency. And second, we demonstrate that the temperature dependence of V_{OC} can be used to determine the a priori unknown energy of the CT state. Additionally, the extended SQ limit is applied to a novel small molecule planar hetero-junction solar cell system based on diindenoperylene (DIP) and derivatives, where open-circuit voltages between 0.9 and 1.4 V, depending on the respective partner, have recently been reported.[14-19] Relevant parameters, such as the energy E_{CT} and absorption coefficient α_{CT} of the CT state – both being crucial for the simulations – are derived from experiment. Furthermore, the comparison of measured $V_{OC}(T)$ data to simulations based on the here presented modification of the SQ theory allows to quantify non-radiative recombination losses in this D/A system.

The paper is organized as follows: In the first part, we will introduce the basic principles of the modified SQ limit, comprising a general discussion of its implications for organic solar cells. Thereby the presentation of the theory is restricted to some basic formulae, as the detailed procedure can be found in Ref.[3,11,13]. Special emphasis will be put on the role of the CT state for the open-circuit voltage and its temperature dependence. The second part will focus on the temperature dependence of the open-circuit voltage of a DIP/C_{60} planar hetero-junction cell and its analysis by the afore-described modified SQ theory.

2. Modified Shockley-Queisser theory

Following to the classic work of Shockley and Queisser, our calculations are based on the principle of detailed balance, which requires equilibrium between incoming sunlight and radiation from the solar cell under open circuit conditions, both assumed as black bodies – though at largely different temperatures (about 5778 K for the surface of the sun and 300 K for the PV cell, respectively).[3] While the basic considerations of the original work – valid for inorganic homo-junction solar cells – can be adapted, some modifications referring to the electronic structure of organic hetero-junctions have to be included. The SQ theory assumes a single-step function for the absorption coefficient, i.e. the absorption of the idealized solar cell equals unity for photon energies above the band gap ($E \geq E_{\mathrm{g}}$), while photons with energies below E_{g} do not induce any effect. In organic solar cells, the high exciton binding energies necessitate the introduction of a D/A hetero-junction with the concomitant possibility to form a CT state with energy E_{CT}, being lower than the optical gap of either of the two semiconductors to ensure successful electron or hole transfer, respectively. The energetic offset ΔE between both energy gaps ($\Delta E = E_{\mathrm{g}} - E_{\mathrm{CT}}$) acts as the driving force for the photoinduced charge transfer (see inset Fig. 1).

Please note that the exciton binding energy itself is already included in the following treatment by the convention that E_g denotes the optical gap of the semiconductor and not the single particle or transport gap. It is also worth mentioning that we will not consider the microscopic nature of the CT state (whether it is localized or delocalized and the decay rate; see ongoing discussion) and also not the question if it is coulombically bound or not.[20,21] In our treatment E_{CT} is simply a parameter that determines at which energy radiative (and non-radiative) recombination – required for detailed balance in a PV cell – occurs, thus governing the open-circuit voltage measured under steady state conditions. How this energy is related to values obtained, e.g. from photoelectron spectroscopy, remains to be investigated.

With the absorption of the CT state, α_{CT}, being in the range of 10^{-4} to 10^{-2} relative to the main absorption α_0 in common bulk hetero-junction organic solar cells[22], the absorption spectrum $\alpha(E)$ has to be extended by an additional step[13], resulting in

$$\alpha(E)=\begin{cases} 0 & \text{for} \quad E<E_{\mathrm{CT}} \\ \alpha_{\mathrm{CT}} & \text{for} \quad E_{\mathrm{CT}}<E<E_{\mathrm{g}} \\ \alpha_0\equiv 1 & \text{for} \quad E>E_{\mathrm{g}} \end{cases}, \tag{1}$$

where E_{g} is the optical gap of either the donor or acceptor material, depending on which of both has the smaller value. This decisive assumption is illustrated in Fig. 1.

In accordance with Planck's law, the number of photons per unit area and time, $N(E_{\mathrm{CT}},T)$, which is absorbed or emitted by the organic solar cell can be calculated as

$$N(E_{\mathrm{CT}},T)=\int_{E_{\mathrm{CT}}}^{\infty}\alpha(E)\cdot n(E,T)\mathrm{d}E=\int_{E_{\mathrm{CT}}}^{\infty}\alpha(E)\cdot\frac{2\pi s}{h^3c^2}\left[\exp\left(\frac{E}{k_{\mathrm{B}}T}\right)-1\right]^{-1}E^2\mathrm{d}E=\frac{j}{q}. \tag{2}$$

Therein $n(E,T)$ is the flux of photons with energy E emitted by a black body at a certain temperature T, h is Planck's constant, c the speed of light in vacuum, k_{B} Boltzmann's constant and q the elementary charge. Following SQ this expression can now be used in two fundamentally different ways: First, to calculate the photocurrent generated in the PV cell by absorption of incoming sunlight; and, second, to quantify the emitted radiation by the PV cell following from radiative recombination of carriers driven by a current through the device (in the absence of illumination).

Under the assumption that each absorbed photon creates exactly one electrical charge, the short circuit current of the solar cell ($j = j_{\mathrm{SC}}$) is determined by the fraction of sunlight being absorbed by the solar cell, with T being the temperature of the sun ($T = T_{\mathrm{S}} \sim 5778$ K) and $s \approx 2.18\cdot10^{-5}$ being a geometrical factor, which accounts for the fraction of solar radiation reaching the earth's surface.[3] In analogy, the solar cell's emitted black body radiation equivalent ($j = j_0$) can be expressed by radiative recombination of carriers under dark conditions, where T now denotes the temperature of the cell $T_{\mathrm{C}} \sim 300$ K and $s = 1$.

When the solar cell is operated under open-circuit conditions, the number of absorbed photons must be equal to the emitted radiation flux. With the emission assumed as black body spectrum at ambient temperature and by taking Shockley's equation for an ideal diode ($j_{\mathrm{diode}} = j_0\cdot(\exp(q\cdot V/k_{\mathrm{B}}\cdot T)-1)$) into account[23], the open circuit voltage V_{OC} of a solar cell can thus be written as

$$V_{\mathrm{OC}}=\frac{k_{\mathrm{B}}T}{q}\cdot\ln\left(\frac{j_{\mathrm{SC}}}{j_0}+1\right). \tag{3}$$

In this context j_0 is often denoted as reverse saturation current of the solar cell, which is experimentally accessible via current-voltage characteristics under dark conditions.[24-26] Note however, that the value extracted from experimental j-V characteristics is – in contrast to its meaning in Eq. (3) – not exclusively of radiative origin, but might contain a considerable amount of non-radiative recombination current (see the discussion at the end of this section for details).

In case of vanishing CT state absorption ($\alpha_{\mathrm{CT}} \to 0$) the theory outlined above exactly describes the radiative limit for an inorganic homo-junction cell with a band gap energy E_{g}, as derived by Shockley and Queisser. As we will show below, the presence of the CT state in molecular D/A cells essentially does not change the short-circuit current j_{SC} (unless the CT absorption becomes comparable to the main material absorption), however, there will be a significant loss in quantum energy affecting the open-circuit voltage already for very low CT absorption strength. The reason is that with $T_{\mathrm{S}} \sim 5778$ K the black-body spectrum of incoming sunlight has its maximum at 0.79 eV and is fairly broad (see Fig. 1), while the corresponding spectrum for radiation emitted by the PV cell at $T_{\mathrm{C}} \sim 300$ K peaks at 0.041 eV (not visible in the graph) and tails off very rapidly towards higher energy. As a matter of fact, there is virtually no overlap with the main absorption at E_g and only recombination processes at E_{CT} will contribute to the recombination current determining V_{OC}. Thus, to minimize the loss in photon energy, smallest possible offset energy ΔE is favored, provided that it suffices for effective photoinduced charge transfer. Veldman *et al.* showed that a minimal driving force of $\Delta E \geq \mathrm{ca.}\, 0.1\,\mathrm{eV}$ is necessary to populate the CT state, whereas usual values for organic photovoltaic cells are found in the range of 0.3-1.1 eV.[27-30]

Based on the considerations introduced above, **Figure 2** shows the calculated short circuit current j_{SC} as a function of the optical gap E_{g}, assuming a fixed driving force for charge transfer $\Delta E = 0.5$ eV and a CT state absorption of $\alpha_{\mathrm{CT}} = 10^{-3}$. There is essentially no difference to the original SQ limit. Even for larger values of ΔE deviations from SQ are too small for visualization, implying that charge generation is mainly determined by the optical gap E_{g} of the contributing donor or acceptor. Both underlying solar spectra, the standardized air mass 1.5 global (AM1.5g) spectrum – used for subsequent calculations – as well as a black body spectrum at 5778 K are depicted in the inset of Fig. 2.

As discussed above, the influence of an existing CT state will be more pronounced, when considering the open-circuit voltage dominated by radiative recombination. **Figure 3** shows V_{OC} calculated from Eq. (3) with AM1.5g illumination at 1 sun and $T_C = 300$ K, as a function of the optical gap for several values of ΔE and α_{CT}.

The limiting case of $\alpha_{CT} \rightarrow 0$ or $\Delta E \rightarrow 0$ represents the original SQ limit, lying already below the voltage equivalent of E_g due to unavoidable radiative recombination losses for finite cell temperature. All other values of α_{CT} and ΔE cause a further decrease of V_{OC}. Thus, larger driving forces for charge separation and higher absorption α_{CT} lead to increased recombination from CT states, which manifests in a reduced maximum achievable open-circuit voltage. The strong influence of ΔE on V_{OC} emphasizes the demand for engineering the HOMO-LUMO gap in optimized organic hetero-junction solar cells, especially since efficient exciton dissociation is already fulfilled for $\Delta E \geq 0.1$ eV. But not only ΔE plays an important role in optimizing V_{OC}; also a tuning of the CT state absorption α_{CT} is necessary. For $\alpha_{CT} = 1$, the hetero-junction equals the case of a homo-junction semiconductor in the classical SQ theory with an effective band gap of $E_g' = E_{CT}$, which indicates the lower limit for V_{OC} in the diagram. This can be achieved, if D and A are intimately mixed in a bulk-hetero junction device, so that absorption from the CT state becomes the dominant electronic transition. However, it is well known that such a situation is not favorable for charge separation and transport.[31]

The power conversion efficiency η of a solar cell is defined as the efficiency at the maximum power point, i.e. $\eta = j_{SC} \cdot V_{OC} \cdot \mathrm{FF} / P_{LI}$, with P_{LI} being the intensity of solar illumination. **Figure 4** shows η as a function of the optical energy gap for several values of ΔE and the CT absorption α_{CT} fixed at 10^{-3}. All curves are characterized by a distinct maximum in efficiency, visualizing the trade-off between preferably low band gap energies for efficient light harvesting (high j_{SC}) and large band gap energies E_g as requirement for high V_{OC}. The calculations predict a severe drop in the maximum achievable efficiency with increasing energy level offset (ΔE) and a slight shift of the peak value to higher gap energies, starting from 33.4 % at a band gap energy of $E_g = 1.34$ eV for the original SQ limit ($\Delta E = 0$) towards a value of about 23.6 % at $E_g = 1.40$ eV for $\Delta E = 0.5$ eV. The inset demonstrates the corresponding behavior of the fill factor. All in all, the decreasing efficiency for increasing offset energy ΔE is mainly ascribed to the drop in open-circuit voltage. The influence of the fill factor is less pronounced and almost no change in the short circuit current (cf. Fig. 2) is observed. A similar dependence was shown by Giebink *et al.*, however, with peak efficiencies being lower in magnitude there. The reason for this deviation can be found in the underlying solar spectrum, which is an AM1.5g spectrum in our case instead of a black body radiation as in Ref.[13]

The calculation of V_{OC} for different CT state absorption strength α_{CT}, as it was shown in Fig. 3, implies a similar effect of α_{CT} on the efficiency. A detailed analysis is depicted in **Figure 5a**, showing both V_{OC} and η as a function of α_{CT} for a fixed value of the charge transfer driving force ($\Delta E = 0.5$ eV) with the cell temperature set to $T_C = 300$ K. Both, V_{OC} as well as η, show a plateau for very low absorption of the CT state ($\alpha_{CT} < 10^{-8}$), indicating the limiting case for $\alpha_{CT} \rightarrow 0$ (SQ limit at 300 K). Within this plateau, V_{OC} reaches approximately 1.6 V entailing a value of η around 25 %.

According to Fig. 5a, the efficiency features a second maximum at $\alpha_{CT} = 1$, because the CT state absorption yields a significant contribution to j_{SC} for α_{CT} exceeding 10^{-2}. For this set of data ($E_g = 1.9$ eV and $\Delta E = 0.5$ eV) the second maximum is even higher than in the limit of $\alpha_{CT} \rightarrow 0$, because one now has a hypothetical semiconductor with an effective gap of $E_g' = E_g - \Delta E = 1.4$ V. However, as discussed before, this case would require an intimate mixture of donor and acceptor molecules, which, in turn, would lead to a full suppression of charge carrier transport due to the absence of percolation paths.[31] For this reason, this second maximum does not represent a case to be considered seriously. Conventional material combinations exhibit values of α_{CT} ranging between 10^{-4} and 10^{-2}, and are thus located around the minimum of the efficiency curve.[22]

These findings clearly show that suppressed CT state absorption and recombination are essential requirements for maximum achievable organic PV efficiency. It was reported recently that recombination rates can be reduced, if intermolecular coupling between donor and acceptor are minimized.[22,32,33] This means that in terms of Marcus energy transfer the electronic coupling matrix element from the CT state to the ground state should be as small as possible, while the molecular reorganization energy should be increased, to maximize V_{OC}. However, too large values of the latter quantity will impede charge carrier and exciton transport, leading to low short-circuit currents and fill factors.

Another characteristic feature predicted by the SQ theory is the temperature dependence of V_{OC}. In the absence of non-radiative recombination, as assumed for the derivation of the SQ limit, $V_{OC}(T)$ shows a temperature dependence given by eq. 3. This can be re-written as[34]

$$V_{OC}(T) = \frac{E_{CT}}{q} - \Delta V_{OC}^{rad}(T)\,, \qquad (4)$$

where ΔV_{OC}^{rad} represents the thermodynamically unavoidable loss in V_{OC} due to radiative recombination at finite temperature.

This is shown as an upper limit (for E_g=1.9 eV, $\alpha_{CT} = 0$ and $\Delta E = 0$) in **Figure 5b** together with different simulated curves for an excitonic solar cell with the same optical gap and ΔE = 0.5eV at various absorption strength of the CT state. All curves with $\alpha_{CT} > 0$ end up in one single value for V_{OC} as T is approaching 0 K, which corresponds to the equivalent energy of the CT state E_{CT}/q, while the curve with $\alpha_{CT} = 0$ describes the original SQ limit for a band gap energy E_g. As already discussed above, the case for $\alpha_{CT} = 1$ (and $\Delta E \neq 0$) corresponds to a homo-junction cell with $E_g' = E_{CT}$. All other curves can be found within these two extremes. Very small CT absorptions ($\alpha_{CT} \leq 10^{-10}$) result in a maximum of V_{OC} at intermediate temperatures; however, these values of α_{CT} approach the limit of physical relevance and can hardly be reached in practice. Interestingly, for a CT absorption close to 10^{-5} a nearly temperature independent behavior of V_{OC} is observed, which indeed has been found in some experimental studies.[35] The important point, again, is that regardless of the value of α_{CT} all curves of $V_{OC}(T)$ extrapolate to the same limiting value at $T = 0$, which represents the energy of the CT state at the D/A interface.

However, before an unambiguous correlation between experimental data and simulations can be drawn, another important factor influencing the temperature behavior of V_{OC} has to be considered, namely the presence of non-radiative recombination losses. Following the reciprocity theorem[36], the losses in V_{OC} due to non-radiative recombination can be expressed via the electroluminescence quantum efficiency of the PV cell operated under forward bias (carrier injection) conditions. Thus the total device current can be split into a fraction j_0 yielding radiative recombination and another one, $j_{non}(T)$, being responsible for non-radiative recombination of charges, which usually is temperature dependent, too. Including this term in Eq. 3 yields:

$$V_{\mathrm{OC}} = \frac{k_{\mathrm{B}} \cdot T}{\mathrm{q}} \cdot \ln\left[\frac{j_{\mathrm{SC}}}{j_0(E_{\mathrm{g}},T) + j_{\mathrm{non}}(T)} + 1 \right]. \tag{5}$$

Taken all together, the open-circuit-voltage of an excitonic solar cell at finite temperature can thus, in analogy to Eq. 4, be expressed as:

$$V_{\mathrm{OC}}(T) = \frac{E_{CT}}{\mathrm{q}} - \Delta V_{\mathrm{OC}}^{\mathrm{rad}}(T) - \Delta V_{\mathrm{OC}}^{\mathrm{non}}(T)\,. \tag{6}$$

(Although we did not make use of it, we would like to mention that analytical expressions for both the radiative and non-radiative losses can be found in Ref.[22])

With that in mind, two important consequences arise from the simulation results shown in Fig. 5. One is that the knowledge of the CT energy and absorption strength for a given OPV system will allow to quantify non-radiative losses from a comparison of simulated and experimentally measured $V_{\mathrm{OC}}(T)$ data, as we will show in the subsequent section. The other is that, if non-radiative recombination is negligible, V_{OC} at 300 K (where a PV cell would normally be operated) can exceed the value of E_{CT}/q, provided that the absorption strength of the CT state is low enough ($\alpha_{\mathrm{CT}} \leq 10^{-5}$), and can finally even reach the value given by the original SQ limit for $\alpha_{\mathrm{CT}} \leq 10^{-8}$. As discussed above, materials development towards this direction entails both a big challenge but also a great potential.[33] Apart from molecular design, tuning of device architectures, process conditions, molecular orientations and film morphologies are additional handles for achieving this goal.

3. Comparison to experiment

After having discussed some general features of the modified SQ theory we will now turn towards its application to device data of an organic planar hetero-junction solar cell based on diindenoperylene (DIP) and C_{60}. Recently, DIP was successfully employed as donor in organic solar cells, with its main advantage being found in the high ionization potential and the favorable energy level alignment with the acceptor C_{60} leading to high open circuit voltages of up to 0.93 V.[14] Moreover, owing to its good transport properties[37-39] combined with a high electron mobility in C_{60}[40,41], PV cells exhibit high fill factors approaching 75 %. We note that even higher V_{OC} can be obtained, when DIP is used as acceptor in combination with oligo- or polythiophenes.[15]

As outlined in the previous section, the temperature dependent measurement of the open-circuit voltage is the most direct way to test the validity of the modified SQ theory for an organic hetero-junction D/A cell and to assess some of its critical parameter values, most importantly the energy E_{CT} of the involved CT state.

Before applying the theory to a real device stack, values for bulk absorption α_0 and the CT state absorption α_{CT} have to be determined. The bulk absorption of the organic semiconductor materials is comparatively easy to obtain: Using standard transmission/reflection measurements of the respective individual materials in combination with thin-film optical modeling yield the absorption. **Figure 6** (inset) shows the spectral dependence of the absorption for thin films of both materials, DIP and C_{60} on glass substrates (in agreement with Ref.[42,43]). The spectra imply that the main contribution to light absorption in a hetero-junction device with comparable layer thickness of both materials (see below) will come from the fullerene. Accordingly, the critical value for the optical gap entering the simulations is the onset of absorption in C_{60} at about 1.9 eV.

As mentioned before, CT absorption features are typically characterized by low absorption coefficients, requiring sensitive spectroscopic techniques. Among the most common methods is photothermal deflection spectroscopy (PDS) based on local heating of the sample even by very weak absorption of light.[44] Furthermore, CT absorption can be detected by Fourier transform photocurrent spectroscopy (FTPS), a very sensitive technique to record the spectral dependence of photocurrent.[45,46]

Here, we use PDS, which allows the determination of values for α_{CT}, being several orders of magnitude smaller as compared to the bulk material absorption. The principles of this technique are described in Ref.[47] For PDS, neat and mixed films of DIP and C_{60} were evaporated on quartz glass substrates. Perfluorohexane was used as deflection medium, which assures high transmittance in the energy region of 0.6 – 6 eV[48] and guarantees for insolubility of both DIP and C_{60}.

Figure 6 shows PDS data of a co-evaporated mixed layer of DIP and C_{60} in comparison to the spectra of the single materials. For absolute values of the absorption coefficient, the PDS signal has to be calibrated using standard reflection/transmission measurements in the high energy region (see inset Fig. 6). In the high and low energy region (above 1.9 eV and below 1.3 eV, respectively) the spectrum of the blend is similar to the combined absorption of the single materials. Based on these findings α_{CT} can be estimated to be around $2.3 \cdot 10^{-3}$ lower than the bulk absorption α_0, which is calculated from the ratio of the CT absorption at an energy of 1.4 eV (see below) and the averaged bulk absorption between 1.9 and 3.3 eV. Note that for the purpose of this paper only the order of magnitude of α_{CT} is required, but not a precise value, as will be discussed in more detail at the end of this section.

A schematic drawing of the planar hetero-junction solar cell architecture – including the used thicknesses – is shown in **Figure 7** together with temperature dependent *j-V* characteristics under white-light illumination. For a detailed description of device fabrication we refer to Wagner *et al*.[14] These electrical measurements were performed in an optical cryostat using liquid nitrogen for sample cooling. An LOT-ORIEL sun simulator with a 150 W Xenon arc lamp equipped with an AM1.5g filter set was used for illumination at an intensity of about 46 mWcm^{-2}, i.e. at roughly half a sun. Current-voltage characteristics were measured using a Keithley 237 High Voltage Source Measure Unit.

The obtained *j-V* characteristics for different temperatures shown in Fig. 7 exhibit an increase of V_{OC} as well as a decrease of j_{SC} for decreasing temperatures, as was similarly reported for other material systems.[35,49-51] The reasons for the continuous decrease in short circuit current may be on the one hand a reduction of charge carrier extraction efficiency due to a lowering of their mobility and on the other hand a decline of exciton transport at lower temperature. Additionally, we observe the appearance of an s-shaped behavior for temperatures below 200 K, which can be ascribed to the contribution of a temperature dependent series resistance R_S.[35] In the present solar cell stack, the increasing series resistance can rather likely be attributed to a non-ohmic contact at the anode/donor interface, which becomes limiting at low temperatures.[52,53] Other material systems show a comparable effect in the temperature dependence of V_{OC}, but can be attributed to a low parallel resistance R_P.[54] A theoretical method explaining the curvature by a Gaussian disorder of the semiconductors with no need of taking resistance limitation into account was given by Manor *et al.*[55] showing promising results for bulk heterojunction (BHJ) devices. With the DIP/C60 PV cell being highly crystalline, disorder considerations should not play a major role.

Before the modified SQ theory, which is based on complete absorption of photons with energy exceeding the band gap of the semiconductor ($\alpha(E > E_g) = 1$), can be applied to our data, the fact that a thin-film device actually does not absorb all photons with energy $E > E_g$ has to be taken into account. Kirchartz *et al*. account for incomplete absorption at finite thickness of the organic semiconductors by a Gaussian-shaped absorption coefficient that is based on experimental results of absorption coefficients and photoluminescence data.[56] Here, we keep the approach of a step-like absorption at E_g, but reduce it for photon energies $E > E_g$

to $\alpha_0 = 0.19$ (see below), with the energy gap of C_{60} ($E_g = 1.9$ eV) being the limiting gap. This effective value of the absorption is estimated from a comparison of simulated and measured short-circuit currents. As j_{SC} is basically only determined by the absorption of the bulk material, the difference between experimentally measured and simulated j_{SC} would correspond to a deviation of the absorption from $\alpha(E > E_g) = 1$, provided that other losses caused by a finite exciton diffusion length and in-complete charge carrier extraction are negligible. From Fig. 2 the simulated value of j_{SC} for a band gap of 1.9 eV can be obtained as $j_{SC}^{sim} \approx 17.1$ mA cm^{-2} for 1 sun. With the experimental data of j_{SC} being 1.46 mA cm^{-2} at about half a sun and $T = 300$ K, the absorption can be set to $\alpha_0 \approx 0.19$, which is consistent with the averaged incident-photon-to-current efficiency (IPCE) value over the relevant wavelength range. Correspondingly, α_{CT} has to be corrected by the same factor. Moreover, it has to be taken into account that the present solar cell is nominally a planar hetero-junction device, however, with a rough D/A interface (see Ref[14] for details). This fact is considered in the simulation by assuming that only about 1/3 of the total active layer thickness contributes to the CT absorption. Both effects reduce α_{CT} to $1\cdot10^{-4} – 2\cdot10^{-4}$. For the simulation we used $1.5\cdot10^{-4}$ being the most reasonable value. We note that the estimations used above may introduce some uncertainty in the simulation. However, this applies mainly to the magnitude of the photocurrent which critically depends on the value of the bulk material absorption α_0, whereas the influence of inaccuracies in α_0, and concomitantly also in α_{CT}, on V_{OC} is only of minor extent (see Fig. 5a).

In this context, we would like to point out that DIP films used in our PV cells exhibit an almost upright standing orientation of the molecules with respect to the substrate plain. Although this orientation is not very favorable for achieving good light absorption and high photocurrents (see above), it probably helps to keep the coupling between the CT state and the ground state low. We thus assume that the perpendicular orientation of DIP/C_{60} yields reduced recombination rates as compared to a parallel one, as it was shown for pentacene/C_{60} by Yi *et al.*[57]

Figure 8 shows the temperature dependence of V_{OC} extracted from *j-V* characteristics in Fig. 7 together with simulations based on the modified SQ theory. As predicted by a very general theoretical approach[58], and experimentally confirmed for a variety of material systems[22], V_{OC} shows an approximately linear temperature dependence over a wide temperature range.

The deviation of the linear behavior for temperatures below 150 K can be attributed to the appearance of an s-shape (cf. Fig. 7), which is induced by a non-ohmic contact at the anode/semiconductor interface, as already mentioned above. As a crude estimation for the energy of the CT state at the D/A interface one can use an extrapolation of the linear behavior towards $T_C = 0$, yielding a value of 1.42 eV (dotted line Fig. 8).

For a detailed analysis we will now use the modified SQ theory to simulate the temperature dependence of V_{OC} as described in the previous section. Taking the parameters (α_0, α_{CT}, E_g) as given above and $E_{CT} = 1.4$ eV (see below) and assuming that all recombination is radiative (Eq. 3), one obtains a behavior of V_{OC} given by the dashed line in Fig. 8. This curve describes the thermodynamically unavoidable radiative loss in V_{OC} with respect to its hypothetical maximum at $T_C = 0$. At room temperature this loss term ΔV_{OC}^{rad} amounts to about 0.12 eV. However, it is obvious that the actually measured $V_{OC}(T)$ data are significantly lower. Thus, one has to take non-radiative recombination losses into account. This is done according to Eq. 5 by introducing an additional contribution j_{non} to the device current, being responsible for non-radiative recombination of carriers. The relative magnitude of this term is determined by a scaling factor $\gamma = j_{non}/j_0$. The solid line shows a fit of the experimental data with equation 5 yielding an excellent description over the whole temperature range. Importantly, this fit results in a CT energy of $E_{CT} = 1.40$ eV differing only slightly from the value given by the linear extrapolation, which emphasizes its suitability to be a reasonable first approach. Moreover, the value of E_{CT} is very close to the intermolecular HOMO-LUMO gap determined as 1.25 eV by photoelectron spectroscopy for this D/A pair.[14]

Further on, the fit allows for an estimation of the non-radiative recombination current. We find that j_{non} indeed scales with j_0, i.e. $j_{non}/j_0 = \text{const.} = 4.8 \cdot 10^6$ (see inset Fig. 8), demonstrating that non-radiative recombination presents the prevailing recombination mechanism leading to an additional loss term ΔV_{OC}^{non} of about 0.40 V. However, this observation does not provide a rule of generality, but might be a special feature of the current solar cell.

Concerning the influence of the CT absorption strength on the ratio of radiative and non-radiative recombination, one has to admit that both parameters are coupled. From Fig. 5 it is evident that an increase of α_{CT} by one order of magnitude also yields a stronger decay of V_{OC} with increasing temperature, which therefore results in a reduction of j_{non}/j_0 of the same order of magnitude. Nevertheless, this would not change the dominant role of non-radiative recombination losses compared to the radiative ones, as even for the unrealistic case of α_{CT} = 1, j_{non} would still exceed j_0 by a factor of 1000. Thus for an independent and unambiguous determination of both the CT absorption strength and the contribution of non-radiative recombination losses further experiments, e.g. measuring the electroluminescence quantum efficiency of a PV cell[59], are required.

Finally, after verification of its applicability to an organic hetero-junction PV cell, the modified SQ theory can serve as a tool to predict the ultimate thermodynamic efficiency limit of a given material system (provided that the cell is a single junction device devoid of additional measures for light management etc.). In the present case (see Fig. 4), one can estimate an upper limit for the power conversion efficiency of about 20%. The major loss term is obviously insufficient light absorption as discussed before. However, the analysis shows that reducing non-radiative recombination could also give the device efficiency a considerable boost. Interestingly, the measured fill factors of almost 75% are not too far from the theoretical limit (inset in Fig. 4). This in turn can be taken as a manifestation of excellent charge extraction in this highly crystalline molecular hetero-junction device.

4. Conclusion

In summary, we have been able to successfully adapt the Shockley-Queisser theory to the peculiarities of organic hetero-junction solar cells, most importantly their excitonic nature. While the D/A concept enables successful photo-induced charge transfer, the introduction of such a hetero-junction is accompanied with additional energy losses as compared to an inorganic homo-junction cell, owing to the presence of a CT state at the D/A interface. Detailed simulations show the important impact of the CT absorption strength on the open-circuit voltage V_{OC}, elucidating the potential of enhancing solar cell efficiencies by keeping the absorption of the CT state as low as possible.

The model is applied to a planar hetero-junction device based on DIP as donor and C_{60} as acceptor. All relevant parameters, such as the energy and absorption coefficient of the CT state – both being crucial for the simulations – are assessed by PDS. Temperature dependent device characteristics, in particular $V_{OC}(T)$, can serve as an experimentally accessible method, which allows for a quantitative test of the model. Thereby, the modified SQ theory provides a refined approach to determine the energy of the CT state – and thus the upper limit of V_{OC} for a given D/A combination. Furthermore, temperature dependent device characteristics serve to quantify recombination losses, emphasizing that non-radiative recombination exceeds their radiative counterpart by orders of magnitude. All in all, our method can provide quantitative predictions of the thermodynamic efficiency limits of molecular D/A solar cells.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft (DFG) within the Priority Program 1355 ("Elementary Processes of Organic Photovoltaics") and the Elite Network of Bavaria within the International Graduate School: Materials Science of Complex Interfaces. We thank Prof. Mark Thompson (Univ. of Southern California) for stimulating discussions.

Received: ((will be filled in by the editorial staff))
Revised: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))

[1] J. Nelson, *The Physics of Solar Cells*, World Scientific, Singapore **2003**.

[2] P. Würfel, *Physics of Solar Cells*, Wiley-VCH, Weinheim **2005**.

[3] W. Shockley and H. J. Queisser, *J. Appl. Phys.* **1961**, *32*, 510.

[4] C. H. Henry, *J. Appl. Phys.* **1980**, *51*, 4494.

[5] W. van Roosbroeck and W. Shockley, *Phys. Rev.* **1954**, *94*, 1558.

[6] N. S. Sariciftci, *Bound neutral excitons or charged polaron pairs, in Primary photoexcitations in conjugated polymers: Molecular excitons versus semiconductor band model*, World Scientific, Singapore **1997**.

[7] C. W. Tang, *Appl. Phys. Lett.* **1986**, *48*, 183.

[8] N. S. Sariciftci, L. Smilowitz, A. J. Heeger and F. Wudl, *Science* **1992**, *258*, 1474.

[9] P. Panda, d. Veldman, J. Sweelssen, J. A. M. Bastiaansen, B. M. W. Langeveld-Voss and Stefan C. J. Meskers, *J. Phys. Chem. B* **2007**, *111*, 5076.

[10] A. Gadisa, M. Svensson, M. R. Andersson and O. Inganäs, *Appl. Phys. Lett.* **2004**, *84*, 1609.

[11] T. Kirchartz, J. Mattheis and U. Rau, *Phys. Rev. B* **2008**, *78*, 235320.

[12] K. Vandewal, K. Tvingstedt, J. V. Manca and O. Inganäs, *IEEE J. Sel. Top. Quant.* **2010**, *16*, 1676.

[13] N. C. Giebink, G. P. Wiederrecht, M. R. Wasielewski and S. R. Forrest, *Phys. Rev. B* **2011**, *83*, 195326.

[14] J. Wagner, M. Gruber, A. Hinderhofer, A. Wilke, B. Bröker, J. Frisch, P. Amsalem, A. Vollmer, A. Opitz, N. Koch, F. Schreiber and W. Brütting, *Adv. Funct. Mater.* **2010**, *20*, 4295.

[15] U. Hörmann, J. Wagner, M. Gruber, A. Opitz and W. Brütting, *Phys. Status Solidi Rapid Res. Lett.* **2011**, *5*, 241.

[16] D. Fujishima, H. Kanno, T. Kinoshita, E. Maruyama, M. Tanaka, M. Shirakawa and K. Shibata, *Sol. Energy Mater. Sol. Cell.* **2009**, *93*, 1029.

[17] J. Meiss, M. Hummert, H. Ziehlke, K. Leo and M. Riede, *Phys. Stat. Sol. RRL* **2010**, *4*, 329.

[18] M. Hirade and C. Adachi, *Appl. Phys. Lett.* **2011**, *99*, 153302.

[19] D. Yokoyama, Z. Q. Wang, Y. Pu, K. Kobayashi, J. Kido and Z. Hong, *Sol. Energy Mater. Sol. Cell.* **2012**, *98*, 472.

[20] J. Brédas, J. E. Norton, J. Cornil and V. Coropceanu, *Acc. Chem. Res.* **2009**, *42*, 1691.

[21] C. Deibel and V. Dyakonov, *Rep. Prog. Phys.* **2010**, *73*, 096401.

[22] K. Vandewal, K. Tvingstedt, A. Gadisa, O. Inganäs and J. V. Manca, *Phys. Rev. B* **2010**, *81*, 125204.

[23] S. M. Sze, Physics of Semiconductor Devices, 3rd ed.,Wiley, New York , 1981.

[24] J. Xue, S. Uchida, B. P. Rand and S. R. Forrest, *Appl. Phys. Lett.* **2004**, *84*, 3013.

[25] S. Yoo, B. Domercq and B. Kippelen, *J. Appl. Phys.* **2005**, *97*, 103706.

[26] J. H. Lee, S. Cho, A. Roy, H.-T. Jung and A. J. Heeger, *Appl. Phys. Lett.* **2010**, *96*, 163303.

[27] D. Veldman, S. c. J. Meskers and R. A. J. Janssen, *Adv. Func. Mater.* **2009**, *19*, 1939.

[28] A. Wilke, T. Mizokuro, R.-P. Blum, J. P. Rabe and N. Koch, *IEEE J. Sel. Top. Quan.* **2010**, *16*, 1732.

[29] Z. Xu, L.-M. Chen, M.-H. Chen, G. Li and Y. Yang, *Appl. Phys. Lett.* **2009**, *95*, 013301.

[30] X. Gong, M. Tong, F. G. Brunetti, J. Seo, Y. Sun, D. Moses, F. Wudl and A. J. Heeger, *Adv. Mater.* **2011**, *23*, 2272.

[31] A. Opitz, J. Wagner, W. Brütting, I. Salzmann, N. Koch, J. Manara, J. Pflaum, A. Hinderhofer and F. Schreiber, *IEEE J. Sel. Top. Quant.* **2010**, *16*, 1707.

[32] M. D. Perez, C. Borek, S. R. Forrest,and M. E. Thompson, *J. Am. Chem. Soc.* **2009**, *131*, 9281.

[33] C. W. Schlenker and M. E. Thompson, *Chem. Commun.* **2011**, *47*, 3702.

[34] R. T. Ross, *J. Chem. Phys.* **1967**, *46*, 4590.

[35] B. P. Rand, D. P. Burk and S. R. Forrest, *Phys. Rev. B* **2007**, *75*, 115327.

[36] U. Rau and J. H. Werner, *Appl. Phys. Lett.* **2004**, *84*, 3735.

[37] N. Karl, *Synth. Met.* **2003**, *133*, 649.

[38] D. Kurrle and J. Pflaum, *Appl. Phys. Lett.* **2008**, *92*, 133306.

[39] M. Horlet, M. Kraus, W. Brütting and A. Opitz, *Appl. Phys. Lett*. **2011**, *98*, 233304.

[40] A. Opitz, M. Bronner and W. Brütting, *J. Appl. Phys.* **2007**, *101*, 063709.

[41] J. J. Kwiatkowski, J. M. Frost and J. Nelson, *Nano Let.* **2009**, *9*, 1085.

[42] U. Heinemeyer, R. Scholz, L Gisslén, M. I. Alonso, J. O. Ossó, M. Garriga, A. Hinderhofer, M. Kytka, S. Kowarik, A. Gerlach and F. Schreiber, *Phys. Rev. B* **2008**, *78*, 085210.

[43] M. K. Kelly, P. Etchegoin, D. Fuchs, W. Krätschmer and K. Fostiropoulos, *Phys. Rev. B* **1992**, *46*, 4963.

[44] L. Goris, K. Haenen, M. Nesladek, P. Wagner, D. Vanderzande, L. De Schepper, J. D'Haen, L. Lutsen and J. V. Manca, *J. Mater. Sci*. **2005**, *40*, 1413.

[45] M. Vanecek and A. Poruba, *Appl. Phys. Lett.* **2002**, *80*, 719.

[46] K. Vandewal, L. Goris, I. Haeldermans, M. Nesladek, K. Haenen, P. Wagner and J. V. Manca, *Thin Solid. Films* **2008**, *516*, 7135.

[47] L. Goris, K. Haenen, M. Nesladek, A. Poruba, M. Vanecek, P. Wagner, L. Lutsen, J. V. Manca, D. Vanderzande and L. De Schepper, *Proc. SPIE-Int. Soc. Opt. Eng.* **2004**, *5464*, 372.

[48] T. Gotoh, S. Nonomura, H. Watanabe, S. Nitta and D. Han, *Phys. Rev. B* **1998**, *58*, 10060.

[49] D. Chirvase, Z. Chiguvare, M. Knipper, J. Parisi, V. Dyakonov and J. C. Hummelen, *J. Appl. Phys.* **2003**, *93*, 3376.

[50] V. Dyakonov, *Appl. Phys. A* **2004**, *79*, 21.

[51] W. J. Potscavage, S. Yoo and B. Kippelen, *Appl. Phys. Lett.* **2008**, *93*, 193308.

[52] J. Wagner, M. Gruber, A. Wilke, Y. Tanaka, K. Topczak, A. Steindamm, U. Hörmann, A. Opitz, Y. Nakayama, H. Ishii, J. Pflaum, N. Koch and W. Brütting, *J. Appl. Phys.* **2012**, *111*, 054509.

[53] D. Rauh, A. Wagenpfahl, C. Deibel and V. Dyakonov, *Appl. Phys. Lett.* **2011**, *98*, 133301.

[54] A. K. Thakur, G. Wantz, G. Garcia-Belmonte, J. Bisquert and L. Hirsch, *Sol. Energy Mater. Sol. Cell.* **2011**, *95*, 2131.

[55] A. Manor and E. A. Katz, *Sol. Energy Mater. Sol. Cell.* **2012**, *97*, 132.

[56] T. Kirchartz, K. Taretto and U. Rau, *J. Phys. Chem. C* **2009**, *113*, 17958.

[57] Y. Yi, V. Coropceanu and J. Brédas, *J. Am. Chem. Soc.* **2009**, *131*, 15777.

[58] M. A. Green, *Prog. Photovolt: Res. Appl.* **2003**, *11*, 333.

[59] K. Tvingstedt, K. Vandewal, A. Gadisa, F. Zhang, J. Manca and O. Inganäs, *J. Am. Chem. Soc.* **2009**, *131*, 11819.

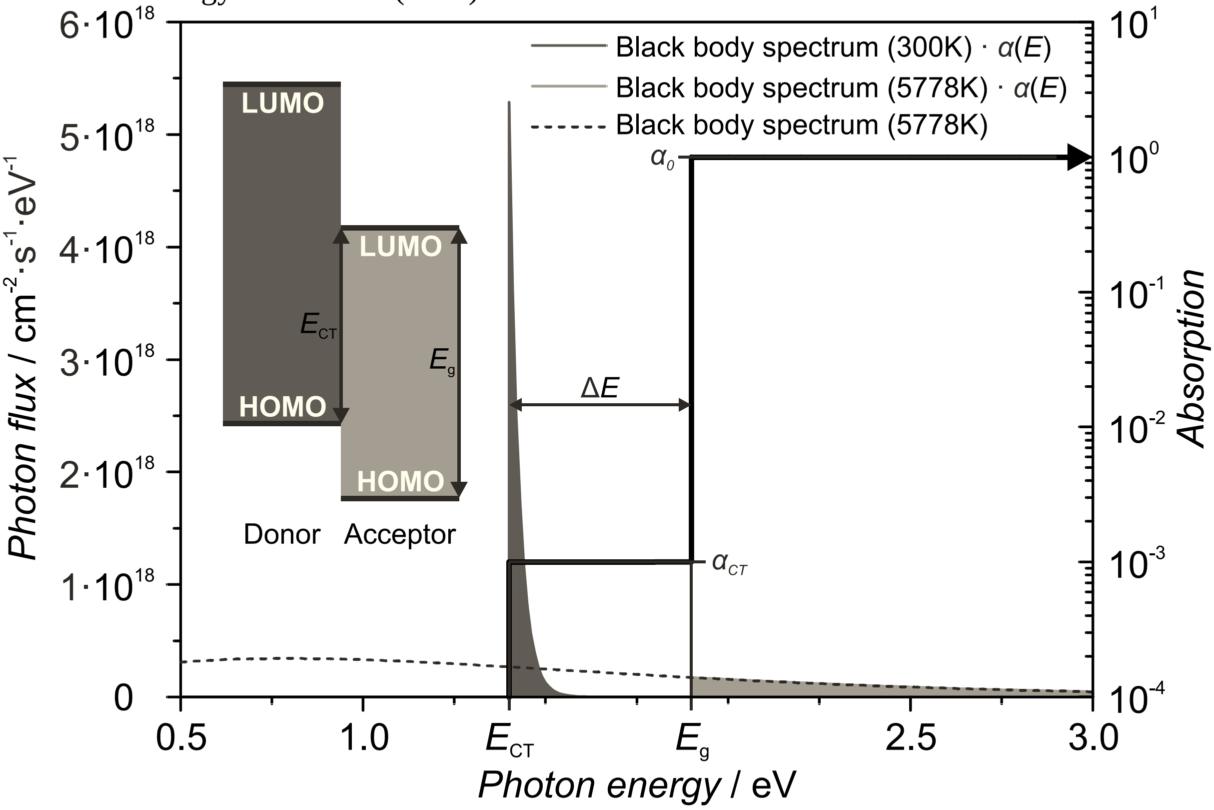


Figure 1. Spectral dependence of photon flux and step-like absorption in a donor/acceptor hetero-junction solar cell. The dashed line shows the incident solar radiation, which after multiplication with the absorption spectrum yields the light grey-shaded area. The dark grey-shaded area represents the emission of the solar cell under open circuit conditions, which has to be equal to the incident photon flux. The inset shows the relative positions of the energy levels and the resulting optical energy gap E_g as well as the energy E_{CT} of the CT state.

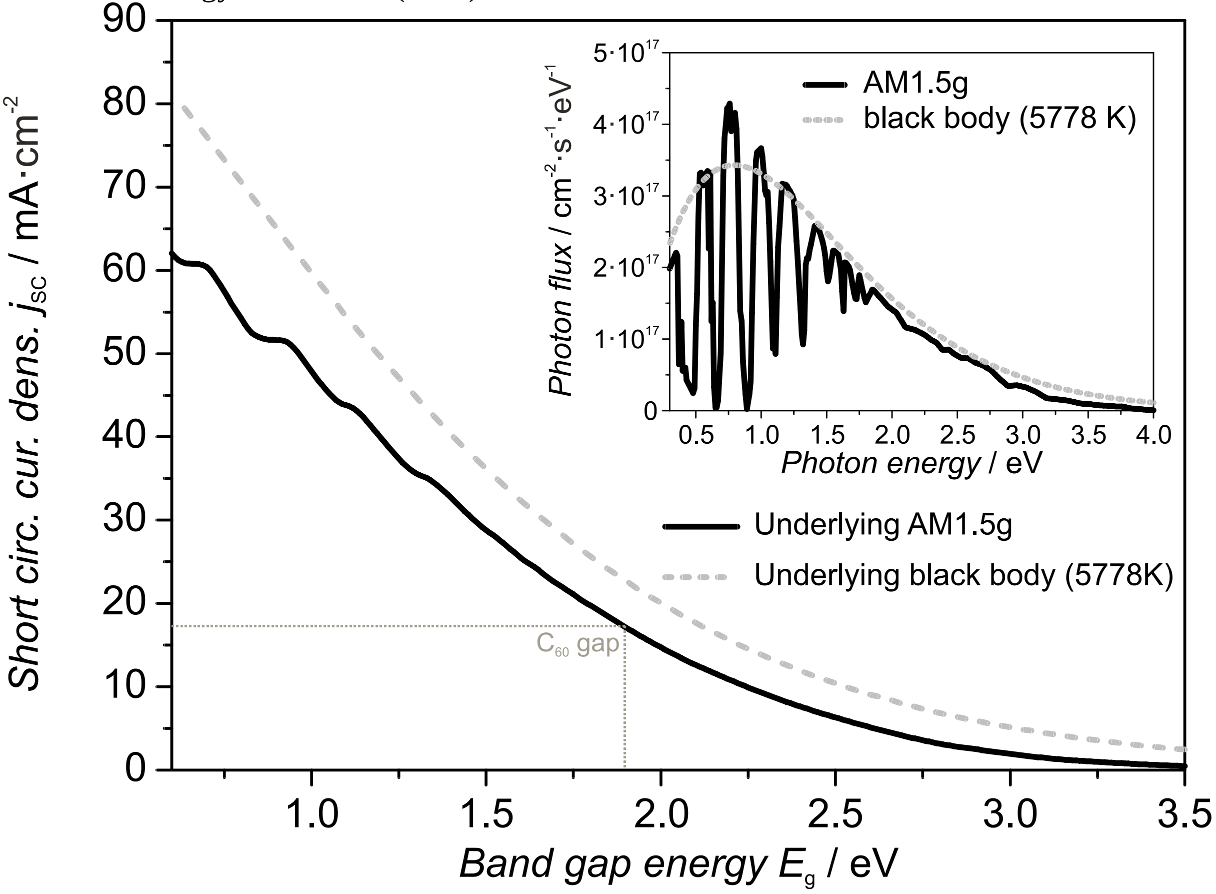


Figure 2. Maximum short circuit current densities j_{SC} predicted for an organic hetero-junction solar cell as a function of band gap energy E_g for $\alpha_{CT} = 10^{-3}$ and $\Delta E = 0.5$ eV, assuming different illumination conditions (AM1.5g and the spectrum of black-body radiation at a temperature of $T_S = 5778$ K). The dotted line marks the C_{60} gap energy $E_g = 1.9$ eV of the solar cell under consideration. The inset shows the corresponding solar radiation spectra.

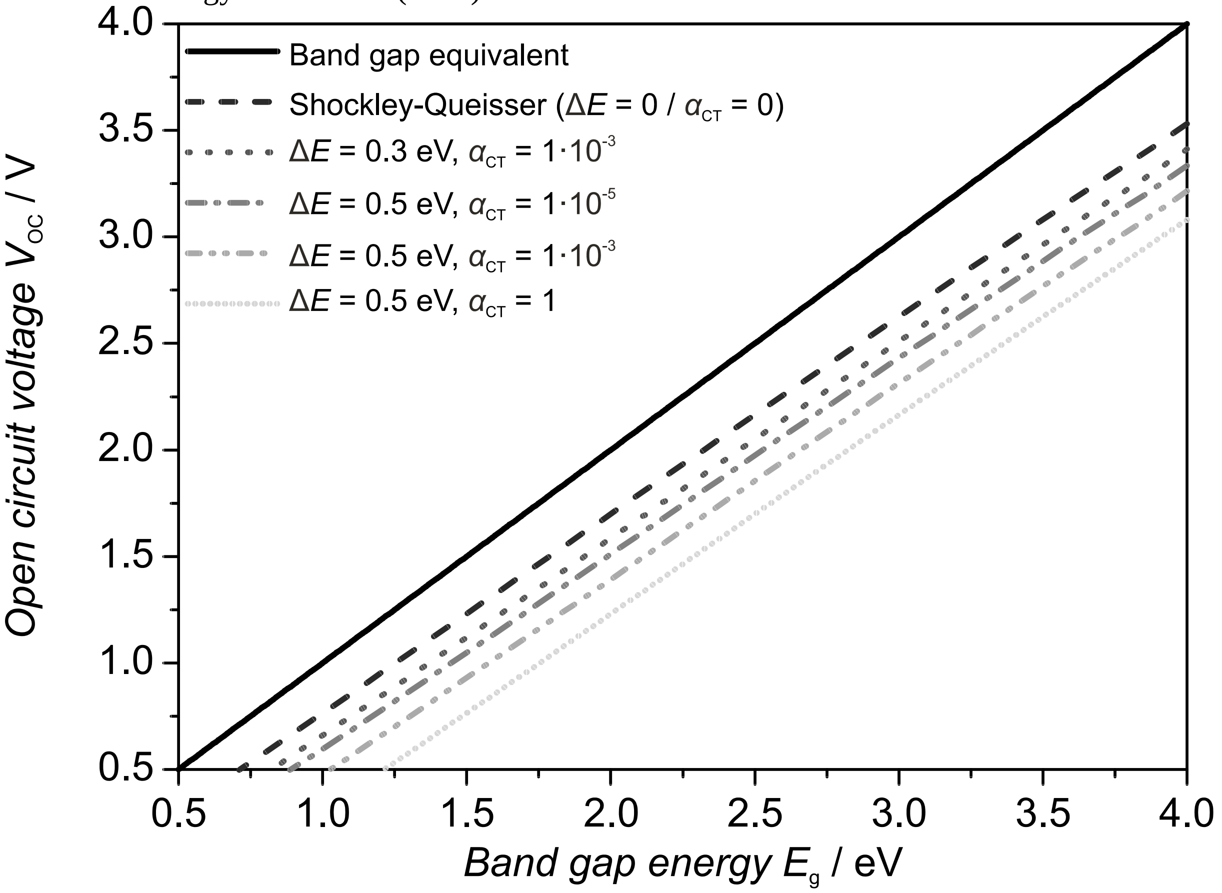


Figure3. Maximum open circuit voltage V_{OC} predicted for an organic hetero-junction solar cell as a function of band gap energy E_g for several different offset energies $\Delta E = E_g - E_{CT}$ and varying CT absorption α_{CT}, assuming the AM1.5g solar radiation spectrum and the solar cell as black body radiator at a temperature $T_C = 300$ K.

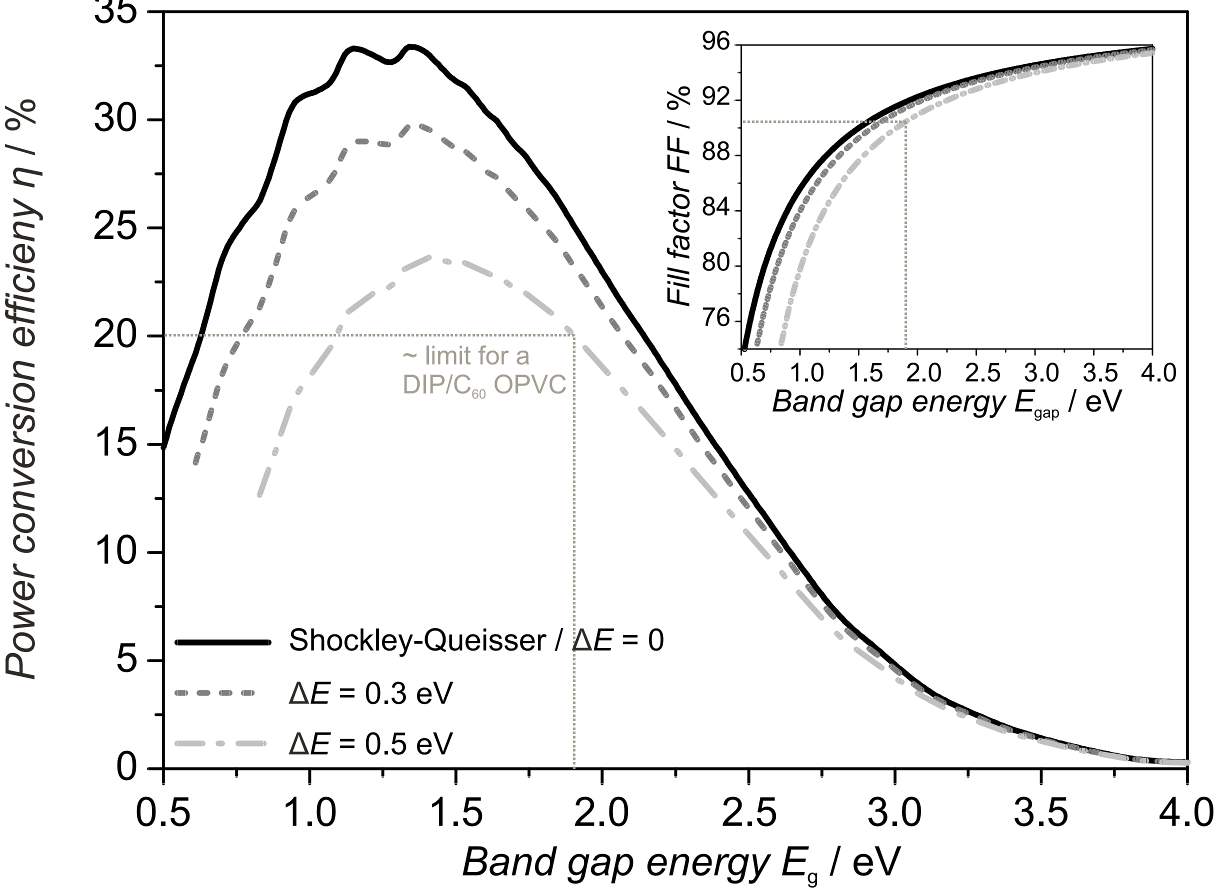
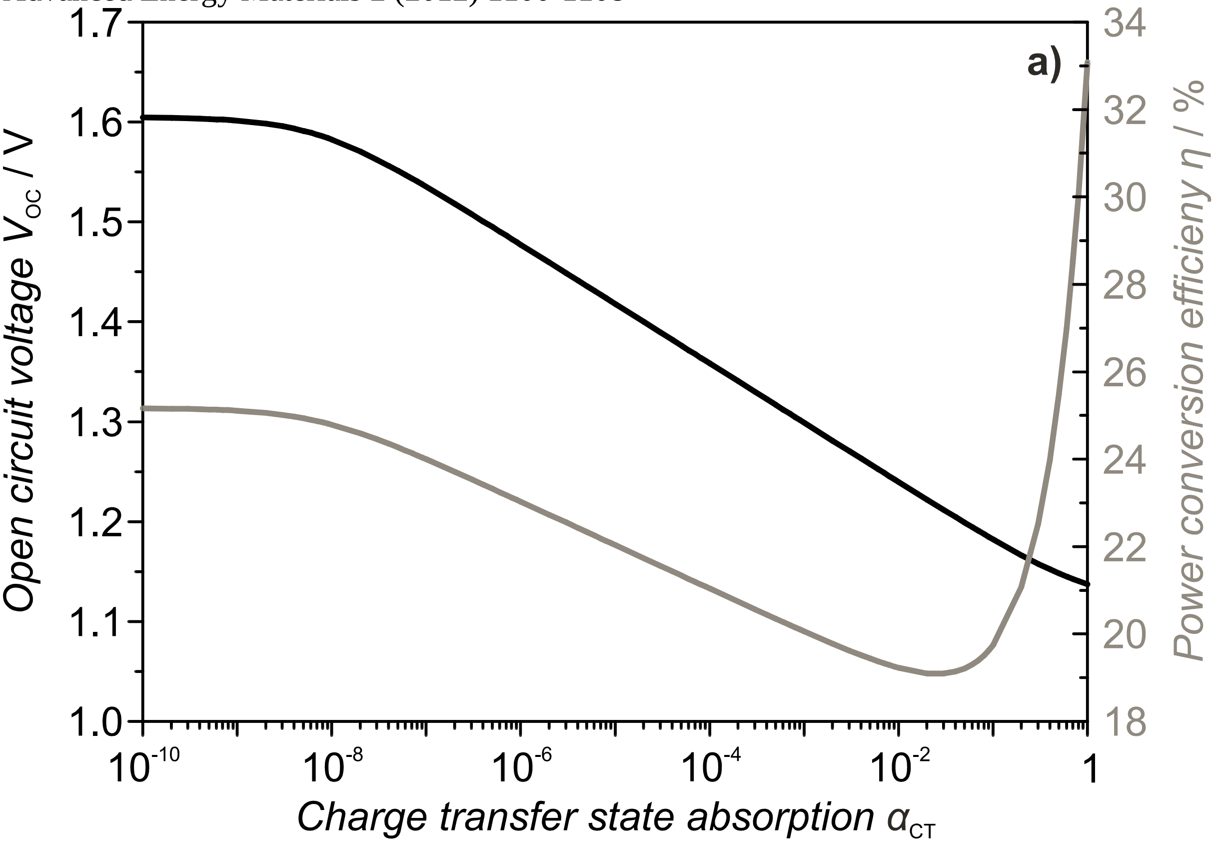


Figure 4. Maximum efficiency η and fill factor FF (inset) predicted for an organic hetero-junction solar cell as a function of band gap energy E_g for $\alpha_{CT} = 10^{-3}$ and several different offset energies ΔE, assuming the AM1.5g solar radiation spectrum and the solar cell as black body radiator at a temperature $T_C = 300$ K. The dotted lines mark the C_{60} gap energy $E_g = 1.9$ eV of the solar cell under consideration.


a)
Open circuit voltage V_{OC} / V
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
Power conversion efficieny η / %
18
20
22
24
26
28
30
32
34
10^{-10}
10^{-8}
10^{-6}
10^{-4}
10^{-2}
1
Charge transfer state absorption α_{CT}

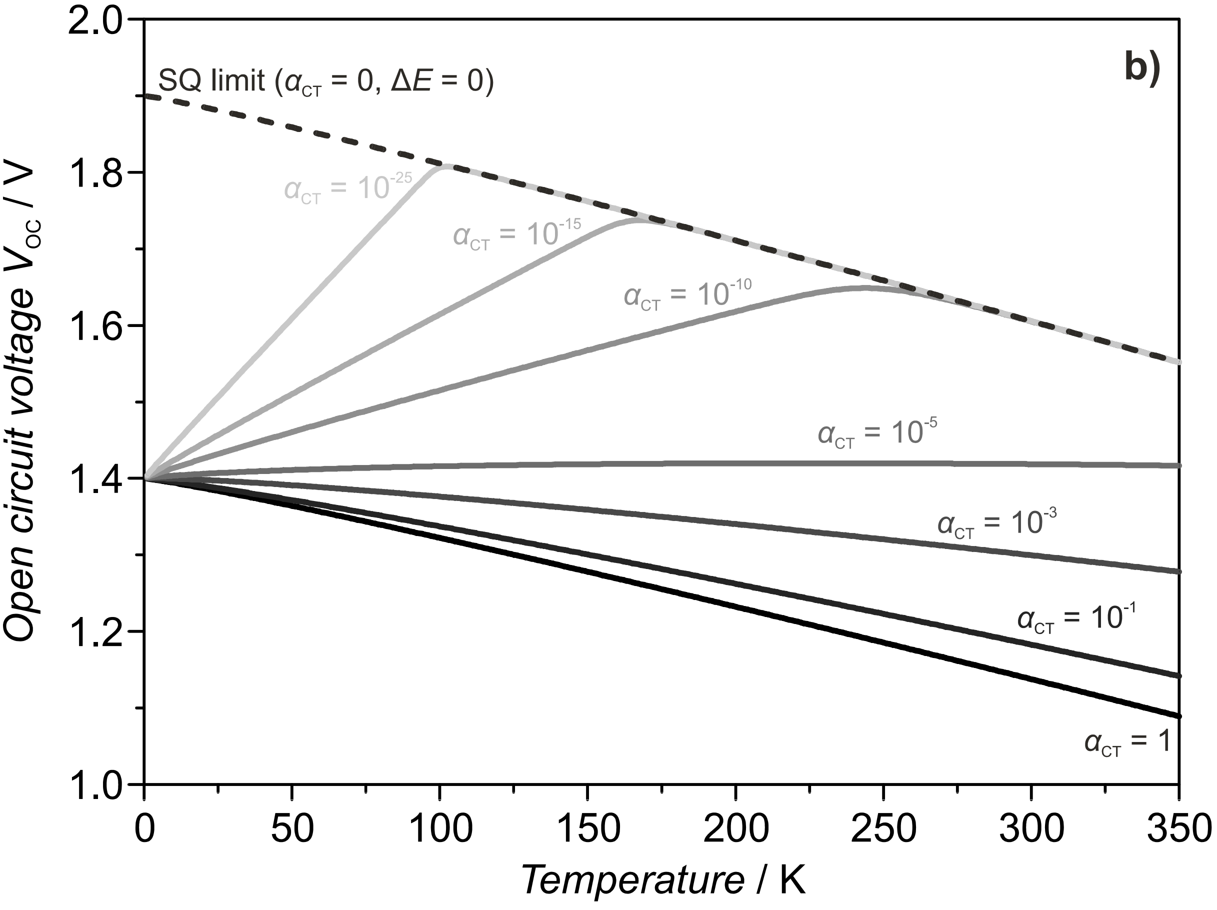

b)
SQ limit (α_{CT} = 0, ΔE = 0)
$\alpha_{CT} = 10^{-25}$
$\alpha_{CT} = 10^{-15}$
$\alpha_{CT} = 10^{-10}$
$\alpha_{CT} = 10^{-5}$
$\alpha_{CT} = 10^{-3}$
$\alpha_{CT} = 10^{-1}$
$\alpha_{CT} = 1$
Open circuit voltage V_{OC} / V
1.0
1.2
1.4
1.6
1.8
2.0
0
50
100
150
200
250
300
350
Temperature / K

Figure 5. a) Maximum open circuit voltage V_{OC} and power conversion efficiency η predicted for an organic hetero-junction solar cell as a function of CT absorption α_{CT}, assuming an offset energy of $\Delta E = 0.5$ eV, a band gap of $E_g = 1.9$ eV and the AM1.5g solar radiation spectrum. The maximum efficiency of 33 % at $\alpha_{CT} = 1$ corresponds to the case of a homo-junction in the classical SQ theory with $E_g' = 1.4$ eV. b) Maximum open circuit voltage V_{OC} predicted for an organic hetero-junction solar cell as a function of temperature T for several different CT absorptions α_{CT}, assuming an offset energy of $\Delta E = 0.5$ eV, a band gap of $E_g = 1.9$ eV and the AM1.5g solar radiation spectrum.

Advanced Energy Materials 2 (2012) 1100-1108

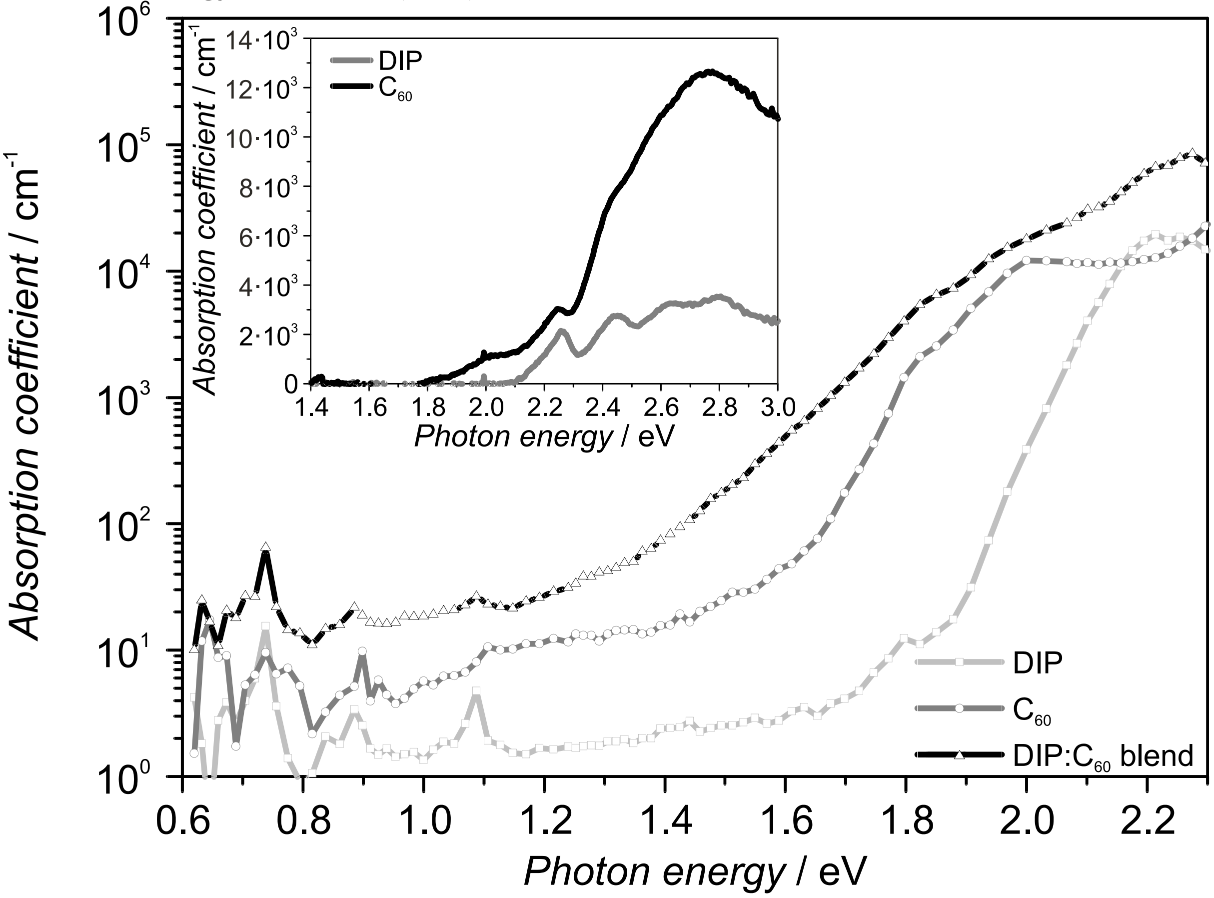


Figure 6. Photothermal deflection spectroscopy (PDS) measurements for a blend of the donor DIP and the acceptor C_{60}. Moreover the single spectra of both materials are plotted to demonstrate the difference caused by additional charge transfer state absorption. The inset shows the absorption coefficients of the single materials extracted from reflection/transmission measurements, which were used to calibrate the PDS data quantitatively.

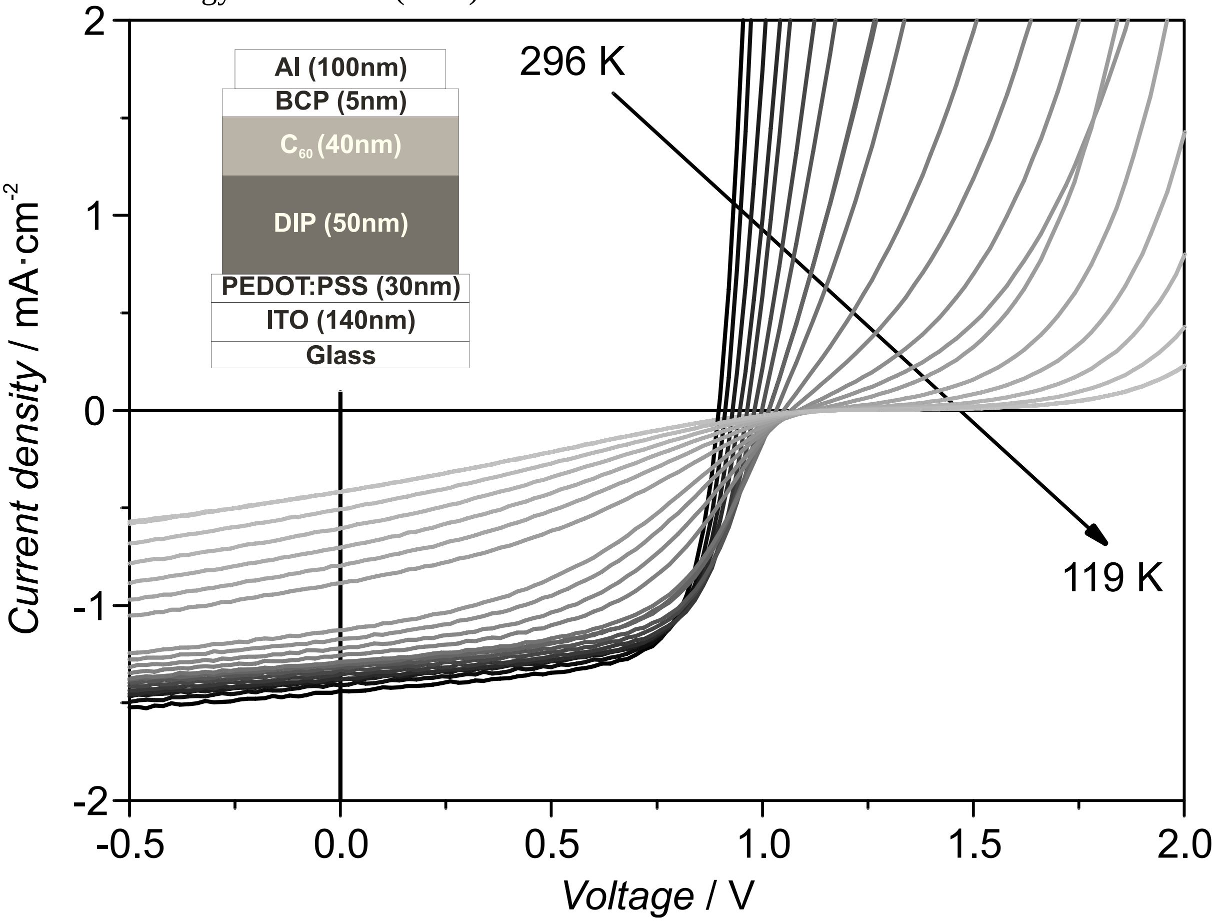


Figure 7. Current density vs. voltage (*j*-*V*) characteristics of a planar hetero-junction solar cell under simulated solar illumination in the temperature range $119\text{K} \leq T \leq 296$ K. The stack (inset) is build-up on a glass substrate and consists of an indium tin oxide (ITO) anode covered by 30 nm poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) as hole injection layer, followed by the active materials diindenoperylene (DIP) and C_{60} with thicknesses of 50 nm and 80 nm, respectively. For exciton blocking and protection against aluminum penetration into the active layer, a 5 nm thick layer of bathocuproine (BCP) is inserted between C_{60} and the aluminum electrode.

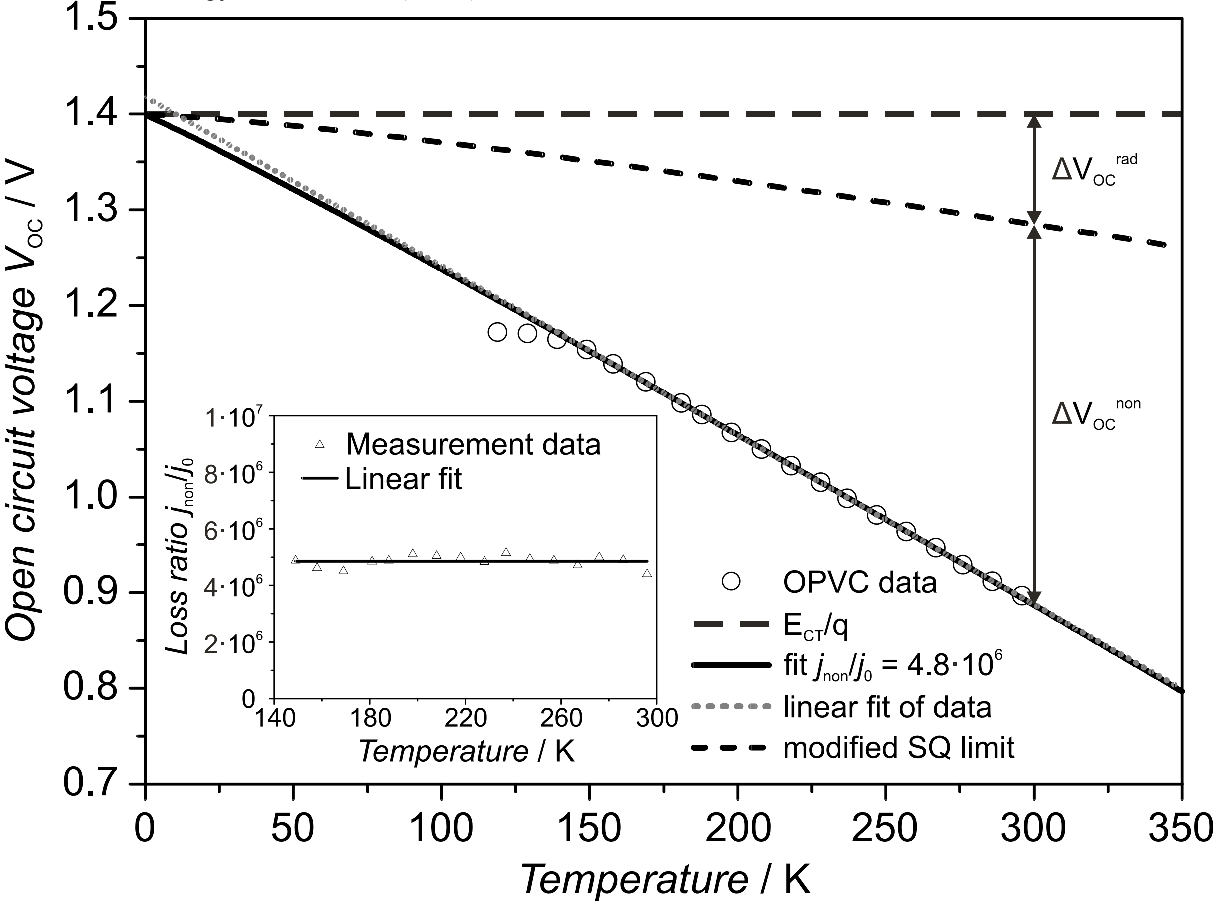


Figure 8. Open circuit voltage V_{OC} as function of temperature extracted from the measurement data of the planar hetero-junction solar cell shown in Figure 7. The data is fitted by equation 5 with $j_{non} = j_0 \cdot 4.8\cdot10^6$ and the C_{60} optical energy gap of $E_g = 1.9$ eV resulting in a CT gap of 1.40 eV. To elucidate the device's potential the solar cell is simulated with the same parameters, excluding non-radiative recombination losses resulting in the modified SQ limit. To point out the similar temperature behavior of j_{non} and j_0, the ratio is plotted vs. temperature (inset).

Advanced Energy Materials 2 (2012) 1100-1108

Modifying the Shockley-Queisser limit with an additional absorption and emission of the charge transfer state leads to a useful tool for describing organic solar cells. The charge transfer energy gap can be determined by fitting the theoretical open circuit voltage to a temperature dependent measurement, whereby non-radiative recombination losses can be quantified.

diindenoperylene, open circuit voltage, organic solar cells

Mark Gruber, Julia Wagner, Konrad Klein, Ulrich Hörmann, Andreas Opitz, Martin Stutzmann, and Wolfgang Brütting

Thermodynamic efficiency limit of donor-acceptor solar cells and its application to diindenoperylene/C_{60} based planar hetero-junction devices