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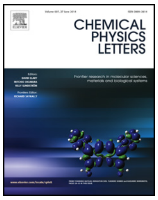

Trap-assisted charge transport at conjugated polymer interfaces

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ABSTRACT

The trap-assisted charge transport in conjugated polymers is numerically investigated in the framework of a one-dimensional tight-binding model. Our findings show that a polaron trapped within an interchain region can be released migrating between the chains at low temperature regimes. Conversely, a trapped bipolaron cannot be released even considering high temperature values. Interestingly, for systems containing more than one polaron, the formation of trapped states is avoided and there is no charge transfer between the chains. Considering more than one bipolaron, the generation of trapped states occurs and a bipolaron can migrates between the chains.

1. Introduction

Bulk heterojunction organic photovoltaics have emerged in the past few years as the most promising solution to the development of new green energy applications [1–3]. Advantages such as malleability, low cost, light-weight, and low environmental impact make these materials interesting for industrial applications. One of the key issue in this photovoltaic technology is to enhance the charge transport efficiency between molecular segments [4,5]. Particularly, trap states are recognized as one of the properties which can limit the charge transport in organic conductors and hence the performance of photovoltaic applications [6]. Therefore, investigations regarding the influence of trap states on the charge transport mechanism are essential to broaden understanding the photovoltaic devices based on organic materials.

Recently, relevant experimental studies have been employed to investigate the influence of trapped states on the charge transport mechanism in organic photovoltaics [7–10]. Behrends and colleagues have investigated the bipolaron formation in organic solar cells and its influence on charge transport [9]. They have pointed out a physical picture consistent with a mechanism called trap-mediated isoenergetic hopping. In this mechanism, when a mobile polaron finds a trapped polaron in the heterojunction (interfacial region), a bonded polaron pair may be formed. Depending on the relative spin orientation of both structures, the mobile polaron may or may not jump to the site of the trapped polaron to form a bipolaron. Once the hopping mechanism occurs along the direction of the applied electric field, it increases the net current. On the other hand, if a mobile polaron encounters a doubly occupied bipolaron state, and both are similar in energy, the isoenergetic hopping can occur. Their results show a very interesting trait in the organic solar cell operation: after optical generation of an exciton and its subsequent dissociation into two oppositely charged polarons, the polarons are transported toward the electrodes. If a polaron encounters another trapped polaron, with same charge signal and parallel spin configuration, the transport channel involving bipolaron formation is avoided, so hindering charge transport to the electrode, and hence lowering the efficiency of the solar cell.

Once one of the fundamental traits in the photovoltaic operation is the charge transport between molecular segments, the intermolecular polaron transport has been extensively investigated at atomic [11–17] and molecular scales [18–23] in the framework of tight-binding methodologies. Johansson and Stafstrom have studied the polaron dynamics in a system composed of coupled conjugated polymer chains in the presence of an external electric field [14]. The objective was to describe how a polaron can migrate between polymer chains. Their results indicated that there are three possible channels for the polaron migration: (a) considering field strengths smaller than 0.8 mV/Å, the polaron moves with constant velocity through the chain, but with considerably small energy to jump over to another neighboring chain, remaining stuck at the end of the first chain; (b) for field strengths ranging from 1.0 to 3.0 mV/Å, the polaron moves along the chain in which is

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initially located, jumps over to the neighboring chain, and keep its motion similarly as on the first chain; (c) for field strengths higher than 3.0 mV/Å, the polaron is dissociated, either before or after the chain jump. For these field regimes the charge transport cannot be described by polaron motion. Importantly, their results show that tight-binding approaches can successfully predict the charge transport mechanism in systems formed by interfaces of organic conductors. Nevertheless, a theoretical description which considers the influence of trap states on the charge transport mechanism in these materials is lacking in the literature, which needs of further investigations.

In this work, the trap-assisted charge transport in conjugated polymers is numerically investigated in the scope of a one-dimensional tight-binding model, which includes lattice relaxation. An Ehrenfest Molecular Dynamics is performed using a modified version of the Su–Schrieffer–Heeger (SSH) model [24,25] which considers the influence of an external electric field, temperature effects, and interchain interactions. The present study is aimed to provide a physical picture about the charge transport mechanism in conjugated polymer interfaces when the presence of trap states is considered, which may enlighten the understanding of this fundamental process in the operation of bulk heterojunction organic photovoltaics.

2. Methodology

The system used here to investigate the influence of trap states on charge transport at organic interfaces is composed by two conjugate polymer chains [26] containing 80 sites each one. In this arrangement, the last 20 sites of the first chain are interacting with the first 20 sites of the second chain. It is important to do so in order to realize the polaron dynamics toward the interfacial region and subsequent trap state formation within the interaction region. In this way, the model Hamiltonian is given by $H = H_{elec} + H_{latt}$. The first term of the Hamiltonian H states the electronic part of the system, which describes the intra- and inter-chain interactions and includes an external electric field and the Brazovskii–Kirova symmetry-breaking [27]

$$\begin{aligned} H_{elec} = & -\sum_{n,s} t_{j,n,s}(C^{\dagger}_{j,n+1,s}C_{j,n,s} + h \cdot c) \\ & -\sum_{n,s}^{l} t_{inter}(C^{\dagger}_{1,n,s}C_{2,n,s} + C^{\dagger}_{2,n,s}C_{1,n,s}). \end{aligned} \tag{1}$$

The index j establishes the chain whereas n runs over the sites of a particular chain. The operator $C^{\dagger}_{j,n,s}$ ($C_{j,n,s}$) creates (annihilates) a π-electron with spin s at the nth site. $t_{n,n+1}$ represents the transfer integral given by $t_{n,n+1} = e^{-i\gamma A(t)}[(1+(-1)^n\delta_0)t_0 - \alpha y_n]$, where t_0 is the transfer integral of a π-electron between nearest neighbor sites in the undimerized chain, δ_0 is the symmetry-breaking term introduced in order to lift the ground-state degeneracy for non-degenerated polymers, α is the strength of the electron-lattice interaction, and y_n is the relative displacement coordinate defined as $y_n \equiv u_{n+1} - u_n$, where u_n is the displacement of an atom at the nth site. $\gamma \equiv ea/(\hbar c)$, where e is the absolute value of the electronic charge, a is the lattice constant, and c is the speed of light. The external electric field $\mathbf{E}(t)$ is taken into account by means of time-dependent vector potential $\mathbf{A}(t)$, where $\mathbf{E}(t) = -(1/c)\dot{\mathbf{A}}(t)$. The two chains are coupled using an interchain interaction term, the last part in H_{elec}, where t_{inter} is the inter-chain hopping integral of a π-electron between pairs of nearest ($t_{\perp}$) or next nearest (t_d) neighboring sites in opposite chains, according represented in Figure 1. The index l refers to the total number of sites which couple the two chains.

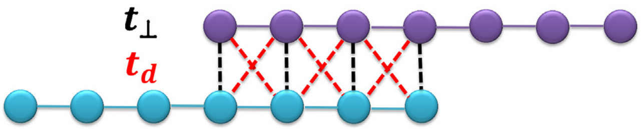

Figure 1. Schematic representation of the inter-chain interactions.

The term H_{latt} of our Hamiltonian model describes the lattice backbone, which is treated classically:

$$H_{latt} = \frac{K}{2}\sum_{i}(u_{i+1} - u_i)^2 + \frac{M}{2}\sum_{i}\dot{u}_i^2, \tag{2}$$

where K is the harmonic constant, which describes a σ bond, and M is the mass of a CH group. The index i runs over the sites of both chains. The parameters implemented here are those commonly used to describe a polyacetylene lattice [28–34]: $t_0 = 2.5$ eV, $t_{\perp} = 0.1$ eV, $t_d = 0.05$ eV, $M = 1349.14$ eV × fs^2/Å^2, $K = 21$ eV Å^{-2}, $\delta_0 = 0.05$, $\alpha = 4.1$ eV Å^{-1}, $a = 1.22$ Å, and a bare optical phonon energy $\hbar\omega_Q = \hbar\sqrt{4K/M} = 0.16\,\text{eV}$.

The initial electronic and lattice configurations for the polymer chains are obtained by solving self-consistent equations for y_n and the electronic wave functions [35]. The time evolution of the system is performed by means of the Ehrenfest Molecular Dynamics, in which the lattice dynamics is carried out classically using the Euler–Lagrange equations and the wave functions are obtained by solving the time-dependent Schrödinger equation [35]. The temperature effects are taken into account using the Langevin equation with a white stochastic signal, as the fluctuation term, and a dissipation term included in order to keep the temperature constant after a transient period, according to described in Ref. [35].

3. Results

In order to investigate the trap-assisted charge transport in coupled conjugated polymer chains, we carried out a systematic numerical investigation considering the influence of an external electric field, interchain interactions, temperature, and the interaction between free charge carriers (with same signal) on this process. It is worth emphasizing that the two polaron have parallel spin configuration in order to prevent the bipolaron formation. It is well known that two acoustic polarons, with same charge and parallel spins, may recombine into a bipolaronic state [36]. Once the present study is aimed to characterize the possible channels for the interchain charge transport considering pairs of same structures (polarons and bipolarons), the recombination process should be avoided. In the first moment, we discuss the temperature influence on the detrapping process of polarons and bipolarons. Subsequently, we present the impact of the interaction between trap states and free charge carriers on the charge transport mechanism. For the sake of clarity, we performed the analysis using the temporal evolution of the mean charge density

$$\bar{\rho}(t) = 1 - [\rho_{n-1}(t) + 2\rho_n(t) + \rho_{n+1}(t)]/4, \tag{3}$$

where we have used the rgb color scheme to depict the polaron dynamics whereas the bipolaron dynamics is depicted using the hot color scheme. It is worth to mention here that the sites of the first chain are labeled from 1 to 80 whereas the sites of the second chain are indexed from 81 to 160.

For the sake of validation of the present model, we begin our discussion by present the field included polaron dynamics in a single polymer chain with 300 sites and periodic boundary conditions. In order to do so, Figure 2 depicts the polaron dynamics, at zero temperature, for electric field strengths raging from 0.5 to 2.5 mV/Åwith increment of 0.5 mV/Å. Figure 2a presents the results for the polaron trajectory. The polaron position is obtained