

# Current-Voltage Characteristics of Bulk Heterojunction Organic Solar Cells: Connection Between Light and Dark Curves

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Organic photovoltaic materials and devices are being intensely investigated owing to their potential to reduce production costs of solar energy.<sup>[1]</sup> The interpenetrated nanostructure formed by a polymer donor and fullerene acceptor molecules acting as the active layer in bulk-heterojunction (BHJ) solar cells has attracted much attention because of its technological application.<sup>[2,3]</sup> It is of special relevance to clarify which operating mechanisms govern the solar cell overall performance, and establish the achievable values for short-circuit current  $j_{sc}$ , open-circuit voltage  $V_{oc}$ , and fill factor FF. Therefore, the analysis of the current-voltage characteristics along with the main factors influencing its shape is a theme of intense research in the field of organic photovoltaics. Very recent analyses relate the shape of the current-voltage ( $j - V$ ) characteristics and the reachable output voltage either to the energetics of the charge transfer state (CTS),<sup>[4,5]</sup> or to the recombination flux of charge carriers,<sup>[6-8]</sup> indicating that the issue is still under discussion. The role of electrostatically bound CTS in establishing the photocurrent level was previously modeled in terms of the Onsager-Braun field-assisted dissociation process.<sup>[9]</sup> However, there exist experimental tests signaling that geminate recombination of CTS does not play a significant role in the BHJ performance in case of some materials combinations as those formed by poly(3-hexylthiophene):[6,6]-phenyl C<sub>61</sub>-butyric acid methyl ester (P3HT:PCBM),<sup>[7,10]</sup> PCDTBT:PC<sub>70</sub>BM,<sup>[11]</sup> or PCPDTBT:PC<sub>70</sub>BM.<sup>[12]</sup> We then focus our analysis on the variation of the carrier recombination flux both on applied voltage and illumination intensity by examining the resistive response of solution-processed P3HT:PCBM photovoltaic devices.

A possible approach for the analysis of  $j - V$  characteristics of organic solar cells is to establish a physical model and solve it by computer calculation. The information extracted from fitting

of a limited number of current-voltage curves is not conclusive with respect to variation of simulation parameters.<sup>[9]</sup> More recent works rely on additional experimental information since fitting is calibrated against light and dark  $j - V$  characteristics, charge extraction curves and transient photovoltage data.<sup>[13]</sup> It is then important to use complementary measurements that probe the solar cell in operation conditions and provide additional information. Impedance spectroscopy is a powerful tool for the study of solar cells that measures differential resistances and capacitances. Furthermore, different internal processes can be separated by the spectroscopy, followed through the variation of the voltage axis, and then interpreted along with the steady state measurement ( $j - V$  curve).<sup>[14]</sup>

There are currently two basic approaches to view the operation of BHJ solar cells. The first assumes that the current decreases, as the voltage increases, by a decrease of an internal electrical field that reduces the rate of exciton separation.<sup>[9]</sup> Another approach views the blend as a homogeneous layer with selective contacts.<sup>[15,16]</sup> In this second approach the current is created by selective extraction of one carrier (electron or hole) at each side of the layer. The voltage  $V_F$  is given by the separation the Fermi level of the distinct carriers at the two contacts,

$$V_F = (E_{Fn} - E_{Fp})/q \quad (1)$$

being  $q$  is the elementary charge. In this model, the reason why the current decreases as the forward bias increases is recombination of the separate photogenerated carriers that contribute to the splitting of the Fermi levels.

A simple model based on this second approach is the following

$$j = j_0 \left[ \exp \left( \beta \frac{q V_F}{k_B T} \right) - 1 \right] - j_{ph} \quad (2)$$

Here  $k_B T$  is the thermal energy, and  $j_0$  accounts for the dark current. The first summand is interpreted in terms of the recombination current  $j_{rec}$ ,

$$j_{rec} = j_0 \exp \left( \beta \frac{q V_F}{k_B T} \right) \quad (3)$$

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and the second one represents the photocurrent  $j_{\text{ph}}$ . The expression in Equation (3) for the recombination current is usually labeled as the  $\beta$ -recombination model that includes the parameter  $\beta$  accounting for the deviation from the diode ideal equation (inverse of the diode ideality factor).<sup>[17]</sup> The rationale for Equation (3) is that the recombination current is proportional to a certain power of the carrier densities, which in turn depend exponentially on the voltage  $V_F$ . For example if only one carrier concentration, e.g. electrons, changes with the applied voltage, and if such carrier is a "conduction band carrier" obeying Boltzmann statistics as  $n_c = n_0 \exp(q V_F / k_B T)$ , then  $\beta$  is an effective order of the recombination. The recombination current can be expressed by

$$j_{\text{rec}} = j_0 \left( \frac{n_c}{n_0} \right)^\beta \quad (4)$$

providing that  $n_c \gg n_0$ . This last expression assumes that carrier concentration is basically homogeneous over the whole film. It is also easy to show that for both electrons in conduction band and holes in valence band,  $p_v$ , it holds that  $n_c p_v = n_0 p_0 \exp(q V_F / k_B T)$ .

One can describe more complex recombination mechanisms that involve carriers in traps, or a combination of extended and localized states, as in amorphous semiconductors.<sup>[6, 18–20]</sup> Different models involving total or trapped charge will lead to various interpretation of the parameter  $\beta$ . However, these last assumptions, leading to Equation (3), are not necessary at this stage of interpretation, as Equation (2) relates current to voltage as required, without statements about a detailed origin of the underlying recombination mechanism. Of course we would like to know, in a complete model, which is the local carrier concentration at each point, the recombination kinetics, the transport rate, and so on. It must be recognized, however, that the distance between such "complete" model and an expression as Equation (2) is huge, because experimentally we just get a voltage dependence of the recombination flux. We remark that Equation (3) is a reasonable assumption validated by several standard models of recombination of semiconductors, which we use as the starting working hypothesis for the recombination flux, although it is not completely general. For example recombination flux mediated by a *single* bandgap state will fail to behave exponentially. Therefore Equation (3) must be confirmed by the analysis of recombination resistance as we discuss later on.

Additional questions should be also clarified concerning the *empirical* behavior of recombination, photogeneration and charge collection. It is essential to know if the recombination term depends on photogeneration rate, or is a single function of *voltage* (valid at different illumination levels) as indicated in Equation (2). This question is a fundamental one related to reciprocity relationships.<sup>[21, 22]</sup> As pointed out by Donolato,<sup>[21]</sup> carrier collection reciprocity states that the current collected by the outer surface in the presence of a source of carriers at a given internal point, is linked with the excess carrier density at such point caused by a carrier density placed on the outer surface. If obeyed it allows connecting local carrier concentrations and output voltage *univocally*. Therefore, the issue is whether  $j - V$

curves in the illuminated solar cell can be related to the carrier concentration present in the same device under forward voltage in the dark.

The barrier to obtain an answer to this question is that recombination current and photocurrent are obviously mixed under illumination, and it cannot be said conclusively if Equation (2) is really realized, just by analysis of  $j - V$  curves. Impedance spectroscopy method is a small perturbation technique (at each voltage point), that experimentally determines differential quantities. The derivative procedure is able to remove an added constant current (the photocurrent) so that only the voltage-dependent term is measured. Thus recombination resistance (per unit volume, being  $L$  the active layer thickness) is defined from the recombination current derivative<sup>[23]</sup>

$$R_{\text{rec}} = L \left( \frac{dj_{\text{rec}}}{dV_F} \right)^{-1} \quad (5)$$

From this we readily arrive at the conclusion that if electronic reciprocity is obeyed (the voltage fixes all local concentrations) then recombination resistance at given voltage must be the same *at all light intensities*. Note furthermore that based on Equation (3)

$$R_{\text{rec}} = L \frac{k_B T}{\beta q j_0} \exp \left( -\beta \frac{q V_F}{k_B T} \right) \approx L \frac{k_B T}{\beta q} j_{\text{rec}}^{-1} \quad (6)$$

Therefore the recombination resistance (*i*) exhibits an exponential dependence on voltage and (*ii*) is inversely proportional to the recombination current. If these features are in fact realized they place strong constraints on detailed models that make statements about local concentration of carriers, their recombination and transport kinetics, and the macroscopic distribution along the active layer.

Another question of great significance towards general empirical conclusions is that we do not find in real cells, even in the best of cases, the ideal behavior of the recombination diode of Equation (2). Indeed voltage and current are distorted with respect to this model by other elements in the device unrelated to the photovoltaic operation of the active layer, so that it is usually found a behavior as

$$j = \frac{1}{1 + R_s/R_p} \left\{ j_0 \left[ \exp \left( \beta \frac{V_{\text{app}} - j A R_s}{k_B T/q} \right) - 1 \right] - \left[ j_{\text{ph}} - \frac{V_{\text{app}}}{R_p A} \right] \right\} \quad (7)$$

Here  $V_{\text{app}}$  stands for the applied voltage, that differs from  $V_F$  by a series voltage due to series resistance  $R_s$ , and current is reduced by shunt resistance  $R_p$ , being  $A$  the active area. It should be noticed that the distortion caused by the series resistance is especially important around the maximum power point, and is furthermore a strong function of the total current through the cell. It is necessary to recognize and consider these elements for a treatment of the  $j - V$  curve, especially when comparing light and dark conditions. Fortunately, we can extract  $R_s$  along with  $R_{\text{rec}}$  from the impedance measurement, and then use the

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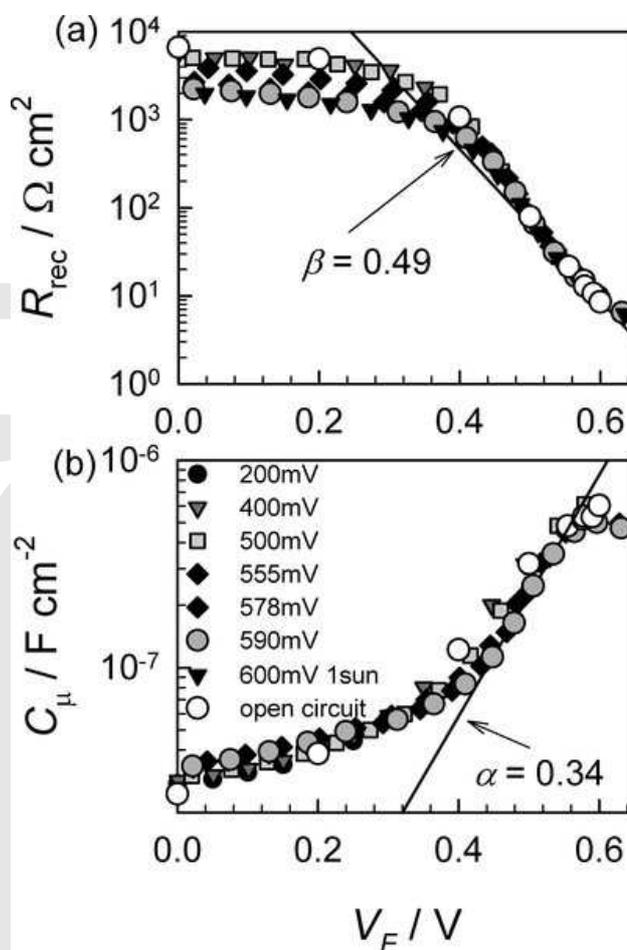
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correct voltage scale  $V_F = V_{app} - jAR_s$  for the analysis of reciprocity and other fundamental recombination properties.

We have reported very recently on the analysis of recombination resistance at different open-circuit voltages.<sup>[14, 23]</sup> Under these experimental conditions the kinetic balance between photogeneration and charge recombination fluxes holds, thus allowing for the analysis of the recombination current without interference of series or transport mechanisms. The impedance analysis has been adopted by others to analyze the effect of acceptor traps on the recombination kinetics,<sup>[24]</sup> or in the analysis of evaporated bulk-heterojunction devices.<sup>[25]</sup> These findings point to the relevance of carrier recombination processes in establishing the solar cell performance. Here, we extend our previous analysis by determining not only the recombination at different open-circuit conditions (which differ in the irradiation level) but also at different voltages across each single  $j$ - $V$  curve. Based on a detailed study of the resistances associated to recombination and series processes, evidence is provided that allows identifying carrier recombination flux as the determining factor of the  $j$ - $V$  curve shape. From the experimental analysis we conclude that (i) photogeneration flux is voltage-independent in accordance to previous analysis,<sup>[26]</sup> (ii) carrier recombination is observed to be independent of the irradiation intensity, and (iii) collection of photogenerated carriers is not a limiting rate factor of the cell performance. We furthermore establish the empirical dependence of the recombination flux on  $V_F$  [Equation (3)]. This provides both a criterion that must be obeyed by detailed recombination models, and a tool for the prediction of the solar cell performance in different conditions, based on a restricted set of measured parameters.

To analyze the above mentioned questions we have performed a series of impedance measurements in P3HT:PCBM BHJ solar cells exhibiting power-conversion efficiency within the range of 2.5 - 3.0 % by varying the applied voltage at different irradiation intensities (see Supporting Information on preparation conditions). The extraction of resistive and capacitive parameters from impedance measurements was explained in previous papers,<sup>[14, 23]</sup> and details are as Supporting Information. The experimental impedance analysis has allowed measuring  $R_{rec}$  as a function of the applied voltage for different illumination intensities, and to determine  $\beta$  parameter, as we will next explain. Additionally the series resistance  $R_s$  and the chemical capacitance  $C_\mu$ , which conveys information about the excess charge storage produced by light or applied voltage, have been extracted from fits.

We show in **Figure 1** the variation of  $R_{rec}$  and  $C_\mu$  as a function of  $V_F$  at different illumination intensities, and also in open-circuit conditions by applying a bias equaling  $V_{oc}$ . In these plots the voltage axis is corrected in order to discount the potential drop at the series resistance as  $jAR_s$  [see Equation (7)]. By examining Figure 1 one can observe that the differential resistance extracted from impedance exhibits a change in the voltage dependence at  $\sim 0.4$  V. Below this voltage the resistance varies with the illumination intensity, increasing for lower light levels, with a total change of a factor of five. For  $V_F > 0.4$  V the response corresponds to an approximate exponential behavior  $R_{rec} = R_0 \exp(-q\beta V_F/k_B T)$  as expected from Equation (6). This observation confirms that the empirical model as-



**Figure 1.** (a) Recombination resistance and (b) chemical capacitance extracted from impedance spectroscopy as a function of the voltage  $V_F = V_{app} - jAR_s$  at different illumination intensities ranging within  $1 \cdot 10^{-3}$  sun (corresponding to the open-circuit voltage signaled). The values obtained at open circuit are also indicated for comparison.  $\beta$ -parameter in the expression  $R_{rec} = R_0 \exp(-q\beta V_F/k_B T)$  is extracted for the high voltage range,  $\beta = 0.49$ . At high-voltages the capacitance follows an approximate exponential dependence on voltage as  $C_\mu = C_0 \exp(q\alpha V_F/k_B T)$  with  $\alpha = 0.34$ .

sumed in the beginning, Equation (3), is appropriate to describe the trends of recombination in these solar cells. A straightforward estimation of the  $\beta$ -parameter is obtained that results in  $\beta = 0.49$ , as observed in Figure 1(a). The chemical capacitance in Figure 1(b) exhibits the expected variation on voltage originated by the carrier occupation of electronic density-of-states (DOS) as  $C_\mu = q^2 g(V_F)$ .<sup>[14]</sup> As observed in Figure 1(b),  $C_\mu = C_0 \exp(\alpha q V_F/k_B T)$  also follows an approximate exponential form with  $\alpha = 0.34$ . At low voltages ( $V_F < 0.4$  V) the measured capacitance is originated by the voltage-modulation of the depletion zone built up at the cathode contact,<sup>[14]</sup> as has been shown in our previous work and is explained later in more detail. We also note that  $R_{rec}$  registered at open-circuit

at different light intensities, follows the response obtained under low-irradiation conditions. Apart from the variation of  $R_{\text{rec}}$  and  $C_{\mu}$  at low voltages, it is worth noting that both parameters collapse into a single curve ( $V_F > 0.4$  V) then indicating that illumination intensity does not affect neither the recombination mechanisms (represented by  $R_{\text{rec}}$ ), nor the excess carrier accumulation (derived from  $C_{\mu}$ ). This finding implies that splitting of the electron and hole Fermi levels at a given  $V_F$  is equivalently produced either by light (measured as a photovoltage) or applied voltage, so that electronic reciprocity is satisfied. Moreover each Fermi level at the edge of the organic layer easily equilibrates to the respective metal Fermi level.

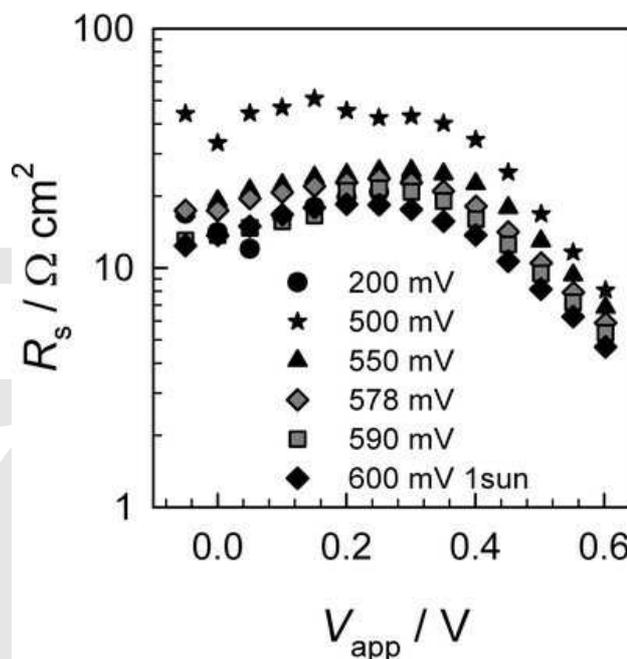
It is worth comparing these last results (irradiation independence of both  $R_{\text{rec}}$  and  $C_{\mu}$  at  $V_F > 0.4$  V) with previous analysis of the recombination fluxes derived from measurements of charge density.<sup>[7]</sup> Our findings entails that excess charge density is not affected by the light intensity but it is fully determined by the voltage. This is in accordance with the electronic reciprocity as commented above. The work by Shuttle et al.<sup>[7]</sup> showed, using the same polymer and fullerene combination, that charge density is independent of light intensity within the high voltage range (0.5 - 0.6 V) in accordance with our observations, and only doubles the dark value with illumination in the low-voltage (< 0.5 V) range. A possible reason for that dependence of charge density on light intensity (at least for voltages within 0.4 - 0.5 V) might be the procedure followed to calculate the series resistance potential drop.  $R_s$  can be just estimated from the slope of the  $j$  -  $V$  curve at large forward bias,<sup>[7]</sup> but determined with high accuracy from the analysis of the high-frequency impedance response at each measured voltage (see Supporting Information and Figure 2). In our analysis the specific  $R_s$  is not constant but decreases steeply at forward bias  $R_s \approx 15 - 5 \Omega \text{ cm}^2$ . This fact suggests that  $R_s$  should be related to transport and interfacial effects in addition to external cable contributions. We also observe that  $R_s$  is rather independent of the intensity of illumination.

We now focus our attention to  $\beta$  parameter and  $R_{\text{rec}}$  measured at open-circuit conditions, at which dc current is zero. This implies from Equation (2) that  $j_{\text{rec}}(V_{\text{oc}}) = j_{\text{ph}}$ , i.e. the solar device functions under the kinetic balance between generation and recombination currents. One of the purposes of this work is to check whether the photogenerated current is independent of the applied voltage. To consider that  $j_{\text{ph}} = j_{\text{sc}}$  along the voltage axis would imply that the exciton dissociation process, which ultimately gives rise to separated free carriers, is not influenced by the electrical field, but by phase segregation and blend morphology.<sup>[27]</sup>

One can infer from Equation (2) and (6) that

$$j_{\text{sc}} = j_{\text{rec}}(V_{\text{oc}}) = L \frac{k_B T}{\beta q R_{\text{rec}}(V_{\text{oc}})} \quad (8)$$

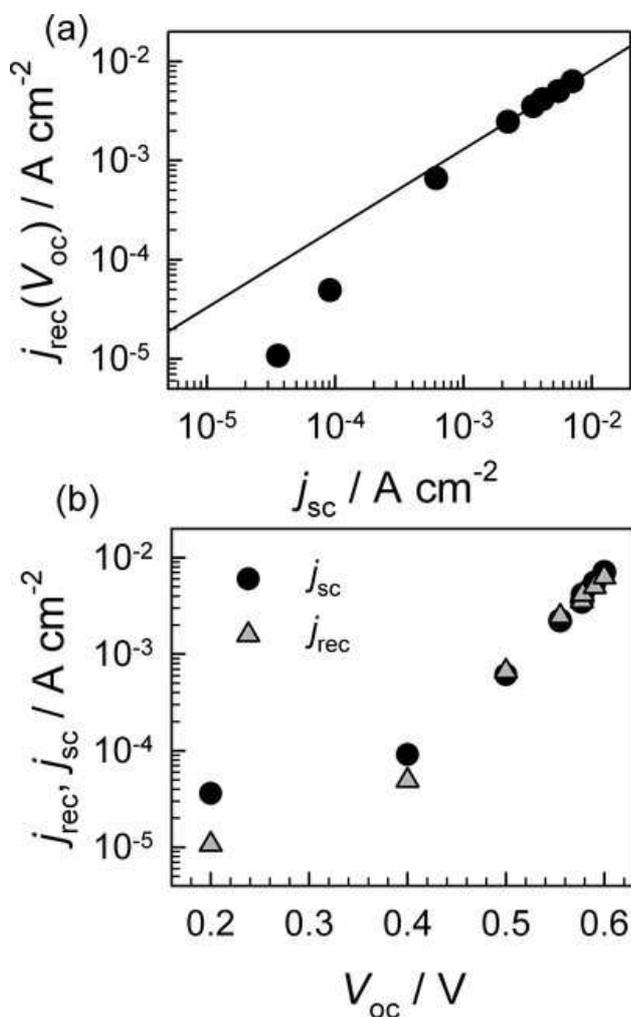
This last expression entails that the current value at short-circuit conditions establishes the derivative of  $j$  -  $V$  curve at open-circuit. The series resistance has no effect at  $V_{\text{oc}}$  because the total current vanishes. This is therefore a convenient prediction that can be tested without need for correction of the voltage.



**Figure 2.** Specific series resistance variation as a function of the applied voltage for different irradiation intensities (marked as the open-circuit voltage reached).

A comparison of calculated recombination current by means of Equation (8), and the experimentally measured  $j_{\text{sc}}$  is feasible. Our results shown in Figure 3 indicate that open-circuit and short-circuit measurements are correlated for P3HT:PCBM photovoltaic devices. In fact the correlation holds extremely well (slope approaches unity) in the high-current (high  $V_{\text{oc}}$ ) interval. At lower currents (low voltage region) deviations appear which coincide with the plateau in resistance dependence on applied voltage observed in Figure 1. It seems clear that within the low-voltage interval ( $V_F < 0.4$  V) Equation (6) underestimates the value for  $j_{\text{rec}}$  [Figure 3(b)]. To regard recombination flux as the key factor determining the cell performance requires quite flat profiles for both electron and hole Fermi levels, aligning to their respective selective contacts. Homogeneous carrier distributions are expected under these conditions, being the recombination process highly position-independent within the active layer. Such a solar cell energy picture is reached as far as the operating voltage overcomes the flat-band voltage originated by the depletion zone built up at the device cathode.<sup>[14]</sup> The capacitance in Figure 1(b) also manifests the occurrence of a depletion zone at  $V_F < 0.4$  V. Flat-band voltages usually reported for P3HT:PCBM-based solar cells lie within the range of 0.3 - 0.5 V.<sup>[14]</sup> At low-irradiation or low-voltage conditions carrier distribution inhomogeneities produced by the band bending near the cathode then alters the recombination process.<sup>[28]</sup> This relates to the resistance and capacitance behavior reported in Figure 1 at low voltages. As a result the calculated  $j_{\text{rec}}$  using the parameter  $\beta$  extracted at higher voltages deviates from  $j_{\text{sc}}$ . As we will next see this deviation has a negligible influence on the overall reconstruction of

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**Figure 3.** (a) Recombination current calculated from the recombination resistance values at different irradiation intensities and  $\beta = 0.49$  using Equation (8) as a function of short-circuit current reached at these irradiation intensities. (b) Comparison of photogeneration and recombination currents as a function of the reached open-circuit voltage.

the  $j$ - $V$  characteristics because at low voltages (high resistance region) the response is completely dominated by  $j_{sc}$  (recombination current is a negligible fraction of the total current).

According to the preceding observations on the correlation at larger short-circuit and recombination currents we propose that currents relevant for device operation are exclusively those related to carrier recombination and generation fluxes. Drift-diffusion currents in the studied, thin active layer ( $< 200$  nm) devices play then a minor role, being the  $j$ - $V$  characteristics mainly associated to the relationship established between generation, on the one hand, and recombination and extraction fluxes, on the other. Therefore, charge carrier transport does not limit the solar cell performance. Moreover, it is derived from the previous analysis that photogeneration processes are highly voltage-independent. We therefore conclude

that for P3HT:PCBM blends the electrical field does not have an influence on carrier transport ( $j_{ph}$  is observed to be voltage-independent, and this entails that the collection efficiency is not limited by a field-driven transport mechanism). Similarly, the electrical field does not affect the photogeneration yield ( $j_{ph}$  is fully cancelled by  $j_{rec}$  at open-circuit voltages in excess of 0.4 V). The shape of the  $j$ - $V$  curve, and then the fill factor, will be linked to the variation of the recombination flux on applied voltage modeled through the  $\beta$ -parameter, and the series resistance voltage loss.

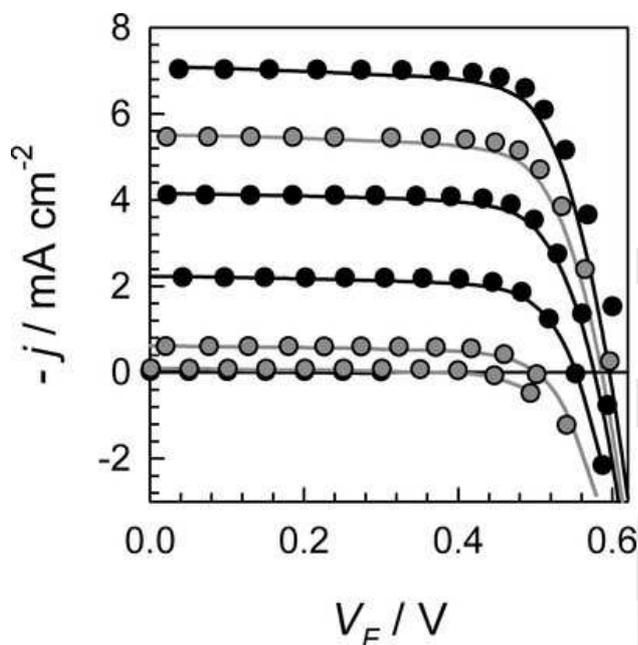
At this point we note that the sole analysis of the device resistances (recombination and series) suffice to reconstruct the most relevant aspects of  $j$ - $V$  characteristics concerning the device performance. This finding has implications of great importance for technological development of the organic solar cells. It means that we can readily determine a few key parameters that establish the performance of the solar cell in any required set of conditions.

To generate an expression for the whole  $j$ - $V$  curve, we combine Equation (2) and (8) and obtain the following expression

$$j = L \frac{k_B T}{q\beta} \left( \frac{1}{R_{rec}(V_F)} - \frac{1}{R_{rec}(V_{oc})} \right) \quad (9)$$

At a given illumination intensity the measurement of the recombination resistance allows generating the  $j$ - $V$  response. This has to be improved by including the effect of the series resistance as in Equation (7) by correcting the applied voltage. We show in Figure 4 a very good correlation between experimental  $j$ - $V$  curves at different illumination intensities of a representative cell and the total current using Equation (9). The resistance analysis then suffices to reconstruct the solar cell performance. Our analysis allows calculating the improvement in power-conversion efficiency at 1 sun illumination (from 2.57% to 3.06%) and FF (from 0.60 to 0.72) that would be obtained by removing the influence of the series resistance.

It is also interesting to observe that the impedance method allows establishing a direct relation between the capacitance and resistance dependences on  $V_F$ , and the kinetics of recombination.<sup>[17]</sup> Since the  $R_{rec}C_{\mu}$  product is a measurement of the effective carrier lifetime  $\tau$ , it is inferred that the recombination kinetics depends on the flux of carrier loss through the parameter  $\beta$ , and not only on the features of the DOS (accessible from the capacitance variation on  $V_F$ ). An estimation of the excess charge carrier density is also accessible by integration of  $C_{\mu}(V_F)$  curve, which mainly describes the occupancy of fullerene LUMO levels as indicated in previous works.<sup>[14,23]</sup> The impedance analysis becomes a convenient experimental method to progress in a detailed kinetic picture of recombination, which is microscopically seen as a bimolecular-like charge transfer process. We note in addition that the achievable output open-circuit voltage does depend on the particularities of the materials energetics through the electron and hole energy level distribution (DOS).<sup>[29]</sup> It is derived therefore that, for a good cell in which  $R_s \ll$ , and  $R_p \gg$ , the fill factor will be mainly determined by the carrier recombination mechanism through the parameter  $\beta$ .



**Figure 4.** Comparison between experimental  $j$  -  $V$  curves (lines) measured at different illumination intensities ranging within  $1 \cdot 10^{-3}$  sun, after correcting the series resistance contribution as  $V_F = V_{app} - jAR_s$ , and the calculated total current (dots) using Equation (9). Recombination resistance is determined at each illumination and  $\beta = 0.49$ .

In summary we propose a new strategy to obtain the central features of the  $j$  -  $V$  curve that is the principal aim of solar cell device modeling, and allows establishing its determining operating factors. Our approach uses the analysis of impedance spectroscopy that provides two essential pieces of information in a single measurement in working conditions: the measurement bypasses the influence of photocurrent and measures directly the (derivative of) recombination flux, and in addition, it determines the series resistance and allows removing the distortion of the voltage scale. Once internal band bending is compensated by sufficient applied voltage, a collapse of recombination resistance and chemical capacitance reveals a unique function with respect to internal voltage that allows us to reconstruct current-voltage characteristics in any desired set of conditions. Recombination current then appears as the unique mechanism which is essential to understand the solar cell  $j$  -  $V$  shape.

### Supporting Information

Supporting Information is available online from the Wiley Online Library or from the author.

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