



Migration of an exciton in organic polymers driven by a nonuniform internal electric field



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ARTICLE INFO

Article history:

Received 31 October 2015

Received in revised form

3 December 2015

Accepted 14 December 2015

Available online xxx

Keywords:

Polymer photovoltaic devices

Exciton migration

Nonuniform electric fields

ABSTRACT

Migration of excitons is of vital importance for the photovoltaic process in polymer-based donor/acceptor (D/A) photovoltaic system. Due to the existence of some trapping charges as well as the mismatch of energy levels at the D/A heterointerface, there will exist a nonuniform internal electric field, which may induce the migration or dissociation of an exciton or charge transfer state generated near the interface. In this work, by choosing the nonuniform internal electric field as a linear gradient form, we theoretically simulate the migration dynamics of an exciton in a polymer. It is found that the exciton will be polarized under the electric field. Especially, the polarized positive and negative charges in the exciton lie in different electric fields, which will induce a net force driving the exciton to migrate. Effects of some factors, such as the electron-phonon (e-ph) coupling, on the exciton migration are analyzed. This research reveals a new exciton migration mechanism in polymer-based D/A photovoltaic system, which might be timely for further understanding their photovoltaic process, and thus provide a new strategy to optimize the photovoltaic efficiency of the devices.

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1. Introduction

Due to the semiconductor-like properties and ease of processing, conjugated polymers have become one of the most promising materials in photoelectric applications [1,2]. Up to now, polymer-based light emitting diodes have been commercially available, and polymer-based solar cells also made a breakthrough in the practical application. Considering the photovoltaic process in a polymer solar cell with a donor/acceptor (D/A) heterojunction structure, exciton migration plays a crucial role, which determines the final working efficiency [3]. It is known that, in polymers, due to the strong electron-phonon (e-ph) coupling, strongly bound electron-hole pairs or excitons are primarily created in these materials after photon absorption [4]. As the generated exciton is energetically instable, it must reach the D/A interface through interchain hopping [5,6] or intrachain migration [7] within its lifetime. As such, the exciton can be dissociated by the driving force induced by the interface potential and then provide photocurrent [8–11]. Therefore, the mechanism or method of exciton migration plays an important role in improving the efficiency of polymer solar

cells.

As we know, most of researchers consider that exciton migration in organic materials behaves in the form of diffusion [1,3,8,12–16]. For example, Samiullah et al. performed an experimental technique to estimate the diffusion length of excitons in a ladder-type conjugated organic semiconductor [12]. They found that the diffusion length is consistent with that obtained by a phenomenological random walk model. Markov et al. studied the exciton diffusion process in a poly(*p*-phenylene vinylene) based derivative and found that the result is in agreement with the theoretical simulation with an exciton diffusion constant $3 \times 10^{-4} \text{cm}^2/\text{s}$ [1]. Besides, Sun et al. studied the collision between a polaron and a triplet exciton in conjugated polymers based on a tight-binding model combined with a nonadiabatic evolution method [17]. They showed that the polaron can push the triplet exciton to move together under a certain uniform electric field. In inorganic devices, another exciton migration mechanism was experimentally reported by Gärtner et al. [18]. They applied a resistive top gate to coupled GaAs quantum wells, in which an in-plane gradient electric field is generated. Interestingly, they found a migration of the exciton towards regions of high electric fields. If there also exists a gradient electric field in organic polymers, how will the exciton behave? As stated above, in actual polymer solar cells, excitons will be dissociated at D/A heterointerfaces and result

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in the formation of free charge carriers. However, at interfaces there will inevitably exist some trapping charges, which induce many local nonuniform electric fields along polymers [19]. Moreover, due to the energy mismatch between the D/A materials, it will induce a potential barrier and consequently make the electric field to be nonuniform near the interface.

For simplicity, we regard the local nonuniform electric field near a D/A interface as a linear gradient form along a polymer chain. Then, we will study the migration dynamics of an exciton in such a system. By this work, we try to find some internal mechanisms for an electrically neutral exciton to migrate along or between polymer chains to improve its migration length, and consequently optimize the efficiency of polymer solar cells. Our model is presented in the following section. The results and discussion are presented in Section 3. Finally in Section 4, a conclusion is given.

2. Model and method

We consider a single polymer chain with a linear gradient electric field included. Such a system can be described by an extended version of the well known Su-Schrieffer-Heeger (SSH) model [20], in which the strong e-ph coupling in polymers is emphasized. The Hamiltonian can be written as

$$H = H_{el} + H_{la} + H_E. \quad (1)$$

H_{el} describes the electron transfer between sites,

$$H_{el} = - \sum_n t_{n,n+1} (C_{n+1}^+ C_n + C_n^+ C_{n+1}), \quad (2)$$

where $t_{n,n+1} = t_0 - \alpha(u_{n+1} - u_n) - (-1)^n t_e$. t_0 is the transfer integral of π -electrons for an undimerized lattice, α the e-ph coupling constant, and u_n the lattice displacement of the n -th site from its equidistant position. t_e is the symmetry-breaking term, determined by the energy difference of the two phases in a polymer with a nondegenerate ground state. The operator C_n^+ (C_n) creates (annihilates) a π -electron at the n -th site, in which the spin index is omitted.

The second term H_{la} in Eq. (1) shows the elastic potential and kinetic energy of a site, which is described classically in the following form

$$H_{la} = \frac{1}{2} K \sum_n (u_{n+1} - u_n)^2 + \frac{1}{2} M \sum_n \dot{u}_n^2. \quad (3)$$

K is the elastic constant between neighboring sites, and M the mass of a site.

The third term H_E in Eq. (1) represents the contribution of the linear gradient electric field to the system,

$$H_E = \frac{e}{2} \sum_n E_n (na + u_n) (C_n^+ C_n - 1). \quad (4)$$

e indicates the electronic charge, a the lattice constant, and E_n shows the electric field value on the n -th site, that is,

$$E_n = w \cdot (na + u_n). \quad (5)$$

Here, we choose the linear coefficient w as a negative value ($w < 0$), and the direction of the internal electric field is consequently from right to left along the polymer chain.

Thus, once an exciton is instantaneously photogenerated in the polymer chain, the internal electric field E_n will induce it to experience an evolution. In the dynamical simulations, we employ a nonadiabatic evolution method similar to Refs. [17,21], in which

evolution of the electronic wave functions $\psi_\mu(n,t)$ can be described by the time-dependent Schrödinger equation,

$$i\hbar \dot{\psi}_\mu(n,t) = -t_{n-1,n} \psi_\mu(n-1,t) - t_{n,n+1} \psi_\mu(n+1,t) + \frac{1}{2} e E_n (na + u_n) \psi_\mu(n,t). \quad (6)$$

Evolution of the lattice u_n is classically described and governed by the Newtonian equation of motion [22–27],

$$M \ddot{u}_n = K(u_{n+1} + u_{n-1} - 2u_n) + 2\alpha[\rho_{n,n+1}(t) - \rho_{n-1,n}(t)] - e E_n [\rho_{n,n}(t) - 1] - \lambda M \dot{u}_n, \quad (7)$$

where the density matrix $\rho_{n,n'}$ ($n' = n \pm 1$) is defined as

$$\rho_{n,n'}(t) = \sum_\nu \psi_\nu^*(n,t) \psi_\nu(n',t). \quad (8)$$

In addition, to describe the energy dissipation into the surrounding medium during the evolution process, we introduce in Eq. (7) a damping term by a tuning parameter λ [27]. The coupled differential Eqs. (6) and (7) are solved by the Runge-Kutta method of order eight with step-size control, which has been widely used and proven to be an effective approach in the study of dynamic processes in conjugated polymers [22,27–30].

The parameters used here are chosen as those generally used for *cis*-polyacetylene, that is, $t_0 = 2.5$ eV, $\alpha = 4.1$ eV/Å, $K = 21.0$ eV/Å², $M = 1349.14$ eV·fs²/Å², $a = 1.22$ Å, $t_e = 0.05$ eV, and $\lambda = 0.05$ fs⁻¹ [31]. Despite all this, the results are expected to be qualitatively valid for other conjugated polymers.

3. Results and discussion

We choose a polymer chain with a length of 150 sites as our model system. At beginning, we suppose that an exciton has formed in the chain, centered at the 50-th site. In a uniform electric field, the exciton will keep its position unchanged, but can be polarized or dissociated [11,32–34], which is dependent on the field strength. However, if the exciton lies in a nonuniform electric field, such as the linear form of Eq. (5), the situation might be much different. Here, we only focus on the dynamical behavior of the exciton under a nonuniform electric field before its dissociation. As such, we set the gradient constant of the nonuniform electric field in the order of $\sim 10^{-5}$ V/Å² to make sure that the field strength on the right end of the polymer chain keeps $\sim 10^{-3}$ V/Å, which is weaker than the excitonic dissociating field ($\sim 10^{-2}$ V/Å or $\sim 10^6$ V/cm [33]). As shown in Fig. 1, evolution of the exciton in the polymer chain is presented, where we give its evolution by the lattice configuration $y_n = (-1)^n (2u_n - u_{n+1} - u_{n-1})/4$, and the gradient constant of the electric field is chosen as $w = -3.0 \times 10^{-5}$ V/Å². It is found that, the exciton begins to migrate from its initial position to the right direction of the polymer chain. At about $t = 20$ ps, the exciton center reaches the 6

3-th site. Thus, the average migration speed of the exciton governed by the gradient electric field is about $v = 0.78$ Å/ps, comparable to the results reported by some experimental works [3,16].

Now, let us focus on the exciton migration mechanism. As stated above, an exciton will be polarized under an electric field [32–34]. Therefore, we firstly calculate the instantaneous net charge distribution q_n [$q_n(t) = \rho_{n,n}(t) - 1$] at $t = 0.5$ ps, as shown by the black solid line in Fig. 2. We can see that there appears an apparent polarization for the exciton, in which the polarized positive charges Q and negative charges $-Q$ are separately distributed on the left and right

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