

SCIENTIFIC REPORTS



OPEN

Fill factor in organic solar cells can exceed the Shockley-Queisser limit

Vasily A. Trukhanov, Vladimir V. Bruevich & Dmitry Yu. Paraschuk

Received: 08 December 2014

Accepted: 21 May 2015

Published: 22 June 2015

The ultimate efficiency of organic solar cells (OSC) is under active debate. The solar cell efficiency is calculated from the current-voltage characteristic as a product of the open-circuit voltage (V_{OC}), short-circuit current (J_{SC}), and the fill factor (FF). While the factors limiting V_{OC} and J_{SC} for OSC were extensively studied, the ultimate FF for OSC is scarcely explored. Using numerical drift-diffusion modeling, we have found that the FF in OSC can exceed the Shockley-Queisser limit (SQL) established for inorganic p - n junction solar cells. Comparing charge generation and recombination in organic donor-acceptor bilayer heterojunction and inorganic p - n junction, we show that such distinctive properties of OSC as interface charge generation and heterojunction facilitate high FF , but the necessary condition for FF exceeding the SQL in OSC is field-dependence of charge recombination at the donor-acceptor interface. These findings can serve as a guideline for further improvement of OSC.

The efficiency of organic solar cells (OSC) has shown an impressive growth for the recent years¹ and their ultimate efficiency is under intense discussion^{2–6}, with the Shockley-Queisser (SQ) model proposed for inorganic solar cells (ISC) being a reference point⁷. The photoactive layer of OSC is based on type-II heterojunction formed by two organic semiconductors with different electron affinities and ionization potentials, one of them is an electron donor, and the other is an electron acceptor⁸. The maximal achieved efficiencies are comparable for two different architectures of heterojunction: over 10% for the bulk one⁹ and 8.4% for the planar one¹⁰. The heterojunction is needed for dissociation of excitons that are generated upon light absorption in organic semiconductors. Exciton dissociation into free charges needs an extra energy so that the ultimate OSC efficiency is generally suggested to be lower than the Shockley-Queisser limit (SQL). This extra energy eventually reduces the solar cell voltage, specifically the open circuit voltage (V_{OC})^{2,11}. However the photocurrent, in particular the short-circuit current density (J_{SC}) for OSC can potentially exceed J_{SC} for a single p - n junction ISC due to the effect of singlet exciton fission, when one photon can produce two pairs of electrons and holes¹². The cell efficiency also determined by the shape of its current-voltage characteristic, and this shape can be characterized by the fill factor (FF) that is the ratio of the maximum output power to the product of short-circuit current and V_{OC} . As a result, the cell efficiency is proportional to the product of V_{OC} , J_{SC} , and FF . The SQ model establishes the theoretical limit for FF as a function of V_{OC} ^{7,13}. For OSC the limiting factors for J_{SC} and V_{OC} were extensively studied^{14–18}, but the ultimate FF for organic solar cells has been discussed only in a few works. The FF is assumed to be lower than that for ISC because of increased charge recombination¹⁹.

As FF is one of the key parameters determining the solar cell efficiency, in this Report we address the issue of the ultimate FF in OSC. We use numerical drift-diffusion modeling, which is a well-established approach in OSC study^{20–23}. Using the model for bilayer organic solar cell described in our previous work²⁴, we show that the FF in planar heterojunction OSC can exceed the SQL and substantiate this result by contrasting charge generation and recombination in organic heterojunction and p - n junction solar cells. Our approach is following: we confront drift-diffusion models for organic planar heterojunction and inorganic p - n junction (homojunction). The homojunction model presents an ideal inorganic solar cell with bulk generation of charges and their radiative recombination as the only loss of them. The most essential differences between these models are the junction type (homo/heterojunction), the charge generation-recombination spatial distribution (bulk/interface), and the recombination dependence on

Faculty of Physics and International Laser Center, M.V. Lomonosov Moscow State University, Moscow, 119991, Russia. Correspondence and requests for materials should be addressed to D.Y.P. (email: paraschuk@gmail.com)

Process/parameter	Organic solar cell planar heterojunction	Inorganic solar cell <i>p-n</i> junction
Generation of free charges	interface	bulk
Junction type	heterojunction	homojunction
Interface recombination	field-dependent	none
Bulk recombination	Langevin	radiative, $\alpha_{rad} = 3 \times 10^{-18} \text{ m}^3/\text{s}$
Band gap, E_g	1.85/2.1 eV	1.12 eV
Electron (hole) mobilities, μ_n (μ_p)	10^{-10} (10^{-7})/ 10^{-7} (10^{-10}) $\text{m}^2/(\text{V s})$	0.12 (0.03) $\text{m}^2/(\text{V s})$
Dielectric constant, ϵ	3/4	12
Doping level, N_d	10^{24} m^{-3}	10^{24} m^{-3}

Table 1. Input parameters of bilayer organic and inorganic *p-n* junction solar cells; for the planar heterojunction, the parameters of donor and acceptor layers are divided by slash marks.

the electric field (dependent/independent). The planar heterojunction model simulates a bilayer OSC^{20,24} in which generation of free charges occurs only at the heterojunction interface, and their recombination happens in the bulk according to the Langevin model²⁵ and at the interface via binding of electrons and holes into a charge-transfer state²⁶. In the ISC model, the *FF* exactly follows the SQ model, whereas, in the OSC model, it can be higher. To reveal the origin of high *FF*, we replace step by step the essential features of the OSC/ISC model by the corresponding features of the ISC/OSC model and observe how the *FF* varies relative to the SQL. For example, we replace the heterojunction by a homojunction in the OSC model and the homojunction by a heterojunction in the ISC model, then we replace the interface recombination by the bulk one, etc. Following this way, we have found that the field-dependent charge recombination is responsible for the *FF* exceeding the SQL: the higher the electric field at the heterojunction interface, the less the interface charge recombination, and the steeper the current-voltage characteristic at voltages near the V_{OC} .

Results

Modeling. In this section, we briefly describe the models of solar cells used in this work.

Current-voltage characteristics of ideal inorganic solar cell. The textbook model for ISC gives the following expression for their current density-voltage (*J-V*) characteristics:

$$J(V) = J_s \left[\exp\left(\frac{eV}{kT}\right) - 1 \right] - J_{ph} = J_{SC} \left[\frac{\exp(eV/kT) - 1}{\exp(eV_{OC}/kT) - 1} - 1 \right] \quad (1)$$

where J_s and J_{ph} are the saturation current and photocurrent densities, which can be uniquely expressed via the J_{SC} and V_{OC} ; e is the electron charge, k is the Boltzmann constant, T is the cell temperature. Equation (1) corresponds to an ideal solar cell with the zero series and infinite shunt resistances and with unity diode ideality factor.

Model of bilayer organic solar cell. We use a numerical model recently developed for bilayer organic solar cells²⁴ that accounts for generation, recombination, drift and diffusion of charge carriers, doping, and space charge effects in the active layers. Briefly, generation and recombination of free charges in OSC model occur via bound electron-hole (e/h) pairs at the donor-acceptor interface (charge transfer states) and depend on the interface electric field. In the bulk of the layers, the charges recombine according to the Langevin model. The input parameters of the model are the charge mobilities, band gap, layer thickness, doping level, and dielectric constant for each layer. As a reference, we use the input parameters for the most studied donor-acceptor material pair, poly-3-hexylthiophene and phenyl- C_{61} -butyric acid methyl ester (P3HT/PCBM), which are given in Table 1. In addition, the active layers are equally doped by majority carriers (donor is *p*-doped, acceptor is *n*-doped) with concentration $N_d = 10^{24} \text{ m}^{-3}$, and the rate of bound e/h-pairs dissociation at zero field $k_{diss}(0)$ is set 100 times higher than the monomolecular recombination rate of bound e/h-pairs k . As a result, the modeled OSC have very high *FF*.

*Model of inorganic *p-n* junction solar cell.* To reveal the origin of the high *FF*, we compare generation, transport, and recombination of charges in the bilayer OSC and *p-n* junction ISC. For this purpose, we developed a drift-diffusion *p-n* junction model for ISC similar to our model for bilayer OSC²⁴. The

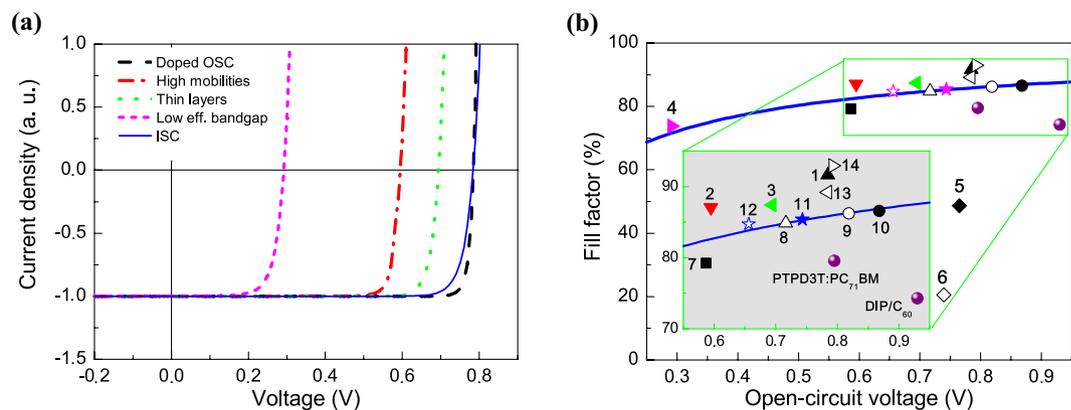


Figure 1. J - V characteristics and FF for high FF solar cells. (a) J - V characteristics for doped (the doping level is 10^{24} m^{-3} , black dashed curve), high-mobility (mobilities of majority carriers $\mu_n = \mu_p = 10^{-5} \text{ m}^2/(\text{V s})$, red dash-dotted curve), thin (donor and acceptor layers thickness 30 nm instead of 50 nm for other OSC, green dotted curve), low-effective-bandgap OSC (acceptor LUMO and donor HOMO were symmetrically shifted so that their difference was lowered from 1.05 eV to 0.6 eV, magenta short-dashed curve) and for ideal inorganic p - n junction solar cell (blue solid curve). Other input parameters are given in Table 1 and are the same as for bilayer OSC, modeled in our previous work²⁴. J - V characteristics for inorganic p - n junction solar cell (blue solid line) is plotted according to equation (1) with the same J_{SC} and V_{OC} as in the doped OSC, the temperature T is 300 K. (b) Shockley-Queisser limit for FF vs V_{OC} (solid line)^{7,13} and calculated FF s for various OSCs (points 1–14). Points (1–4) correspond to high- FF OSCs, their J - V curves are presented in Fig. 1a, other points (5–14) are our results which are described in the text: modeled OSC with bulk charge generation for different generation regions $\Delta x = 1 \text{ nm}$ and 10 nm (points 5 and 6 correspondingly), OSC with homojunction (point 7), OSC with constant interface recombination for different constant bound e/h -pair dissociation rates $k_{diss} = k_{diss}(0)$, $k_{diss}(E_{BI})$ and $k_{diss}(2E_{BI})$ (points 8, 9 and 10 correspondingly), ISC (point 11) and ISC with interface field dependent charge recombination similar to OSC (point 12), OSC with linear (point 13) and exponential-square-root (point 14) dependences of bound e/h -pair dissociation rate $k_{diss}(E_i)$. The highest experimental FF for OSC (PTPD3T:PCBM polymer bulk heterojunction cell²⁷ and DIP/C₆₀ low-molecular bilayer solar cell²⁸) are shown by spheres. The descriptions of each point are also given in Table 2.

details of the p - n junction model are given in Methods. The main difference between these models is that the generation of free charge carriers occurs in the bulk, i.e. in the whole volume of the active layer, and there is the only recombination channel via bulk bimolecular radiative recombination. As the input parameters, we use those typical to silicon p - n junction solar cells. Table 1 compares the features of OSC and ISC models.

Organic solar cells with FF exceeding the Shockley-Queisser limit. The bilayer OSC model gives J - V characteristics with FF exceeding the SQL for a number of the input parameters sets. Figure 1a illustrates such four J - V characteristics (broken lines) for a doped, high-mobility, thin, and low-effective-bandgap OSC, which are described in details in the figure caption and in Table 2. The last three OSC are undoped. For comparison, p - n junction J - V curve calculated according to equation (1) (solid line) is plotted in Fig. 1a with the same J_{SC} and V_{OC} as for the doped OSC. As the ultimate FF of an inorganic p - n junction solar cell is a function of V_{OC} and does not depend on J_{SC} ^{7,13}, one can use current-normalized J - V curves to compare the maximum possible FF in the OSC and ISC. In all the figures, the current density is normalized to the product eG_s , where G_s is the interface generation rate of bound electron-hole pairs.

Figure 1b displays FF vs V_{OC} for various solar cells. The FF s of the doped (point 1), high-mobility (point 2), thin (point 3) and low-effective-bandgap OSC (point 4) are higher than that of the ideal inorganic p - n junction cell (solid line). The lower V_{OC} in the high-mobility OSC is due to the higher Langevin recombination rate within the layers. Although doping is not the necessary condition for FF exceeding the SQL, the most pronounced exceeding of the SQL by 7% is observed for the doped OSC ($FF = 91.7\%$). Because of this, further we study the nature of high FF using mainly the doped bilayer OSC. Moreover, the latter one can have higher performance than the undoped one: if the layers are doped by majority carriers (i.e., the donor layer is p -doped, and the acceptor layer is n -doped), all the photovoltaic parameters (J_{SC} , V_{OC} , FF and efficiency) can be increased with doping²⁴. The reason is in a significant increase of the electric field at the donor-acceptor interface due to space charge caused by doping²⁴. The other points in Fig. 1b (5–14) refer to our numerical experiments described below in the next sections.

Point number	Cell type	Description	V_{OC} (V)	FF (%)	SQL for FF (%)
1	Organic	Non-modified (doped)	0.785	91.6	85.8
2	Organic	$N_d = 0, \mu_n = \mu_p = 10^{-5} \text{ m}^2/\text{V s}$	0.595	87.1	82.6
3	Organic	$N_d = 0$, thin active layers $L_{1,2} = 30 \text{ nm}$	0.694	87.4	84.5
4	Organic	$N_d = 0$, LUMO(A)-HOMO(D) = 0,6 V	0.292	73.7	71.6
5	Organic	Homojunction	0.587	79.3	82.4
6	Organic	Bulk generation, $\Delta x = 1 \text{ nm}$	0.765	48.7	85.6
7	Organic	Bulk generation, $\Delta x = 10 \text{ nm}$	0.739	20.5	85.2
8	Organic	$k_{diss}(E) = k_{diss}(0) = const$	0.716	84.8	84.8
9	Organic	$k_{diss}(E) = k_{diss}(E_{BI}) = const$	0.819	86.2	86.3
10	Organic	$k_{diss}(E) = k_{diss}(2E_{BI}) = const$	0.868	86.6	86.9
11	Inorganic	Non-modified	0.744	85.3	85.3
12	Inorganic	Field-dependent interface recombination	0.656	84.7	83.8
13	Organic	Linear $k_{diss}(E)$	0.784	89.2	85.8
14	Organic	Exponential square-root $k_{diss}(E)$	0.793	92.9	85.9
–	Organic	Bulk heterojunction PTPD3T:PCBM ²⁷	0.795	79.6	86.0
–	Organic	Planar heterojunction DIP/C ₆₀ ²⁸	0.930	74.3	87.5

Table 2. Open-circuit voltages (V_{OC}) and fill factors (FF) of modeled (rows 1–14) and experimental (the last two rows)^{27,28} solar cells. The last column shows the FF according to the Shockley-Queisser limit (SQL). All the data are also presented in Fig. 1b.

Table 2 summarizes all the data presented in Fig. 1b and compares the modeled FFs with the SQL for FF. The best experimental values for FF reported for bulk²⁷ and planar²⁸ heterojunction OSC are presented in Fig. 1b by spheres.

In the next sections, following our approach mentioned above, we study the origin of high FF in OSC.

Generation of free charges: bulk vs interface. First, we investigated how substitution of interface generation of free charges in the high-FF OSC for their bulk generation affects its J - V characteristics (*interface*→*bulk charge generation in OSC*). We replaced the interface generation of free charges in the OSC with bulk generation in a part of the active layer near the interface, Δx (see the details in SI). Figure 2 compares the results for OSC with the interface and bulk generation of free charges: panel (a) demonstrates J - V characteristics, panel (b) shows the band diagrams, and panel (c) displays the recombination rate of free charges. As Fig. 2a shows, the shapes of the J - V curves for the bulk charge generation are significantly different from that for the interfacial generation. The substitution of the interface generation for the bulk one leads to a strong drop of FF below the SQL (see Fig. 1b, points 5 and 6). We suggest that FF is low due to high recombination (Fig. 2c) of charge carriers within and near their generation region (Fig. 2b), this is discussed in details in SI.

In a symmetric numerical experiment (*bulk*→*interface charge generation in ISC*), we take the inorganic p - n junction solar cell and change charge generation in it from bulk to surface one at the interface between p and n -layers. As a result, the FF does not increase and remains to be equal to the SQL; moreover, the J - V characteristic does not change. This is expected, as the only loss mechanism in the inorganic solar cell is radiative recombination that is the same in the cells with bulk and interface charge generation. Thus, we conclude that the type of free charge generation (interface or bulk) is not a key parameter that can result in a FF exceeding the SQL.

Junction type: homojunction vs heterojunction. Consider whether the junction type, i.e., hetero- or homojunction, could be responsible for FF exceeding the SQL. We start from the high-FF OSC and substitute in it the heterojunction for a homojunction (*heterojunction*→*homojunction in OSC*). We shift the donor lowest unoccupied molecular orbital (LUMO) and acceptor highest occupied molecular orbital (HOMO) energies of the OSC so that the heterojunction transformed into a hypothetical homojunction with a band gap of 1.05 eV and an electron affinity of 4.0 eV, with the other parameters unchanged. We will refer the donor and acceptor layers in the homojunction cell as p -layer and n -layer, respectively. Figure 3 compares the key characteristics of the hetero- and homojunction solar cells: J - V characteristics (a), band diagrams (b), concentrations of free electrons and holes (c) and recombination rates (d). The transformation of hetero- to homojunction decreases both V_{OC} and FF. The FF of the homojunction cell is given in Fig. 1b as a square (point 7), and it is significantly lower than the SQL. The reason for this is similar to the previous case (*interface*→*bulk charge generation in OSC*) — increase of the charge

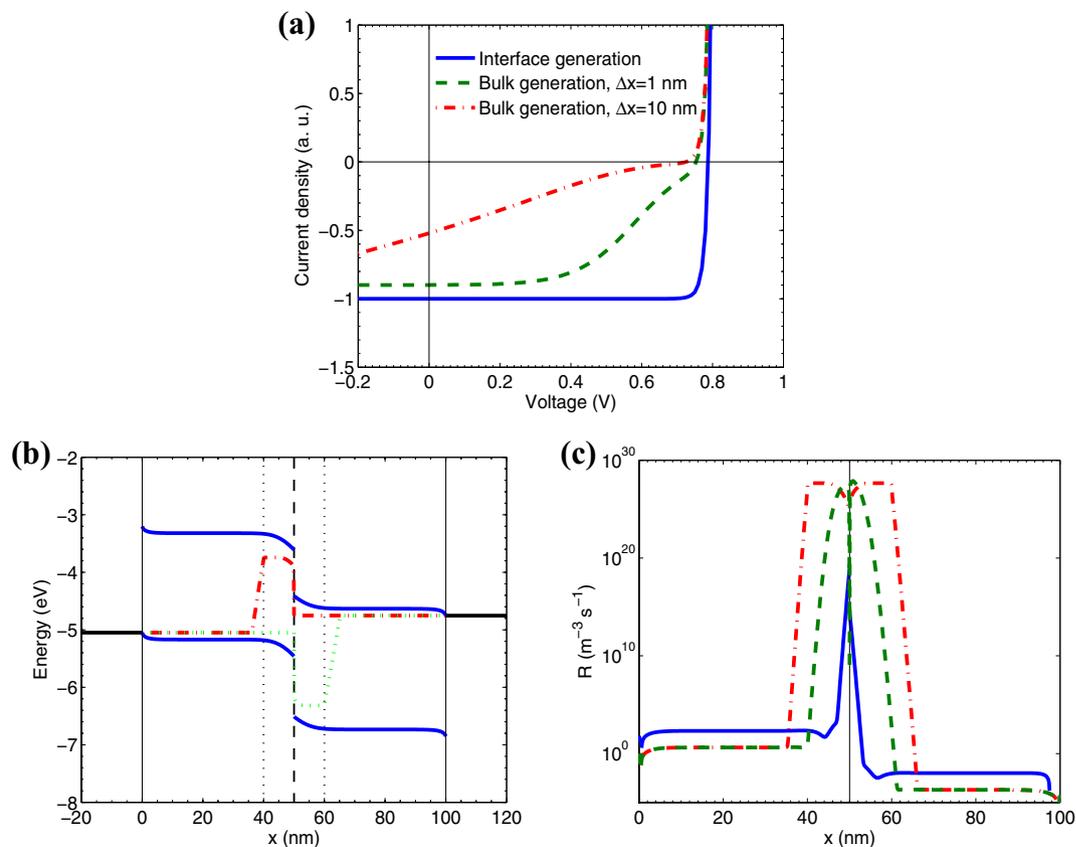


Figure 2. Bulk vs interface generation of free charges in OSC. (a) J - V characteristics for a OSC with interface (solid line) and bulk generation of free charges for two different widths of the generation region $\Delta x = 1$ nm (dashed line) and $\Delta x = 10$ nm (dash-dotted line). (b) Band diagram for the cell with bulk generation ($\Delta x = 10$ nm). The vertical black solid lines denote the active layer-electrode interfaces, the vertical dashed line shows the interlayer interface, the solid lines are lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) energies, the dash-dotted/dotted line is the electron/hole quasi-Fermi level. The Fermi levels of electrodes are denoted by horizontal black solid lines. The vertical black dot lines denote the boundaries of the generation region. (c) Recombination rate of free charges $R = \alpha(np - n_{int}^2)$ in the bulk of the active layer; α is the Langevin recombination constant²⁵, and n_{int} is the intrinsic concentration of charge carriers²⁴. Plots (b) and (c) are given for the maximum power point.

recombination rate in the bulk of the active layer (as shown in Fig. 3d) due to increased concentrations of minority charge carriers, i.e. electrons in p -layer and holes in n -layer (Fig. 3c). High concentrations of minority carriers appear due to lowered energy barriers at the interface in the homojunction OSC (Fig. 3b). The other details are described in SI.

In the corresponding symmetric numerical experiment, we transform the homojunction to a heterojunction (*homojunction* \rightarrow *heterojunction* in ISC) by shifting the energy levels in the p - n junction solar cell model: the conducting band edge E_c of the p -layer is shifted up, and the valence band edge E_v is shifted down. As in the above numerical experiment related to the free charge generation type, the J - V characteristics are unchanged, and the FF remains within the SQL. Therefore, the junction type is not a key parameter responsible for FF exceeding the SQL.

Note that from the comparison of homo- and heterojunction in OSC and ISC one can show that the band gap also is not a parameter that is responsible for FF exceeding the SQL.

Using the same approach, we have tested the effect of charge mobility and dielectric constants on FF . In the OSC/ISC, we have substituted the charge mobilities (dielectric constants) for those of the ISC/OSC (Table 1). As a result, the FF decreases below the SQL in the OSC, but it remains within the SQL in the ISC. Therefore, neither the charge mobilities nor the dielectric constants are responsible for FF exceeding the SQL.

Field-dependent charge recombination. In OSC, light-induced charge generation is considered as a multistep process. Excitons formed after photon absorption diffuse to the donor-acceptor interface and dissociate there into bound e/h -pairs with the electrons in the acceptor phase and the holes in the donor

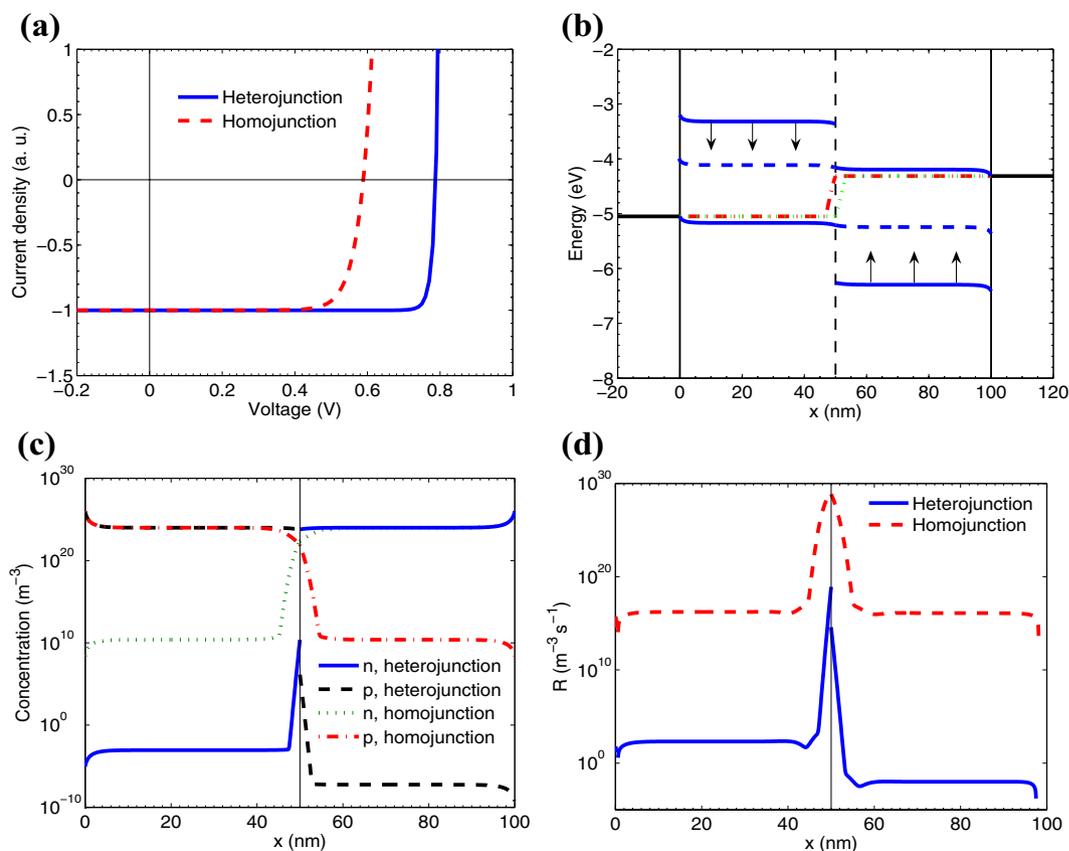


Figure 3. Hetero- vs homojunction. (a) J - V characteristics for the organic heterojunction solar cell (solid line) and for the corresponding hypothetical homojunction cell (dashed line). (b) Band diagrams for the heterojunction (solid lines) and homojunction (dashed lines) cells, respectively. Vertical arrows indicate the offset of the energy levels in the transition from hetero- to homojunction. Distribution of free electrons (n) and holes (p) concentrations (c) and the recombination rate $R = \alpha(np - n_{int}^2)$ (d) in the active layer for the hetero- and homojunction. The data in panels (b–d) are calculated in the maximum power point. For other details see the caption to Fig. 2.

phase. Then these bound e/h -pairs can either recombine monomolecularly with the rate k_f or dissociate into free charge carriers with the rate k_{diss} , which increases with the electric field at the interface E_i . The free charges can move to the electrodes or can diffuse back to the interface and form bound e/h -pairs. If $k_{diss}(E_i) \gg k_f$, the free charge generation rate is proportional to $k_{diss}(E_i)/(k_f + k_{diss}(E_i)) \sim 1$ and hence weakly depends on E_i . However, the recombination rate of free charges R depends on the E_i as $R \sim k_f/k_{diss}(E_i)$, so it decreases with increasing the E_i , which is almost proportional to the difference between the applied voltage V and the built-in voltage V_{BI} . Therefore, the photocurrent J_{ph} (see eq. (1)) in OSC increases as the V decreases from the V_{OC} down to zero (short circuit condition). This is in contrast with ISC, where the J_{ph} does not depend on the voltage as photon absorption directly generates free charges and recombination is independent of the electric field. Accordingly, in OSC, the J - V curve will be steeper and the FF can be higher than that given by equation (1). Consequently, we suggest that the key reason for unexpectedly high FF in OSC is field-dependent charge recombination at the donor-acceptor interface.

To substantiate our suggestion, we used the OSC model and made there the interface recombination field-independent (with other parameters unchanged): the bound e/h -pair dissociation rate $k_{diss}(E_i)$ was replaced by the constants $k_{diss}(0)$, $k_{diss}(E_{BI})$ or $k_{diss}(2E_{BI}) = const$, where $E_{BI} = V_{BI}/(L_1 + L_2)$ are the donor and acceptor layer thicknesses, correspondingly. As a result, the FF decreased to the SQL as shown in Fig. 1b by points 8–10. Figure 4a compares J - V characteristics of the OSC with field-dependent and field-independent recombination for the three different constant rates k_{diss} . The J - V curves for the field-independent k_{diss} are less steep than that for the field-dependent k_{diss} . As a result, the FF for the constant k_{diss} is equal to or just below the SQL. However, for the field-dependent k_{diss} , the FF is 91.7%, which exceeds by 7% the SQL at $V_{OC} = 0.785$ V. In the corresponding symmetric experiment, we took the ISC model and introduced there the field-dependent interface recombination from the OSC model with the other parameters unchanged. Figure 4b compares J - V characteristics for the ISC model with and without the field-dependent interface recombination. For the former, the V_{OC} significantly drops, but the FF slightly exceeds the SQL as shown in Fig. 1b by point 12. Without the interface recombination,

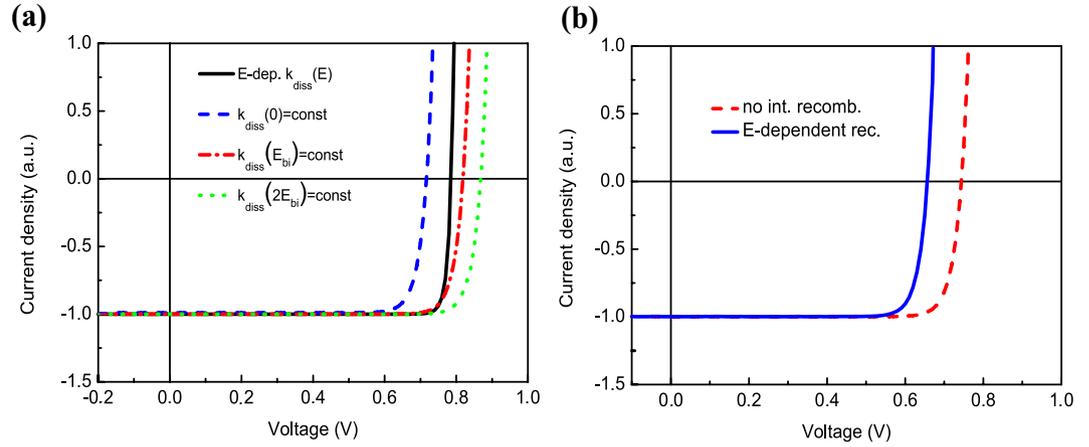


Figure 4. Field-dependent vs field-independent interface recombination. J - V characteristics for the OSC (a) and ISC (b) models with field-dependent (solid curves) and field-independent (broken curves) recombination rates at the interface between the donor/acceptor and p/n layers, respectively.

the FF is equal to the SQL (85.3% at $V_{OC}=0.744$ V, point 11 in Fig. 1b) and, with the field-dependent recombination, the FF reaches 84.7% exceeding by 1% the SQL at $V_{OC}=0.656$ V. Therefore, using both the OSC and ISC models, we have found that the interface field-dependent recombination can result in FF exceeding the SQL.

The form of $k_{diss}(E_i)$ dependence. The field dependence of the interface recombination rate is determined by the bound e/h -pair dissociation rate k_{diss} , which depends on the E_i . The above results were obtained for the specific dependence $k_{diss}(E_i)$ from Ref.²⁰ describing electron thermoemission from a Coulombic potential well under the electric field E_i :

$$k_{diss}(E_i) = k_{diss}(0) \frac{2}{M} \left[e^M \left(1 - \frac{1}{M} \right) + \frac{1}{M} \right], \text{ where } M = \frac{e}{kT} \sqrt{\frac{e|E_i|}{\pi\epsilon\epsilon_0}} \quad (2)$$

The parameter M is the ratio of the energy, by which the thermoemission barrier is lowered due to the electric field, to the thermal energy.

Obviously, this function, $k_{diss}(E_i)$, is not universal and depends on the model. To reveal how the FF in OSC is sensitive to the field dependence of $k_{diss}(E_i)$, we modeled J - V characteristics for smoother and steeper field dependences than that given by equation (2). As a smoother $k_{diss}(E_i)$, we used the linear function of E_i

$$k_{diss}(E_i) = k_{diss}(0) (1 + M^2) \quad (3)$$

As a steeper $k_{diss}(E_i)$, we used the exponential-square-root function of E_i

$$k_{diss}(E_i) = k_{diss}(0) \exp(M) \quad (4)$$

Figure 5 shows J - V characteristics for OSC with these three different dependences $k_{diss}(E_i)$ and for the constant $k_{diss}(E_i)=k_{diss}(0)$. The corresponding FF s are plotted in Fig. 1b by triangles (points 1, 8, 13 and 14). For the cell with the linear $k_{diss}(E_i)$ (Eq. (3)) the FF is 89.2% that is higher by 4% than the SQL at $V_{OC}=0.784$ V. For the cell with the exponential-square-root $k_{diss}(E_i)$ (Eq. (4)) the FF is 92.9% that is higher by 8% than the SQL limit at $V_{OC}=0.793$ V. Therefore, our calculations show that for OSC with FF exceeding the SQL the E_i -dependence of $k_{diss}(E_i)$ must be an increasing function, and the form of this dependence is not essential. Nevertheless, the steeper the function $k_{diss}(E_i)$, the steeper the corresponding J - V curve near V_{OC} , and the higher FF can be reached.

Discussion

Using numerical drift-diffusion modeling, we have shown that the FF in a bilayer OSC can be higher than the SQL for FF established for ISC. The OSC model with various numerical parameters (charge mobilities, band gaps, doping level) can result in J - V curves with the FF higher than the SQL for a given V_{OC} (see Fig. 1b). Confronting the drift-diffusion models of OSC (planar heterojunction) and ISC (p - n junction), we have identified the reason responsible for high FF in OSC. Such OSC properties as heterojunction and interface charge generation facilitate a high FF in OSC as compared to the homojunction and bulk charge generation in ISC because of lower charge recombination; however, they cannot provide the FF beyond the SQL. Such a high FF is due to interface charge recombination that

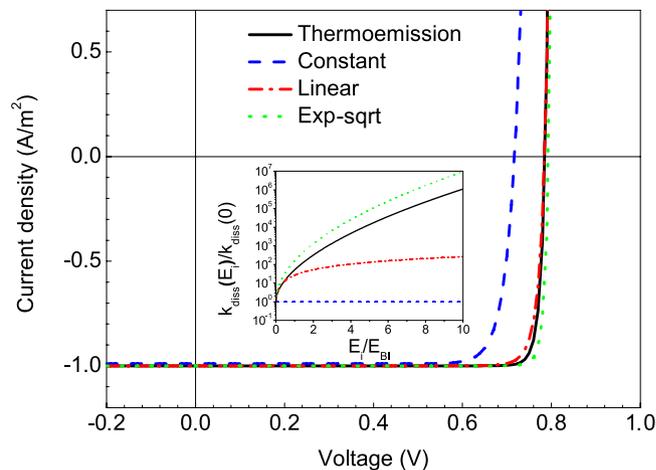


Figure 5. J - V characteristics of OSC with different forms of bound e/h -pair dissociation rate field dependences $k_{diss}(E_i)$. Inset displays the $k_{diss}(E_i)$ dependences described by equations (2–4).

must decrease with increasing the electric field at the heterojunction interface. Indeed, on the one hand, the FF drops lower than the SQL if we use an OSC model similar to a p - n junction cell by making the recombination of free charges field-independent. On the other hand, the FF increases above the SQL if we introduce field-dependent interface recombination in the p - n homojunction model. Thereby we claim that the FF in OSC can exceed the theoretical limit for inorganic p - n junction solar cells, and this is due to field-dependent recombination of free charges at the donor-acceptor interface. The rate of such field-dependent recombination should be much lower than the free charge generation rate, in other words the dissociation rate of bound e/h -pairs $k_{diss}(0)$ should be much higher than monomolecular recombination rate of bound e/h -pairs k_r . If this condition is not satisfied, the recombination will decrease the FF in organic solar cells¹⁹. To summarize, field-dependent recombination is the necessary but not sufficient condition for FF exceeding SQL.

Note that the model used does not account for light absorption, exciton diffusion, and formation of bound electron-hole pairs at the donor-acceptor interface. All these processes determine the generation rate of bound electron-hole pairs G_S , which is an input parameter in the model, and we put it constant in our numerical studies; moreover, we normalized all the J - V characteristics to G_S . In addition, when we changed the heterojunction for the homojunction, the donor and acceptor band gaps narrowed, and the donor LUMO – acceptor LUMO energy difference reduced. The former increases the number of absorbed photons, and the latter decreases the driving force that splits excitons. Evidently, this will influence G_S and the device efficiency. However, we put G_S constant in our numerical studies as our aim was to show how the differences in free charge generation, recombination, and transport in organic and inorganic solar cells can lead to an unexpectedly high FF in the former.

In this study, we assumed the presence of a sharp and flat interface between the donor and acceptor layers. Note that a two layer organic structure, e.g., P3HT/PCBM, is susceptible to intermixing²⁹. However, intermixing at the donor-acceptor interface could be suppressed by using cross-linked donor or/and acceptor layers^{30,31}. Essentially, the results obtained in our work for bilayer OSC can be naturally extrapolated to ordered bulk heterojunction OSC, i.e., those with large-area non-planar heterojunction interface where the donor (acceptor) phase is in contact with anode (cathode) and not with cathode (anode).

The maximal experimental values of FF achieved in OSC are high (about 80%) but still lower than the SQL (the spheres in Fig. 1b and the last two rows in Table 2). This is because in real OSC it is rather difficult to achieve the conditions, which can provide the ultimate FF . The model used does not take into account a number of effects that can limit the FF in real devices such as disorder of energy states in organic semiconductors, defect- and contact-mediated recombination, etc. However, such effects can be incorporated in the model and at least in principle can be strongly suppressed. Importantly, the ultimate efficiency of OSC is obviously below the SQ efficiency limit for a single-junction cell because of an extra energy loss for exciton dissociation. This energy loss generally decreases the V_{OC} ; however, the FF is already not limited by the SQ model. As a result, the J - V curves can be steeper than that in the SQ model but with lower V_{OC} .

In conclusion, drift-diffusion modeling shows that the FF in OSC can exceed the SQL for FF established for p - n junction ISC. We conclude that the field-dependent recombination of free charges at the donor-acceptor interface is responsible for the FF beyond the SQL. This recombination rate must drop with increasing the electric field at the donor-acceptor interface, and the dissociation rate of bound e/h -pairs should be much higher than the rate of their monomolecular recombination; the form of the recombination rate dependence on the electric field is not crucial, but the steeper it, the higher FF can be

reached. On the one hand, field dependence of the charge recombination rate is the necessary condition for FF exceeding SQL but it is not sufficient. On the other hand, heterojunction and interface generation in OSC facilitate reaching high FF but are not necessary conditions for FF exceeding SQL . Our findings highlight an unnoticed advantage of OSC and can be used in their further improvement.

Methods

Drift-diffusion p - n junction model. The p - n junction model for ISC is based on the same equations used in the bilayer OSC model²⁴; Poisson equation, current-continuity equations for electrons and holes, and drift-diffusion equations for electron and hole currents. The current-continuity equations are:

$$\begin{cases} \frac{1}{e} \frac{dj_{n,i}}{dx} = G - \alpha_{rad}(n_i p_i - n_{int}^2) \\ -\frac{1}{e} \frac{dj_{p,i}}{dx} = G - \alpha_{rad}(n_i p_i - n_{int}^2) \end{cases} \quad (5)$$

where $j_{n,i}$ and $j_{p,i}$ are current densities of electrons and holes, G is the charge generation rate, α_{rad} is the bimolecular radiation recombination rate, n_i and p_i are the electron and hole concentrations, index $i = 1$ and 2 corresponds to the p and n -layer respectively.

As the surface generation and recombination at the interface between p - and n -type layers are absent, the matching conditions for the electron and hole current densities are:

$$\begin{cases} j_{n,1}|_{x=L_1} = j_{n,2}|_{x=L_1} \\ j_{p,1}|_{x=L_1} = j_{p,2}|_{x=L_1} \end{cases} \quad (6)$$

where L_1 and L_2 are the p - and n -layer thicknesses, correspondingly. In the p - n junction model, the numerical value of bulk generation rate G is taken such that the total quantity of absorbed photons equals to the quantity of photogenerated bound electron-hole pairs at the donor-acceptor interface in the OSC model:

$$G \cdot (L_1 + L_2) = G_S. \quad (7)$$

Another difference between the bilayer OSC and p - n junction models is in the boundary conditions. In the latter, we suggest ideal contacts, i.e., membranes that are permeable for the majority charge carriers and block the minority charge carriers³². Therefore, the current densities of the latter at the contacts with electrodes are equal to zero:

$$\begin{cases} j_{n,1}|_{x=0} = 0 \\ j_{p,2}|_{x=L_1+L_2} = 0. \end{cases} \quad (8)$$

References

- Green, M. A., Emery, K., Hishikawa, Y., Warta, W. & Dunlop, E. D. Solar cell efficiency tables (version 43). *Progress in Photovoltaics: Research and Applications* **22**, 1–9 (2014).
- Scharber, M. C. *et al.* Design rules for donors in bulk-heterojunction solar cells - Towards 10% energy-conversion efficiency. *Adv. Mater.* **18**, 789–794 (2006).
- Godovsky, D. Modeling the ultimate efficiency of polymer solar cell using Marcus theory of electron transfer. *Org. Electron.* **12**, 190–194 (2011).
- Giebink, N. C., Wiederrecht, G. P., Wasielewski, M. R. & Forrest, S. R. Thermodynamic efficiency limit of excitonic solar cells. *Phys. Rev. B* **83**, 195326 (2011).
- Koster, L. J. A., Shaheen, S. E. & Hummelen, J. C. Pathways to a New Efficiency Regime for Organic Solar Cells. *Adv. Energy Mater.* **2**, 1246–1253 (2012).
- Kirchartz, T., Taretto, K. & Rau, U. Efficiency Limits of Organic Bulk Heterojunction Solar Cells. *J. Phys. Chem. C* **113**, 17958–17966 (2009).
- Shockley, W. & Queisser, H. J. Detailed Balance Limit of Efficiency of p - n Junction Solar Cells. *J. Appl. Phys.* **32**, 510–519 (1961).
- Tang, C. W. 2-Layer Organic Photovoltaic Cell. *Appl. Phys. Lett.* **48**, 183–185 (1986).
- Liu, Y. *et al.* Aggregation and morphology control enables multiple cases of high-efficiency polymer solar cells. *Nat. Commun.* **5**, 5293 (2014).
- Cnops, K. *et al.* 8.4% efficient fullerene-free organic solar cells exploiting long-range exciton energy transfer. *Nat. Commun.* **5**, 3406 (2014).
- Brabec, C. J. Origin of the open circuit voltage of plastic solar cells. *Adv. Funct. Mater.* **11**, 374–380 (2001).
- Congreve, D. N. *et al.* External Quantum Efficiency Above 100% in a Singlet-Exciton-Fission-Based Organic Photovoltaic Cell. *Science* **340**, 334–337 (2013).
- Green, M. A. General Solar-Cell Curve Factors Including Effects of Ideality Factor, Temperature and Series Resistance. *Solid State Electron.* **20**, 265–266 (1977).

14. Janssen, R. A. J. & Nelson, J. Factors Limiting Device Efficiency in Organic Photovoltaics. *Adv. Mater.* **25**, 1847–1858 (2013).
15. Brabec, C. J., Sariciftci, N. S. & Hummelen, J. C. Plastic solar cells. *Adv. Funct. Mater.* **11**, 15–26 (2001).
16. Mihailetschi, V. D., Blom, P. W. M., Hummelen, J. C. & Rispen, M. T. Cathode dependence of the open-circuit voltage of polymer:fullerene bulk heterojunction solar cells. *J. Appl. Phys.* **94**, 6849–6854 (2003).
17. Koster, L. J. A., Mihailetschi, V. D., Ramaker, R. & Blom, P. W. M. Light intensity dependence of open-circuit voltage of polymer : fullerene solar cells. *Appl. Phys. Lett.* **86**, 123509 (2005).
18. Qi, B. & Wang, J. Open-circuit voltage in organic solar cells. *J. Mater. Chem.* **22**, 24315–24325 (2012).
19. Dibb, G. F. A., Jamieson, F. C., Maurano, A., Nelson, J. & Durrant, J. R. Limits on the Fill Factor in Organic Photovoltaics: Distinguishing Nongeminate and Geminate Recombination Mechanisms. *J. Phys. Chem. Lett.* **4**, 803–808 (2013).
20. Barker, J. A., Ramsdale, C. M. & Greenham, N. C. Modeling the current-voltage characteristics of bilayer polymer photovoltaic devices. *Phys. Rev. B* **67**, 075205 (2003).
21. Koster, L. J. A., Smits, E. C. P., Mihailetschi, V. D. & Blom, P. W. M. Device model for the operation of polymer/fullerene bulk heterojunction solar cells. *Phys. Rev. B* **72**, 085205 (2005).
22. Deibel, C., Wagenpfahl, A. & Dyakonov, V. Influence of charge carrier mobility on the performance of organic solar cells. *Phys. Status Solidi-Rapid Res. Lett.* **2**, 175–177 (2008).
23. de Falco, C., Sacco, R. & Verri, M. Analytical and numerical study of photocurrent transients in organic polymer solar cells. *Computer Methods in Applied Mechanics and Engineering* **199**, 1722–1732 (2010).
24. Trukhanov, V. A., Bruevich, V. V. & Paraschuk, D. Y. Effect of doping on performance of organic solar cells. *Phys. Rev. B* **84**, 205318 (2011).
25. Langevin, P. The recombination and mobilities of ions in gases. *Ann. Chim. Phys.* **28**, 433–530 (1903).
26. Deibel, C., Strobel, T. & Dyakonov, V. Role of the Charge Transfer State in Organic Donor-Acceptor Solar Cells. *Adv. Mater.* **22**, 4097–4111 (2010).
27. Guo, X. G. *et al.* Polymer solar cells with enhanced fill factors. *Nat. Photonics* **7**, 825–833 (2013).
28. Wagner, J. *et al.* High Fill Factor and Open Circuit Voltage in Organic Photovoltaic Cells with Diindenoperylene as Donor Material. *Adv. Funct. Mater.* **20**, 4295–4303 (2010).
29. Treat, N. D. *et al.* Interdiffusion of PCBM and P3HT Reveals Miscibility in a Photovoltaically Active Blend. *Adv. Energy. Mater.* **1**, 82–89 (2011).
30. Kim, B. J., Miyamoto, Y., Ma, B. & Fréchet, J. M. J. Photocrosslinkable Polythiophenes for Efficient, Thermally Stable, Organic Photovoltaics. *Adv. Funct. Mater.* **19**, 2273–2281 (2009).
31. Hsieh, C.-H. *et al.* Highly Efficient and Stable Inverted Polymer Solar Cells Integrated with a Cross-Linked Fullerene Material as an Interlayer. *J. Am. Chem. Soc.* **132**, 4887–4893 (2010).
32. Würfel, P. *Physics of Solar Cells: From principles to New Concepts.* (Wiley, 2005).

Acknowledgments

The work is supported by Russian Foundation for Basic Research (grant 14-02-31823 mol_a) and M.V. Lomonosov Moscow State University Program of Development. The authors thank T. Markwart for fruitful discussions.

Author Contributions

V.A.T. carried out the numerical modeling, V.V.B. generated the approach, and D.Y.P. supervised the work. All authors discussed the results and wrote the manuscript.

Additional Information

Supplementary information accompanies this paper at <http://www.nature.com/srep>

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Trukhanov, V.A. *et al.* Fill factor in organic solar cells can exceed the Shockley-Queisser limit. *Sci. Rep.* **5**, 11478; doi: 10.1038/srep11478 (2015).



This work is licensed under a Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder to reproduce the material. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>