

Study of the mechanism and rate of exciton dissociation at the donor-acceptor interface in bulk-heterojunction organic solar cells

Monishka Rita Narayan and Jai Singh

Citation: [Journal of Applied Physics](#) **114**, 073510 (2013); doi: 10.1063/1.4818813

View online: <http://dx.doi.org/10.1063/1.4818813>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jap/114/7?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Exciton dissociation at donor-acceptor heterojunctions: Dynamics using the collective effective mode representation of the spin-boson model](#)

J. Chem. Phys. **140**, 044104 (2014); 10.1063/1.4861853

[Dynamic Monte Carlo modeling of exciton dissociation in organic donor-acceptor solar cells](#)

J. Chem. Phys. **137**, 014903 (2012); 10.1063/1.4731698

[Effect of metal cathode reflectance on the exciton-dissociation efficiency in heterojunction organic solar cells](#)

Appl. Phys. Lett. **94**, 103303 (2009); 10.1063/1.3098472

[The dissociation of excitons at indium tin oxide-copper phthalocyanine interface in organic solar cells](#)

J. Appl. Phys. **104**, 103702 (2008); 10.1063/1.3020525

[Exciton dissociation dynamics in model donor-acceptor polymer heterojunctions. I. Energetics and spectra](#)

J. Chem. Phys. **122**, 214719 (2005); 10.1063/1.1924540



AIP | Journal of
Applied Physics

Journal of Applied Physics is pleased to
announce **André Anders** as its new Editor-in-Chief

Study of the mechanism and rate of exciton dissociation at the donor-acceptor interface in bulk-heterojunction organic solar cells

Monishka Rita Narayan¹ and Jai Singh^{2,a)}

¹Centre for Renewable Energy, Research Institute of the Environment and Livelihoods, Charles Darwin University, 0909 Darwin, NT, Australia

²School of Engineering and IT, Charles Darwin University, 0909 Darwin, NT, Australia

(Received 5 June 2013; accepted 2 August 2013; published online 20 August 2013)

In this paper, a comprehensive study is carried out on the dissociation mechanism of excitons in bulk-heterojunction organic solar cells. It is proposed that at the donor-acceptor interface, a Frenkel exciton relaxes to a charge transfer exciton and then dissociates into free charge carriers with the aid of molecular vibrational energy. The interaction operator between the charge transfer exciton and molecular vibrational energy is derived and used to formulate and calculate the rates of dissociation of singlet and triplet excitons into free charge carriers. The dissociation rates are found to be dependent on the binding energy, lowest unoccupied molecular orbital offset between the donor and acceptor, the phonon energy, reduced excitonic mass, excitonic Bohr radius, and the dielectric constant of the organic material. Using the proposed dissociation mechanism, three points have also been highlighted that could provide possible reasons as to why the performance of bulk-heterojunction organic solar cell is low. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4818813>]

I. INTRODUCTION

Research interest in organic solar cells (OSCs) has escalated recently due to their cost effectiveness, easy fabrication techniques, and large scale production.¹ There are various types of OSCs, but the most prominent and successful at present is the bulk-heterojunction OSC.² Here, the donor and acceptor organic materials are mixed together to form an interface.³ In bulk-heterojunction OSCs, the principle processes of operation include: (1) photon absorption and exciton formation,^{4,5} (2) exciton diffusion to the donor-acceptor interface,⁶ (3) exciton dissociation at the interface,⁷ and (4) transport of respective free charge carriers to opposite electrodes.⁸

These four processes are interdependent and contribute to the conversion efficiency of bulk-heterojunction OSCs. If any of the above processes gets hindered, it affects the overall performance of an OSC. This is one of the reasons why the conversion efficiency of OSCs prepared to-date is relatively low (5%–9.2%).^{9–12} When photons are absorbed, the excited electron and hole pairs instantly form excitons due to the higher binding energy, E_B , in organic materials having low dielectric constant ($\epsilon = 3$ –4).^{13–15} After this process, excitons have to be dissociated to form free electrons and holes, a process that is known to occur at the donor-acceptor interface. Thus, after their creations, first the excited excitons are required to diffuse to the interface and then dissociate. Finally, free charge carriers thus created need to be separated and transported to the opposite electrodes. Apparently, only few research efforts have been made in studying these processes in OSCs, systematically.^{16–19} We have recently studied the first two processes of exciton formation^{4,5} and diffusion, theoretically.⁶ However, the third and fourth processes have

not yet been studied explicitly, neither experimentally nor theoretically.

Following the seminal work of Tang *et al.*,¹⁶ it is very well accepted that the exciton dissociation is facilitated by the presence of a donor-acceptor interface in OSCs and most of the OSCs till date are fabricated with such a design. However, the mechanism of exciton dissociation occurring at the interface is not yet understood very well. To the best of our knowledge, no interaction operator between an exciton and a donor-acceptor interface has yet been discovered to dissociate excitons in OSCs. In this study, a time-dependent interaction operator responsible for the dissociation of excitons at the donor-acceptor interface is derived. Using this interaction operator, the rate of exciton dissociation is derived and calculated for the dissociation of singlet and triplet excitons. It is expected that such rates of exciton dissociation may help in understanding the operation of OSCs and improving their photovoltaic performance.

II. MECHANISM OF EXCITON DISSOCIATION AT DONOR-ACCEPTOR INTERFACE

In this section, we have derived a time-dependent exciton-donor acceptor interaction operator responsible for the dissociation of excitons at the interface in bulk-heterojunction OSCs. Considering that the absorption of a photon of energy larger than or equal to the band gap of the donor organic material excites a pair of electron (e) and a hole (h), the electron is excited to the lowest unoccupied molecular orbital (LUMO), leaving a hole in the highest occupied molecular orbital (HOMO). These excited pairs of charge carriers instantly form excitons due to their strong Coulomb interaction caused by the low dielectric constant, ϵ , in organic solids.^{13–15} As the electronic intermolecular interaction is weak in organics, the formation of such excitons is usually of Frenkel type with a

^{a)}Author to whom correspondence should be addressed. Electronic mail: jai.singh@cdu.edu.au

high binding energy, E_B , (0.06–0.80 eV).⁶ The formation of Frenkel excitons in OSCs has been extensively studied in our previous works.^{4–6}

The Hamiltonian of a free Frenkel exciton, \hat{H}_{FE} , is given by²⁰

$$\hat{H}_{FE} = \sum_{n=1}^N E_n B_n^+(S) B_n(S), \quad (1)$$

where $E_n = E_{LUMO} - E_{HOMO} - E_B$ is the exciton's energy, E_{LUMO} is the LUMO energy, and E_{HOMO} is the HOMO energy of the organic donor molecule at site, n . $B_n^+(S)$ and $B_n(S)$ are the exciton creation and annihilation operators, respectively, with spin S and are expressed as

$$B_n^+(S) = \sum_{\sigma_e, \sigma_h} a_{nL}^+(\sigma_e) d_{nH}^+(\sigma_h), \quad (2a)$$

$$B_n(S) = \sum_{\sigma_e, \sigma_h} a_{nL}(\sigma_e) d_{nH}(\sigma_h), \quad (2b)$$

here $a_{nL}^+(a_{nL})$ represents the creation (annihilation) operator of an electron with spin σ_e in the LUMO level and $d_{nH}^+(d_{nH})$ represents the creation (annihilation) operator of a hole with spin σ_h in the HOMO level. The sums over spin in Eq. (2) give rise to a singlet and triplet exciton state, $S = \sigma_e + \sigma_h$, whereby $S=0$ and $S=1$ for a singlet and triplet excitons, respectively.

After its formation, a singlet Frenkel exciton in the donor diffuses via the Förster energy transfer and a triplet exciton through the Dexter transfer mechanism⁶ to the interface and dissociates. Here, we propose that the mechanism of exciton dissociation occurs through two steps: (1) As the energy of acceptor's LUMO is lower than that of donor's LUMO, a Frenkel exciton relaxes first to a charge transfer (CT) exciton state where electron gets transferred to the acceptor's LUMO²¹ as shown in Fig. 1(a). It is to be noted that the CT exciton is not yet dissociated because for dissociation it requires an external energy at least equal to the binding energy.¹⁹ This external energy comes from the excess

vibrational energy released due to the formation of CT exciton. This excess vibrational energy, if adequate, may impact back to the CT exciton causing it to dissociate into free charge carriers as shown in Fig. 1(b). Free electrons, thus generated, are drawn towards the cathode and holes towards the anode due to the potential energy difference caused by the difference in work functions of the two electrodes,^{3,22} which will be discussed later in this study.

In organic solids, the intramolecular vibrations play a more significant role in the exciton dissociation than the intermolecular vibrations due to the larger intermolecular separation. The vibrational Hamiltonian, H_v , in organic solids may be written as²³

$$\hat{H}_v = \sum_{n=1}^N \sum_{v=1}^n \hbar \omega_v (b_{nv}^+ b_{nv} + 1/2), \quad (3)$$

where \hbar is the reduced Planck's constant, ω_v is the phonon frequency, and b_{nv}^+ (b_{nv}) is the phonon creation (annihilation) operator in the vibrational mode, v and N is the number of molecules.

As shown in Fig. 1, the formation of a CT exciton involves emission of phonons at the donor-acceptor interface site, which then impact back to CT exciton and dissociate it into free charge carriers. Following the theory of molecular vibration, the interaction operator, \hat{H}_d , between excitons and phonons can be written as²³

$$\hat{H}_d = \sum_{n=1}^N \sum_{v=1}^n \hbar \omega_v G_v B_n^+(S) B_n(S) (b_{nv}^+ + b_{nv}), \quad (4)$$

where G_v is the exciton-phonon coupling constant, which is a dimensionless linear displacement in the excited state of a molecule associated with the vibrational mode, v and is given by

$$G_v = \sqrt{\frac{\mu_x \omega_v}{2\hbar}} (q_{v0} - q_{00}), \quad (5)$$

where $\mu_x = \frac{m_e m_h}{m_e + m_h}$ is the reduced excitonic mass and m_e and m_h are the free electron and hole masses,⁶ respectively, q_{v0}

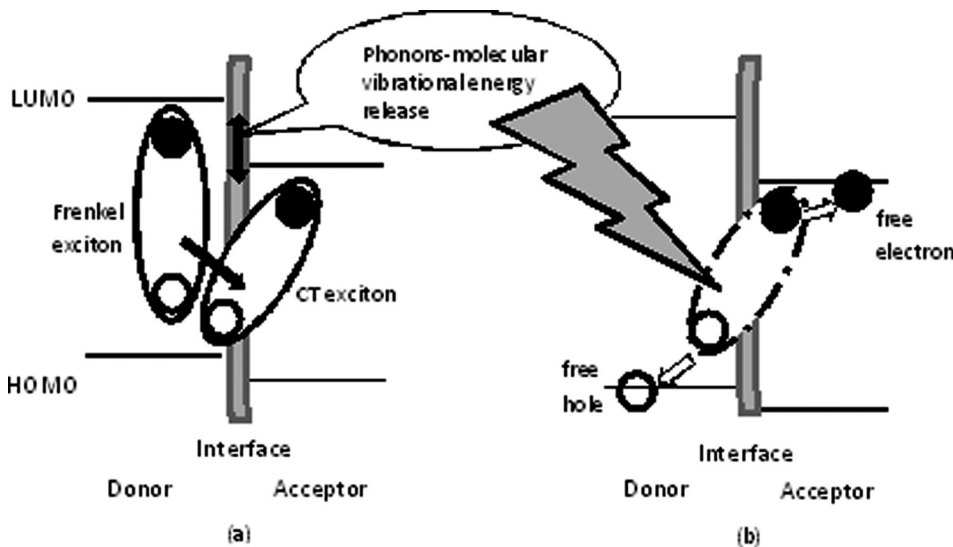


FIG. 1. (a) The Frenkel exciton in the donor relaxes to the CT exciton at the donor-acceptor interface whereby the electron moves to the acceptor LUMO. Molecular vibrational energy in the form of phonons is released when the Frenkel exciton relaxes to the CT state. (b) The excess molecular vibrational energy, thus released, causes the CT exciton to dissociate into free charge carriers. Finally, dissociated electrons move to the cathode and holes to the anode due to the potential energy difference provided by the difference in work functions of the two electrodes.

denotes the displacement associated with the ν th vibrational mode by which a molecule gets shifted when excited from HOMO to LUMO and q_{oo} is the equilibrium position in the ground state along the dimensionless coordinate, λ , which is given by $\lambda = (q_{vo} - q_{oo})\sqrt{\mu_x\omega/2\hbar}$ as shown in Fig. 2.²³

Substituting Eq. (2) into Eq. (4), \hat{H}_d is obtained as

$$\hat{H}_d = \sum_{g,h,i,j,k,\nu_2} \sum_{\sigma_1,\sigma_2,\sigma_3,\sigma_4} \hbar\omega_{kv_2} G_{\nu_2} a_{gL_2}^+(\sigma_1) d_{hH_2}^+(\sigma_2) a_{iL_2}^+ \times (\sigma_3) d_{jH_2}^+(\sigma_4) (b_{kv_2}^+ + b_{kv_2}). \quad (6)$$

For the dissociation of an exciton at the donor-acceptor interface in a bulk-heterojunction OSC, the initial state, $|i\rangle$, can be considered to consist of a CT exciton and a phonon, and the final state, $|f\rangle$, consists of dissociated free electron and hole. Thus, the initial state can be expressed as²⁴

$$|i\rangle = N^{-3/2} \sum_{\ell,m,n} \sum_{\sigma_e,\sigma_h,\nu} a_{\ell L}^+(\sigma_e) d_{mH}^+(\sigma_h) b_{n\nu}^+ |0; \nu\rangle, \quad (7)$$

where the electron is created at a site ℓ of the acceptor's LUMO, L and hole at the site m of the donor's HOMO, H , and $|0; \nu\rangle = |0\rangle|v\rangle$, where $|0\rangle$ represents the electronic vacuum state with the LUMO completely empty and HOMO completely full and $|v\rangle$ represents the occupation of the vibration state. And the final state can be written as

$$|f\rangle = N^{-3/2} \sum_{\ell_1,m_1} \sum_{\sigma'_e,\sigma'_h,\nu_1} a_{\ell_1 L_1}^+(\sigma'_e) d_{m_1 H_1}^+(\sigma'_h) |0; \nu_1\rangle, \quad (8)$$

where the electron is created at site ℓ_1 of LUMO, L_1 of the acceptor molecule and hole at site m_1 of HOMO, H_1 of the donor molecule.

Using Eqs. (6)–(8), the transition matrix element is obtained as

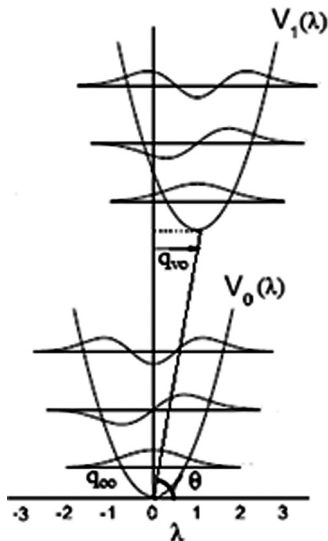


FIG. 2. Schematic energy diagram for the vibrational potentials of ground (V_o) and excited (V_i) state along the dimensionless coordinate, λ . The excited state potential is displaced on the λ -axis by q_{vo} .²³

$$\langle f | H_d | i \rangle = N^{-1} \sum_n \hbar\omega_{nv} G_{\nu} n_{\nu}, \quad (9)$$

where n_{ν} is the number of phonons required to dissociate a CT exciton.

Using Fermi's Golden Rule, the rate of exciton dissociation, R_d , can be expressed as⁴

$$R_d = \frac{2\pi}{\hbar} |\langle f | H_d | i \rangle|^2 \delta(E_f - E_i + \hbar\omega), \quad (10)$$

where E_i is the initial energy and E_f is the final energy of the dissociation process at the donor (D) and acceptor (A) interface, which can be expressed as

$$E_i = E_{LUMO}^D = E_{LUMO}^A + n_{\nu} \hbar\omega \quad (11)$$

and

$$E_f = E_{LUMO}^A + E_B + n_1 \hbar\omega, \quad (12)$$

where ($n_1 \geq 0$) is the remaining number of phonons after dissociation of the CT excitons.

Substituting Eqs. (9), (11), and (12) into Eq. (10), we get R_d as

$$R_d = \frac{2\pi}{\hbar E_B} \sum_{n_1} (\hbar\omega)^2 n_{\nu}^2 G_{\nu}^2 \delta\left(1 - (n_{\nu} - n_1) \frac{\hbar\omega_{\nu}}{E_B}\right). \quad (13)$$

Using $(n_{\nu} - n_1) \frac{\hbar\omega_{\nu}}{E_B} = 1$ within Eq. (13), we get $n_1 = n_{\nu} - \frac{E_B}{\hbar\omega_{\nu}}$, and then the rate, R_d , becomes

$$R_d = \frac{2\pi(\hbar\omega_{\nu})^2}{\hbar E_B} G_{\nu}^2 \left(n_{\nu} - \frac{E_B}{\hbar\omega_{\nu}}\right)^2. \quad (14)$$

In Fig. 2, $q_{vo} - q_{oo} = r \cos\theta$, where r is the average separation between an e and h in a CT exciton before its dissociation. Using this in Eq. (5) and integrating over the whole solid angle, $d\Omega = \cos\theta d\theta d\phi$, we get

$$(q_{vo} - q_{oo})^2 = r^2 \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \int_0^{2\pi} \cos^2\theta \cos\theta d\theta d\phi = \frac{8\pi}{3} r^2, \quad (15)$$

where the average separation, r , can be written in terms of excitonic Bohr radius, a_x as $r = a_x/\epsilon$.⁶

Substituting Eqs. (5) and (15) in Eq. (14), we get R_d as

$$R_d = \frac{2\pi}{\hbar E_B} (n_{\nu} \hbar\omega_{\nu} - E_B)^2 \frac{\mu_x \omega_{\nu}}{2\hbar} \frac{8\pi}{3} \left(\frac{a_x}{\epsilon}\right)^2. \quad (16)$$

Finally, substituting Eq. (11) into Eq. (16), R_d in bulk-heterojunction OSCs is obtained as

$$R_d = \frac{8\pi^2}{3\hbar^3 \epsilon^2 E_B} [(E_{LUMO}^D - E_{LUMO}^A) - E_B]^2 (\hbar\omega_{\nu}) \mu_x a_x^2 \quad (17)$$

provided $(E_{LUMO}^D - E_{LUMO}^A) \geq E_B$. The advantage of obtaining the rate of dissociation in the above form is that all

quantities can be estimated from the known parameters of materials used as donor and acceptor in bulk-heterojunction OSCs.

III. RESULTS AND DISCUSSIONS

From the rate derived in Eq. (17), the dissociation of a Frenkel exciton into free charge carriers at the interface of any pair of donor and acceptor can be calculated in bulk-heterojunction OSCs. According to Eq. (17), the exciton dissociation rate depends on the binding energy of an exciton, LUMO offset between donor and acceptor, molecular vibrational energy produced when the Frenkel exciton relaxes to CT exciton, reduced excitonic mass, excitonic Bohr radius, and the dielectric constant of the donor material. The inverse of the rate in Eq. (17) gives the time of dissociation of a Frenkel exciton into free charge carriers: $\tau_d = (R_d)^{-1}$. Thus, the rate and time of dissociation of a Frenkel exciton can be calculated for any LUMO offset between the donor and acceptor provided $(E_{LUMO}^D - E_{LUMO}^A) > E_B$.

In this study, we have proposed that upon light absorption in a bulk-heterojunction OSC, a Frenkel exciton (either singlet or triplet type) is formed in the donor. It may then diffuse to the donor-acceptor interface⁶ and relax to a CT exciton because the LUMO of the acceptor is at a lower energy. The excess molecular vibrational energy thus generated is released in the form of phonons, which can be transferred back to the CT exciton thus formed to dissociate it into free charge carriers. However, it is important to note that dissociation can only occur if the excess molecular vibrational energy is greater than or equal to the exciton binding energy.

As singlet and triplet excitons have different binding energies and excitonic Bohr radius, different rates and times of dissociation will be obtained, respectively. Using Eq. (17), the rate, R_d^S and time, τ_d^S (where the superscript *S* denotes singlet) of dissociation for singlet exciton can be calculated if E_B^S , μ_x , a_x^S , and ϵ are known. For organic semiconductors, R_d^S and time, τ_d^S have been calculated using the

following known input parameters:⁶ $E_B^S = 0.059$ eV, $\mu_x = 4.66 \times 10^{-31}$ kg, $a_x^S = 4.352$ nm, and $\epsilon = 3$. These input parameters are calculated for a few organic materials used for fabricating OSCs elsewhere.⁶ The calculated rate and time of dissociation of singlet excitons are plotted as a function of the LUMO offset in Fig. 3.

We have also calculated the corresponding triplet exciton dissociation rate, R_d^T and time, τ_d^T (where the superscript *T* denotes triplet) in organic semiconductors, using $E_B^T = 0.759$ eV and $a_x^T = 0.317$ nm.⁶ Other parameters remain the same as for the case of singlet excitons. These rates and times of dissociation for a triplet exciton are plotted as a function of the LUMO offset in Fig. 4.

According to Figs. 3 and 4, the time of dissociation of both singlet and triplet excitons decreases and the corresponding rate increases, with increasing LUMO offset between the donor and acceptor. This is because a higher LUMO offset means a higher excess energy is available to overcome the exciton binding energy and hence a quicker dissociation is expected. The rate of dissociation of a singlet exciton is about three orders of magnitude faster than that of a triplet exciton. For example, at an offset of 0.10 eV, the rate of singlet exciton dissociation is $1.84 \times 10^{15} \text{ s}^{-1}$ and the corresponding dissociation time is $0.54 \times 10^{-15} \text{ s}$ (less than 1 fs). While for a triplet exciton, at 0.80 eV offset, the rate of dissociation is $6.08 \times 10^{12} \text{ s}^{-1}$ and the corresponding time is $0.16 \times 10^{-12} \text{ s}$ (less than 1 ps). The dissociation time of a singlet exciton agrees very well with experimental results.^{25,26} However, the underlying question arises that if the rate of singlet and triplet exciton dissociations is so high, then why the conversion efficiencies of bulk-heterojunction OSCs obtained so far are limited to 5%–9.2%, experimentally?^{9–12} An attempt is made to answer this question below.

On the experimental side, the LUMO offset in bulk-heterojunction OSCs vary from 0.3 to 0.5 eV.^{27–29} In the case of triplet exciton, dissociation can only commence at an offset of ≥ 0.759 eV. Hence, a triplet exciton cannot be dissociated at such an experimentally available offset and hence

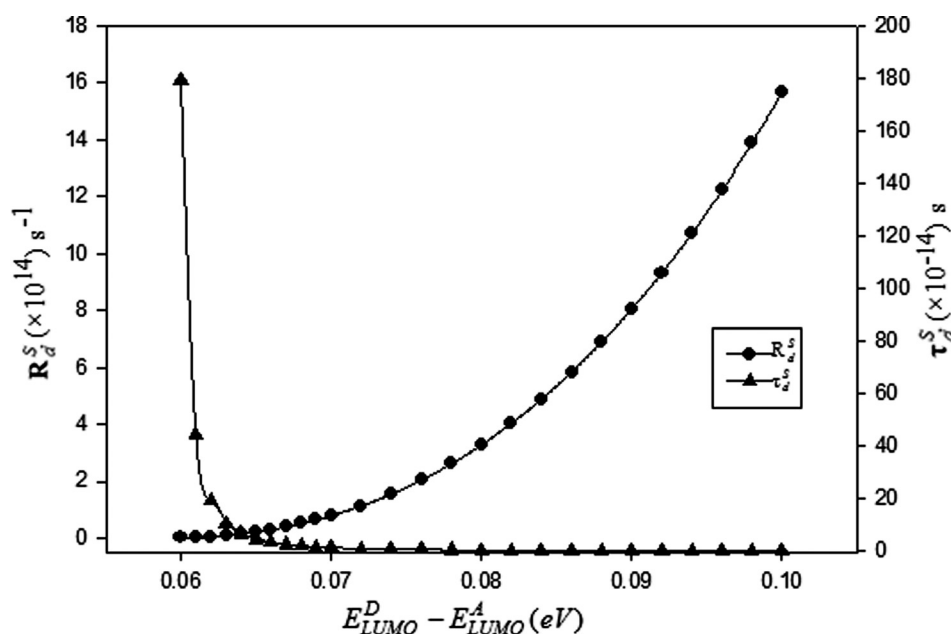


FIG. 3. The rate, R_d^S , [Eq. (17)] and time, τ_d^S , of dissociation of a singlet exciton as plotted as a function of LUMO offset between donor and acceptor, $(E_{LUMO}^D - E_{LUMO}^A)$ in a bulk-heterojunction OSC.

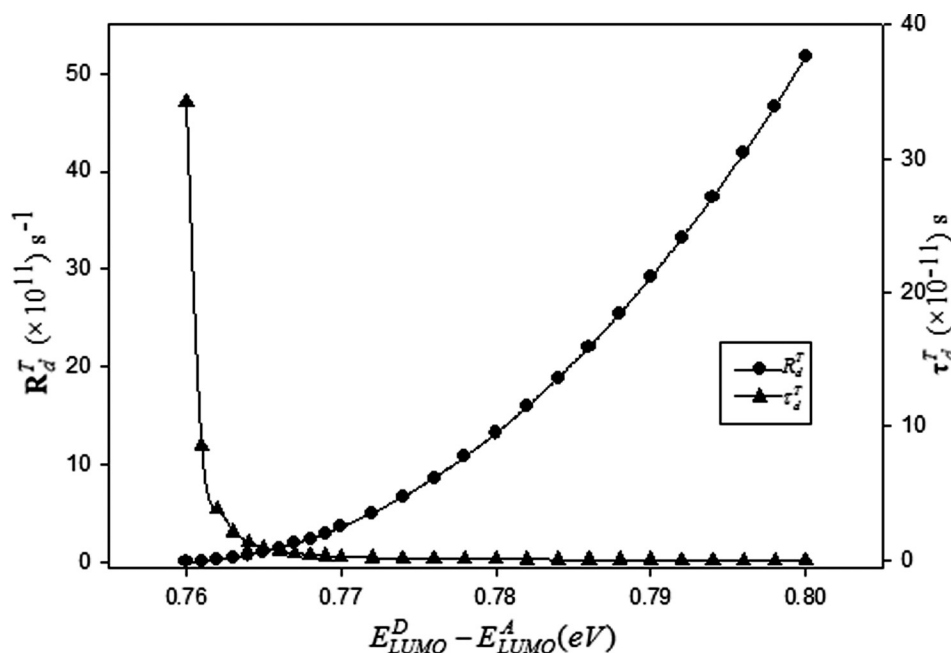


FIG. 4. The rate, R_d^T , [Eq. (17)] and time, τ_d^T , of dissociation of a triplet exciton as plotted as a function of LUMO offset between donor and acceptor, $(E_{LUMO}^D - E_{LUMO}^A)$ in a bulk-heterojunction OSC.

cannot contribute to the photovoltaic performance of bulk-heterojunction OSCs.

Comparing the formation of singlet and triplet excitons in OSCs with that in the organic light emitting devices (OLEDs), where electrons and holes are injected from the opposite electrodes, one may think that it is more probable to create triplet excitons than singlet excitons. This is because statistically, on average, the formation of triplet excitons in OLEDs is three times more probable than singlet excitons.^{30–32} As the triplet exciton energies are lower, one may expect to excite more triplets than singlets. This implies that unless one can dissociate triplet excitons in OSCs, more than half of the absorbed energy may be lost through triplet excitons. It is to be noted that triplet excitons cannot also recombine radiatively due to spin restrictions and cannot dissociate due to insufficient LUMO offset. Hence, they may lose their energy through non-radiative recombinations.

One of the possibilities of such loss may be due to the creation of high density triplet excitons within a thin film to enable them to interact with each other and dissociate non-radiatively. In our previous study, it has been found out that in triplet excitation, incorporation of heavy metal atom enhances the rate of absorption of triplet excitons due to the enhanced spin-orbit-interaction which flips the spin to a singlet form. This leads to a faster dissociation of triplet excitons and hence an overall enhancement in the conversion efficiency of organic solar cells.⁵

In addition, contributing to the loss of energy due to high density triplet excitons, there are other possibilities as well which need to be considered. These are due to three different inefficient processes: (1) transport of created excitons towards the interface, (2) transfer of vibrational energy back to CT for its dissociation, and (3) transport of dissociated charge carriers to opposite electrodes. Impact of these three possibilities on the performance of an OSC is discussed below:

(1) Inefficient transfer of excitons to the donor-acceptor interface

An exciton created by the absorption of a solar photon is an electrically neutral entity as electron and hole are bound together through Coulomb interaction. An exciton created at a molecule can move in any direction of outward solid angle, Ω . Considering the fractional solid angle, $d\Omega = \sin\theta d\theta d\varphi$, we get the whole solid angle as $\int d\Omega = 4\pi$. This means that the probability of an exciton created at a molecule to move to any one particular direction is $1/4\pi$. If this molecule is next to the interface then the transfer should be multiplied by $1/4\pi$. However, if this interface is a few molecules away from the excited molecule, the rate of transfer should be multiplied by $1/4\pi$ at each such molecular step. Thus, the probability that an exciton created n molecules away from the interface will reach the interface becomes $(1/4\pi)^n$. As $4\pi > 10$, the farther the exciton is from the interface, much less is the probability that it will reach the interface to form a CT exciton. This basically means that every single step away from the interface will reduce the probability by at least one order of magnitude.

From this analysis, one may conclude that the only efficient way of ensuring that an exciton reaches the interface is that each donor molecule must be next to an acceptor molecule. If the fabrication is based on solution method, this implies that in a heterojunction OSC, donor-acceptor concentration should be equal (1:1).

(2) Inefficient transfer of vibrational energy back to CT exciton for dissociation

When an exciton from a donor molecule converts itself to a CT exciton by transferring its electron to an acceptor molecule, the excess energy released will excite molecular vibrations. This vibrational energy can be dissipated in any direction from the excited molecule. The probability that it will be transferred back to the CT exciton to dissociate it is only one of the possible directions of a solid angle. Therefore, the transition matrix element of dissociation [Eq. (9)] of excitons must be multiplied by $1/4\pi$. This means that the rate of dissociation reduces by a factor of $(1/4\pi)^2$,

which is nearly three orders of magnitude less than that obtained from Eq. (17) and hence the dissociation time will be longer by three orders of magnitude.

(3) Inefficient transport of free charge carriers to opposite electrodes

After the dissociation of an exciton, free charge carriers are drawn to the opposite electrodes, solely by the difference between the ionisation potential of the anode and the electron affinity of the cathode. The potential difference due to the work functions, ϕ (in eV) between the anode and cathode is given as: $\Delta V = \phi_a - \phi_c$, where ϕ_a and ϕ_c are the work functions of the anode and cathode, respectively. The force, F , required for a charge carrier to be drawn towards the electrode is given as

$$F = \frac{\phi_a - \phi_c}{r}, \quad (18)$$

where r is the inter-electrode distance. In bulk-heterojunction OSCs, normally ITO is used as the anode, $\phi_{ITO} = 4.7$ eV (Ref. 33) and aluminium (Al) as the cathode, $\phi_{Al} = 4.3$ eV (Ref. 34), which provides $\Delta V = 0.4$ eV. The inter-electrode distance is around 100 nm (Ref. 35) and using Eq. (18), the effective force for charge diffusion to the electrode is $F = 0.64$ pN. According to Eq. (18), in order to enhance the force for charge diffusion to the electrodes, the potential difference should be larger and the inter-electrode distance should be smaller. Hence, calcium (Ca), $\phi_{Ca} = 2.9$ eV (Ref. 36) and caesium (Cs), $\phi_{Cs} = 2.1$ eV may be employed as potential cathodes to enhance the potential difference to strengthen the force. The charge mobilities should also be high for efficient charge diffusion to the electrodes.

Furthermore, the exciton dissociation rate in Eq. (17) can also be postulated for bulk-heterojunction hybrid OSCs. These OSCs are similar to bulk-heterojunction OSCs but the acceptor material is usually an inorganic semiconductor such as cadmium selenide, zinc oxide, and titanium oxide.^{37–39} In bulk-heterojunction hybrid OSCs, blends of the inorganic nanoparticles are mixed with the organic polymer to form an active layer.⁴⁰ The inorganic semiconductor nanoparticles provide the advantages of high absorption coefficients and tuning ability of the optical band-gap and electron affinity to the nanoparticle size.⁴¹ The rate of exciton dissociation in a bulk-heterojunction hybrid OSC can be written as

$$R_d = \frac{8\pi^2}{3\hbar^3 \epsilon^2 E_B} [(E_{LUMO}^D - E_{CB}^A) - E_B]^2 (\hbar\omega_v) \mu_x a_x^2, \quad (19)$$

where E_{CB}^A is the energy level at the conduction band of the inorganic acceptor material. Other parameters remain the same as in Eq. (17). This dissociation rate can be modeled for various organic donor and inorganic acceptor materials.

IV. CONCLUSIONS

A time-dependent interaction operator for the dissociation of an exciton into free charge carriers in bulk-heterojunction OSCs has been derived. It is proposed that at the donor-acceptor interface, the molecular vibrational energy generated when a Frenkel exciton relaxes to a charge

transfer exciton provides the excess energy for the self-dissociation of the charge transfer exciton into free charge carriers. For such a mechanism of dissociation, the rate of dissociation of a Frenkel exciton into free charge carriers is derived, which depends on the LUMO offset between the donor and acceptor, molecular vibrational energy, reduced excitonic mass, binding energy, dielectric constant, and the excitonic Bohr radius.

For a bulk-heterojunction OSC, increasing the LUMO offset between the donor and acceptor may lead to faster dissociation of both singlet and triplet excitons and hence may enhance the conversion efficiency. However, despite the dissociation rate being very fast, the conversion efficiency is still low. Possible reasons for this are inefficient transport of created excitons towards the interface, transfer of vibrational energy back to CT for its dissociation, and transport of dissociated charge carriers to opposite electrodes. The exciton dissociation rate is also postulated for bulk-heterojunction hybrid OSCs.

- ¹N. Yeh and P. Yeh, *Renewable Sustainable Energy Rev.* **21**, 421 (2013).
- ²M. T. Dang, L. Hirsch, and G. Wantz, *Adv. Mater.* **23**, 3597 (2011).
- ³I. Bruder, thesis, Max-Planck-Institut für Festkörperforschung, 2010.
- ⁴M. R. Narayan and J. Singh, *Eur. Phys. J. B* **86**, 1 (2013).
- ⁵M. R. Narayan and J. Singh, "Effect of simultaneous excitation of both singlet and triplet excitons on the operation of organic solar cells," *J. Chem. Phys.* (unpublished).
- ⁶M. R. Narayan and J. Singh, *Phys. Status Solidi C* **9**, 2386 (2012).
- ⁷K. Tvingstedt, K. Vandewal, F. Zhang, and O. Inganäs, *J. Phys. Chem. C* **114**, 21824 (2010).
- ⁸C.-W. Chu, V. Shrotriya, G. Li, and Y. Yang, *Appl. Phys. Lett.* **88**, 153504 (2006).
- ⁹W. Cai, X. Gong, and Y. Cao, *Sol. Energy Mater. Sol. Cells* **94**, 114 (2010).
- ¹⁰G. Zhao, Y. He, and Y. Li, *Adv. Mater.* **22**, 4355 (2010).
- ¹¹Y. Liang, D. Feng, Y. Wu, S.-T. Tsai, G. Li, C. Ray, and L. Yu, *J. Am. Chem. Soc.* **131**, 7792 (2009).
- ¹²Z. He, C. Zhong, S. Su, M. Xu, H. Wu, and Y. Cao, *Nat. Photonics* **6**, 593 (2012).
- ¹³J. Roncali, *Acc. Chem. Res.* **42**, 1719 (2009).
- ¹⁴B. Kippelen and J. L. Brédas, *Energy Environ. Sci.* **2**, 251 (2009).
- ¹⁵J. L. Brédas, J. E. Norton, J. Cornil, and V. Coropceanu, *Acc. Chem. Res.* **42**, 1691 (2009).
- ¹⁶C. Tang, *Appl. Phys. Lett.* **48**, 183 (1986).
- ¹⁷Y. Liang, Z. Xu, J. Xia, S. T. Tsai, Y. Wu, G. Li, C. Ray, and L. Yu, *Adv. Mater.* **22**, E135 (2010).
- ¹⁸H. Ohkita and S. Ito, *Polymer* **52**, 4397 (2011).
- ¹⁹M. C. Scharber, D. Mühlbacher, M. Koppe, P. Denk, C. Waldauf, A. J. Heeger, and C. J. Brabec, *Adv. Mater.* **18**, 789 (2006).
- ²⁰S. M. Sze, *Semiconductor Devices: Physics and Technology* (John Wiley & Sons, New York, 2008).
- ²¹X.-Y. Zhu, Q. Yang, and M. Muntwiler, *Acc. Chem. Res.* **42**, 1779 (2009).
- ²²M. J. Kendrick, A. Neunzert, M. M. Payne, B. Purushothaman, B. D. Rose, J. E. Anthony, M. M. Haley, and O. Ostroverkhova, *J. Phys. Chem. C* **116**, 18108 (2012).
- ²³J. Knoester and V. M. Agranovich, *Frenkel and Charge-Transfer Excitons in Organic Solids* (Academic Press, 2003), Vol. 31.
- ²⁴P. L. Taylor, *A Quantum Approach to the Solid State* (Prentice-Hall, 1970).
- ²⁵R. Mauer, thesis, Johannes Gutenberg-University Mainz, 2012.
- ²⁶L. Koster, E. Smits, V. Mihailetschi, and P. Blom, *Phys. Rev. B* **72**, 085205 (2005).
- ²⁷L. Koster, V. Mihailetschi, and P. Blom, *Appl. Phys. Lett.* **88**, 093511 (2006).
- ²⁸M. Lenes, G. J. A. Wetzelaer, F. B. Kooistra, S. C. Veenstra, J. C. Hummelen, and P. W. Blom, *Adv. Mater.* **20**, 2116 (2008).
- ²⁹J. D. Servaites, M. A. Ratner, and T. J. Marks, *Appl. Phys. Lett.* **95**, 163302 (2009).

- ³⁰J. Singh, *Phys. Status Solidi C* **7**, 984 (2010).
- ³¹J. Singh, *Excitation Energy Transfer Processes in Condensed Matter: Theory and Applications* (Plenum Press, 1994).
- ³²J. Singh, *Phys. Rev. B* **76**, 085205 (2007).
- ³³J. S. Kim, J. H. Park, J. H. Lee, J. Jo, D.-Y. Kim, and K. Cho, *Appl. Phys. Lett.* **91**, 112111 (2007).
- ³⁴S. Gunes, H. Neugebauer, and N. S. Sariciftci, *Chem. Rev.* **107**, 1324 (2007).
- ³⁵A. J. Moulé, J. B. Bonekamp, and K. Meerholz, *J. Appl. Phys.* **100**, 094503 (2006).
- ³⁶R. Friend, R. Gymer, A. Holmes, J. Burroughes, R. Marks, C. Taliani, D. Bradley, D. Dos Santos, J. Bredas, and M. Lögdlund, *Nature* **397**, 121 (1999).
- ³⁷J. Weickert, R. B. Dunbar, H. C. Hesse, W. Wiedemann, and L. Schmidt-Mende, *Adv. Mater.* **23**, 1810 (2011).
- ³⁸Y. Zhou, M. Eck, and M. Krüger, *Organic-Inorganic Hybrid Solar Cells: State of the Art, Challenges and Perspectives* (Intech, 2011).
- ³⁹M. Wright and A. Uddin, *Sol. Energy Mater. Sol. Cells* **107**, 87 (2012).
- ⁴⁰E. Arici, N. S. Sariciftci, and D. Meissner, *Encyclopedia Nanosci. Nanotechnol.* **3**, 929 (2004).
- ⁴¹S. Günes and N. S. Sariciftci, *Inorg. Chim. Acta* **361**, 581 (2008).