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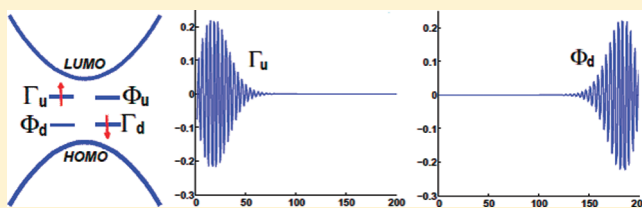
# Forbidden Singlet Exciton Transitions Induced by Localization in Polymer Light-Emitting Diodes in a Strong Electric Field

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**ABSTRACT:** Through combining the electron transition process and dipole moment evolution as well as electron–phonon coupling, molecular dynamics calculations show that the radiative decay of singlet excitons in a conjugated polymer, such as a polymer light-emitting diode (PLED), is largely determined by the evolution of the dipole moment. Without an electric field, the decay life of a singlet exciton is about 1 ns. Once an electric field is applied and exceeds a critical value, with electron–phonon coupling, the original lattice structure evolves into two new localized lattice distortions, consistent with the experimental results. Owing to the new lattice structure and self-trapping, the dipole moment rapidly decreases to zero within 5 fs, eliminating the radiative decay of the singlet exciton.



## 1. INTRODUCTION

The basic characteristics of conjugated polymers are determined by the conjugation breaks or lattice distortion along the chain, where conformational subunits couple to neighboring subunits to form nanoscale excitons.<sup>1</sup> The exciton is formed due to an electron–hole pair and not only contributes electroluminescence, but also has an influence on the polymer optical properties.<sup>2</sup>

Above all, by virtue of the one-dimensional nature of a conjugated polymer, the lattice is sensitive to the change of electronic structure. This means that, once the electronic state is changed, the bond structure of the polymer undergoes distortion accordingly. Subsequently, some new electronic bound states are reformed by the bond distortion, which is the self-trapping effect in a conjugated polymer.<sup>3</sup> This effect entails coupling between the electron and localized lattice distortion, resulting in a self-trapped exciton. Further, the binding energy of the self-trapped exciton is about 0.4 eV, which not only makes the exciton stable even at room temperature, but also becomes the main contribution to luminescence in polymer light-emitting diodes (PLEDs).<sup>4,5</sup>

In 2005 and 2007, it was reported that the exciton spans several groups/segments along the polymer chain, and the relaxation of the created exciton mainly takes place on an ultrafast time scale.<sup>6</sup> The exciton lifetimes for different polymer layers range from 260 ps for unsubstituted *meso*-tetraphenylporphyrin to 800 ps for *meso*-tetra(4-ethylphenyl)-porphyrin.<sup>7</sup> Thus, if an electric field is applied along the polymeric chain and exceeds a certain threshold, the intensity of electroluminescence of a PLED will sharply decrease, which is believed to be a result of dissociation of the exciton at higher current densities.<sup>8–11</sup> In 2008, Tamura et al. experimentally found that for a donor–acceptor heterojunction embedded in

a polymeric material, the dissociation of the exciton is indeed driven by phonons.<sup>12</sup> This suggests that electron–phonon coupling plays a key role in the dissociation of an exciton driven by an external electric field, leading to the luminescence quenching phenomenon in PLEDs.

Besides the phonons, recently it was observed that exciton dissociation is actually an intrachain process. In particular, the dissociation only takes place after the exciton is localized on a conjugated segment of a single polymer chain.<sup>13</sup> More importantly, it was discovered that both the decay of the exciton and its dynamic relaxation strongly depend on the dipole moment of the transition. Devizis et al. also pointed out the localization is able to largely exert influence on the property of the excited state.<sup>14</sup>

On the basis of the discussion above, combining the electron–phonon coupling, localization, and dipole moment of the electron transition in a conjugated polymer makes it possible to exhibit a panoramic view of luminescence quenching caused by exciton dissociation in a strong electric field, which is the purpose of this paper. We will begin with the Su–Schrieffer–Heeger–Hubbard Hamiltonian, which not only includes electron–phonon interactions but also accounts for the dynamic relaxation of carriers upon coupling with the molecular dynamics. A challenge is how to introduce the dipole moment of the electron transition into the Su–Schrieffer–Heeger–Hubbard Hamiltonian, where we will embed the transition dipole moment within the molecular dynamics, then link this to the Hamiltonian, and finally complete the composite picture of the luminescence quenching caused by exciton dissociation.

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## II. DIPOLE MOMENT OF TRANSITION AND MODELING HAMILTONIAN

The sandwich structure of a PLED generally consists of three layers, where an electroluminescent polymeric material is inserted between two electrodes. Due to the applied bias voltage between the electrodes, the electron from the highest occupied molecular orbital (HOMO) and the hole of the lowest unoccupied molecular orbital (LUMO) are injected into the polymer from the electrodes. Combining the prominent self-trapping effect of the polymer with the attraction between the electron and hole, the original HOMO and LUMO states move to the center of the gap to form two localized states— $\Gamma_u$  and  $\Gamma_d$ —leading to an exciton.

If  $|u\rangle$  and  $|d\rangle$  are the wave functions of the localized states  $\Gamma_u$  and  $\Phi_d$  whose energies are  $E_u$  and  $E_d$  ( $E_u > E_d$ ), without the restriction of Pauli repulsion, the electron in  $\Gamma_u$  can transit to  $\Phi_d$  and the transition dipole moment of the two localized states can be expressed as

$$p = e\langle u|r|d\rangle \quad (1)$$

where  $r$  is the dipole operator. Thus, the transition rate  $\gamma_{ud}$  between these states becomes

$$\gamma_{ud} = \frac{4e^2(E_u - E_d)^3}{3\hbar^4 c^3} \langle u|r|d\rangle^2 = \frac{4(E_u - E_d)^3}{3\hbar^4 c^3} p^2 \quad (2)$$

The evolution of the electron populations  $P_u$  and  $P_d$  of  $\Gamma_u$  and  $\Phi_d$  due to the electron transition are expressed by the rate equation

$$\frac{dP_u}{dt} = -\gamma_{ud}P_u, \quad P_d = n - P_u \quad (3)$$

where  $n$  is the total electron number. Considering the formation of the exciton as a spin-independent process, the resultant excitons are divided into two groups: one is a triplet with  $S = 1$  and the other is a singlet with  $S = 0$ . Thanks to the forbidden electron transition of Pauli repulsion, the singlet exciton is an emissive carrier while the triplet exciton is not. Through the transition rate and the above rate equation, the evolutions of electron populations of  $\Gamma_u$  can be well described.

Accompanying the electronic transition dipole moment, the prominent electron–phonon coupling in the conjugated also changes the lattice structure. Furthermore, as mentioned in the Introduction, the exciton dissociation in a PLED is the result of an intrachain effect. Fortunately, the extended Hubbard–Su–Schreiffer–Heeger Hamiltonian provides an accurate description. Along a single conjugated polymer, the Hamiltonian for the electron–phonon interaction can be expressed as

$$H_{e-p} = - \sum_{l,s} [t_0 + \alpha(u_{l+1} - u_l) + (-1)^l t_e] [c_{l+1,s}^\dagger c_{l,s} + Hc] \quad (4)$$

where  $t_0$  is a hopping constant,  $\alpha$  is an electron–lattice coupling constant,  $c_{l,s}^\dagger$  ( $c_{l,s}$ ) denotes the electron creation (annihilation) operator with spin  $s$  at unit cluster/group  $l$ ,  $u_l$  is the displacement of unit cluster/group  $l$ , and  $t_e$  is the Brazovskii–Kirova term. The elastic potential energy of lattice oscillations and electron interactions in a conjugated polymer chain can be depicted as

$$H_l + H_e = \frac{K}{2} \sum_l (u_{l+1} - u_l)^2 + U \sum_{l,s} n_{l,\uparrow} n_{l,\downarrow} \quad (5)$$

where  $K$  is an elastic constant,  $t_e$  is the Brazovskii–Kirova term, and  $U$  is the on-site Coulomb repulsion strength, respectively.

With the electric field  $E$  directed along the polymer chain, the interaction between electron and electric field is

$$H_E = \sum_{l,s} Ee \left( l - \frac{N+1}{2} \right) a n_{l,s} \quad (6)$$

where  $E$  is the electric field strength, and  $N$  is the number of lattice sites. Thus, the total Hamiltonian describing the properties of conjugated polymer becomes<sup>15–17</sup>

$$H = H_{e-p} + H_l + H_e + H_E \quad (7)$$

In order to describe the electron's behavior, we have to know its energy spectrum  $\varepsilon_\mu$  and wave function  $\Phi_\mu$ , which are functionals of the lattice displacement  $u_l$ , as determined by the eigenequation

$$H\Phi_\mu = \varepsilon_\mu \Phi_\mu \quad (8)$$

Realizing that atoms are much heavier than electrons and using the Feynman–Hellmann theorem, we can describe the atomic movement of the lattice through classical dynamics by the equation

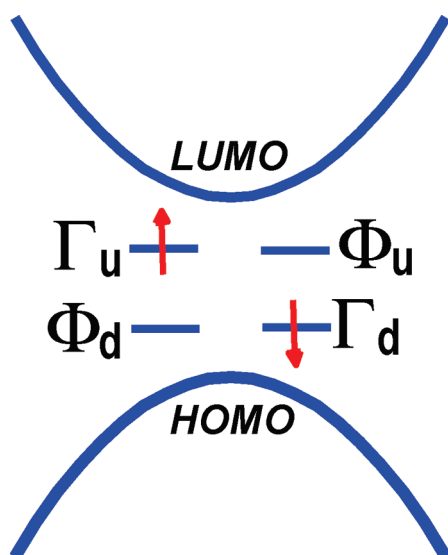
$$M \frac{d^2 u_l}{dt^2} = - \sum_{\mu}^{\text{occ}} \frac{\partial \varepsilon_\mu}{\partial u_l} + K(2u_l - u_{l+1} - u_{l-1}) \quad (9)$$

Assuming an electronic wave function  $\Phi_\mu = \{Z_{n,\mu}^s\}$ , where  $Z_{n,\mu}^s$  is the value for the electron at the  $n$ th site in state  $\mu$  with spin  $s$ , the charge distribution can be represented as  $\rho_n^\alpha = \sum_{\mu} |Z_{n,\mu}^s|^2 - n_0$ ;  $n_0$  is the density of the positively charged background and “occ” stands for the occupation or population of electrons. Since the polymer is not a strongly correlated system, by using the above coupled equations and conventional molecular dynamics, we can quantitatively describe the dynamic evolution of not only the electronic states but also the lattice structure in a conjugated polymer chain.

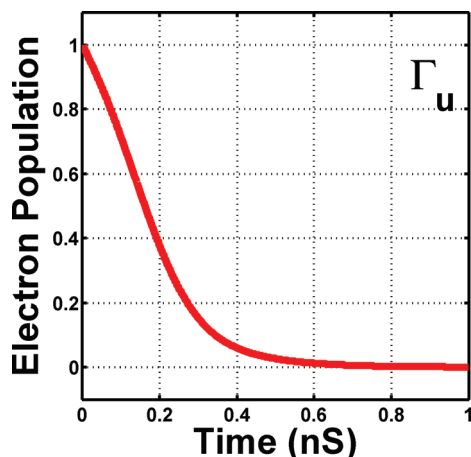
## III. RADIATIVE DECAY OF A SINGLET EXCITON

As mentioned in section II, a PLED is generally comprised of three layers, with a luminescent polymer layer embedded between two electrodes. Once the bias voltage between the two electrodes is applied, both electrons and holes are injected into the polymer layer from the negative and positive electrodes. Following this, the attraction between the electron and hole binds them together to form an exciton, leading to two localized states,  $\Gamma_u$  and  $\Gamma_d$ , at the center of the band gap. The resultant excitons can be divided into two kinds: one is a triplet exciton with  $S = 1$  and the other is a singlet with  $S = 0$ . For the triplet, due to the Pauli exclusion principle, an electronic transition between the localized states is forbidden, which makes the triplet exciton a nonemissive carrier, while the singlet exciton is not. As shown in Figure 1, for the two localized states,  $\Gamma_u$  and  $\Gamma_d$ , of the singlet exciton, each state is occupied by one electron with different spin. For clarity, the state occupied by a spin-up/spin-down electron is arranged at the left-/right-hand side. During the decay of the exciton, considering Pauli repulsion, the electron in  $\Gamma_u$  only transits to  $\Phi_d$  and emits light.

Let us first concentrate on the dynamic process of the decay of the singlet exciton that contributes to the luminescence of PLEDs, which changes the electron occupations in  $\Gamma_u$  and  $\Phi_d$ . Due to the self-trapping effect, the electron excitation as a

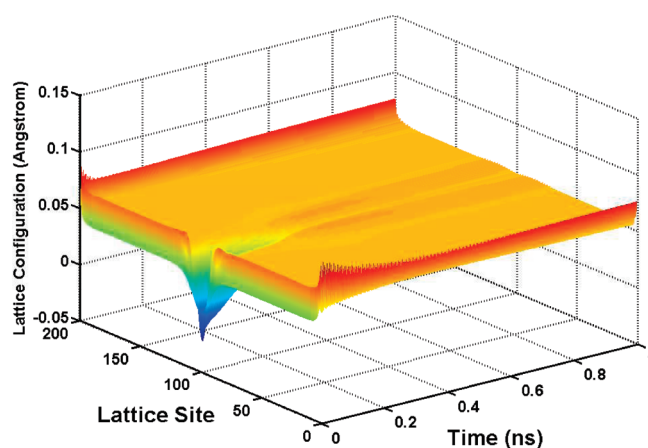


**Figure 1.** Electronic structure of a singlet exciton with the state  $\Gamma_u/\Gamma_d$  occupied by a spin-up/spin-down electron.



**Figure 2.** Evolution of the electron population  $\Gamma_u$  during the radiative decay of a singlet exciton in a PLED.

singlet exciton induces distortion of the lattice structure. As an example, we choose a conjugated polymer consisting of 200 unit clusters/groups. If the displacement of the  $l$ th unit cluster/group is  $u_l$ , we use the lattice configuration  $\phi_l = (-1)^{l_u l}$  to describe the evolution of the lattice structure. Thus, the whole process of the electron population of  $\Gamma_u$  is described by Figure 2, where at the beginning of the decay, i.e., at 0 ps, the electron population of each localized state is 1.0 because each state of  $\Gamma_u$  and  $\Gamma_d$  is occupied by one electron with opposite spin. Also, as illustrated in Figure 3, at this instant, the localized lattice distortion along the polymer chain is 0.013 Å. When time reaches 0.2 ns, the electron population of the up state  $\Gamma_u$  changes to 0.38 from the original 1.0. Up to 0.9 ns, the electron population of  $\Gamma_u$  is 0.08, as depicted in Figure 2. Along with the electronic transition, the lattice structure of the conjugated polymer gradually goes back to the homogeneous lattice dimerization, as seen from Figure 3. Once time reaches 1 ns, the localized lattice configuration no longer exists, which not only means this moment is the end of the electronic transition, but also indicates the life of the exciton to be about



**Figure 3.** Lattice configuration of the singlet exciton at the beginning of the radiative decay.

1 ns. Along with the electronic transition of the singlet exciton, the polymer has been emitting light.

#### IV. FORBIDDEN SINGLET EXCITON TRANSITIONS

As demonstrated experimentally by Devizis et al.,<sup>14</sup> the localization exerts influence largely on the property of the excited state, which means that the evolution of the localized states  $\Gamma_u$  and  $\Phi_d$  of the exciton probably changes the transition process. Furthermore, Devizis et al. point out that both the decay of the exciton and its dynamic relaxation strongly depend on the dipole moment of the transition.

Based on eqs 2 and 3, the transition process is determined by the transition rate

$$\gamma_{ud} = \frac{4(E_u - E_d)^3}{3\hbar^4 c^3} p^2$$

and electron population, where  $p$  is the dipole moment between  $\Gamma_u$  and  $\Phi_d$ . If  $|u\rangle$  and  $|d\rangle$  are the wave functions of the localized states  $\Gamma_u$  and  $\Phi_d$ , with the dipole moment as  $p = e\langle u|r|d\rangle$ , the transition rate becomes

$$\gamma_{ud} = \frac{4(E_u - E_d)^3 e^2}{3\hbar^4 c^3} \langle u|r|d\rangle^2$$

If an electric field is applied along the polymer chain and its strength exceeds the threshold value 4.5 MV/cm,<sup>18–22</sup> the wave functions for the states  $\Gamma_u$  (Figure 4a) and  $\Phi_d$  (Figure 4b) at 3.5 fs indicate that not only are both wave functions localized, but also their localized positions overlap. In turn,  $p^2 = e^2 \langle u|r|d\rangle^2$  should be a certain positive value. However, from 4.0 fs on, the electric field dissociates the original localized lattice distortion of singlet exciton, reaching the situation illustrated by Figure 5 at 7.0 fs where the localized  $\Gamma_u$  moves to the left side of the polymer chain (Figure 5a), and simultaneously the localized  $\Phi_d$  is driven from the center of the polymer chain to the right (Figure 5b). More importantly, because both are localized states, with large aberrance of their positions as shown in Figure 5, where one is at the left while another is at the right side, the dipole moment  $p = e\langle u|r|d\rangle$  can be estimated to be zero.

Actually, just within a short time span, due to the applied electric field, the change of location of the localized wave leads to a large decrease in the dipole moment. The time-dependent

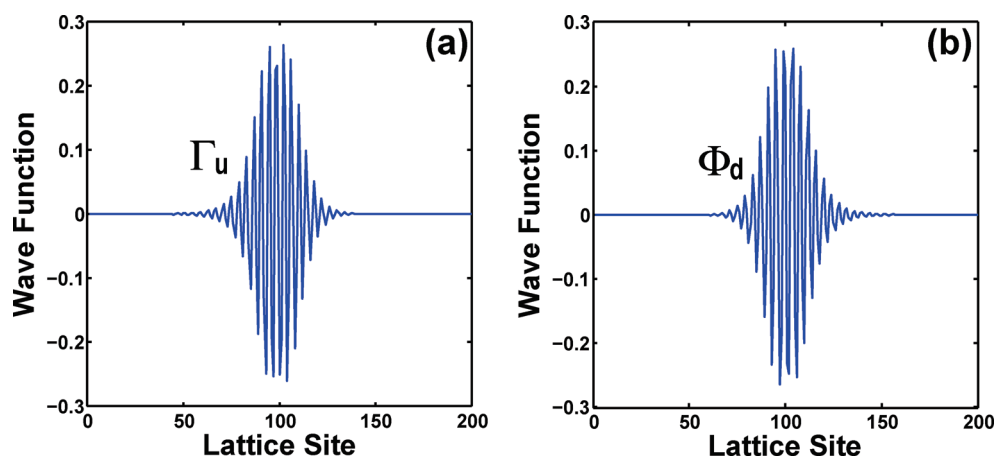


Figure 4. After applying the electric field  $E = 4.5$  MV/cm: (a) wave function of state  $\Gamma_u$  at 3.5 fs and (b) wave function of state  $\Phi_d$  at 3.5 fs.

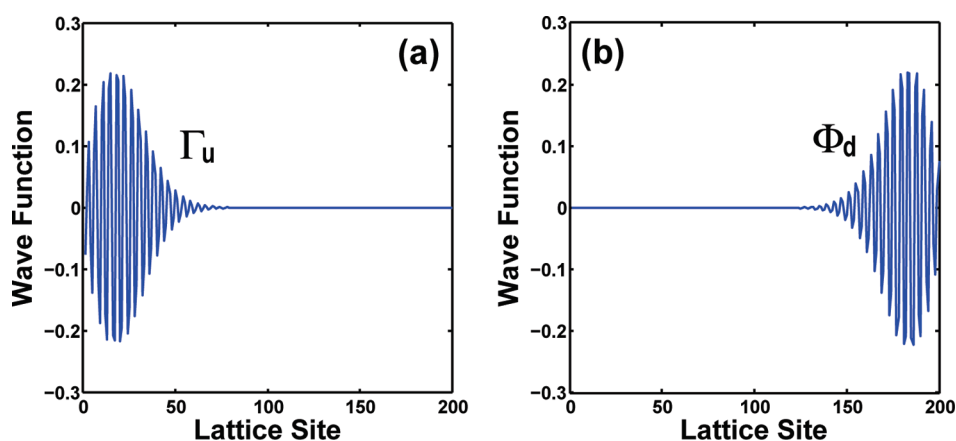


Figure 5. With the help of a strong electric field  $E = 4.5$  MV/cm: (a) wave function of state  $\Gamma_u$  at 7.0 fs and (b) wave function of state  $\Phi_d$  at 7.0 fs.

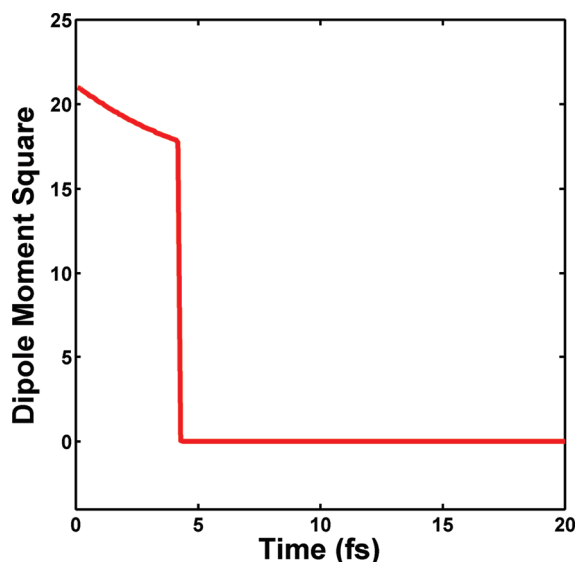


Figure 6. Time-dependent dipole moment square  $p^2$  between  $\Gamma_u$  and  $\Phi_d$ .

dipole moment evolution is depicted in Figure 6. Before an electric field is applied,  $p^2$  is  $17.99 \text{ e}^2 \text{ \AA}^2$ . After a  $4.5 \text{ MV/cm}$  electric field is applied along the polymer chain and time reaches

$4.3 \text{ fs}$ ,  $p^2$  immediately becomes  $0.07 \text{ e}^2 \text{ \AA}^2$ , and then  $p^2$  soon tends to zero, with the transition rate

$$\gamma_{ud} = \frac{4(E_u - E_d)^3}{3\hbar^4 c^3} p^2$$

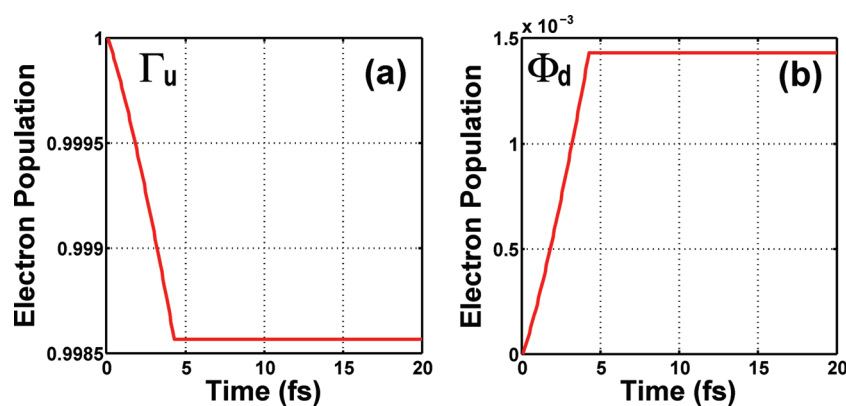
also going to zero.

As discussed earlier, the evolution of the electron population of  $\Gamma_u$  is described as  $dP_u/dt = -\gamma_{ud}P_u$ . The zero value of the transition rate gives  $dP_u/dt = 0$ , and it can be expected that the evolution of the electron population  $P_u$  at  $\Gamma_u$  is stopped.

Therefore, the electronic transition for a singlet exciton indeed ceases, as illustrated in Figure 7. At the beginning of the application of the external electric field, the electron of  $\Gamma_u$  transits to the empty state  $\Phi_d$  in the middle of the gap, which is free of the Pauli repulsion, gradually inducing a decrease of the electron population in  $\Gamma_u$ . Associated with this, the electron population of  $\Phi_d$  increases. However, up to  $4.4 \text{ fs}$ , as shown in Figure 5,  $p^2$  inclines soon to 0, causing the transition rate  $\gamma_{ud}$  to be zero. At that point, the electron populations of  $\Gamma_u$  and  $\Phi_d$  are fixed at  $0.9986$  and  $0.0014$ , respectively, which means that the electronic transition between  $\Gamma_u$  and  $\Phi_d$  ceases. Naturally, this ends the radiative decay of the singlet exciton.

Hence, the whole dynamics for the failure of light emission can be described as follows: Without an electric field or under a weak electric field, the light emission of a conjugated polymer is





**Figure 7.** Under a strong electric field  $E = 4.5$  MV/cm: (a) time-dependent electron populations in state  $\Gamma_u$  and (b) time-dependent electron populations in state  $\Phi_d$ .

attributed to the radiative electronic transition for a singlet exciton. Once the applied electric field surpasses a certain threshold, the original lattice distortion of the singlet exciton is dissociated into two localized parts. Associated with the evolution of lattice structure, it also forms two localized states that do not overlap. The aberrance of the positions of the two localized states leads to both the dipole moment and transition rate as being zero, thus stopping the radiative decay of the singlet exciton.

In conclusion, both electronic transitions and the evolution of the dipole moment are embedded within our newly developed molecule dynamics. Based on the dynamic process, it is found that the radiative decay of a singlet exciton in a conjugated polymer, such as a PLED, is largely determined by the evolution of the dipole moment. Without an electric field, the decay time of the singlet exciton is about 1 ns. Once an electric field is applied and exceeds a critical value, the original lattice structure is dissociated into two new localized lattice distortions. Owing to the new lattice structure and the electron–phonon coupling, the dipole moment rapidly becomes zero within 5 fs, thus ending the electronic transition.

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