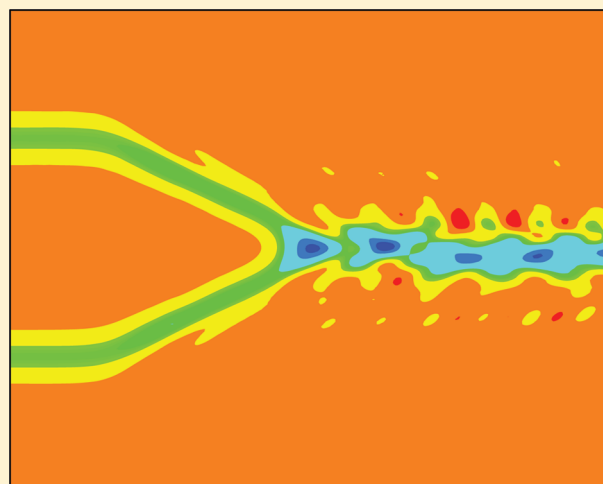


# Formation and Evolution Dynamics of Bipolarons in Conjugated Polymers

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**ABSTRACT:** Combining the one-dimensional tight-binding Su–Schrieffer–Heeger (SSH) model and the extended Hubbard model (EHM), we analyze the scattering and combination in conjugated polymers of two polarons with the same charges and parallel or antiparallel spins using a nonadiabatic evolution method. Results show that collisions between the two same charge polarons with parallel spin are essentially elastic due to strong Pauli repulsion, whereas the two same charge polarons with antiparallel spins can combine into a singlet bipolaronic state. The dynamics of bipolarons on two coupled polymer chains and at the interface of a polymer/polymer heterojunction are discussed in detail. This knowledge will serve to understand the dynamics of the system when many polarons are created in the system, e.g., by electroluminescence.



## ■ INTRODUCTION

The discovery of electroluminescence in conjugated polymer thin films has opened a new chapter in the story of devices based on polymer light-emitting diodes (PLEDs).<sup>1–3</sup> Generally, the quantum efficiency for electroluminescence in PLEDs is taken to be the ratio of the number of emitted photons to the number of emissive singlet excitons. If exciton combination in PLEDs is a spin-independent process, the maximum quantum efficiency of the PLEDs is limited to 25%.<sup>4</sup> In order to break the limitation of 25%, there have been many experiments which have attempted to improve the quantum efficiency, and the results of these experiments have shown that some organic electroluminescence efficiencies can reach 22–60%.<sup>5–9</sup> On the theoretical side, there have been extensive investigations to identify the physical principles leading to improvement of the efficiencies. For example, our previous research shows that the yield of the neutral excitons which are formed by oppositely charged polarons colliding and combining depends sensitively on the strength of the applied fields.<sup>10</sup> The collision between a positive polaron and a neutral triplet exciton can then induce the exciton to emit light and the maximum quantum efficiency of the PLEDs can reach about 61.6%.<sup>11</sup>

In contrast to self-localized electron states called spin-bearing polarons (spin 1/2, charge  $\pm|e|$ ),<sup>12</sup> bipolarons (spinless species, charge  $\pm 2|e|$ ) are also charge carriers generated upon doping or photoexcitation in organic semiconductors especially in highly conjugated conducting polymers. The bipolarons are important because they can scatter into a singlet biexcitonic state which can decay to the ground state by radiating two photons. A number of experimental and theoretical studies have shown the existence of bipolarons especially in doped polymers.<sup>13–15</sup> The formation,

stability, and dynamical evolution of polarons and bipolarons have been simulated by many researchers. For example, bipolarons can be created in organic LEDs where charge injection results in a large concentration of polarons.<sup>16</sup> The charges injected from a metal electrode into a nondegenerate polymer chain can favor the formation of electron (hole) bipolarons which have better stability than two polarons.<sup>17</sup> Two acoustic polarons with the same charges and antiparallel spins can also combine with each other to form an acoustic bipolaron.<sup>18</sup> The stability of a bipolaron is a function of the strength of the Coulomb electron–electron interactions and the electron–phonon coupling. It has been shown that the energies of two isolated polarons are greater than that of one bipolaron, so a bipolaron is energetically more stable than a separated pair of polarons for weak electron–electron interactions.<sup>19,20</sup> The conversion of polarons to bipolarons<sup>21</sup> and the propagation of a moving charged bipolaron<sup>22</sup> have also been studied numerically on a single conjugated polymeric chain, and our previous research has shown that interactions of a bipolaron–exciton pair and/or a polaron–bipolaron pair open channels that enhance the quantum efficiency of electroluminescence.<sup>23,24</sup> Based on this previous work, it can be verified that the bipolaron, like the polaron, is a common type of self-localized excitation that plays an important role in conjugated polymers.

In the actual materials used in PLEDs, it has been found that a multiple-layer polymer structure can remarkably improve the performance of PLEDs.<sup>6,25,26</sup> In addition, such a structure can balance electron and hole injection. The behavior of polarons at

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the polymer/polymer heterojunction interface is believed to play an important role in PLEDs. Our previous results<sup>27</sup> suggest that the charged polaron can either migrate through the interface or be blocked at the interface, due to the potential barrier, depending on the parameters used in the calculation. Subsequently, blocked polarons can meet and collide at the interface between the two polymers. Moreover, studies<sup>28</sup> have also shown that for low fields, when the polaron reaches the region where the coupled conjugated polymer chains interact, the polaron can get stuck at the end of first chain. However, at slightly higher field strengths, the polaron oscillates and remains at the end of the first chain for some time and then jumps over to the second chain. These previous results therefore imply that polarons have a certain probability to meet and collide in the region of coupled polymer chains and/or at the polymer/polymer heterojunction interface, with the result that bipolarons can be created in organic LEDs whenever charge injection results in a large concentration of polarons.

In this work, combining the SSH and EHM models, we focus on investigating, using a nonadiabatic evolution method, whether the collision of two electron-polarons will result in an electron-bipolaron on an isolated single polymer chain, on coupled polymer chains, or at the interface of a polymer/polymer heterojunction structure. We also study whether or not the electron-bipolarons can be blocked in the overlapping region of coupled polymer chains and/or at the interface of polymer/polymer heterojunction structures. The results are also valid for the formation and evolution dynamics of hole-bipolarons in conjugated polymers. In this way, we are able to gain a basic understanding of the formation of bipolarons as well as the dynamical properties of systems with many polarons and/or bipolarons. These results are also expected to be helpful in future work on the scattering and combination of oppositely charged bipolarons. Stable oppositely charged bipolarons states can be scattered into a singlet biexcitonic state, and the formation of these biexcitons must be taken into account to understand the experimental observation of the high internal quantum efficiency (60%)<sup>9</sup> observed in PLEDs. The formation and dynamics of bipolarons and other charged excitations will therefore be important for designing PLEDs with higher electroluminescent efficiency in future work.

## MODEL AND NUMERICAL METHOD

In our simulations, the electrons are treated by solving the time-dependent Schrödinger equation with transitions between instantaneous eigenstates, while the lattice is described classically.<sup>29–31</sup> The Hamiltonian of an isolated single polymer chain is given as

$$H = H_e + H_{\text{ext}} + H_{\text{latt}} = \sum_{n,n',s} c_{n,s}^\dagger h_{nn'}^s c_{n',s} + H_{\text{latt}} \quad (1)$$

where  $h_{nn'}^s$  accounts for both the electron term and the contribution from the applied electric field. The electron part includes both the electron–phonon interaction<sup>12</sup> with a Brazoskii–Kirova-type symmetry-breaking term<sup>2</sup> and the electron–electron interactions<sup>32,33</sup>

$$\begin{aligned} H_e = & - \sum_{n,s} [t_n + (-1)^n t_e] (c_{n+1,s}^\dagger c_{n,s} + \text{hc}) \\ & + \frac{U}{2} \sum_{n,s} \left( c_{n,s}^\dagger c_{n,s} - \frac{1}{2} \right) \left( c_{n,-s}^\dagger c_{n,-s} - \frac{1}{2} \right) \\ & + V \sum_{n,s,s'} \left( c_{n,s}^\dagger c_{n,s'} - \frac{1}{2} \right) \left( c_{n+1,s'}^\dagger c_{n+1,s} - \frac{1}{2} \right) \quad (2) \end{aligned}$$

where  $t_n = t_0 - \alpha(u_{n+1} - u_n)$  with  $t_0$  being the transfer integral of  $\pi$ -electrons in a regular lattice,  $\alpha$  is the electron–lattice coupling constant, and  $u_n$  is the lattice displacement of the  $n$ th site from its equidistant position. The quantity  $t_e$  is introduced to lift the ground-state degeneracy for nondegenerate polymers. The operator  $c_n^\dagger$  ( $c_n$ ) creates (annihilates) a  $\pi$ -electron at the  $n$ th site.  $U$  gives the strength of the on-site Coulomb interactions and  $V$  gives that of the nearest-neighbor interactions. In this paper, these extended-Hubbard-type interactions are treated within the unrestricted Hartree–Fock approximation.<sup>18</sup>

The applied electric field contribution to the Hamiltonian is

$$H_{\text{ext}} = |e| \sum_{n,s} (na + u_n) \left( c_{n,s}^\dagger c_{n,s} - \frac{1}{2} \right) E(t) \quad (3)$$

where  $e$  is the electron charge and  $a$  the lattice constant. The applied field  $E(t)$  is half Gaussian/constant<sup>28</sup> with an amplitude  $E_0$  centered around  $t_c = 75$  fs and a width of  $t_w = 25$  fs.

The Hamiltonian of the lattice is described classically by

$$H_{\text{latt}} = \frac{1}{2} K \sum_n (u_{n+1} - u_n)^2 + \frac{1}{2} M \sum_n \dot{u}_n^2 \quad (4)$$

where<sup>12</sup>  $K$  is the elastic constant and  $M$  is the mass of a CH group. Though the model parameters are those generally chosen for polyacetylene:  $t_0 = 2.5$  eV,  $\alpha = 4.1$  eV/Å,  $t_e = 0.05$  eV,  $K = 21.0$  eV/Å<sup>2</sup>,  $M = 1349.14$  eV fs<sup>2</sup>/Å<sup>2</sup>, and  $a = 1.22$  Å, the results are expected to be qualitatively valid for other conjugated polymers with nondegenerate ground states. Since the electron–phonon interaction is dominant for the tight-binding electron–phonon interaction model,<sup>29</sup> it is expected that our results should be valid in any system with weak electron–electron interactions which are set here to be  $U = V = 0.5$  eV.

The initial bond configuration and electron structure can be obtained by solving the self-consistent equations of the bond configuration  $\{u_n\}$  and all electron wave functions  $\{\phi_k^i(n)\}$ . Once  $\{u_n\}$  and  $\{\phi_k^i(n)\}$  are determined, the temporal evolution of the lattice configuration is determined by the equation of motion for the atom displacements

$$\begin{aligned} M\ddot{u}_n(t) = & -K[2u_n(t) - u_{n+1}(t) - u_{n-1}(t)] \\ & + 2\alpha \sum_s [\rho_{n,n+1}^s(t) - \rho_{n,n-1}^s(t)] \\ & + |e|E(t) \sum_s \left[ \rho_{n,n}^s(t) - \frac{1}{2} \right] \quad (5) \end{aligned}$$

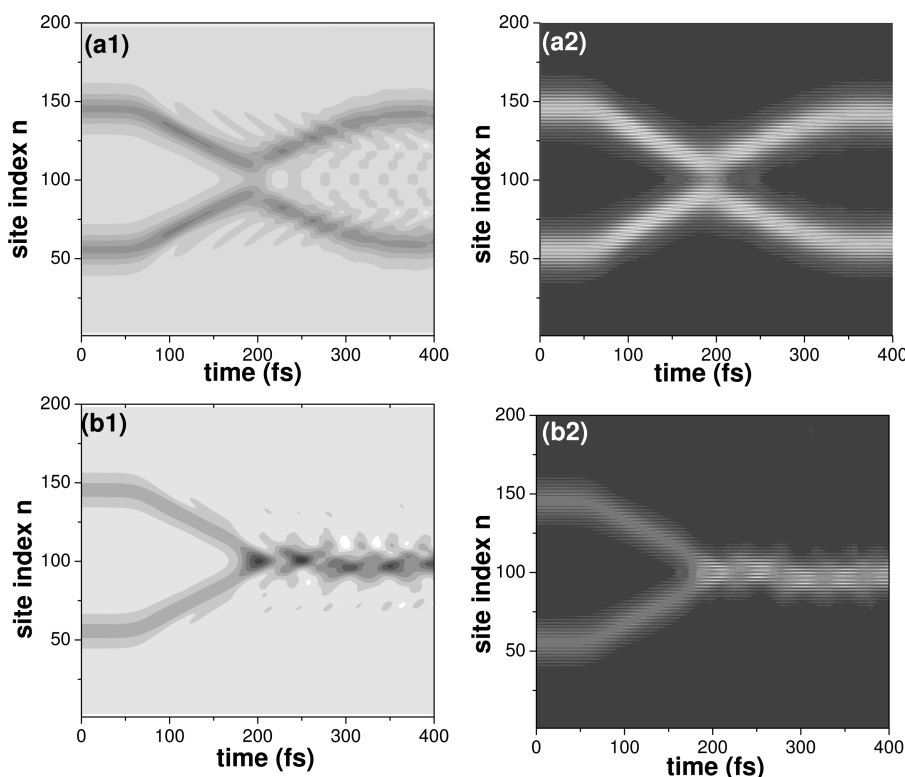
where  $\rho_{n,n'}^s(t) = \sum_k \psi_k^{s*}(n,t) f_{k,s} \psi_k^s(n',t)$ , and  $f_{k,s}$  ( $=0,1$ ) is the time-independent distribution function and is determined by the initial state. The electron wave functions  $\psi_k^s(n,t)$  are the solutions of the time-dependent Schrödinger equation

$$i\hbar \dot{\psi}_k^s(n,t) = \sum_{n'} h_{nn'}^s \psi_k^s(n',t) \quad (6)$$

The coupled differential eqs 5 and 6 are solved using the same technique as in refs 28, 33, and 34, i.e., the Runge–Kutta method of order 8 with step-size control, which has been proven to be an effective approach for investigating polaron and bipolaron dynamics in conjugated polymers.

## RESULTS AND DISCUSSION

**Collision between Two Polarons with Parallel or Antiparallel Spins on an Isolated Single Polymer Chain.** In this



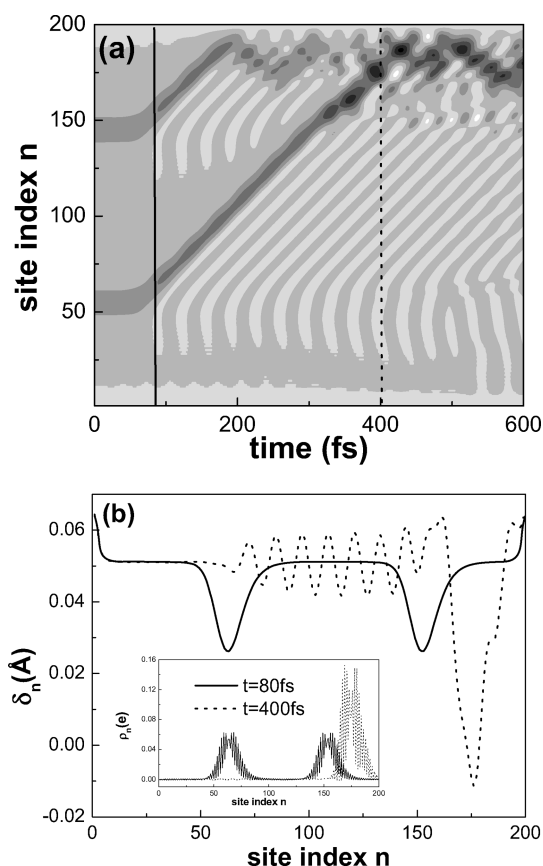
**Figure 1.** Evolution of the staggered bond order parameter distribution  $\delta_n$  (left column) and the charge distribution  $\rho_n$  (right column) between two electron-polarons with parallel and antiparallel spins for an intermediate electric field strength,  $E_0 = 1.5$  mV/Å: (a) two electron-polarons with parallel spin; (b) two electron-polarons with antiparallel spins.

section, we consider a polymer chain with a total of 200 sites which contains two electron-polarons, one near each end of the chain. This polymer chain is long enough to contain two independent polarons and to eliminate chain-end effects. Since our purpose here is to study the interactions of polarons, we use an electric field to launch each polaron and then turn the field off when the polarons have reached a constant velocity. To this end, we subject each of the two polarons to electric fields pointing in opposite directions. When the external electric fields turn on, the two polarons approach each other and then collide. Before their collision, the motion of the polarons is the same as that reported in ref 33; that is, each polaron moves as one entity consisting of both charge and lattice defect.

First, we describe the scattering processes for a pair of polarons with parallel spins. The dynamical evolution of the staggered bond order parameter  $\delta_n \equiv (-1)^n(2u_n - u_{n+1} - u_{n-1})/4$  and the charge distribution  $\rho_n$  are shown in Figure 1. We have carried out similar calculations by changing  $E$  from 0.05 to 4.5 mV/Å and found the effect of the  $E$  is only to vary the relative velocity between the polarons before collision. With the electric field in this direction mode, the two polarons approach each other. When two polarons reach constant velocities at about 100 fs, the electric field is turned off. Figure 1a suggests that the repulsive interaction between two polarons with parallel spin is predominantly determined by the Pauli exclusion principle and the effect of the interaction between charges. The Pauli exclusion force is so strong that there is no chance for the two quasi-particles to be unified. This means that the collision should be almost elastic. Changes in the electric field strength and other parameters show that these collisions are always reflective and that the two quasi-particles

never pass through each other. We have observed no case where unification of the two quasi-particles was realized.

Second, it is interesting to investigate the collision of two polarons with antiparallel spin orientations. We have obtained results for cases where the oppositely oriented electric field strengths varied from 0.05 to 6.0 mV/Å, and all results show that two isolated polarons can form a bipolaron. For example, Figure 1b shows results for the case of an intermediate electric field  $E_0 = 1.5$  mV/Å. The results can be understood in the following way. When two polarons with antiparallel spins approach each other, now without the Pauli exclusion effect, if the strength of the Coulomb repulsion between the electrons of the two polarons is smaller than the strength of the attractive interaction between the two polarons, i.e., the values of  $U$  and  $V$ , and the magnitudes of the electric fields are suitable for forming a stable state, they will combine with each other to form a bipolaron, at least temporarily. Since the lattice distortions involved in a polaron and in a bipolaron are quite different, and the energies of two isolated polarons are greater than that of a bipolaron, two isolated polarons can approach and possibly form a bipolaron. Lattice displacements accompanying the formation of a bipolaron-like distortion will cause excitations of lattice vibrational modes (phonons) which can be emitted to the region outside the bipolaron, thus carrying away the excess energy. Thus, two colliding polarons which form a potential bipolaron lattice distortion can lose energy through transfer to a phonon. To illustrate the situation clearly, Figure 1b2 shows the charge distribution  $\rho_n$  of the collision process corresponding to the staggered bond order parameter distribution  $\delta_n$  shown in Figure 1b1. It can be seen that the charge distribution  $\rho_n$  is an excitation which includes two



**Figure 2.** Dynamics of two electron-polarons with antiparallel spins combining into an electron-bipolaron at the end of an isolated single polymer chain for  $E_0 = 1.5$  mV/Å: (a) evolution of the staggered bond order parameter distribution  $\delta_n$ ; (b) staggered bond order parameter  $\delta_n$  and the charge distribution  $\rho_n$  (inset) before and after the collision.

electrons and  $\delta_n$  represents a bipolaron lattice distortion after the collision.

There is another type of behavior that can be seen in the collision between two polarons on an isolated single polymer chain. In this case, when the electric field (its direction is from the right to the left) turns on, the two polarons both move to the end of chain and then collide driven by the applied electric field. The staggered bond order parameter  $\delta_n$  and the charge distribution  $\rho_n$  (inset) before and after the collision are shown in Figure 2. It can be seen that a polaron arrives at the end of the chain at about 180 fs, and then oscillates back and forth at the end under the electric field until the other polaron also arrives at about 350 fs. The two polarons then meet and finally form a bipolaron. The inset of Figure 2b shows the change of the total charge in different segments. From the inset, one can see that the electron charges are initially independent. After the collision, the total charge is that of a bipolaron, in which two electrons are trapped. The reason for their collision resulting in a stable bipolaron is the same that for Figure 1b.

**Formation and Dynamics of Bipolarons on Two Coupled Polymer Chains.** In the previous section, the dynamical properties of two polarons with antiparallel spins merging into a bipolaron on an isolated single polymer chain were considered when the interchain interactions were completely ignored. In fact, although the interchain interactions between the polymer chains are weak in comparison with the intrachain interactions,

they play important roles in actual materials used in polymer light-emitting diodes (PLEDs). Extensive studies of the dynamics of polarons in a system of coupled conjugated polymer chains under the influence of an external force have been carried out by Johansson and Stafström.<sup>28</sup> Studies show that in low fields when the polaron reaches the region where the coupled conjugated polymer chains interact, the polaron (both charge and distortion) gets stuck at the end of first chain. With a slightly higher field strength, the polaron oscillates and remains at the end of the first chain for some time and then jumps over to the second chain. This delay at the end of the chain implies, therefore, that polarons have a significant chance of meeting and colliding in the region where polymer chains are coupled.

The questions then arise as to whether or not (i) a bipolaron can form in the region where the chains interact and (ii) if the bipolaron formed moves to the region where the chains are coupled, the bipolaron can jump over to the other chain or whether it will be blocked in the coupled chain area. All these results will help to understand the scattering and combination of oppositely charged bipolarons in conjugated polymers. In this section, we consider the formation and dynamics of bipolarons on two coupled polymer chains.

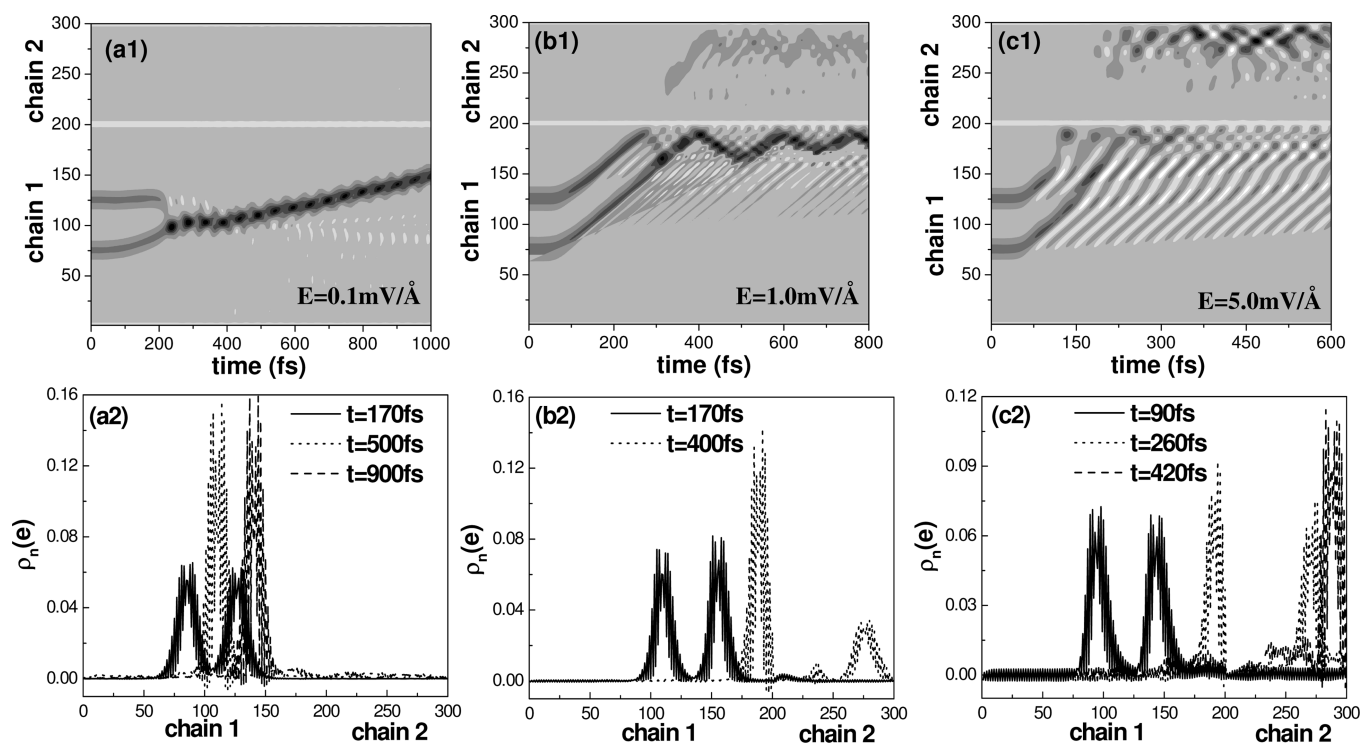
In order to describe the two coupled polymer chain structures, we consider the interchain coupling Hamiltonian<sup>35–37</sup>

$$H_{\text{int c}} = - \sum_{n, s} [t_1 + (-1)^n t_2] (c_{1, n, s}^\dagger c_{2, n, s} + \text{hc}) + \sum_{n, s, s'} U_0 \left( c_{1, n, s}^\dagger c_{1, n, s} - \frac{1}{2} \right) \left( c_{2, n, s'}^\dagger c_{2, n, s'} - \frac{1}{2} \right) \quad (7)$$

where  $t_1$  ( $t_2$ ) denotes the transfer integral and  $U_0$  is the interchain e–e interaction term.

Next, we study the formation of bipolarons on two coupled polymer chains. We turn to a system consisting of two chains placed beside each other and overlapping by 50 sites. The first chain consists of 200 sites and contains two electron-polarons at the 75th and 125th sites, respectively, while the other chain is a perfectly dimerized 100-site chain. The strengths of the interchain interactions are set to  $t_1 = 0.1$  eV,  $t_2 = 0.15$  eV and the interchain e–e interaction term is set to  $U_0 = 0.1$  eV.<sup>35–37</sup> These parameters are appropriate for physical systems such as LEDs. Simulations were carried out for a number of different field strengths ranging from 0.05 to 6.0 mV/Å. Results for three values of the field strength corresponding to markedly different behaviors in the polaron collision dynamics are shown in Figure 3. When the electric field turns on, both the left polaron and the right polaron move along chain 1 approaching the region where the chains interact. In all cases the two polarons start to move on the first chain with constant speed as discussed above.<sup>33</sup> We identify basically three regions of the electric field strength. In a weak field ( $E_0 < 0.3$  mV/Å), e.g., 0.1 mV/Å, two polarons have relatively small velocities before collision; see Figure 3a. When the left polaron meets the right polaron which requires some waiting time to gain enough energy for further motion, the two particles have a chance to approach and finally merge into a single entity (bipolaron). The bipolaron then continues to move along the first chain to the overlap area. If we increase the electric field strength, two polarons can gain enough energy from the electric field and have no need for some waiting time. The two polarons then scatter into a bipolaron state in the overlap area. As an example, Figure 3b shows the propagation of the lattice deformation

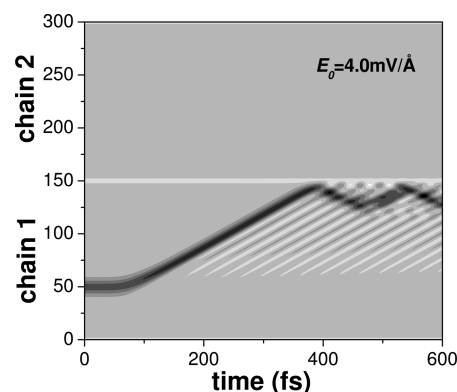




**Figure 3.** Evolution of the staggered bond order parameter  $\delta_n$  of two antiparallel spin electron-polarons combining into an electron-bipolaron as a function of time (upper row), and the charge distribution  $\rho_n$  at a time before and after the scattering (lower row) for different electric field strengths: (a)  $E_0 = 0.1 \text{ mV/\AA}$ ; (b)  $E_0 = 1.0 \text{ mV/\AA}$ ; and (c)  $E_0 = 5.0 \text{ mV/\AA}$ .

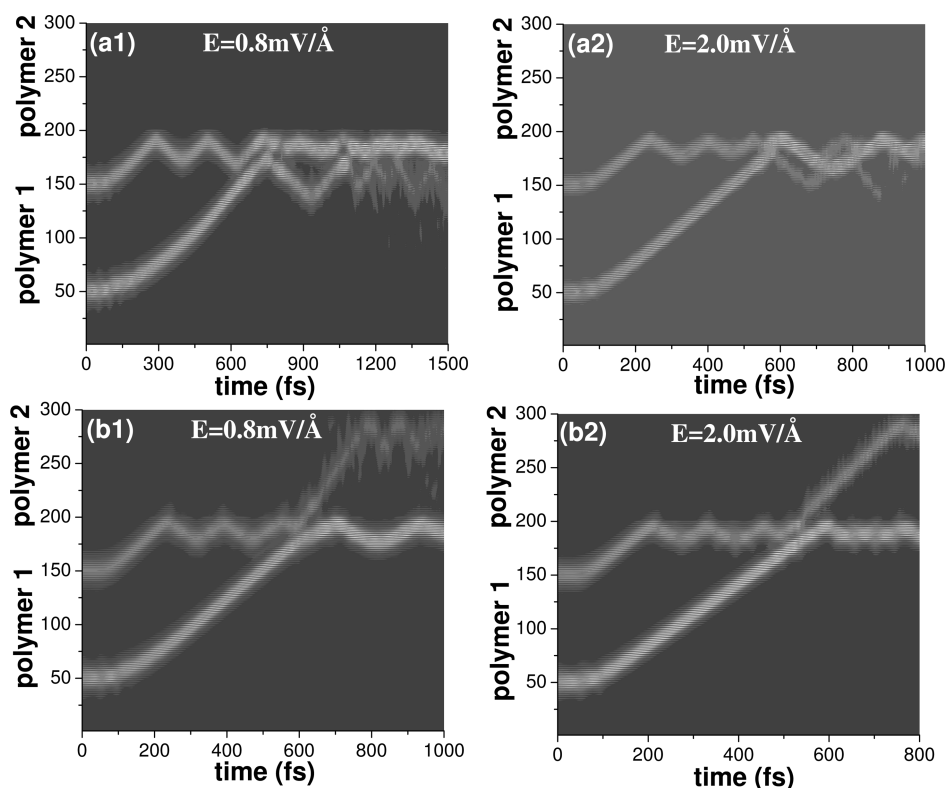
under an intermediate electric field of  $1.0 \text{ mV/\AA}$ . One can see that both polarons start to move due to the electric field, then maintain constant velocities before colliding. At about  $250 \text{ fs}$ , the right polaron reaches the end of chain 1, and then oscillates back and forth for about  $100 \text{ fs}$  in order to gain enough energy from the electric field to jump over to chain 2. In this “waiting time”, it meets the left polaron at about  $350 \text{ fs}$ . They approach and finally merge into a mix of a bipolaron and a polaron. It also can be seen that partial charges jump over to chain 2, and that the charge can be recollected and appears to be localized on chain 2. The product formation probabilities can also be analyzed through their occupation numbers (not shown). This suggests that there is a high formation probability for bipolarons in the coupled region, and low probability of the polaron jumping over to chain 2. In a yet stronger electric field  $E_0 > 4.5 \text{ mV/\AA}$  (in a real physical system, e.g., a PLED, the field strengths are generally lower than in this case), the two polarons break into irregular lattice vibrations after passing through the coupling region. For example, the evolution of the lattice distribution  $\delta_n$  with time is shown in Figure 3c, for  $E_0 = 5.0 \text{ mV/\AA}$ . One can see that the two polarons have a higher velocity, and at about  $150$  and  $260 \text{ fs}$ , the two polarons reach the overlap area then jump over to chain 2, respectively. However, when the two polarons meet at the end of the second chain, the free charges appear to be collected, the localized lattice deformations of the two polarons break into irregular lattice vibrations, and this case can no longer be regarded as a stable polaron-pair and/or bipolaron.

Since, as shown above, the bipolaron can be formed on coupled polymer chains under appropriate conditions, we now investigate the dynamics of bipolarons on two coupled polymer chains using field strengths ranging from  $0.05$  to  $10.0 \text{ mV/\AA}$  and other parameters as above. Figure 4 shows an electron-bipolaron



**Figure 4.** Time dependence of the staggered bond order parameter  $\delta_n$  of an electron-bipolaron moving in a system consisting of two coupled chains, for electric field strengths  $E_0 = 4.0 \text{ mV/\AA}$ .

as it starts to move along chain 1 and reaches a constant speed. When it reaches the end of chain 1, i.e., the region where the chains interact, it oscillates back and forth due to the potential of the electric field and the energy minimum for the bipolaron at the middle of the chain. If the “waiting time” is sufficiently long, the bipolaron (both charge and distortion) gets stuck. This behavior survives up to a field strength of about  $10.0 \text{ mV/\AA}$ . Thus, bipolaron transport with jumping from the first to the second chain is impossible with the electric field strengths used in normal devices. For sufficiently high fields (this behavior is not displayed in Figure 4), the charge of the bipolaron appears to be delocalized in the coupled chain area and has difficulty recollecting. It is possible to see that some localized lattice distortions continue to travel along the chain and are scattered at the chain end, but these



**Figure 5.** Time dependence of the charge distribution  $\rho_n$  of two antiparallel spin electron-polarons colliding at the interface of a polymer/polymer structure with a 0.2 eV potential barrier for different hopping integrals: (a)  $t_h = 1.0$  eV, (b)  $t_h = 2.0$  eV.

distortions can no longer be regarded as a bipolaron. These results indicate that at the field strengths used in normal devices most of the bipolarons are blocked and collect at the region where the chains interact.

**Formation and Dynamics of Bipolarons at the Interface of a Polymer/Polymer Heterojunction Structure.** In actual polymer light-emitting diodes, it has been noted that the efficiency is higher in multilayer materials.<sup>6,25,26</sup> The reason may be related to the existence of bipolarons in the multilayer conjugated polymer interface. Transport studies of polarons in a system with a polymer/polymer interface and under the influence of an external force have been carried out in our previous work.<sup>27</sup> The results showed that the transport of a polaron through a polymer/polymer heterojunction interface depends sensitively on the hopping integrals at the polymer/polymer interface ( $t_h$ ), the interface potential barrier ( $\Delta_e$ ), and the applied electric field strength ( $E_0$ ). These results suggested that for different parameter values the polaron can either migrate through the interface or be blocked at the interface due to the potential barrier, and that blocked polarons can meet and collide to form bipolarons at the polymer/polymer heterojunction interface. In this section, the formation and dynamics of bipolarons at the interface of a polymer/polymer heterojunction structure are discussed in detail.

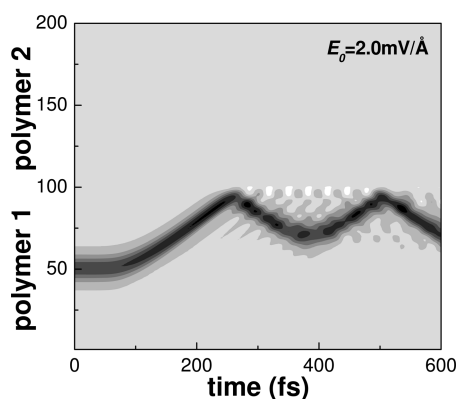
The coupling Hamiltonian used to describe the polymer/polymer interface is<sup>27</sup>

$$H_{\text{intf}} = -t_h(C_{1,N}^\dagger C_{2,1} + C_{2,1}^\dagger C_{1,N}) \quad (8)$$

where  $t_h$  is the hopping integral between the end site of polymer 1 and the first site of polymer 2.

First, the formation of bipolarons at the interface of a polymer/polymer heterojunction structure was studied. For the different

types of heterojunction formed between dissimilar organic semiconductors, the offsets between the conduction edges and valence band edges are of many types;<sup>6,25–27</sup> e.g., the PPV/CN-PPV heterojunction typical of LEDs is designated as “type II”, i.e., the energy gap of the electron-transporting layer (polymer 1 in our case, e.g. CN-PPV) is smaller than that of the hole-transporting layer (polymer 2 in our case, e.g., PPV.) Figure 5 shows the trajectories of two electron-polarons with antiparallel spins that combine into an electron-bipolaron at the interface of a polymer/polymer heterojunction structure. The formation of the bipolaron shows different behavior at the interface region. For the weak interface coupling case, e.g.,  $t_h = 1.0$  eV, the two electron-polarons eventually merge into an electron-bipolaron, as shown in Figure 5a. However, in contrast to the weak coupling case, when the hopping integral is increased, as shown in Figure 5b, the two polarons gradually merge into a mix of polaron and bipolaron states. Simultaneously, the partial polaron jumps over to polymer 2 and the charge appears to be localized on chain 2. The stronger the interface coupling is, the higher the probability that the polaron will jump over to polymer 2; i.e., there is only a low probability of finding bipolarons at the interface. Similarly, the stronger the electric field is, the lower is the formation probability of bipolarons at the interface. However, in realistic PPV/CN-PPV multilayer LEDs, it should be noted that the potential barrier is about 0.2 eV, the electric field strength is about 1.0 mV/Å, and the hopping integral at the interface is about 1.0 eV. For these parameters, calculated results indicate that most of the polarons are blocked by the interface. Thus, polarons with the same charges and antiparallel spins should eventually merge into a bipolaron at the interface of actual PPV/CN-PPV heterojunctions.



**Figure 6.** Time dependence of the staggered bond order parameter  $\delta_n$  of an electron-bipolaron moving at the interface of a polymer/polymer heterojunction with electric field strengths  $E_0 = 2.0$  mV/Å.

Finally, we discuss the dynamical behavior of bipolarons at the interface of polymer/polymer LEDs when the field strengths range from 0.05 to 10.0 mV/Å, the potential barrier of interface is 0.2 eV and the hopping integral at the interface is 1.0 eV. Figure 6 shows that the electron-bipolarons will get stuck and oscillate at the interface region; i.e., they collect at the interface. This behavior survives up to a field strength about 10.0 mV/Å, the highest field we studied. The bipolaron oscillation is due to the dual effects of the potential barrier induced by the energy mismatch at the polymer/polymer interface and the hopping integrals at polymer/polymer interface which effectively reduce the potential barrier at the interface.

The formation and evolution dynamics of hole-bipolarons are similar to the case for electron-bipolarons in conjugated polymers, and details are not given here. The above results are also valid for  $U, V$  below the critical values  $U \sim 4.0$  eV and  $V \sim 2.0$  eV. These results indicate that most of both the electron-bipolarons and hole-bipolarons can be blocked and collected at the electron-transporting layer and the hole-transporting layer, respectively. Thus, the combination of oppositely charged bipolarons to form biexcitons can occur in an isolated single polymer chain, in two coupled polymer chains, and at the heterojunction interface of polymer/polymer structures. As a result, the existence and evolution dynamics of bipolarons are likely to play an important role in understanding the operation of optoelectronic devices based on conjugated polymers.

## SUMMARY

In summary, by combining the one-dimensional tight-binding SSH model and the extended Hubbard model, the scattering and combination of polarons with the same charge and with parallel and antiparallel spins in conjugated polymers have been investigated using a nonadiabatic evolution method. Results show that polarons with the same charge and antiparallel spins can scatter into bipolaron states, and the bipolarons can collect in the region where the chains interact and at the interface in polymer/polymer heterojunction materials. The formation and evolution dynamics of bipolarons depend sensitively on the electric field strength, the interchain interaction hopping integral, and the strength of the coupling at the interface of the two polymers in a heterojunction. This work has shown that we are able to get a basis for understanding the formation of bipolarons and the dynamical properties of systems with many polarons and/or

bipolarons. In particular, it will be helpful for investigating the singlet biexcitons formed by the scattering of oppositely charged bipolarons in conjugated polymer materials.

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