Combined influence of carrier mobility and dielectric constant on the performance of organic bulk heterojunction solar cells

M. L. Inche Ibrahim, Zubair Ahmad, Khaulah Sulaiman, and S. V. Muniandy

---

Articles you may be interested in

Balanced charge carrier mobilities in bulk heterojunction organic solar cells
Appl. Phys. Lett. **101**, 073302 (2012); 10.1063/1.4745602

Effects of aging on the mobility and lifetime of carriers in organic bulk heterojunction solar cells
J. Renewable Sustainable Energy **3**, 063111 (2011); 10.1063/1.3670411

Imbalanced charge mobility in oxygen treated polythiophene/fullerene based bulk heterojunction solar cells
Appl. Phys. Lett. **95**, 263305 (2009); 10.1063/1.3279135

Effects of semiconducting and metallic single-walled carbon nanotubes on performance of bulk heterojunction organic solar cells
Appl. Phys. Lett. **94**, 233309 (2009); 10.1063/1.3153514

Optimum charge carrier mobility in organic solar cells
Appl. Phys. Lett. **90**, 133504 (2007); 10.1063/1.2711534

Combined influence of carrier mobility and dielectric constant on the performance of organic bulk heterojunction solar cells

M. L. Inche Ibrahim,[a] Zubair Ahmad, Khaulah Sulaiman, and S. V. Muniandy
Department of Physics, University of Malaya, 50603 Kuala Lumpur, Malaysia

It has been shown that there is an optimum charge carrier mobility that leads to a peak in the efficiency for organic bulk heterojunction solar cells with mobility-dependent recombination rate. Hence, improving the mobility is considered as one of the ways to increase the efficiency. In this study, we investigate the combined influence of charge carrier mobility and dielectric constant on the performance of organic bulk heterojunction solar cells by performing drift-diffusion calculations. We find that a higher dielectric constant leads to a higher peak efficiency together with a lower optimum mobility. We also find that if the dielectric constant of the active material can be increased significantly (to around 8 or higher), it is then possible that the mobility of the active material need not to be improved in order to achieve the maximum efficiency. This study demonstrates the importance of knowing the interplay between the mobility and the dielectric constant with regard to the efficiency. © *2014 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License.* [http://dx.doi.org/10.1063/1.4881080]

I. INTRODUCTION

Organic bulk heterojunction (BHJ) solar cell is a promising candidate as a source of energy due to its low cost of fabrication compared to inorganic solar cells. However, their efficiencies are still significantly lower than the efficiencies of inorganic solar cells. This is generally attributed to poor material properties such as low charge carrier mobilities, low dielectric constants, and poor band offsets.[1] Hence, optimization of these properties is crucial in order to achieve a higher efficiency.

Drift-diffusion model has been extensively used and shown to be a powerful tool in modeling organic BHJ solar cells.[2] This general model can help us to describe experimental measurements, to study specific device models, as well as to predict the influences of various parameters on the performance of organic BHJ solar cells, thus guiding us to improve the efficiency.

The charge carrier mobility is an important factor that influences the efficiency and its effects has been extensively studied.[3–7] It has been shown that there is an optimum value of the mobility that leads to a peak efficiency.[3–6] Mobilities lower than the optimum value lead to lower efficiencies due to significant reductions in the dissociation rate of polaron pairs into free charge carriers,[3] together with less efficient charge extractions. Mobilities above the optimum value lead to decreases in the open circuit voltage and no significant increase in the dissociation rate of polaron pairs.[3] This leads to a lower voltage at the maximum power point, thus reducing the efficiency.[3] Tress *et al.*[4] showed that Langevin type recombination leads to an optimum mobility while mobility-independent recombination leads to no optimum value.

Another important factor that influences the performance is the dielectric constant of the active layer. Koster *et al.*[1] pointed out that increasing the dielectric constant is crucial in order to significantly increase the efficiency of organic solar cells. However, previous studies only concentrated on either

---

[a]lukman@um.edu.my

4, 057133-1

mobility or dielectric constant alone, while the combined effect of both parameters has been ignored. In order to maximize the efficiency, it is important to know if there is any interplay between the mobility and the dielectric constant with regard to the efficiency.

In this study, we investigate how the mobility and the dielectric constant jointly affect the performance of organic BHJ solar cells. The drift-diffusion model is used for simulations. We adopt the widely used models such as the Onsager-Braun model for polaron pair dissociation[8–10] and the Langevin recombination model, which have been shown to well describe the experimental data of organic solar cells. Based on the results, we show that it is important to know the combined influence of mobility and dielectric constant in order to improve the efficiency of organic BHJ solar cells.

II. MODEL

The drift diffusion model essentially solves the continuity and the Poisson equations using numerical schemes.[2, 11] The continuity equations are given by

$$\frac{dn(x)}{dt} = \frac{1}{q}\frac{dJ_{\mathrm{n}}(x)}{dx} - R(x) + G_{\mathrm{n}}(x), \tag{1a}$$

$$\frac{dp(x)}{dt} = -\frac{1}{q}\frac{dJ_{\mathrm{p}}(x)}{dx} - R(x) + G_{\mathrm{p}}(x), \tag{1b}$$

where n is the density of electrons, p is the density of holes, q is the elementary charge, J_{n} is the electron current density, J_{p} is the hole current density, G_{n} is the generation rate of electron density, and G_{p} is the generation rate of hole density. J_{n} and J_{p} consist of the drift and the diffusion current components.

The recombination rate follows the bimolecular Langevin recombination, which is given by

$$R(x) = \zeta\gamma n(x)p(x), \tag{2}$$

where $\gamma = \frac{(\mu_{\mathrm{n}}+\mu_{\mathrm{p}})q}{\varepsilon_0\varepsilon_{\mathrm{r}}}$, with μ_{n} is the electron mobility, μ_{p} is the hole mobility, ε_0 is the vacuum permittivity, and ε_{r} is the dielectric constant. The recombination pre-factor ζ is introduced in order to capture the effect of reduced Langevin recombination.[12] For the boundary conditions, Boltzmann statistics is used to determine the charge carrier densities at the contacts. The built in potential is taken as the difference between the work functions of the electrodes.

The active layer is considered to be one semiconducting material where the effective band gap E_{g} of the layer is the difference between the LUMO (lowest unoccupied molecular orbital) of the electron accepting material and the HOMO (highest occupied molecular orbital) of the electron donating material. The absorption of light by the active layer first generates excitons, which can then dissociate into polaron pairs (PP) when they reach the donor-acceptor interfaces. The PPs either dissociate into free electrons and holes or decay to the ground state. Furthermore, free electrons and holes can recombine to produce PPs. The continuity equation for PPs is given by

$$\frac{dS(x)}{dt} = G(x) - k_{\mathrm{f}}S(x) - k_{\mathrm{d}}S(x) + R(x), \tag{3}$$

where S is the density of polaron pairs, G is the generation rate of PPs per unit volume, k_{f} is the decay rate coefficient of PPs, k_{d} is the dissociation rate coefficient of PPs, and R is the recombination rate [see Eq. (2)].

The dissociation rate coefficient k_{d} is taken to follow the Onsager-Braun model[8, 9] as proposed by Mihailetchi *et al.*,[10] which has dependencies on both the mobility and the dielectric constant. The dissociation probability of PPs into free carriers is defined as

$$P = \frac{k_{\mathrm{d}}}{k_{\mathrm{d}} + k_{\mathrm{f}}}. \tag{4}$$

Rearranging Eq. (4) by writing $k_{\mathrm{d}} = [P/(1 - P)]k_{\mathrm{f}}$, we can write Eq. (3) in steady-state condition as

$$k_{\mathrm{d}}S(x) = PG(x) + PR(x). \tag{5}$$

TABLE I. Values of the parameters used in the simulations.

Parameter	Value for OC_1C_{10}-PPV/PCBM	Value for P3HT/PCBM
Effective band gap, E_g	1.34 eV	1 eV
Effective density of states, N_c	2.5×10^{25} m^{-3}	2×10^{26} m^{-3}
Generation rate, G	2.7×10^{27} m^{-3}s^{-1}	7.4×10^{27} m^{-3}s^{-1}
Polaron pair decay rate, k_f	1.5×10^6 s^{-1}	2×10^4 s^{-1}
Polaron pair separation, a	1.3 nm	1.8 nm
Recombination pre-factor, ζ	0.5	0.1
Active layer thickness, L	100 nm	100 nm
Temperature, T	300 K	300 K

Using Eq. (5) with $k_d S = G_n = G_p$, the continuity equations for electrons and holes [Eqs. (1a) and (1b)] in steady-state condition can be alternatively written as

$$-\frac{1}{q}\frac{d J_n(x)}{dx} = PG(x) - (1-P)R(x),$$

(6a)

$$\frac{1}{q}\frac{d J_p(x)}{dx} = PG(x) - (1-P)R(x).$$

(6b)

In this study, we investigate the combined influence of mobility μ and dielectric constant ε_r on the efficiency using two different active layers that represent the properties (obviously except the varied mobility μ and dielectric constant ε_r) of OC_1C_{10}-PPV/PCBM (poly[2-methoxy-5-(3′, 7′-dimethyloctyloxy)-*p*-phenylene vinylene] and [6,6]-phenyl C_{61}-butyric acid methyl ester) and P3HT/PCBM (poly(3-hexylthiophene) and phenyl-C_{61}-butyric acid methyl ester) solar cells. We assume that there are no injection barriers at the contacts. The parameters used for the calculations are shown in Table I. The properties of OC_1C_{10}-PPV/PCBM are taken from Ref. 2, where the recombination pre-factor ζ is taken as 0.5 since Ref. 2 used spatially average mobility for the Langevin recombination. The parameters for P3HT/PCBM shown in Table I produce a short circuit current of 103 A/m^2, an open circuit voltage of 0.5782 V, and a fill factor of 0.63 for $\varepsilon_r = 3.5$ and $\mu_n = \mu_p = 1 \times 10^{-8}$ m^2/Vs.

III. RESULTS

A. OC_1C_{10}-PPV/PCBM solar cell

1. The effect of mobility and dielectric constant on short circuit current, open circuit voltage, and fill factor

First, we discuss the effect of mobility μ and dielectric constant ε_r on the short circuit current J_{sc}, the open circuit voltage V_{oc}, and the fill factor FF. Integrating Eq. (6a) over x (distance from the anode), we can write

$$U = PG - (1-P)R$$

(7)

where $U = [J_n(0) - J_n(L)]/qL$ is the average net generation rate of charge carriers, R is now the average recombination rate, and P is now the average dissociation probability. It can be seen from Eq. (7) that μ and ε_r affect U through P and R. From Eq. (7), the recombination yield R_y is defined as

$$R_y = 1 - \frac{U}{PG} = \frac{(1-P)R}{PG},$$

(8)

and is used as a measure of the loss in the charge carriers normalized to the generated charge carriers. The open circuit voltage V_{oc} can be described by[13]

$$V_{oc} = \frac{E_g}{q} - \frac{kT}{q} \ln \left(\frac{(1-P)\zeta \gamma N_c^2}{PG} \right), \qquad (9)$$

where k is the Boltzmann constant. From Eq. (9), μ and ε_r affect V_{oc} through P and the Langevin recombination coefficient γ [see Eq. (2)]. We can also apply the definition of γ into Eq. (9) and write

$$V_{oc} = \frac{E_g}{q} - \frac{kT}{q} \left(\ln \frac{(1-P)\zeta q N_c^2}{PG} + \ln(\mu_n + \mu_p) - \ln \varepsilon_0 \varepsilon_r \right). \qquad (10)$$

Figure 1 shows the short circuit current J_{sc}, the open circuit voltage V_{oc}, and the fill factor FF as functions of charge carrier mobility μ (with equal electron and hole mobilities) and dielectric constant ε_r. To help understanding the results in Fig. 1, Fig. 2 shows the average dissociation probability P and the recombination yield R_y [see Eq. (8)] at short circuit, open circuit, and maximum power point as functions of mobility μ for different dielectric constants ε_r.

It can be seen in Fig. 1(a) that J_{sc} basically increases with both mobility μ and dielectric constant ε_r. Starting from low mobilities, J_{sc} increases quite rapidly until it is close to a saturated value, where a higher ε_r makes J_{sc} to rise and reach the saturated value more quickly. When μ is too low (e.g. $\mu = 10^{-10}$ m^2/Vs), J_{sc} remains significantly lower than the saturated value even if ε_r is increased to a high value. The reasons behind the results in Fig. 1(a) is clear when considering how the mobility μ and the dielectric constant ε_r affect the dissociation probability P at short circuit, as shown in Fig. 2(a). As shown by Eq. (7), the recombination rate R also influences U (thus J_{sc}). However, the influence is small at short circuit because when R is large enough compared to G, the net recombination rate [i.e. $(1-P)R$] is small.

From Fig. 1(b), the open circuit voltage V_{oc} increases with dielectric constant ε_r but decreases with carrier mobility μ. Furthermore, it can be seen that the increase in V_{oc} becomes lower as ε_r is kept increased. These results can be understood by referring to Eq. (10) together with the dissociation probability P as a function of μ and ε_r at open circuit as shown in Fig. 2(b). It can be seen in Fig. 2(b) that the recombination yield R_y is not always 1 at open circuit. This is because the loss of the current density is not only due to recombination, but also due to the extraction of the charge carriers at the "wrong" electrodes.

From Fig. 1(c), it can be seen that the fill factor FF behaves similar to J_{sc} as a function of μ and ε_r, except that the fill factor has a peak value instead of a saturated value. The fill factor decreases slowly after it reaches the peak value. Free charge carriers that are not extracted by the electrodes have to recombine. Hence, a high recombination yield R_y indicates a low fill factor FF. The results in Fig. 1(c) can be understood by considering the behavior of R_y as a function of μ and ε_r at maximum power point as shown in Fig. 2(c). The decrease in FF (after the peak value) as the mobility is increased indicates a significant increase in another loss at maximum power point where the charge carriers are collected at the "wrong" electrodes. The increase in the mobility increases the diffusion coefficient, thus helping the charge carriers to diffuse to the wrong electrodes.

B. The effect of mobility and dielectric constant on the efficiency

Figure 3 shows the efficiency η as a function of charge carrier mobility (where $\mu_n = \mu_p$) for different dielectric constants ε_r of the active layer. The results in Fig. 3 originate from the behaviors of the short circuit current J_{sc}, the open circuit voltage V_{oc}, and the fill factor FF as functions of mobility μ and dielectric constant ε_r, which are shown in Fig. 1. It can be seen in Fig. 3 that for a given ε_r, there is an optimum mobility that leads to a peak efficiency. This can be deduced from Fig. 1 where the optimum mobility occurs when the product of J_{sc}, V_{oc}, and FF is the highest. The influence of mobility on the efficiency and the existence of an optimum mobility have been well discussed in previous studies.[3–6]

From Fig. 3, a higher dielectric constant ε_r leads to a higher efficiency, thus a higher peak efficiency. For example, increasing ε_r from 4 to 8 increases the peak efficiency from around 2.45%
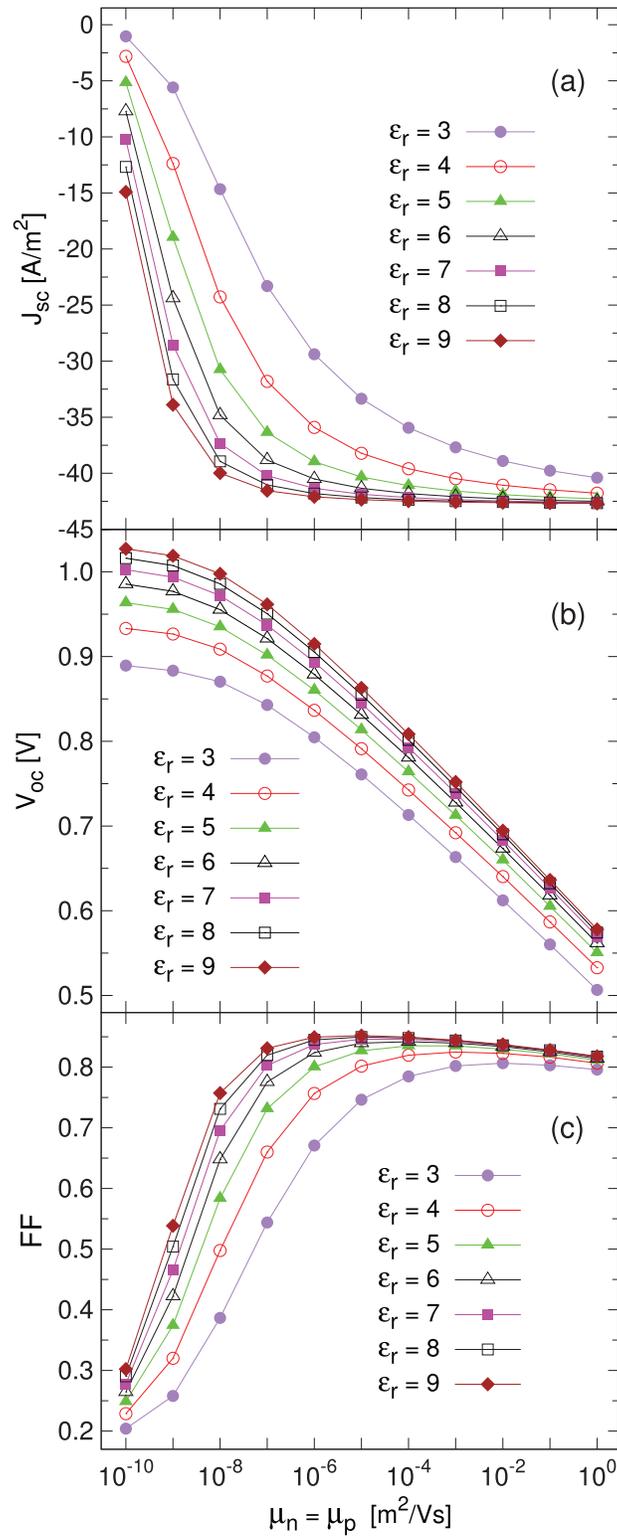
FIG. 1. (a) Short circuit current density J_{sc}, (b) open circuit voltage V_{oc}, and (c) fill factor FF of the OC_1C_{10}-PPV/PCBM solar cell as functions of charge carrier mobility (with $\mu_n = \mu_p$) and dielectric constant ε_r.
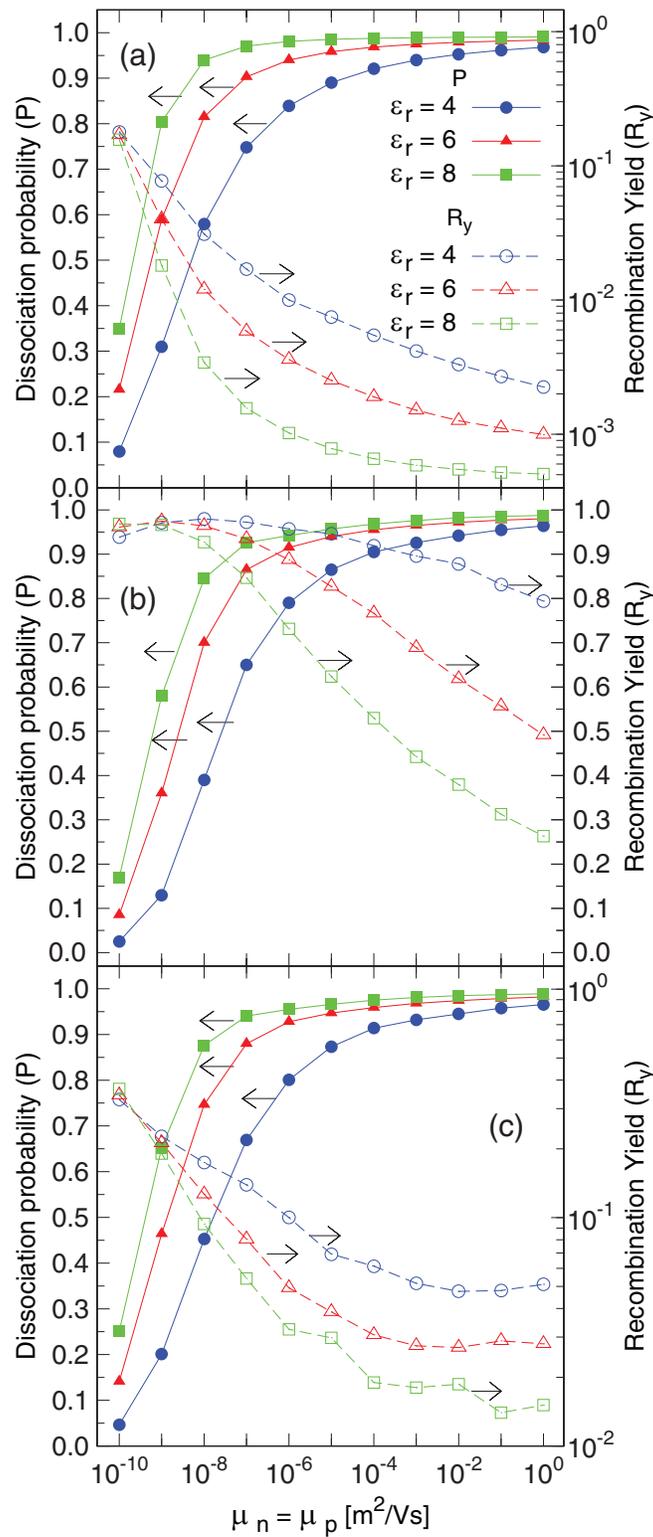
FIG. 2. Average dissociation probability P and recombination yield R_y of the OC_1C_{10}-PPV/PCBM solar cell at (a) short circuit, (b) open circuit, and (c) maximum power point as functions of charge carrier mobility ($\mu_n = \mu_p$) for different dielectric constants ε_r. The symbols for panels (b) and (c) are the same as the symbols for panel (a).
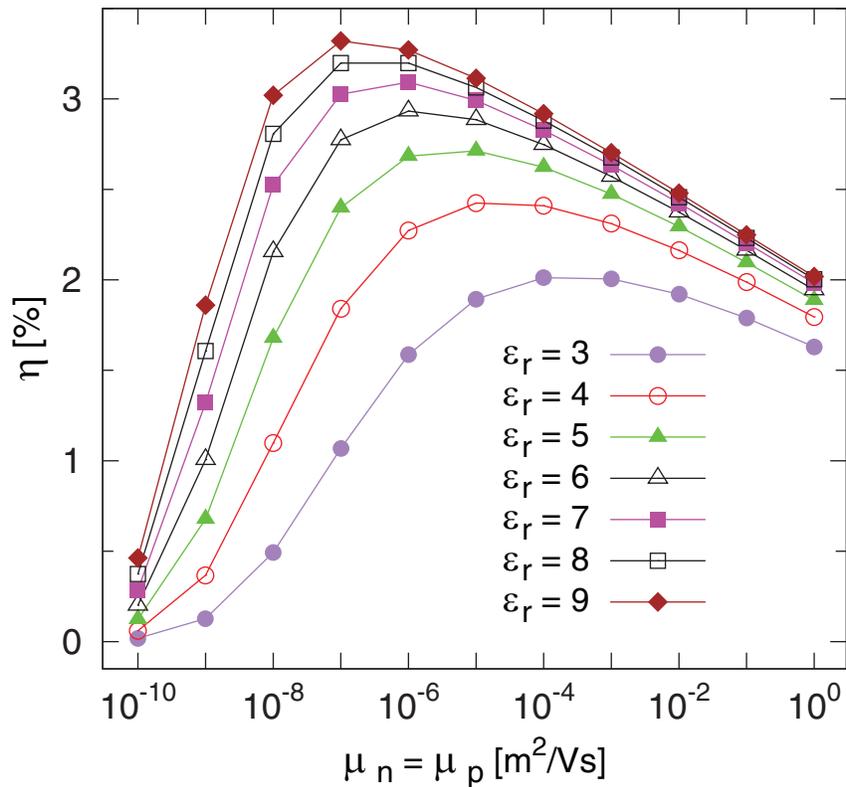
FIG. 3. Efficiency η of the OC$_1$C$_{10}$-PPV/PCBM solar cell as a function of charge carrier mobility (where $\mu_n = \mu_p$) for different dielectric constants ε_r of the active layer.

to around 3.2%. By looking at Figs. 1(a) and 1(c), it is clear that a higher ε_r makes J_{sc} and FF to increase more rapidly with mobility and reach their maximum values at lower mobilities. Since a lower mobility gives a higher V_{oc} [see Fig. 1(b)], this leads to a higher product of J_{sc}, V_{oc}, and FF, hence a higher (peak) efficiency.

A higher dielectric constant ε_r also leads to a lower optimum mobility. When ε_r is increased from 3 to 9 for example, the optimum mobility decreases from around 10^{-4} m^2/Vs to around 10^{-7} m^2/Vs. As just mentioned above, a higher ε_r makes J_{sc} and FF to rise more rapidly with mobility and reach their maximum values at lower mobilities, thus leading to a lower optimum mobility. In turn, this is because a higher ε_r causes the dissociation probability P to increase more rapidly as the mobility is increased, thus requiring a lower mobility in order to reach the maximum value of P (see Fig. 2).

Figure 3 also indicates that the reduction in the optimum mobility due to the increase in ε_r becomes less noticeable at high dielectric constants ε_r (particularly starting from $\varepsilon_r = 8$). The reason for this is clear when looking at Figs. 1(a) and 1(c). It can be seen that when ε_r is increased, the reductions in the mobilities that are required in order to reach the maximum values of J_{sc} and FF are less noticeable at high dielectric constants ε_r.

Furthermore, increasing the dielectric constant ε_r does not significantly improve the efficiency when the mobility is too low (e.g. $\mu = 10^{-10}$ m^2/Vs), and also when the mobility is too high (e.g. $\mu = 1$ m^2/Vs) if ε_r is already relatively high (e.g. $\varepsilon_r = 5$). The origin of this can be explained by looking at J_{sc}, V_{oc}, and FF as ε_r is increased at very low and very high mobilities, as shown in Fig. 1.

The results in Fig. 3 demonstrate the importance of knowing the relationship between the charge carrier mobility and the dielectric constant ε_r when trying to improve and maximize the efficiency of organic solar cells. For example, the average electron and hole mobility for OC$_1$C$_{10}$-PPV/PCBM solar cells is 1.4×10^{-7} m^2/Vs and the typical $\varepsilon_r \approx 3.4$.[2] If the dielectric constant ε_r can be increased to $\varepsilon_r \approx 8$ or higher, then we are very close to achieving the peak efficiency without
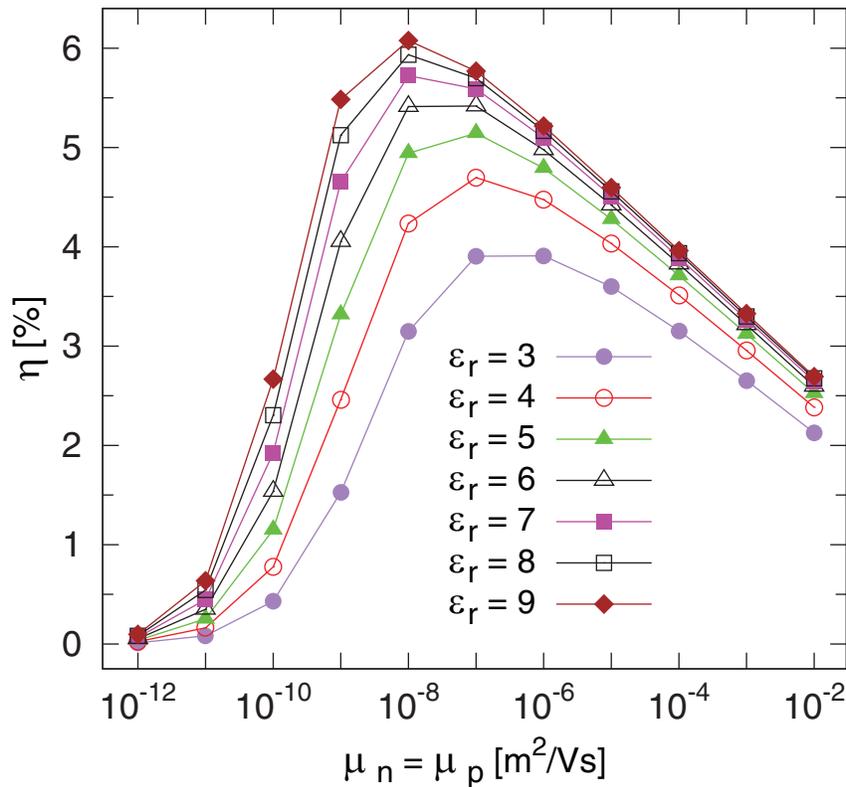
FIG. 4. Efficiency η of the P3HT/PCBM solar cell as a function of charge carrier mobility (where $\mu_n = \mu_p$) for different dielectric constants ε_r of the active layer.

the need to improve the carrier mobility. Furthermore, this would also give a significantly higher efficiency compared to improving to the mobility to the optimum value alone.

C. P3HT/PCBM solar cell

Figure 4 shows the efficiency η of the P3HT/PCBM solar cell as a function of charge carrier mobility (where $\mu_n = \mu_p$) and dielectric constants ε_r. It can be seen that the optimum mobility for the P3HT/PCBM solar cell with typical dielectric constants ε_r (between 3–4) is around 10^{-7} m^2/Vs, similar as found by Mandoc *et al.*[3] With typical mobilities of around 10^{-8} m^2/Vs (Ref. [6]), the optimum mobility can be obtained by increasing the dielectric constant to $\varepsilon_r \approx 7$ or higher.

The basic features of the efficiency with varying mobility and dielectric constant for OC$_1$C$_{10}$-PPV/PCBM and P3HT/PCBM solar cells are the same (see Figs. 3 and 4). The results in Fig. 4 can be derived from the short circuit current J_{sc}, the open circuit voltage V_{oc}, and the fill factor FF as functions of mobility μ and dielectric constant ε_r, which are shown in Fig. 5. Figure 6 shows the average dissociation probability P and the recombination yield R_y as functions of charge carrier mobility μ for different dielectric constants ε_r of the active layer. The results here can be similarly explained as for the OC$_1$C$_{10}$-PPV/PCBM solar cell.

Apart from the values of the efficiency and the optimum mobility, the other noticeable difference between the P3HT/PCBM and the OC$_1$C$_{10}$-PPV/PCBM solar cells is the reduction in the optimum mobility when the dielectric constant ε_r is increased (see Figs. 3 and 4). For example, when ε_r is increased from 3 to 9, the optimum mobility for the P3HT/PCBM solar cell decreases from around 5 $\times$ 10^{-7} m^2/Vs to around 1×10^{-8} m^2/Vs, while for the OC$_1$C$_{10}$-PPV/PCBM solar cell, the optimum mobility decreases from around 1×10^{-4} m^2/Vs to around 1×10^{-7} m^2/Vs. Referring to Figs. 1 and 5, this is because the reductions in the mobilities that are required in order to reach the maximum values of J_{sc} and FF when ε_r is increased are lower for the P3HT/PCBM solar cell. In turn, this is
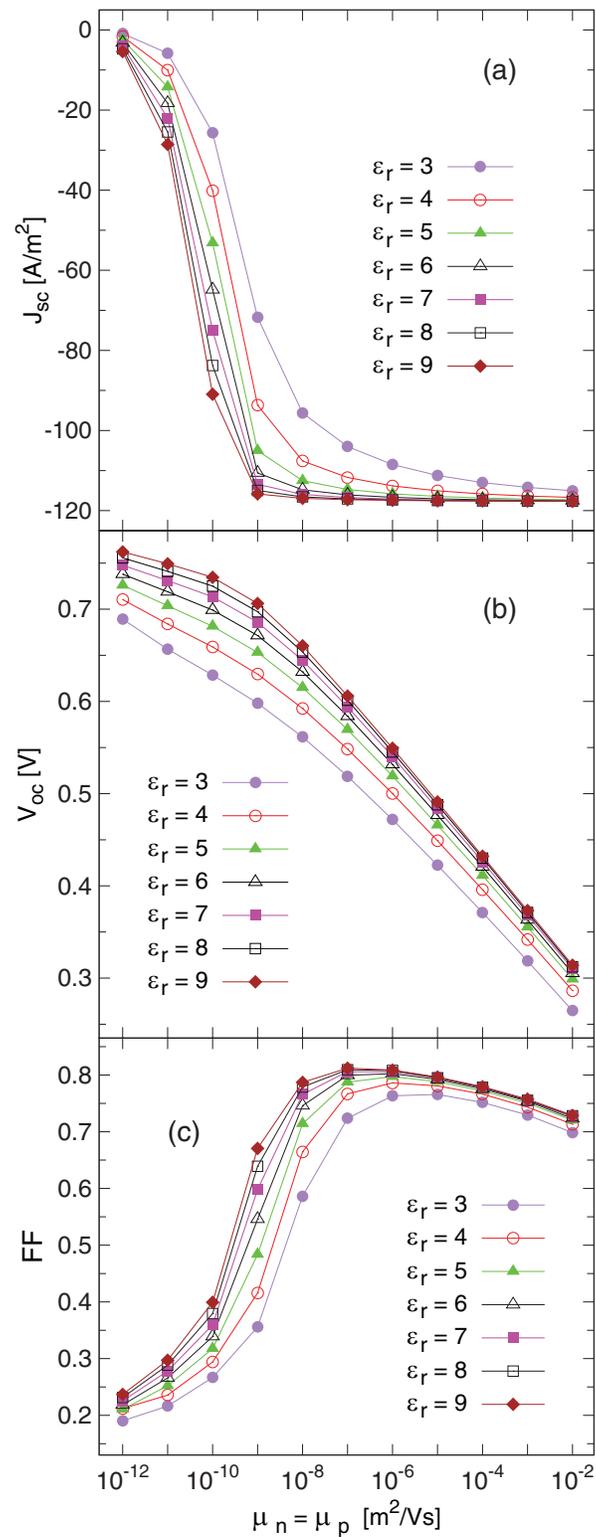
FIG. 5. (a) Short circuit current density J_{sc}, (b) open circuit voltage V_{oc}, and (c) fill factor FF of the P3HT/PCBM solar cell as functions of charge carrier mobility (with $\mu_n = \mu_p$) and dielectric constant ε_r.
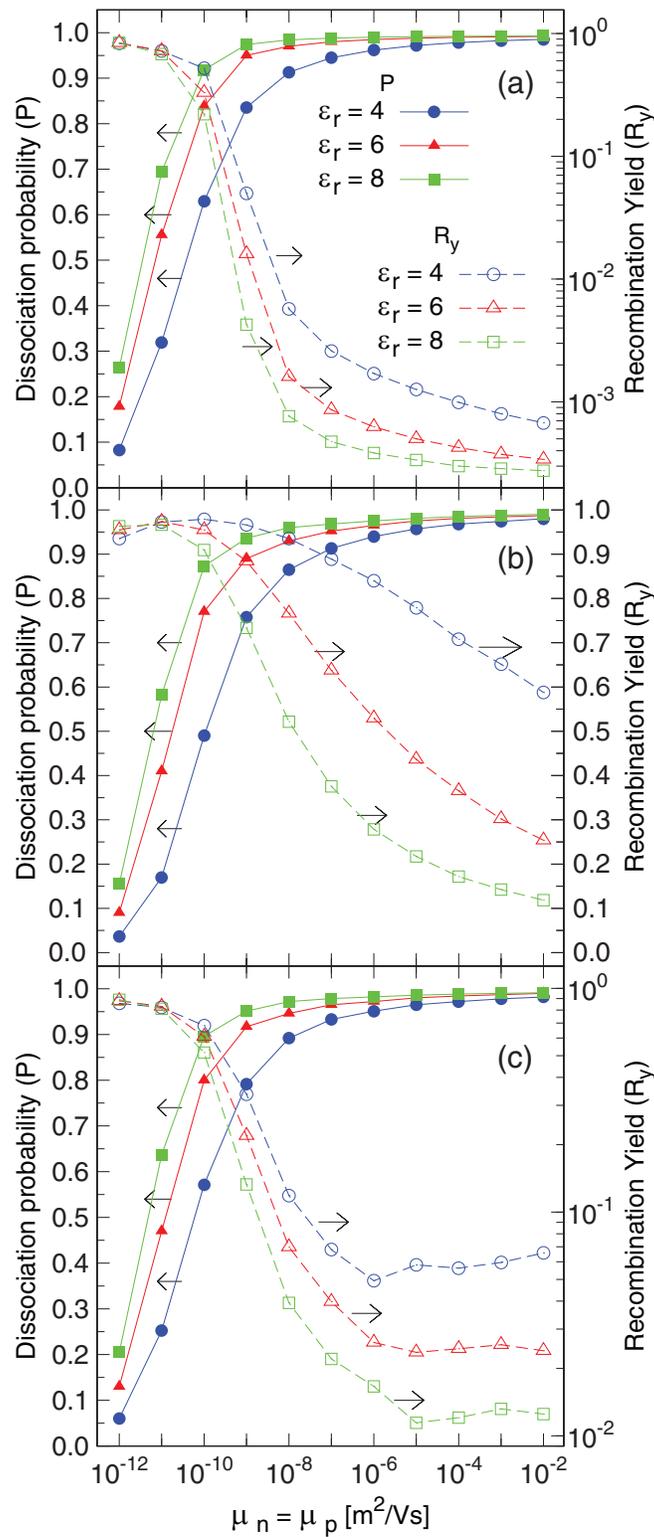
FIG. 6. Average dissociation probability P and recombination yield R_y of the P3HT/PCBM solar cell at (a) short circuit, (b) open circuit, and (c) maximum power point as functions of charge carrier mobility ($\mu_n = \mu_p$) for different dielectric constants ε_r of the active layer. The symbols for panels (b) and (c) are the same as the symbols for panel (a).

because the reduction in the mobility that is required in order to reach the maximum dissociation probability P when ε_r is increased is lower for the P3HT/PCBM solar cell, which can be seen by comparing Figs. 2 and 6. Furthermore, it can also be seen from Figs. 3 and 4 that at high dielectric constants (starting from $\varepsilon_r = 8$ and $\varepsilon_r = 7$ for OC$_1$C$_{10}$-PPV/PCBM and P3HT/PCBM solar cells, respectively), the reductions in the optimum mobility for both solar cells when ε_r is increased start to become insignificant.

IV. CONCLUSIONS

We have performed simulations using a drift-diffusion model to investigate the combined influence of charge carrier mobility and dielectric constant on the performance of organic BHJ solar cells. We apply the widely used models which have been shown to well describe the experimental data of organic solar cells, such as the Onsager-Braun model for polaron pair dissociation, the Langevin recombination model, and the effective band gap approach. It is well known that there is an optimum mobility that would result in a peak efficiency. Hence, improving the mobility is considered as one of the ways to increase the efficiency. Here, we found that a higher dielectric constant leads to a higher peak efficiency together with a lower optimum mobility. This is because a higher dielectric constant causes the dissociation probability to increase more rapidly as the mobility is increased, thus requiring a lower mobility in order to reach the maximum value of dissociation probability. Using two different active materials that represent the properties of OC$_1$C$_{10}$-PPV/PCBM and P3HT/PCBM solar cells, we found that if the dielectric constants ε_r can be increased to $\varepsilon_r \approx 8$ or higher, then the optimum mobilities can be achieved without improving the charge carrier mobility. Our results demonstrate the importance of knowing the interplay between the mobility and the dielectric constant with regard to the efficiency.

ACKNOWLEDGMENTS

[1] L. J. A. Koster, S. E. Shaheen, and J. C. Hummelen, Adv. Energy Mater. **2**, 1246–1253 (2012).
[2] L. J. A. Koster, E. C. P. Smits, V. D. Mihailetchi, and P. W. M. Blom, Phys. Rev. B **72**, 085205 (2005).
[3] M. M. Mandoc, L. J. A. Koster, and P. W. M. Blom, Appl. Phys. Lett. **90**, 133504 (2007).
[4] W. Tress, K. Leo, and M. Riede, Phys Rev B **85**, 155201 (2012).
[5] J.-T. Shieh, C.-H. Liu, H.-F. Meng, S.-R. Tseng, Y.-C. Chao, and S.-F. Horng, J. Appl. Phys. **107**, 084503 (2010).
[6] C. Deibel, A. Wagenpfahl, and V. Dyakonov, Phys. Status Solidi 2, **175** (2008).
[7] Y.-X. Wang, S.-R. Tseng, H.-F. Meng, K.-C. Lee, C.-H. Liu, and S.-F. Horng, Appl. Phys. Lett. **93**, 133501 (2008).
[8] L. Onsager, Phys. Rev. **54**, 554 (1938).
[9] C. L. Braun, J. Chem. Phys. **80**, 4157 (1984).
[10] V. D. Mihailetchi, L. J. A. Koster, J. C. Hummelen, and P. W. M. Blom, Phys. Rev. Lett. **93**, 216601 (2004).
[11] R. Hausermann, E. Knapp, M. Moos, N. A. Reinke, T. Flatz, and B. Ruhstaller, J. Appl. Phys. **106**, 104507 (2009).
[12] G. Juska, K. Arlauskas, J. Stuchlik, and R. Osterbacka, J. Non-Cryst. Solids **352**, 1167 (2006).
[13] L. J. A. Koster, V. D. Mihailetchi, R. Ramaker, and P. W. M. Blom, Appl. Phys. Lett. **86**, 123509 (2005).