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Effects of Energetic Disorder and Mobility Anisotropy on Geminate Electron-hole Recombination in the Presence of a Donor-Acceptor Heterojunction†

Mariusz Wojcik,* Przemyslaw Michalak, and M. Tachiya‡,*

Institute of Applied Radiation Chemistry, Technical University of Lodz, Wroblewskiego 15, 93-590 Lodz, Poland
**E-mail: mariusz.wojcik@mitr.p.lodz.pl*
*‡National Institute of Advanced Industrial Science and Technology (AIST), AIST Tsukuba Central 5, Tsukuba, Ibaraki 305-8565, Japan. *E-mail: m.tachiya@aist.go.jp*
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Geminate electron-hole recombination in organic solids in the presence of a donor-acceptor heterojunction is studied by computer simulations. We analyze how the charge-pair separation probability in such systems is affected by energetic disorder of the media, anisotropy of charge-carrier mobilities, and other factors. We show that in energetically disordered systems the effect of heterojunction on the charge-pair separation probability is stronger than that in idealized systems without disorder. We also show that a mismatch between electron and hole mobilities reduces the separation probability, although in energetically disordered systems this effect is weaker compared to the case of no energetic disorder. We demonstrate that the most important factor that determines the charge-pair separation probability is the ratio of the sum of electron and hole mobilities to the rate constant of recombination reaction. We also consider systems with mobility anisotropy and calculate the electric field dependence of the charge-pair separation probability for all possible orientations of high-mobility axes in the donor and acceptor phases. We theoretically show that it is possible to increase the charge-pair separation probability by controlling the mobility anisotropy in heterojunction systems and in consequence to achieve higher efficiencies of organic photovoltaic devices.

Key Words : Organic solar cells, Photogeneration, Charge carriers, Simulation

Introduction

Geminate electron-hole pairs are formed as a result of light absorption in photoconductive organic materials. They can be produced either directly by photoionization or via dissociation of excited states (excitons). The geminate particles subsequently recombine or escape from the mutual Coulomb attraction to become free charge carriers. The geminate charge-pair separation probability, φ, is significantly lower than unity in many systems of practical importance including organic solar cells, where geminate recombination is considered as one of the main energy loss channels.[1-3] Good understanding of the electron-hole recombination processes may help to improve the efficiency of organic photovoltaic devices.

Analytical theories of geminate charge recombination are available only for homogeneous systems. They are based on the Smoluchowski equation[4]

$$\frac{\partial w(\mathbf{r},t)}{\partial t} = D\left[\nabla^2 w(\mathbf{r},t) + \frac{1}{k_B T}\nabla w(\mathbf{r},t)\nabla V(\mathbf{r})\right], \qquad (1)$$

which describes the time evolution of the probability density $w(\mathbf{r},t)$ that the charge pair is separated by $\mathbf{r}$ at time t. Here, $V(\mathbf{r})$ is the interaction potential, D is the sum of diffusion coefficients of electron and hole, and k_BT is the Boltzmann factor. By integrating $w(\mathbf{r},t)$ over the space variables, one obtains the time-dependent pair survival probability

$$W(t) = \int w(\mathbf{r},t)d\mathbf{r} \qquad (2)$$

that describes the kinetics of the recombination process. The ultimate charge-pair separation probability (escape probability) is determined as the long-time limit of $W(t)$

$$\varphi = \lim_{t\to\infty} W(t)\,. \qquad (3)$$

Instead of using Eqs. (1)-(3), it is much more convenient to calculate the geminate charge-pair separation probability by directly solving the following equation[5,6]

$$\nabla_{r_0}^2 \varphi(\mathbf{r}_0) - \frac{1}{k_B T}\nabla_{r_0}\varphi(\mathbf{r}_0)\nabla_{r_0} V(\mathbf{r}_0) = 0\,, \qquad (4)$$

where $\mathbf{r}_0$ denotes the initial distance between the geminate particles and the differentiation is done with respect to $\mathbf{r}_0$. Formal equivalence of the above two approaches to calculating the escape probability was proven based on the theory of adjoint differential equations.[6]

To describe the electron-hole recombination in photofunctional devices, one needs to know how the charge-pair separation probability depends on the applied electric field $\mathbf{F}$. This problem was solved by Onsager,[5] who derived the following expression

†This paper is to commemorate Professor Kook Joe Shin's honourable retirement.

$$\varphi(r_0, \vartheta, F) = \exp[-\beta r_0(1+\cos\vartheta)] \int_{r_c/r_0}^{\infty} J_0\{2[-\beta r_0(1+\cos\vartheta)s]^{1/2}\} e^{-s} ds \,. \quad (5)$$

Here, ϑ denotes the angle between $\mathbf{r}_0$ and $\mathbf{F}$, $\beta = eF/2k_BT$, and J_0 is a zeroth-order Bessel function of the first kind. More convenient expressions are also available[7] that describe the angularly-averaged escape probability through infinite series summations. For $F = 0$, eq. (5) reduces to the well-known formula

$$\varphi(r_0) = \exp\left(-\frac{r_c}{r_0}\right), \quad (6)$$

where r_c, termed the Onsager radius, is defined as $r_c = e^2/\varepsilon k_BT$. Here, e is the elementary charge and ε is the dielectric constant.

Although Onsager's theory has been widely used to interpret experimental data, it has a serious limitation that questions its applicability. Onsager assumed that the geminate particles ultimately recombine when they approach each other to the distance equal to zero. When the distance between the electron and hole approaches zero, the inward flux of the electron to the hole becomes infinite, so the recombination process is fully diffusion controlled. Such a situation is rarely observed in real systems.

An extension of the Onsager theory by taking into account a non-zero reaction radius R and finite intrinsic reactivity was done by Sano and Tachiya.[6] They solved eq. (4) with an appropriate boundary condition at $r_0 = R$ and obtained the following expression

$$\varphi(r_0, F=0) = \frac{\exp\left(-\frac{r_c}{r_0}\right) - \left(1-\frac{Dr_c}{pR^2}\right)\exp\left(-\frac{r_c}{R}\right)}{1-\left(1-\frac{Dr_c}{pR^2}\right)\exp\left(-\frac{r_c}{R}\right)} \quad (7)$$

that describes the escape probability in the case of partially diffusion-controlled recombination. Here, p is a reactivity parameter, which can be approximately related to the intrinsic first-order recombination rate, k_0, by $p = k_0R$. An analytical solution is also available that generalizes eq. (7) to the case of a non-zero external field.[8,9] However, this solution is mathematically complicated and requires employing numerical methods in its practical applications.[9]

The Onsager theory was also extended to an even more realistic case in which recombination takes place over a range of distances and is described by a distance-dependent rate constant $k(r)$. Then, the escape probability can be obtained by solving the following equation[10]

$$D\left[\nabla_{r_0}^2 \varphi(\mathbf{r}_0) - \frac{1}{k_BT}\nabla_{r_0}\varphi(\mathbf{r}_0)\nabla_{r_0}V(\mathbf{r}_0)\right] - k(\mathbf{r}_0)\varphi(\mathbf{r}_0) = 0 \quad (8)$$

with the reflective boundary condition imposed at $r_0 = R$. Unfortunately, no analytical solutions of eq. (8) exist and it has to be solved numerically.[9,11]

When discussing the Onsager theory and its extensions, it is also worth while to mention a different approach to calculating the escape probability that was used by Braun.[12] He described geminate recombination as a competition between charge-pair separation and reaction, both treated as first-order processes. Although this theory has been widely used to interpret experimental data, it should be realized that the charge separation process involves diffusion and as such cannot be described by a first-order rate constant. Therefore, the approach of Braun is physically incorrect. This issue was widely discussed in Ref. 9.

The theories of geminate recombination presented above refer to homogeneous systems and cannot be directly applied to model charge-pair separation processes in heterojunction systems that are widely used to construct organic solar cells.[13,14] In such systems, two organic conductive materials with significant energy offsets between respective HOMO levels and between respective LUMO levels are in contact with each other. At an interface between the two phases, dissociation of excitons into electron-hole pairs is very efficient. Moreover, since the motions of electrons and holes are restricted to the electron acceptor and donor phases, respectively, and the reaction between them is possible only at the interface, the charge-pair separation probability in such systems is expected to be much higher than that in homogeneous media.

Unfortunately, it is extremely difficult to obtain an analytical solution for the geminate charge separation probability in heterojunction systems. Therefore, computer simulations have been used to study this problem.[15-19] In our recent paper,[19] we calculated the electric-field dependence of the charge-pair separation probability by using a lattice simulation model. The simulation was first carried out for a homogeneous system and tested against the analytical results obtained by solving eq. (8). A very good agreement between the simulation and theory was obtained for a fine lattice spacing $d = 1$ Å. At larger values of d, the escape probability was found to be lower compared to the results of the analytical theory, which assumes ideal diffusion ($d \to 0$). In the main part of Ref. 19, we introduced a heterojunction into our simulation model and clearly demonstrated that in binary donor-acceptor systems the charge-pair separation probability can be as much as an order of magnitude higher compared to homogeneous systems. We also carried out a systematic study of the effect of mobility mismatch between the electron and hole on their separation probability. We found that the mobility mismatch decreases the separation probability, so it has a negative effect on the efficiency of organic solar cells.

Although the results presented in Ref. 19 are, in our opinion, quite convincing, the simulation model applied in that study was rather simple. In particular, it completely neglected a structural disorder that characterizes all amorphous media. It is known that the disorder may affect both the charge transport[20,21] and recombination processes[22,23] in homogeneous systems. Therefore, it is interesting to see to what extent the presence of disorder affects the geminate charge recombination in systems with a heterojunction. This issue is also

important because in another simulation study of a disordered heterojunction system by Groves *et al.*,[17] it was found that a large mobility mismatch between the electron and hole may result in an increase of the charge separation probability, contrary to what was reported in Ref. 19. An analysis of the effect of disorder on geminate charge separation probability in the presence of a heterojunction is one of the main goals of the present work.

In addition to analyzing the effects of disorder, we also aim to extend the results obtained in Ref. 19 by a more detailed study of the role of charge mobility in geminate recombination in heterojunction systems. The mobility of charge carriers in organic materials often exhibits strong local anisotropy. This is observed in conductive polymer systems where intrachain charge transport is much faster than interchain charge transport.[21,24-26] Another example of conductive anisotropic systems is discotic liquid crystals[27-29] in which self-organization of molecules leads to formation of columnar structures with high charge-mobility along the columns. While construction of photofunctional devices with highly controlled local morphology is still not attainable with current technologies, it may be possible in the future. Then, it might also be possible to control orientation of polymer chains or, more generally, the high-mobility direction with respect to the heterojunction. We think it is interesting to assess how the mobility anisotropy in heterojunction systems would affect the electron-hole separation process. We calculate the charge-pair separation probability for various orientations of the high-mobility axes with respect to the heterojunction and for different degrees of anisotropy, both in the absence and presence of disorder.

Method of Calculation

To calculate the charge-pair separation probability, we use a kinetic Monte Carlo method similar to the one used in Ref. 19. We model the hopping motion of an electron and a hole on a regular cubic lattice. An electron is initially placed at (0,0,0) and a hole at (–*d*,0,0), where *d* is the lattice constant. The particles may hop to their nearest lattice sites, with the restriction that electron hops only to the sites at $x \geq 0$ and hole hops only to the sites at $x < 0$ are allowed. Thus, the lattice sites at negative *x* values represent the donor phase and those at zero or positive *x* values represent the acceptor phase, with a planar heterojunction located at $x = -d/2$.

In the course of the simulation, the hopping rates from one site to another are calculated by using the expression

$$k_{qi} = v_{qi} \times \begin{cases} \exp(-\Delta U/k_B T) & \Delta U \geq 0 \\ 1 & \Delta U < 0 \end{cases}, \qquad (9)$$

where index *q* denotes either the electron ($q = e$) or the hole ($q = h$), and index *i* refers to the hops along each of the Cartesian coordinates ($i = x,y,z$). ΔU is the potential energy difference between two sites, which is calculated by taking into account both the Coulomb potential and the potential due to an external electric field *F*. We assume that the external field is applied in *x* direction.

To study the effects of disorder, we add a random component to the energy of each lattice site. This random energies are sampled from the Gaussian distribution of zero mean value and an assumed standard deviation σ.

The charge transport anisotropy can be included in our simulation model by allowing the mobilities of electron and hole along each Cartesian coordinate to be set independently. We denote the charge mobility in the absence of energetic disorder as $\mu_q = (\mu_{qx}, \mu_{qy}, \mu_{qz})$. The mobility components μ_{qi} are related to the hop frequency factors v_{qi} in Eq. (9) through

$$v_{qi} = \frac{2k_B T}{ed^2}\mu_{qi}. \qquad (10)$$

At each simulation step, we calculate the rates of all possible hops for the electron and hole by using Eq. (9). We also calculate the rate of recombination which is assumed to depend exponentially on the separation between the electron and hole

$$k(r) = k_0 \exp[-\alpha(r-R)]. \qquad (11)$$

Which event actually occurs among all possible hops and the recombination is determined probabilistically under the condition that the probability of occurrence of each event is proportional to the rate given by Eq. (9) or (11). Each simulation run is carried out until either the recombination occurs, or the particles get separated from each other to a large distance r_{max}. By repeating the simulation runs ~10^4 times, we determine the charge-pair separation probability.

Effect of Energetic Disorder on the Charge-Pair Separation Probability

The simulation results on the effect of energetic disorder on the electric field dependence of the charge-pair separation probability in heterojunction systems are presented in Figure 1. The four panels of this Figure correspond to different values of the standard deviation of the random energy component, from $\sigma = 0$ (no energetic disorder, Figure 1(a)) to $\sigma = 0.1$ eV (Figure 1(d)). The simulation results represented by squares correspond to the homogeneous systems, while those represented by circles were obtained in the presence of heterojunction. All results shown in Figure 1 were calculated for isotropic mobilities of both electrons and holes ($\mu_{qx} = \mu_{qy} = \mu_{qz} = \mu_q$). The data shown by closed symbols were calculated for equal electron and hole mobilities, $\mu_e = \mu_h$, and those shown by open symbols correspond to mismatched mobilities, $\mu_e = r_\mu \mu$ and $\mu_h = (1 - r_\mu)\mu$, where r_μ changes between 0.5 and 1. Note that the sum of electron and hole mobilities is always constant and equal to μ. The parameter values assumed in these calculations were as follows: $\mu = 10^{-6}$ m^2/Vs, $k_0 = 10^7$ s^{-1}, $\alpha = 10$ nm^{-1}, $d = R = 1$ nm, $r_{max} = 800$ nm, $\varepsilon = 4$, $T = 298$ K.

Figure 1 indicates that the effect of energetic disorder on geminate charge separation is quite significant. In homogeneous systems, the charge pair separation probability

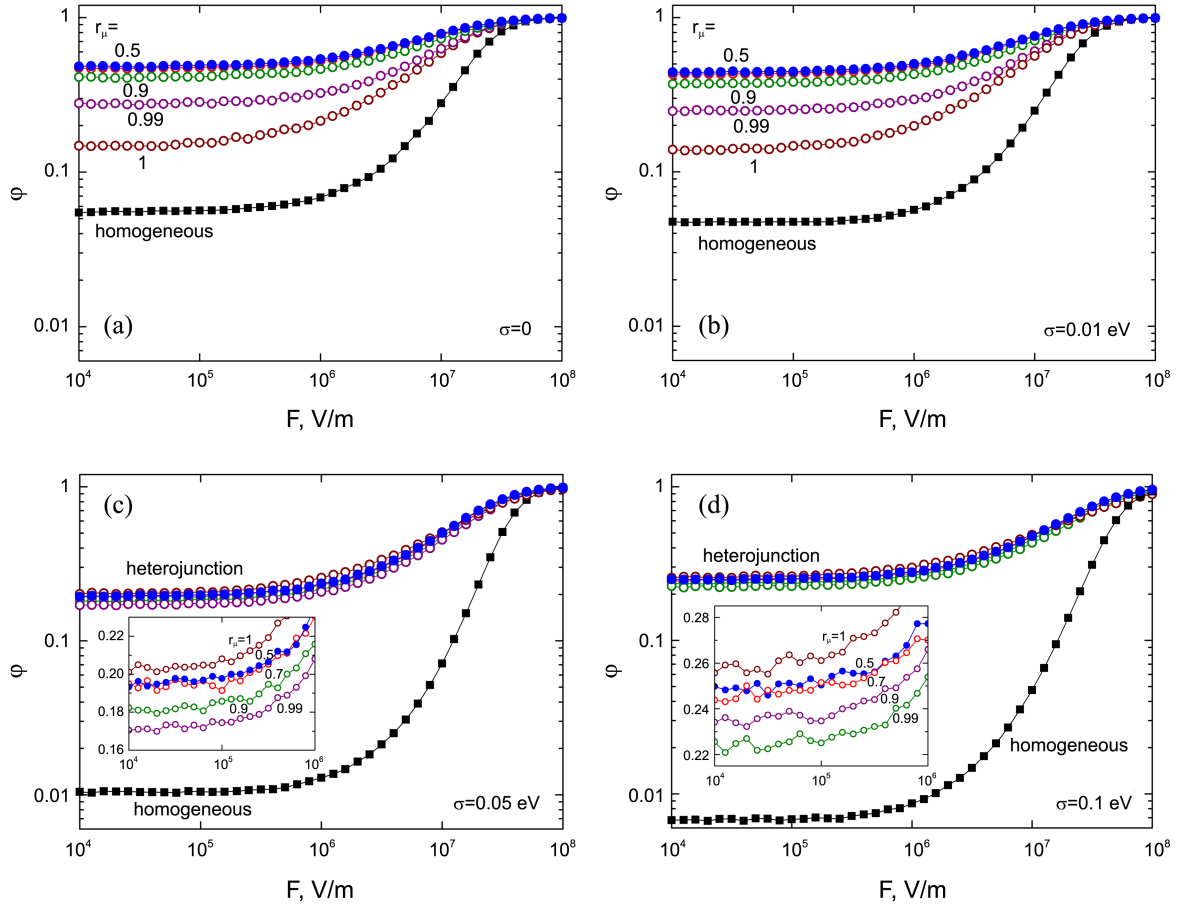

Figure 1. Electric field dependence of the electron-hole separation probability in energetically disordered systems in the presence of heterojunction. (a) $\sigma = 0$, (b) $\sigma = 0.01$ eV, (c) $\sigma = 0.05$ eV, (d) $\sigma = 0.1$ eV. Closed and open circles show the simulation results obtained, respectively, for equal and mismatched electron and hole mobilities. The data in (a) and (b) correspond to (from top to bottom) $r_\mu = 0.5$, 0.7, 0.9, 0.99, and 1. The order of data in (c) and (d) is shown by the values of r_μ attached to different data sets presented, in magnification, in the insets. The simulation results obtained for homogeneous systems are shown by squares. The parameters were assumed as: $\mu = 10^{-6}$ m^2/Vs, $k_0 = 10^7$ s^{-1}, $\alpha = 10$ nm^{-1}, $d = R = 1$ nm, $\varepsilon = 4$, $T = 298$ K. The data in (a) are the same as in Figure 2 of Ref. 19.

decreases with increasing energetic disorder. For $\sigma = 0.1$ eV it is almost an order of magnitude lower (at low external fields) compared to the system with $\sigma = 0$. In the presence of heterojunction, and at equal electron and hole mobilities, the separation probability initially also decreases with increasing energetic disorder. However, this decrease is slower than that in homogeneous systems and the trend changes at larger σ values (at $\sigma = 0.1$ eV the separation probability is slightly higher than that at 0.05 eV). Comparing the separation probability for the homogeneous case with those for the heterojunction cases in Figure 1(a)-(d), we see that the effect of heterojunction on enhancing geminate charge-pair separation probability is significantly stronger in energetically disordered systems compared to those with no energetic disorder. At $\sigma = 0.1$ eV, which is considered as a typical value of this parameter in real systems,[21] the calculated separation probability in the presence of heterojunction (at low external fields) is as much as 40 times higher than that in the corresponding homogeneous system.

We now assess how the mismatch in mobility between the

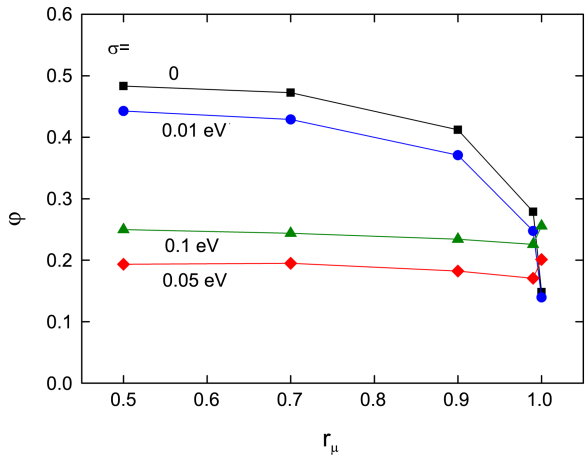

Figure 2. Electron-hole separation probability in heterojunction systems (at an external field $F = 10^4$ V/m) as a function of the mobility mismatch parameter r_μ. Different data sets correspond to different values of the disorder parameter σ, as indicated in the figure. Other parameters are the same as in Figure 1.

electron and hole affects the charge-pair separation probability in heterojunction systems with energetic disorder (note that in homogeneous systems this probability does not depend on the mobility mismatch). In the case of small energetic disorder ($\sigma = 0.01$ eV, Figure 1(b)), the effect of mobility mismatch is very similar to that observed in Figure 1(a) (at no energetic disorder). With increasing mobility mismatch, the separation probability becomes lower, although this effect is not very strong as long as the difference between the electron and hole mobilities is less than an order of magnitude. When the energetic disorder becomes larger (see Figures 1(c) and 1(d)), the effect of mobility mismatch weakens and the separation probability shows only small changes in the whole range of the parameter r_μ. The combined effects of mobility mismatch and energetic disorder are more clearly seen in Figure 2, where the separation probability (at a low external field) is plotted as a function of r_μ for different values of σ. We see that at $\sigma = 0.05$ and 0.1 eV, the separation probability slowly decreases with increasing mobility mismatch up to $r_\mu = 0.99$. However, when r_μ reaches 1 (one of the charge carriers is stationary), the separation probability abruptly increases and exceeds the values obtained in the case of no mismatch. This result is in accord with the corresponding result of Groves *et al*.[17] which shows that if energetic disorder is large, the separation probability in the case when one charge carrier is stationary is higher than that in the case of no electron and hole mobility mismatch (cf. Figure 2(c) of Ref. 17). However, another result of Groves *et al.* which shows an increase of the separation probability at a much lower mobility mismatch contradicts our results presented in Figures 1 and 2. We think that the effect observed at a low mobility mismatch in Ref. 17 probably results from statistical error of simulation or uncertainties related to a larger number of approximations in their simulation methodology in comparison with our approach. It should also be reminded that at a very large mobility mismatch (when $r_\mu \approx 1$), space-charge effects dominate the charge-carrier transport, so the simulation results obtained at $r_\mu = 1$ might not be applicable to real systems.

The effects of energetic disorder on geminate charge separation presented above can be explained by the following arguments. In the presence of energetic disorder, charge carriers are trapped at low energy sites and spend some time residing there. If an electron and hole are trapped near the interface, they have more time to undergo recombination reaction. This explains the fact that the charge separation probability decreases with increasing energetic disorder, as shown in different panels of Figure 1. A similar argument can be called to explain the fact that the energetic disorder reduces the effect of mobility mismatch on the charge separation probability in heterojunction systems. The rate of release of charge carriers from traps depends exponentially on the trap energy [cf. Eq. (9)]. On the other hand, the prefactor in Eq. (9) depends linearly on the parameter r_μ that describes the mobility mismatch. Therefore, the effects due to mobility mismatch between electron and hole are expected to be relatively weaker in disordered systems compared to those resulting from trapping of charge carriers. The important role of the process of carrier release from the traps is also supported by the fact that at $\sigma = 0.01$ eV, which is lower compared to the thermal energy $k_BT \approx 0.025$ eV, the effect of energetic disorder is hardly observable. However, it becomes quite strong at $\sigma = 0.05$ and 0.1 eV, when a significant fraction of trapping sites are energetically deeper than k_BT.

Effect of Mobility Anisotropy on the Charge-Pair Separation Probability

Before analyzing in detail the effect of mobility anisotropy on geminate electron-hole separation in heterojunction systems, it is worth while to see how the separation probability in such systems is affected by the sum of electron and hole mobilities ($\mu = \mu_e + \mu_h$) and another important quantity - the rate constant of recombination reaction (k_0). Figure 3 shows the electric field dependences of the separation probability in the heterojunction system calculated for three different values of total mobility μ by assuming no mobility mismatch ($r_\mu = 0.5$) and no energetic disorder. The data represented by squares are the same as those shown in Figure 1(a), while those represented by diamonds and circles were calculated using, respectively, ten times higher and ten times lower μ. We see that the effect of changing μ on the separation probability φ is very significant. When μ is ten times decreased, the separation probability decreases by almost an order of magnitude. In the opposite case, φ strongly increases and almost approaches unity. We also performed calculations on the effect of changing the value of the recombination rate constant k_0 [cf. Eq. (11)]. We found that the effect of multiplying k_0 by a certain factor is the same as that of dividing the total mobility μ by the same factor. Therefore, we may conclude that the geminate charge-pair separation probability in heterojunction systems is determined by the ratio μ/k_0, as already pointed out in Ref. 19. We indicate this by attaching the corresponding values of μ/k_0 to different

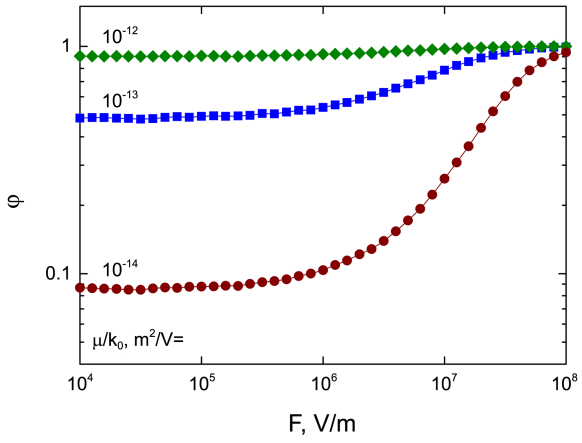

Figure 3. Electric field dependence of the electron-hole separation probability in heterojunction systems of equal electron and hole mobilities calculated for different values of the ratio μ/k_0, as indicated in the figure. Other parameters are the same as in Figure 1.

data sets plotted in Figure 3.

We now proceed to the effect of charge transport anisotropy on the charge separation probability in heterojunction systems. In the first stage of these calculations, we modeled donor-acceptor systems in which the mobility of only one carrier (for example, the electron) is anisotropic. We assumed that the electron mobility along one coordinate (μ_1) is much higher than those along the other two coordinates (μ_0). The components of the hole mobility were all taken equal to μ_0. The electron high-mobility axis can be either parallel or perpendicular to the heterojunction, so we have the following two cases.

case (a): $\mu_h = (\mu_0, \mu_0, \mu_0)$, $\mu_e = (\mu_0, \mu_1, \mu_0)$,

case (b): $\mu_h = (\mu_0, \mu_0, \mu_0)$, $\mu_e = (\mu_1, \mu_0, \mu_0)$.

We calculated the electric-field dependence of the charge-pair separation probability, φ, for cases (a) and (b) for two different degrees of anisotropy. The results presented in Figure 4(A) were obtained for $\mu_0 = 5 \times 10^{-8}$ m^2/Vs and $\mu_1 = 5 \times 10^{-6}$ m^2/Vs ($r_a = \mu_1 / \mu_0 = 10^2$). The data shown in Figure 4(B) correspond to a case of higher anisotropy in which μ_1 is increased to 5×10^{-5} m^2/Vs ($r_a = 10^3$). We also present the results obtained for an energetically disordered system (Figure 4(C)), where $\mu_1 = 5 \times 10^{-5}$ m^2/Vs and $\sigma = 0.05$ eV. In all cases, the values of the other parameters used are the same as in Figure 1. For comparison, in all three panels of Figure 4 we also show the charge-pair separation probability calculated for the corresponding isotropic cases in which all components of the electron and hole mobilities are equal to μ_0 or μ_1.

We see from Figures 4(A) and 4(B) that the separation probability in the case when the electron high-mobility axis is perpendicular to the heterojunction (curves (b)) is higher than that in the case when it is parallel to the heterojunction (curves (a)). However, the magnitude of this effect strongly depends on the applied field. While the effect is rather weak at low fields, it becomes quite significant at the field strength on the order of 10^5 - 10^6 V/m. For $r_a = 10^2$ (Figure 4(A)), the ratio of the charge-pair separation probability in case (b) to that in case (a) is 1.8 at $F = 10^7$ V/m. At a higher mobility anisotropy ($r_a = 10^3$, Figure 4(B)), this ratio increases to 2.1. In the presence of energetic disorder (Figure 4(C)), this ratio further increases to 2.5. The observed difference in the shape of the $\varphi(F)$ curve between cases (a) and (b) may be understood if one notes that the charge-pair separation is easier if the electron with anisotropic mobility moves with higher mobility along the direction of an external field. Figure 4 also shows that the charge-pair separation probability in cases in which one component of the electron mobility is much larger (μ_1) but the others are normal (μ_0) is significantly higher than that in the isotropic case in which all components of the electron mobility are normal. When all mobility components are made equal to the higher value μ_1, the increase of the separation probability is so strong that the $\varphi(F)$ curves almost reach unity.

We also carried out calculations for model systems in which both the electron and hole mobilities are anisotropic. In such systems not only the orientation of the high-mobility axes of electrons and holes with respect to the heterojunction but also their relative orientation with respect to each other are expected to be important factors to determine the charge-pair separation probability. We assume for both electrons

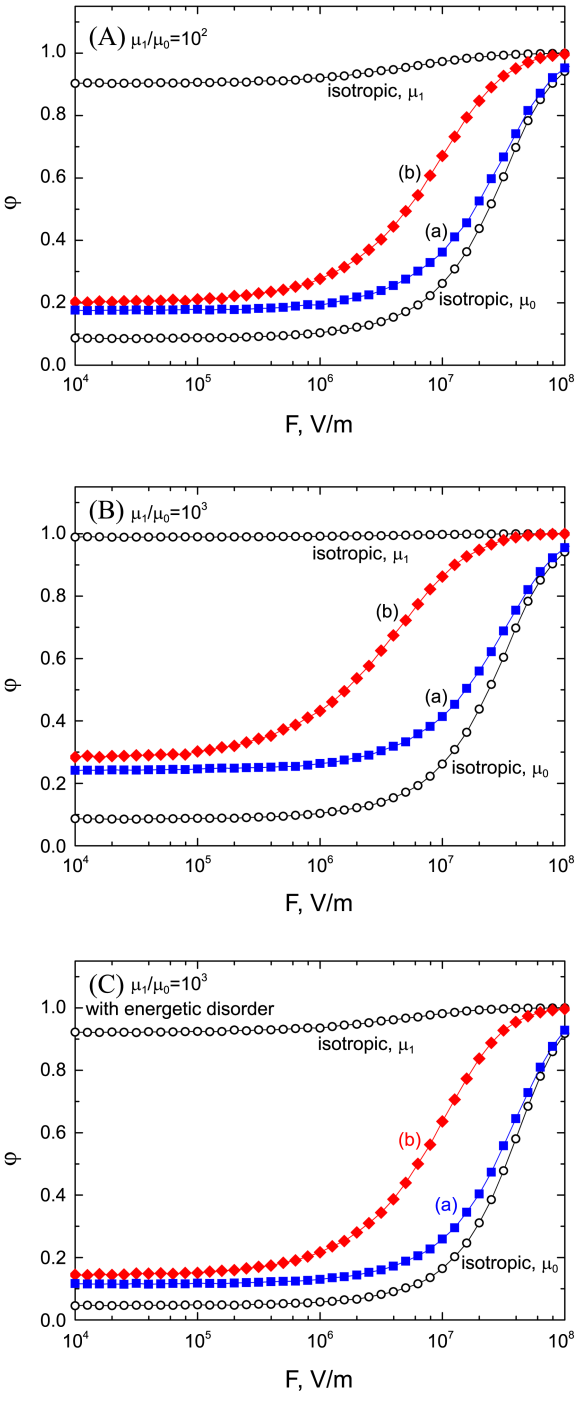

Figure 4. Electric field dependence of the electron-hole separation probability in heterojunction systems. The simulation results obtained for isotropic systems (open symbols, $\mu_e = \mu_h = \mu_0$ or μ_1) and for the systems where the mobility of one charge carrier is anisotropic (closed symbols). The letters (a) and (b) attached to the data correspond to different orientations of the high-mobility axis, as described in the text. (A) $\mu_1 = 5 \times 10^{-6}$ m^2/Vs; (B) $\mu_1 = 5 \times 10^{-5}$ m^2/Vs; (C) $\mu_1 = 5 \times 10^{-5}$ m^2/Vs, an energy disorder included ($\sigma = 0.05$ eV). $\mu_0 = 5 \times 10^{-8}$ m^2/Vs. Other parameters are the same as in Figure 1.

and holes that the charge mobility along one coordinate (μ_1) is much higher than those along the other two coordinates (μ_0). This gives us the following four distinct cases:

case (c): $\mu_h = (\mu_0, \mu_1, \mu_0)$, $\mu_e = (\mu_0, \mu_1, \mu_0)$,
case (d): $\mu_h = (\mu_0, \mu_1, \mu_0)$, $\mu_e = (\mu_0, \mu_0, \mu_1)$,
case (e): $\mu_h = (\mu_0, \mu_1, \mu_0)$, $\mu_e = (\mu_1, \mu_0, \mu_0)$,
case (f): $\mu_h = (\mu_1, \mu_0, \mu_0)$, $\mu_e = (\mu_1, \mu_0, \mu_0)$.

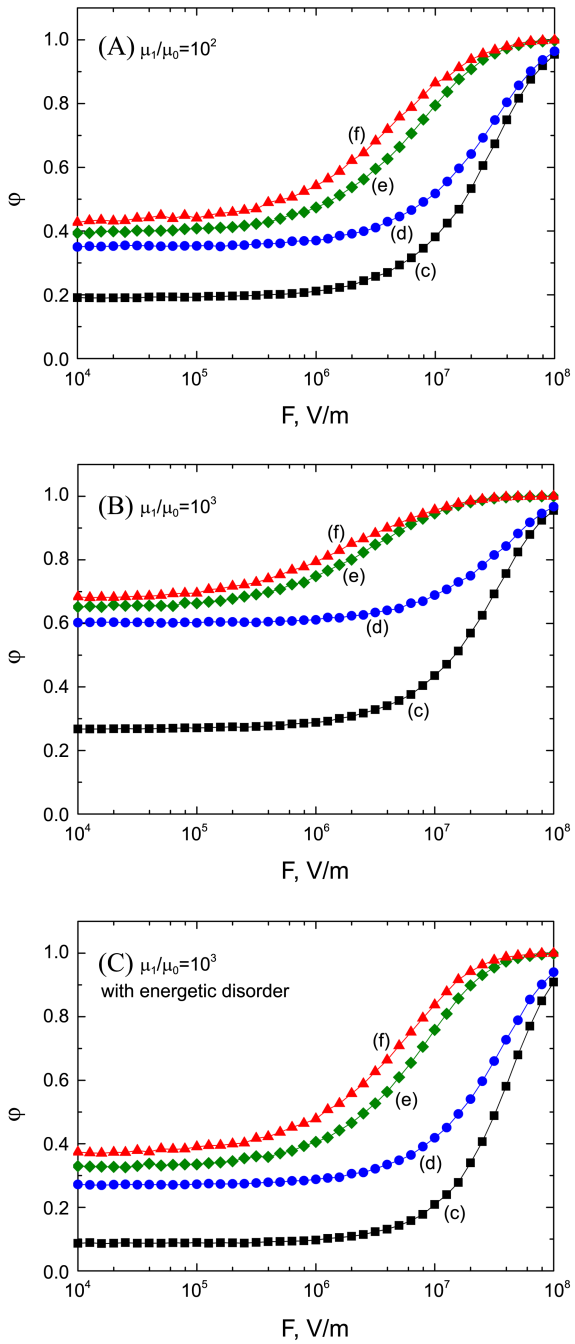

Figure 5. Electric field dependence of the electron-hole separation probability in heterojunction systems where both the electron and hole mobilities are anisotropic. The letters (c)-(f) attached to the data correspond to different orientations of the high-mobility axes, as described in the text. (A) $\mu_1 = 5 \times 10^{-6}$ m^2/Vs; (B) $\mu_1 = 5 \times 10^{-5}$ m^2/Vs; (C) $\mu_1 = 5 \times 10^{-5}$ m^2/Vs, an energy disorder included (σ = 0.05 eV). Other parameters are the same as in Figure 1.

The results of our calculations in cases (c)-(f) for two different degrees of anisotropy, namely, $r_a = 10^2$ and 10^3 are shown in Figures 5(A) and 5(B), respectively. Figure 5(C) shows the corresponding results obtained for the energetically disordered system with $r_a = 10^3$ and $\sigma = 0.05$ eV. The values of the other parameters used are the same as in Figure 4.

We start an analysis of the simulation data presented in Figure 5 by comparing the results obtained when both (case (f)) or one (case (e)) of the electron and the hole has high mobility along the direction perpendicular to the heterojunction. As we can see, the $\varphi(F)$ curve is very similar in these two cases. Although the separation probability in case (e) is slightly lower than in case (f), we may conclude that the applied field separate charge pairs very efficiently in systems in which the high-mobility axis of at least one carrier is oriented perpendicularly to the heterojunction.

When both of the electron and the hole have high mobility along the directions parallel to the heterojunction (curves (c) and (d) in Figure 5), we see that the charge-pair separation probability strongly depends on whether the high-mobility axes are parallel (case (c)) or perpendicular (case (d)) to each other. The values of φ in case (c) are significantly lower than those in case (d) over a wide range of F. At low electric fields, the ratio of the separation probability in case (d) to that in case (c) is about 1.8 and 2.3 for $r_a = 10^2$ and 10^3, respectively. In the presence of energetic disorder, this ratio is even higher and equal to 3.1. The reduced charge-pair separation probability in case (c) compared to case (d) can be explained in the following way. If the high mobility directions of an electron and a hole are parallel, they will have a better chance to meet and in consequence to recombine, compared to the case when their high mobility directions are perpendicular.

When we compare cases (d) and (e), we see that in all panels of Figure 5 the shape of the $\varphi(F)$ curve in case (d) is quite different from that in case (e). At low fields the separation probability in case (d) is only slightly lower than that in case (e). However, the field effect in case (d) is much weaker at low and intermediate electric fields than that in case (e). As a consequence, in case (d) the separation probability starts to increase significantly only at much higher fields than in case (e).

We expect that the progress in materials technology will make it possible in the future to create photovoltaic devices with highly controlled molecular alignment. In this situation our results will give useful guidelines to develop new efficient device architectures. For example, if one can construct a bi-layer device in which one or both layers are made of conductive polymers oriented perpendicularly to the heterojunction, it will achieve high charge-pair separation probabilities. Our theory predicts a strong enhancement of the separation probability in such systems at the field strengths on the order of 10^6-10^7 V/m, which correspond to the typical internal fields in organic photovoltaic cells under short-circuit conditions.[18]

We admit that the lattice simulation model applied here is idealized. Moreover, the geminate electron-hole recombi-

nation studied here is only one of the factors that limit the efficiency of organic solar cells. Light absorption in the cell material, exciton dissociation, charge collection at the electrodes, and other processes also affect the light conversion efficiency, and optimization of one of those processes may have opposing effects on the optimization of other processes.

Conclusions

In this work, we studied the effects of heterojunction, energetic disorder, mobility magnitudes, mobility mismatch, and mobility anisotropy on geminate electron-hole recombination in organic photoconductive systems. We theoretically showed that energetic disorder reduces the charge-pair separation probability both in homogeneous and heterojunction systems. This effect is weaker in heterojunction systems compared to homogeneous systems. As a result, the effect of heterojunction on enhancing the charge-pair separation probability is greater in energetically disordered media in comparison with idealized systems with no energetic disorder. We also showed that mismatch between the electron and hole mobilities decreases the pair separation probability in heterojunction system. However, in the presence of energetic disorder, this effect is not so significant as that in the systems without disorder.

The geminate charge-pair separation probability in heterojunction systems is found to strongly depend on the sum of electron and hole mobilities. As this quantity increases, the separation probability is also increased. An opposite effect is caused by increasing the rate constant of recombination reaction. In consequence, the geminate charge-pair separation probability is determined by the ratio of the sum of electron and hole mobilities to the recombination rate constant.

By studying the effects of mobility anisotropy on geminate electron-hole recombination, we showed that the charge-pair separation probability depends on the orientation of high-mobility axes of electrons and holes with respect to the heterojunction, as well as with respect to each other. A significantly higher separation probability, especially at external fields above 10^6 V/m, is predicted for systems where the high-mobility axis of at least one charge carrier is oriented perpendicularly to the heterojunction.

We hope the results of this work will contribute to better understanding of charge separation processes in photofunctional devices. We also hope that our theoretical predictions, especially those obtained for anisotropic systems, will give useful guidelines for constructing new device architectures and achieving higher efficiencies of organic photovoltaic cells.

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