



The effect of bias light on the spectral responsivity of organic solar cells

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ABSTRACT

The spectral responsivity, S , and the related spectrally resolved photon-to-electron external quantum efficiency, EQE , are standard device characteristics of organic solar cells and can be used to determine the short-circuit current density and power conversion efficiency under standardized test conditions by integrating over the spectral irradiance of the solar emission. However, in organic solar cells S and EQE can change profoundly with light intensity as a result of processes that vary non-linearly with light intensity such as bimolecular recombination of electrons and holes or space charge effects. To determine the S under representative solar light conditions, it is common to use modulated monochromatic light and lock-in detection in combination with simulated solar bias light to bring the cell close to 1 sun equivalent operating conditions. In this paper we demonstrate analytically and experimentally that the S obtained with this method is in fact the differential spectral responsivity, DS , and that the real S and the experimental DS can differ significantly when the solar cells exhibit loss processes that vary non-linearly with light intensity. In these cases the experimental DS will be less than the real S . We propose a new, simple, experimental method to more accurately determine S and EQE under bias illumination. With the new method it is possible to accurately estimate the power conversion efficiency of organic solar cells.

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1. Introduction

Compared to solar cells based on crystalline inorganic semiconductors, organic photovoltaic devices suffer from the moderate hole and electron mobilities associated with amorphous organic semiconductors and higher charge recombination rates due to a lower dielectric permittivity. As a result, non-linear light-intensity-dependent loss processes are generally more significant in organic solar cells than in inorganic solar cells. Well-established examples are bimolecular recombination [1–5] or space charge effects [6,7] that depend in a non-linear fashion on the concentration of photogenerated charge carriers. As a consequence the short-circuit current density (J_{sc}) of organic solar cells often varies sub-linearly with light intensity and the spectral responsivity (S) is not constant.

The spectral responsivity is related to the external quantum efficiency (EQE), which is the fraction of collected charges to incoming photons, and given by:

$$S(\lambda) = EQE(\lambda) \cdot \frac{q\lambda}{hc} \quad (1)$$

with q the elementary charge, h the Planck constant, and c and λ the speed and wavelength of light, respectively. Both S and EQE can provide important information about optical and electrical processes involved in the generation and collection of charges and are standard device characteristics. Under conditions where S and EQE are dependent on light intensity it is important to determine them under relevant test conditions. To compare the performance of photovoltaic cells, standard test conditions (STCs) have been defined. Under STC, the test cell has a temperature of 25 °C and is irradiated by the AM 1.5 G (AM:air mass) global reference spectrum at an intensity (irradiance) of $I = 100 \text{ mW/cm}^2$ [8,9].

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To avoid overestimation of S or EQE , the intensity-dependent losses are taken into account by illuminating the test cell at 1 sun equivalent bias light intensity during the measurement of S or EQE . In practice, the $S(\lambda)$ under illumination is determined by applying a continuous simulated solar light bias at 1 sun equivalent intensity and measuring the additional short-circuit current density generated by calibrated modulated monochromatic light with a low intensity amplitude $dI(\lambda)$. By using lock-in detection (LID), the modulation of the short-circuit current density (dJ_{SC}) generated by the modulated monochromatic illumination $dI(\lambda)$ in the test cell is determined. The measured spectral responsivity $S(\lambda)$ at given wavelength λ of monochromatic illumination is then obtained by the fraction: $dJ_{SC}/dI(\lambda)$.

At this point it is important to point out that the spectral responsivity ($dJ_{SC}/dI(\lambda)$) measured with lock-in detection is not precisely the spectral responsivity ($S(\lambda) = J_{SC}/I(\lambda)$) but rather the differential spectral responsivity $DS(\lambda) = dJ_{SC}/dI(\lambda)$ [10], i.e. the first derivative of the short-circuit current density with intensity. In fact, the differential spectral responsivity equals the slope of the short-circuit current density–light intensity (J_{SC} – I) curve. When J_{SC} is non-linear with I , the spectral responsivity S is different from the differential spectral responsivity DS as discussed by Metzendorf [10]. To our knowledge, this difference has not been explicitly noticed by the organic solar cell community. As we will show below, the difference between the commonly measured $DS(\lambda)$ and the actual $S(\lambda)$ can lead to an underestimation of $S(\lambda)$, $EQE(\lambda)$, and J_{SC} at STC.

In this paper we first summarize the measurement protocols for an accurate estimate of the power conversion efficiency, η , of a solar cell and then illustrate theoretically how the differential spectral responsivity DS measured with lock-in detection leads to an underestimation of S and EQE when J_{SC} is sub-linear with light intensity. Subsequently, we present experimental results on an efficient small band gap organic solar cell in which J_{SC} is sub-linear with light intensity to illustrate the problem. Finally, we suggest a simple procedure to determine the correct S , EQE , J_{SC} and η under AM 1.5 G illumination.

2. Experimental

2.1. Device fabrication and materials

Solar cells were prepared by spin coating a layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Clevios P, VP Al4083) on a pre-cleaned, patterned indium tin oxide (ITO) glass substrate. After annealing the PEDOT:PSS layer for 10 min at 140 °C in an inert atmosphere, the active layer was spin coated from a chloroform:*o*-DCB (9:1 v/v) solution of 7 mg/ml poly[(2,5-bis(2'-hexyldecyl)-3,6-bis(4'-decyloxy-[2,2'-bithiophen]-5,5'-diyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione)-*alt*-(1,4-phenylene)] (PDPP4TOP) [11] as electron donor and 14 mg/ml [6,6]phenyl-C₆₁-butyric acid methyl ester (PCBM), also in an inert atmosphere. As top electrode 1 nm LiF and 100 nm Al were evaporated under 10^{−7} mbar vacuum.

The PEDOT:PSS and the active layer thicknesses of the solar cell were ~35 and ~220 nm, respectively as determined with a Veeco Dektak 150 Surface Profiler.

2.2. Experimental setup and method

Current density–voltage (J – V) characteristics were measured with a Keithley 2400 source meter under ~100 mW/cm² simulated solar light illumination from a tungsten-halogen lamp (Philips Brilliantline, 50 W) filtered by a Schott GG385 UV filter and a Hoya LB120 daylight filter. Spectral responsivity measurements were conducted at different illumination intensities by biasing the solar cell with simulated solar light illumination from the tungsten-halogen lamp through the daylight filter. A lens was used to focus the illumination spot on the active area of the solar cell and a set of neutral density filters (New Focus, OD range 0.04–1.0) was used to vary the illumination intensity. We checked that (combinations of) these neutral density filters did not significantly distort the illumination spectrum. The device was kept in a nitrogen filled box behind a quartz window and irradiated with modulated monochromatic light, generated from a 50 W tungsten-halogen lamp (Philips focusline) and monochromator (Ortel, Cornerstone 130) with the use of a mechanical chopper. The spectral responsivity was recorded as a voltage over a 50 Ohm resistor using a lock-in amplifier (Stanford research Systems SR830) relative to a calibrated silicon solar cell as reference. The steady state short-circuit current density as a function of simulated solar light bias intensity of the solar cell was recorded with a Keithley 2400 source meter and using the simulated solar light bias source of the spectral responsivity setup. The average standard deviation in measuring the wavelength dependent EQE measurement in this setup is less than 0.005 in electrons/photons for wavelengths in the range of 350–800 nm where the $EQE > 0.1$. Only below 400 nm, the standard deviation reaches more than 0.01 occasionally.

2.3. Mismatch factor

The short-circuit current density (J_{SC}) under AM 1.5 G illumination is determined from the J_{SC} measured under simulated solar light illumination by mismatch correction following the procedure outlined in Section 3.1. First the intensity correction and then the spectral mismatch correction are performed. The intensity correction factor is given by the ratio between the short-circuit current of the silicon reference cell measured under simulated solar light illumination (7.62 mA) and the short-circuit current at AM 1.5 G illumination (7.13 mA). The intensity correction factor is then: 7.62 mA/7.13 mA = 1.069. To account for the spectral mismatch between the simulated solar light illumination and AM 1.5 G illumination and the spectral mismatch between the spectral responsivity of the reference cell and the solar cell, the mismatch correction factor (M) was calculated. The lamp spectrum was recorded with an Avantes NIR/vis spectrometer. The spectral mismatch factor was determined to $M = 1.084$. The J_{SC} under AM 1.5 G illumination is given by $J_{SC} = J_{SC}(E_s)/(1.069 \times 1.084)$, with

$J_{SC}(E_S)$ the short-circuit current density measured under simulated solar light illumination of the solar simulator.

3. Theory

3.1. Power conversion efficiency

The power conversion efficiency of an organic solar can be determined from the current–density–voltage characteristics (J – V) of the solar cell recorded under AM 1.5 G illumination:

$$\eta = \frac{J_{SC} V_{OC} FF}{I_{AM1.5G}} \quad (2)$$

with J_{SC} the short-circuit current density, V_{OC} the open-circuit voltage, FF the fill factor, and $I_{AM1.5G} = 100 \text{ mW/cm}^2$ the intensity of the AM 1.5 G spectral irradiance.

To measure a solar cell under AM 1.5 G irradiance outdoor or indoor is difficult. Outdoor, the AM 1.5 G spectrum is only obtained when the sky is free of clouds and when the solar light passes through the earth atmosphere at a zenith angle of 48.2° . Indoor, a solar simulator has to be used that simulates the AM 1.5 G spectrum. In practice, the shape of the spectral irradiance of the solar simulator $E_S(\lambda)$ always deviates from the shape of the spectral irradiance of the reference AM 1.5 G emission $E_R(\lambda)$. The standard technique to measure η under AM 1.5 G illumination with a solar simulator involves two steps. First, because V_{OC} and FF are not significantly influenced by a spectral mismatch between the simulator and the AM 1.5 G illumination they can be determined from the J – V characteristics under simulated solar light. The J_{SC} , however, scales directly to the light intensity and is strongly dependent on the exact shape of the illumination spectrum because the solar cell has a specific absorption spectrum. Consequently, the measured J_{SC} with simulated illumination $E_S(\lambda)$ will be off from the J_{SC} under the reference AM 1.5 G illumination $E_R(\lambda)$. This offset will be larger when the solar cell absorbs in a region where the solar simulator and the AM 1.5 G spectra do not match exactly. Therefore, in a second step, J_{SC} must be determined more precisely. Two main methods exist to evaluate the J_{SC} at AM 1.5 G illumination.

The first method is based on a spectral mismatch correction which takes into account the difference between the simulator spectrum and the AM 1.5 G reference spectrum as well as the difference between the spectral responsivity of the test cell and the reference cell that is used to set the light intensity [12–15]. Basically, the solar simulator has to be adjusted to an equivalent intensity such that the solar cell under test delivers the same short-circuit current density as it would under AM 1.5 G illumination. The intensity of the solar simulator is calibrated with a stable reference cell by adjusting the intensity to a target J_{SC} of the reference cell. The target J_{SC} of the reference cell is determined by the mismatch correction which takes into account the spectral mismatch between the spectral irradiance of solar simulator (E_S) and the AM 1.5 G reference (E_R) spectrum and the mismatch between the spectral responsivity of the reference cell (S_R) and solar cell under test (S_T).

$$M = \frac{\int S_R(\lambda) E_R(\lambda) d\lambda}{\int S_R(\lambda) E_S(\lambda) d\lambda} \cdot \frac{\int S_T(\lambda) E_S(\lambda) d\lambda}{\int S_T(\lambda) E_R(\lambda) d\lambda} \quad (3)$$

To determine the mismatch correction factor M and consequently the target J_{SC} , the spectral responsivity of the solar cell and the irradiance spectrum of the solar simulator have to be measured [13–15]. We note that for calculating M using Eq. (3), normalized values for $S_R(\lambda)$, $S_T(\lambda)$ and $E_R(\lambda)$ suffice and absolute values need not be used. Eq. (3) further shows that to minimize deviation of M from unity, $S_R(\lambda)$ and $S_T(\lambda)$ preferably have the same shape as well as $E_S(\lambda)$ and $E_R(\lambda)$.

The second method to obtain J_{SC} under standard solar illumination is to measure the absolute spectral responsivity $S_T(\lambda)$ of the test cell and then integrate $S_T(\lambda)$ over the AM 1.5 G reference spectrum ($E_R(\lambda)$ at 100 mW/cm^2):

$$J_{SC} = \int S_T(\lambda, E_R) E_R(\lambda) d\lambda \quad (4)$$

Here $S_T(\lambda, E_R)$ signifies that the absolute spectral responsivity depends on λ and should be measured under a bias illumination that preferably matches the reference AM 1.5 G spectrum (E_R) and intensity (100 mW/cm^2).

3.2. Spectral responsivity

In this section we analyze under which conditions the differential spectral responsivity (DS) as it is commonly measured by lock-in detection (LID) deviates from the spectral responsivity (S). Typically, the $DS(\lambda)$ is measured to determine the wavelength dependent $S(\lambda)$ of a solar cell when biased with continuous simulated solar light bias illumination. By using modulated monochromatic light in combination with LID, it is possible to distinguish the contribution to the photocurrent of the low-intensity monochromatic illumination from the contribution of the high-intensity simulated solar light illumination. The amplitude measured with the lock-in amplifier is proportional to the amplitude of the short-circuit current density (dJ_{SC}) generated by the modulated monochromatic illumination ($dI(\lambda)$). The differential spectral responsivity (DS) is obtained by dividing the amplitude of the modulated photocurrent (dJ_{SC}) by the amplitude of the light intensity ($dI(\lambda)$) of the modulated monochromatic illumination: $DS(\lambda) = dJ_{SC}/dI(\lambda)$ [10]. To relate the spectral responsivity S to the differential spectral responsivity DS , we differentiate the photocurrent with respect to the light intensity. The photocurrent density is given by the product of the intensity (I) and spectral responsivity (S):

$$J = S \cdot I \quad (5)$$

Differentiating the photocurrent with respect to the intensity we obtain:

$$DS = \frac{dJ}{dI} = S + I \frac{dS}{dI} \quad (6)$$

The important consequence of Eq. (6) is that DS is only equal to the S when S is independent of the light intensity I . Eq. (5) shows that this condition only holds when the photocurrent varies linearly with light intensity. When the photocurrent is sub-linear with light intensity, e.g.

due to light-intensity-dependent losses [5], the differential spectral responsivity DS measured with the LID technique is not equal to the spectral responsivity S , but off by the second term on the right in Eq. (6).

To illustrate the difference between DS measured with LID and S , we calculated both S and DS from the J_{SC} – I curve obtained from a simple analytical photocurrent model [5]. In this photocurrent model, drift, diffusion, and bimolecular recombination of charge carriers are considered but space charge effects are neglected. The derivation of the photocurrent model and the exact expression of the photocurrent as a function of voltage, generation rate and other device parameters can be found in the paper of Koster et al. [5]. In the model we consider equal hole and electron mobility of $10^{-8} \text{ m}^2/\text{Vs}$ an active layer thickness of 100 nm, a reduced Langevin recombination (pre-factor of 0.1), and an intensity of 1 sun corresponding to a generation rate of $10^{27} \text{ m}^{-3} \text{ s}^{-1}$. Since bimolecular recombination is considered in the analytical photocurrent model, the photocurrent varies sub-linearly with light intensity as shown in Fig. 1a.

The spectral responsivity is calculated by taking the ratio of the photocurrent and the light intensity $S = J_{SC}/I$ while the differential spectral responsivity is obtained by differentiating the photocurrent with respect to the light intensity $DS = dJ_{SC}/dI$. Fig. 1b shows the normalized spectral responsivity and the differential spectral responsivity as a function

of light intensity. As expected from Eq. (6), the normalized S and DS both deviate from 1 as soon as the photocurrent becomes non-linear with light intensity. Since the photocurrent is sub-linear with light intensity, DS is less than S in the sub-linear intensity regime.

This analysis and model calculations show that when the spectral responsivity (S) is measured with LID under bias light illumination and the organic solar cell possesses non-linear light-intensity-dependent losses, the measured data represent the differential spectral responsivity (DS) rather than the spectral responsivity S , and DS is expected to be lower than S .

4. Results and discussion

To experimentally illustrate the effect of a sub-linear J_{SC} – I regime on the measured S and EQE measured with LID we use a polymer:fullerene bulk-heterojunction solar cell with a thick active layer ($\sim 220 \text{ nm}$) consisting of a blend of PDPP4TOP:PCBM. PDPP4TOP is a small band gap donor polymer based on diketopyrrolopyrrole unit alternating with conjugated segment consisting of four thiophene and one benzene ring that provides a power conversion efficiency of $\sim 4.7\%$ in combination with PCBM as acceptor for 100 nm films [11]. For $\sim 220 \text{ nm}$ layers the device presents a clear sub-linear light intensity dependence of J_{SC} at 1 sun and is therefore well suited to demonstrate experimentally the difference between S and DS .

The J – V characteristics of the PDPP4TOP:PCBM solar cell with a 220 nm thick active layer are shown in Fig. 2a under illumination with a solar simulator and in the dark. For this cell $V_{OC} = 0.50 \text{ V}$, $FF = 0.47$, $J_{SC} = 16.30 \text{ mA}/\text{cm}^2$, and $\eta = 3.9\%$ are obtained. The spectral irradiance of the solar simulator does not exactly match the AM 1.5 G spectrum and therefore the measured J_{SC} is off from the real J_{SC} at AM 1.5 G illumination. To obtain the J_{SC} under AM 1.5 G illumination, the $S(\lambda)$ can be measured, followed by integrating $S(\lambda)$ with the AM 1.5 G spectral irradiance using Eq. (4).

Fig. 2b depicts the measured EQE spectra when the solar cell is biased with simulated solar light at ~ 1 sun intensity and when the solar cell is not biased with simulated solar light. A significant reduction of the EQE by 15% is observed under simulated solar light bias. Integrating the EQE spectra with the AM 1.5 G solar spectrum using Eqs. (1) and (4), $J_{SC} = 15.15 \text{ mA}/\text{cm}^2$ without bias and $J_{SC} = 12.81 \text{ mA}/\text{cm}^2$ with bias are obtained.

The reduction of the measured EQE with light bias has often been interpreted as a reduction of the real EQE due to non-linear light-intensity-dependent losses. However, this interpretation is partly incorrect because the experimental EQE measured with LID represents $DS(\lambda)$ rather than $S(\lambda)$ ($EQE_{LID}(\lambda) = (hc/e\lambda) \cdot DS(\lambda)$). In Section 3.2 we have shown that for a sub-linear dependence of J_{SC} with light intensity, DS is less than S and hence EQE_{LID} is lower than the real EQE.

Fig. 3a shows the J_{SC} of the PDPP4TOP:PCBM solar cell for different simulated solar light illumination intensities I . The relation between J_{SC} and I is sub-linear. At

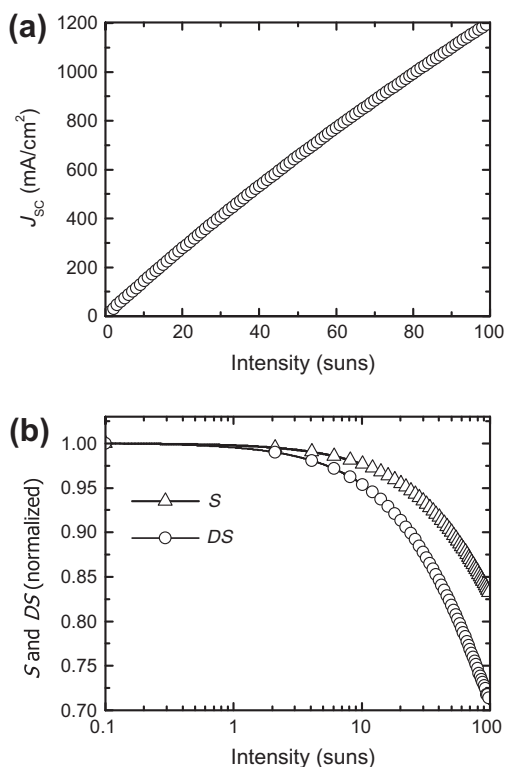


Fig. 1. (a) Calculated photocurrent (J_{SC} , open markers) from a simple analytical model as a function of light intensity (I). (b) Spectral responsivity (S) and differential spectral responsivity (DS) as a function of light intensity, normalized at low light intensities.

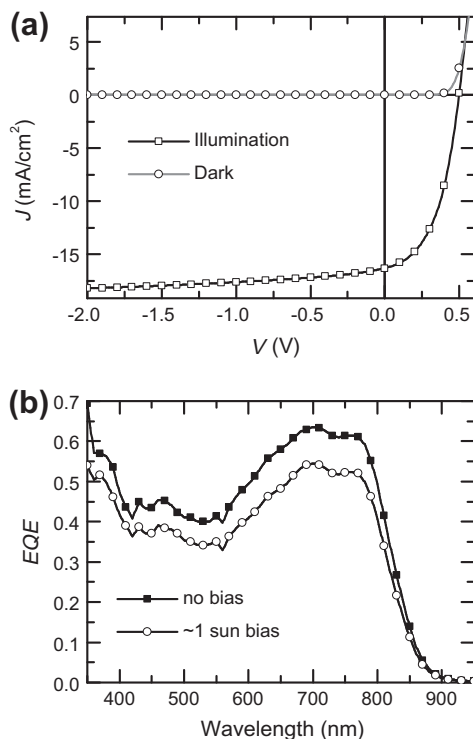


Fig. 2. (a) J - V characteristics of a PDPP4TOP:PCBM solar cell with $J_{SC} = 16.63 \text{ mA/cm}^2$, $V_{OC} = 0.50 \text{ V}$, $FF = 0.47$, and $\eta = 3.9\%$. (b) EQE measured with ~ 1 sun equivalent simulated solar light bias illumination and without light bias. The AM 1.5 G spectrally integrated short-circuit currents obtained from Eq. (3) are $J_{SC} = 15.15 \text{ mA/cm}^2$ without light bias and $J_{SC} = 12.81 \text{ mA/cm}^2$ at ~ 1 sun bias.

$I = 70 \text{ mW/cm}^2$, i.e. below ~ 1 sun intensity (100 mW/cm^2), the deviation of the short-circuit current density from a linear dependence is clearly noticeable. At much lower light intensities J_{SC} essentially varies linearly with light intensity. Hence, at low light intensity the experimental EQE_{LID} corresponds to the real EQE but at somewhat higher light intensities, where J_{SC} varies non-linearly with light intensity, the measured EQE_{LID} will deviate from the real EQE. To compare the measured EQE_{LID} to the real EQE we measured the EQE spectra (Fig. 3b) over the same simulated solar light bias intensity range as J_{SC} .

From the J_{SC} - I curve we obtain the spectrally averaged external quantum efficiency $\langle EQE \rangle$ via:

$$\langle EQE \rangle = \frac{J_{SC}}{q\Phi} = \frac{1}{A} \cdot \frac{J_{SC}}{I} \quad (7)$$

where Φ is the total photon flux of the illumination source, and A is a constant that depends on the shape of the spectral irradiance of the lamp $E_S(\lambda)$, but is independent of I . It is important to note that $\langle EQE \rangle$ in Eq. (7) corresponds to the definition of the real $\langle EQE \rangle$.

The measured EQE spectra at different simulated solar light intensities from Fig. 3b can be integrated with the AM 1.5 G reference spectrum $E_R(\lambda)$ according to Eqs. (1) and (4) to obtain an estimated short-circuit current density, via:

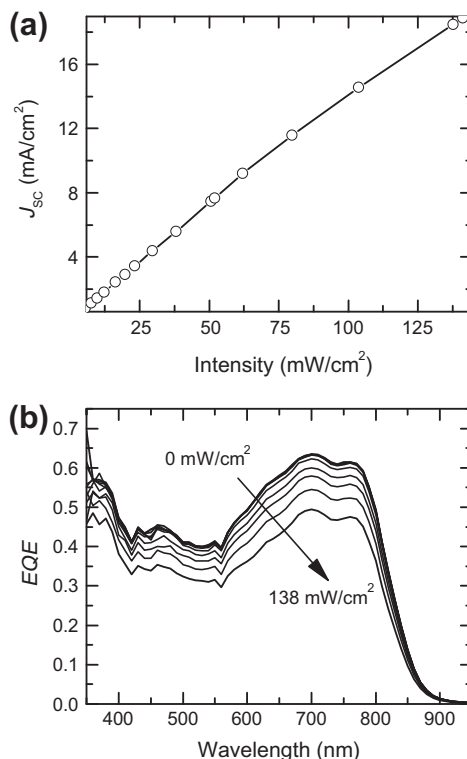


Fig. 3. (a) Short-circuit current density (J_{SC} , open markers) as a function of simulated solar light illumination intensity of a 220 nm active layer PDPP4TOP:PCBM solar cell. (b) Measured EQE spectra at varying simulated solar light bias illumination intensities (0, 5, 9, 12, 16, 37, 60, 78, 101, 138 mW/cm^2). The curve recorded at 37 mW/cm^2 is the first that deviates visibly from the one without light bias.

$$J'_{SC} = \int EQE_{LID}(\lambda) E_R(\lambda) \frac{\lambda}{hc} d\lambda \quad (8)$$

where we use the prime in J'_{SC} to indicate that the short-circuit current density has been determined by spectral integration of the EQE determined with LID. In analogy with Eq. (7) we define the corresponding spectrally averaged external quantum efficiency determined with lock-in detection as $\langle EQE_{LID} \rangle$:

$$\langle EQE_{LID} \rangle = \frac{1}{A'} \cdot \frac{J'_{SC}}{I} \quad (9)$$

where I is the intensity of the simulated solar bias illumination and A' is a constant that depends on the shape of the AM 1.5 G spectrum and on the shape of the simulated solar light used.

Without knowing A and A' in Eqs. (7) and (9), it is still possible to compare $\langle EQE \rangle$ with $\langle EQE_{LID} \rangle$, by normalizing them at the lowest measured bias intensity to unity and using the two normalization factors to scale the data. These normalized $\langle EQE \rangle_n$ and $\langle EQE_{LID} \rangle_n$ are plotted in Fig. 4a as function of simulated solar light bias intensity. At low bias illumination intensity, $\langle EQE \rangle_n$ and $\langle EQE_{LID} \rangle_n$ are equal and remain very close to unity because of the absence of non-linear light-intensity-dependent losses. At higher bias illumination, $\langle EQE \rangle_n$ becomes less than unity with increasing

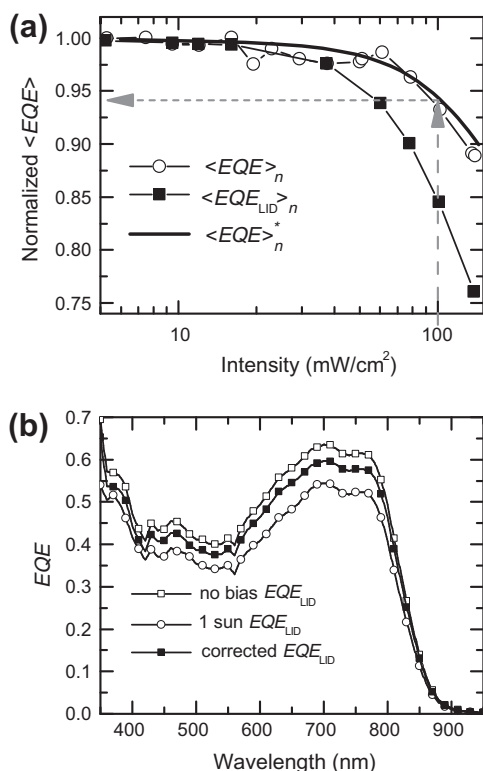


Fig. 4. (a) Normalized spectrally averaged $\langle EQE \rangle_n$ s of a ~ 220 nm active layer PDPP4TOP:PCBM solar cell as a function of bias intensity obtained from measuring the short-circuit current density ($\langle EQE \rangle_n$), from integrating the measured EQE_{LID} spectra with the AM 1.5 G spectral irradiance ($\langle EQE_{LID} \rangle_n$), and from $\langle EQE \rangle_n^*$ as defined in Eq. (10). Arrows indicates the scaling factor f at 1 sun illumination that can be used to obtain the correct EQE spectrum at 1 sun illumination. (b) EQE spectra measured with LID without and with 1 sun bias illumination and the corrected EQE spectrum at 1 sun illumination.

bias light intensity. The normalized measured $\langle EQE_{LID} \rangle_n$ also decreases with increasing bias intensity from unity, but at a higher rate than $\langle EQE \rangle_n$. This is in agreement with the fact that the measured $\langle EQE_{LID} \rangle_n$ scales with DS as explained in Section 3.2 of this paper while $\langle EQE \rangle_n$ scales with S (compare Fig. 1b).

To confirm that the measured $\langle EQE_{LID} \rangle_n$ scales with the differential short-circuit current density rather than with the short-circuit current density itself, the normalized $\langle EQE_{LID} \rangle_n$ is integrated over the intensity and then divided by the light intensity to give:

$$\langle EQE \rangle_n^* = \frac{\int \langle EQE_{LID} \rangle_n dI}{I} \quad (10)$$

Fig. 4a shows that $\langle EQE \rangle_n$ and $\langle EQE \rangle_n^*$ are virtually identical. This confirms that the measured $\langle EQE_{LID} \rangle_n$ scales with the differential short-circuit current density, and $\langle EQE \rangle_n^*$ with the real short-circuit current density.

To determine the correct $EQE(\lambda)$ spectrum at 1 sun simulated solar light intensity the normalized $\langle EQE \rangle_n$ or the integrated $\langle EQE \rangle_n^*$ at 1 sun intensity ($100 \text{ mW}/\text{cm}^2$, see arrow in Fig. 4a) can be used to scale the EQE spectrum. For the specific PDPP4TOP:PCBM solar cells used here, a

scaling factor of $f = 0.94$ at 1 sun intensity is obtained from $\langle EQE \rangle_n^*$. Multiplying the $EQE(\lambda)$ measured without bias illumination with the scaling factor $f = 0.94$, provides the correct $EQE(\lambda)$ spectrum at 1 sun intensity. Fig. 4b compares the $EQE(\lambda)$ spectra measured with LID without bias illumination and with 1 sun bias illumination, with the corrected $EQE(\lambda)$ spectrum. Integration of the corrected $EQE(\lambda)$ spectrum at 1 sun intensity analogous to Eq. (8), provides an estimate of the short-circuit current density under AM 1.5 G conditions of $J_{SC}' = 14.24 \text{ mA}/\text{cm}^2$.

As mentioned in Section 3.1, the short-circuit current density at AM 1.5 G irradiance can also be determined from the short-circuit current density measured with the solar simulator setup (Fig. 2a) by performing a mismatch correction. For our setup and this particular solar cell a correction factor of 1.1588 is calculated (see Section 2.3). Dividing the J_{SC} measured with the solar simulator ($16.30 \text{ mA}/\text{cm}^2$) with 1.1588, provides the corrected $J_{SC} = 14.07 \text{ mA}/\text{cm}^2$ for AM 1.5 G illumination. This matches very closely to $J_{SC}' = 14.24 \text{ mA}/\text{cm}^2$ obtained from the corrected $EQE(\lambda)$ spectrum and confirms independently that scaling the EQE_{LID} spectrum with f can be used to obtain an accurate EQE (and S) and the correct short-circuit current density at AM 1.5 G illumination. The resulting estimates for the AM 1.5 G power conversion efficiency are $\eta = 3.31\%$ and $\eta' = 3.35\%$.

5. Synopsis

Based on these results we propose a simple method to determine the correct $EQE(\lambda)$ spectrum under 1 sun simulated solar light intensity. In the simplest approximation it suffices to measure $EQE_{LID}(\lambda)$ without bias illumination and to measure J_{SC} versus light intensity I (maintaining a constant spectral shape of the light). J_{SC}/I is proportional to the spectrally averaged $\langle EQE \rangle$ and by normalizing J_{SC}/I at the lowest light intensity, as is done in Fig. 4a, it is possible to find the scaling factor f at $I = 100 \text{ mW}/\text{cm}^2$ that is needed to scale the measured $EQE_{LID}(\lambda)$ and obtain the correct $EQE(\lambda)$ under 1 sun illumination conditions. In this method it is important to check that at low I , the normalized J_{SC}/I is virtually constant and shows a plateau region as shown in Fig. 4a.

A more sensitive technique to measure J_{SC}/I as function of light intensity involves measuring the $EQE_{LID}(\lambda)$ under different bias light intensities (as shown in Fig. 3b), followed by determining the spectrally integrated $\langle EQE_{LID} \rangle$ by Eq. (8), and the intensity integrated $\langle EQE \rangle^*$ by Eq. (10) as function of I . By normalizing $\langle EQE \rangle^*$ to unity at the lowest I , the scaling factor f can be found as the value of $\langle EQE \rangle_n^*$ at $I = 100 \text{ mW}/\text{cm}^2$.

Using spectral integration over the AM 1.5 G irradiance, the corrected $EQE(\lambda)$ can be used to obtain an accurate estimate of the short-circuit current density (J_{SC}) under AM 1.5 G conditions.

6. Conclusion

We have shown theoretically and experimentally that the spectral responsivity $S_{LID}(\lambda)$ and external quantum

efficiency $EQE_{\text{LID}}(\lambda)$, measured with lock-in detection deviate from the real $S(\lambda)$ and $EQE(\lambda)$ when the short-circuit current density is non-linear with light intensity. The prime reason for the deviation is that S_{LID} actually represents the differential spectral responsivity DS , rather than S . We further developed a simple method to determine the correct $S(\lambda)$ and $EQE(\lambda)$ spectra under 1 sun illumination conditions from the $EQE_{\text{LID}}(\lambda)$ measured without illumination and the simulated solar-light intensity-dependence of short-circuit current density. By integrating the corrected $S(\lambda)$ with the AM 1.5 G spectral irradiance it is possible to accurately estimate the short-circuit current density of the solar cell under standard test conditions.

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References

- [1] I. Riedel, N. Martin, F. Giacalone, J.L. Segura, D. Chivase, J. Parisi, V. Dyakonov, Polymer solar cells with novel fullerene-based acceptor, *Thin Solid Films* 451 (2004) 43–47.
- [2] M.M. Mandoc, F.B. Kooistra, J.C. Hummelen, B. de Boer, P.W.M. Blom, Effect of traps on the performance of bulk heterojunction organic solar cells, *Appl. Phys. Lett.* 91 (2008) 263505/1–263505/3.
- [3] H. Azimi, A. Senes, M.C. Scharber, K. Hingerl, C.J. Brabec, Charge transport and recombination in low-bandgap bulk heterojunction solar cell using bis-adduct fullerene, *Adv. Energy Mater.* 1 (2011) 1162–1168.
- [4] G.F.A. Dibb, T. Kirchartz, D. Credgington, J.R. Durrant, J. Nelson, Analysis of the relationship between linearity of corrected photocurrent and the order of recombination in organic solar cells, *J. Phys. Chem. Lett.* 2 (2011) 2407–2411.
- [5] L.J.A. Koster, M. Kemerink, M.M. Wienk, K. Maturová, R.A.J. Janssen, Quantifying bimolecular recombination losses in organic bulk heterojunction solar cells, *Adv. Mater.* 23 (2011) 1670–1674.
- [6] V.D. Mihailescu, L.J.A. Koster, P.W.M. Blom, Space-charge limited photocurrent, *Phys. Rev. Lett.* 94 (2005) 126602/1–126602/4.
- [7] J. Szymkowski, The influence of the thickness, recombination and space charge on the loss of photocurrent in organic semiconductors: an analytical model, *J. Phys. D: Appl. Phys.* 40 (2007) 3352–3357.
- [8] ASTM Standard G173, Standard Tables for Reference Solar Spectral Irradiances: Direct Normal and Hemispherical on 37° Tilted Surface, American Society for Testing and Materials, West Conshohocken, PA, USA.
- [9] NREL, <<http://rredc.nrel.gov/solar/spectra/am1.5/>>, (accessed 23.08.12).
- [10] J. Metzendorf, Calibration of solar cells. 1: the differential spectral responsivity method, *Appl. Opt.* 26 (1987) 1701–1708.
- [11] K.H. Hendriks, in preparation.
- [12] C.H. Seaman, Calibration of solar cells by the reference cell method – the spectral mismatch problem, *Solar Energy* 29 (1982) 291–298.
- [13] J.M. Kroon, M.M. Wienk, W.J.H. Verhees, J.C. Hummelen, Accurate efficiency determination and stability studies of conjugated polymer/fullerene solar cells, *Thin Solid Films* 403 (2002) 223–228.
- [14] V. Shrotriya, G. Li, Y. Yao, T. Moriarty, K. Emery, Y. Yang, Accurate measurement and characterization of organic solar cells, *Adv. Funct. Mater.* 16 (2006) 2016–2023.
- [15] H.J. Snaith, How should you measure your excitonic solar cells?, *Energy Environ. Sci.* 5 (2012) 6513–6520.