

# Localization and Relaxation of Singlet Exciton Formation in Conjugated Polymers under Photoexcitation

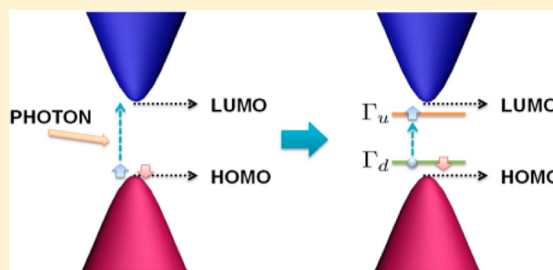
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**ABSTRACT:** This paper employs a molecular dynamics approach to uncover the time profile of exciton formation, which can be divided into two stages: localization of electron–hole pairs and relaxation process (nuclear and electronic). Under photoexcitation, an electron–hole pair is formed by an electronic transition, and the pair in turn becomes localized through the electron–lattice interaction, which triggers the total energy to shift violently and oscillate. The oscillation during the first 40 fs induces the excitation to step into the second stage, i.e., relaxation. After the relaxation process of about 850 fs, the total energy, lattice energy, and electron energy reach certain values whereas the lattice configuration and electron remain localized, indicating the formation of a singlet exciton.



## I. INTRODUCTION

Polymer light-emitting diodes (PLEDs) generally consist of a layer of luminescent conjugated polymer between two metal electrodes.<sup>1</sup> For this sandwich structure, once an external voltage between two metal electrodes is applied, electrons and holes are injected into the semiconductor emission layer, forming electron–hole pairs, i.e., excitons, due to the attraction between electrons and holes. Radiative decay of the excitons leads to light emission of the PLEDs.<sup>1</sup>

To discover the mechanism of solar cells, the first step has been to explore the dynamic process, where time-resolved emission studies, Monte Carlo simulations and ultrafast transient absorption polarization measurements have been carried out<sup>2–7</sup> on the basis of the polymer MEH-PPV and its derivatives.<sup>8–11</sup> An organic semiconductor material undergoing an external optical excitation yields electron–hole pairs, being the basis of the polymer solar cells.<sup>12–21</sup>

Actually, after a conjugated polymer, such as MEH-PPV or poly(3-hexylthiophene) (P3HT), undergoes photoexcitation, neutral excitation occurs in the energy bands. Recently, an ultrafast emission study of poly(3-hexylthiophene) (P3HT) in spin-cast thin films and dilute chlorobenzene solution demonstrated that self-localization of the exciton (less than 100 fs) is an ultrafast process.<sup>22,23</sup> However, compared with this self-localization, the exciton formation per se in a single polymeric molecule is relatively slow, about 1 ps.<sup>22,23</sup> The question arises as to why the time of self-localization of the exciton is different from the time of its formation? To answer this, we focus on the process after exciton formation. As observed for depolarization, spectral red shifts, and changes in the vibronic structure, once an exciton is formed, it can hop to other sites with lower energy or to a slow conformational

planarization of the polymer chain. The intrapolymeric or interpolymeric hopping of an exciton is regarded as the part of the relaxation process. This leads to a possible assumption that, after self-localization from photoexcitation, relaxation could occur until exciton formation. If true, how to describe the relaxation and to tell its difference from self-localization due to photoexcitation becomes particularly important in understanding the behavioral mechanism of excitons after photoexcitation, especially in solar cells.

Although the time-dependent aspects of a polymer generally can be well depicted by the conventional molecular dynamics method, when the polymer undergoes external excitation, this method is unable to provide the temporal evolution of the emission spectrum during the evolution of the exciton. The absence of a valid theoretical method depicting the coupling between the external light field and polymer results in a gap between the experimental and theoretical research. Fortunately, in 2009, Devižis et al. found that the dipole moment of the transition might depend strongly on the relaxation of the exciton.<sup>24</sup> Thus, the external light field, as one of the factors to determine the electron transition, can be introduced to the molecular dynamics, which also provides a bridge between theory and experiment.

Here, we report on a developed molecular dynamics approach that not only involves the coupling between the external light field and conjugated polymer but also introduces time-dependent electron transitions and the evolution of the lattice configuration into the molecular dynamics. On this basis,

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the dynamical process after self-localization of photoexcitation is exhibited in detail until the formation of the exciton, leading to the underlying mechanism that causes the mismatch between self-localization of photoexcitation and formation of the exciton. Further, it also reveals the dependence of the self-localization on the intensity of the external light field.

## II. MODELING THE COUPLING BETWEEN THE EXTERNAL LIGHT FIELD AND CONJUGATED POLYMER

The strong electron–phonon interaction in a conjugated polymer reflects the prominent one-dimensional aspect, which also can lead to the self-trapping effect of carriers in the polymer. Considering electron–phonon and electron–electron interactions along with the elastic potential energy of lattice, the Hamiltonian for the conjugated polymer be written as

$$\begin{aligned}
 H &= H_{e-p} + H_{e-e} + H_l \\
 H_{e-p} &= - \sum_{l,s} [t_0 + \alpha(u_{l+1} - u_l) + (-1)^l t_e] \\
 &\quad \times [c_{l+1,s}^\dagger c_{l,s} + \text{H.c.}] \\
 H_{e-e} &= U \sum_l n_{l,\uparrow} n_{l,\downarrow} + V \sum_{l,s,s'} n_{l,s} n_{l+1,s'} \\
 H_l &= \frac{K}{2} \sum_l (u_{l+1} - u_l)^2
 \end{aligned} \quad (1)$$

where  $t_0$  is a hopping constant (2.5 eV),  $\alpha$  is an electron–lattice coupling constant (4.78 eV/nm),  $c_{l,s}^\dagger (c_{l,s})$  denotes the electron creation (annihilation) operator with spin  $s$  at unit cluster/group  $l$  with displacement  $u_l$ , and  $t_e$  is the Brazovskii–Kirova term (0.12 eV). Including the elastic potential energy of lattice oscillations,  $K$  is an elastic constant (176.86 eV/nm<sup>2</sup>),  $U$  (2.0–5.0 eV) and  $V$  (0.5–2.0 eV) are the on-site and nearest-neighbor Coulomb interactions, and  $a$  (0.12–0.60 nm) is the lattice constant, respectively. The total Hamiltonian describing the polymer chain is called the extended Su–Schreiffer–Heeger–Hubbard Hamiltonian.<sup>25–27</sup>

To describe the electron's behavior, we have to know its energy spectrum  $\varepsilon_\mu$  and wave function  $\Phi_\mu = \{Z_{l,\mu}^s\}$ , which are functionals of the lattice displacement  $u_l$  as determined by the eigenvalue equation

$$H\Phi_\mu = \varepsilon_\mu \Phi_\mu \quad (2)$$

The electron–electron interaction is treated in the Hartree–Fock approximation, whereby the eigenvalue equation above can be written as follows:

$$\begin{aligned}
 \varepsilon_\mu Z_{l,\mu}^s &= \left[ U \left( \rho_l^{-s} - \frac{1}{2} \right) + V \left( \sum_{s'} \rho_{l-1}^{s'} + \sum_{s'} \rho_{l+1}^{s'} - 2 \right) \right] Z_{l,\mu}^s \\
 &\quad - [V \sum_\mu Z_{l,\mu}^s Z_{l-1,\mu}^s + t_0 + \alpha(u_{l-1} - u_l) + (-1)^{l-1} t_e] Z_{l-1,\mu}^s \\
 &\quad - [V \sum_\mu Z_{l,\mu}^s Z_{l+1,\mu}^s + t_0 + \alpha(u_{l+1} - u_l) + (-1)^{l+1} t_e] Z_{l+1,\mu}^s
 \end{aligned} \quad (3)$$

The charge distribution is defined as  $\rho_l^s = \sum_\mu^{\text{occ}} |Z_{l,\mu}^s|^2 - n_0$ , where  $n_0$  is the density of the positively charged background.

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

$$M \frac{d^2 u_l}{dt^2} = - \sum_\mu^{\text{occ}} \frac{\partial \varepsilon_\mu}{\partial u_l} + K(2u_l - u_{l+1} - u_{l-1}) \quad (4)$$

where “occ” stands for the occupation or population of electrons. Because the polymer is not a strongly correlated system, by using the above coupled equations and conventional molecular dynamics, we can quantitatively describe the dynamical evolution of not only the electronic states but also the lattice structure in a conjugated polymer chain.

When an external optical pulse/beam focuses on a PLED or polymer solar cell and its photon's energy just matches the band gap of the polymer, there are two energy levels ( $\Gamma_u$  and  $\Gamma_d$ ) that comprise a singlet exciton. To begin,  $|u\rangle$  and  $|d\rangle$  are taken as the wave functions of the energy levels  $\Gamma_u$  and  $\Gamma_d$ , whose energies are  $E_u$  and  $E_d$  ( $E_u > E_d$ ), and the electron population of  $\Gamma_u/\Gamma_d$  is  $P_u/P_d$ .<sup>28</sup> Without the restriction of Pauli repulsion, the dipole moment of the two localized states can be expressed as  $p = \langle u|r|d\rangle$ , where  $r(n) = na + (-1)^n u_n$  is the dipole operator and  $n$  is the unit number in the polymer chain. When an appropriate external optical field with frequency  $\omega$  and energy density  $I$  is applied to these two energy states of the energy spectrum of the conjugated polymer molecules, photon absorption occurs, and the electron in energy level  $\Gamma_d$  is pumped to level  $\Gamma_u$ .

Within the time span  $\Delta t$ , the change of the population  $\Delta P_u$  of energy level  $\Gamma_u$  consists of two parts: one is the result of stimulated transition  $\Delta P_{d \rightarrow u}$  and the other is contributed by spontaneous transition  $\Delta P_{u \rightarrow d}$  as follows:

$$\Delta P_u = \Delta P_{d \rightarrow u} + \Delta P_{u \rightarrow d} \quad (5)$$

The stimulated transition rate between two levels can be written as

$$W_{d \rightarrow u} = \frac{4\pi^2}{3\hbar^2} p^2 \rho(\omega) \delta\left(\omega - \frac{E_u - E_d}{\hbar}\right) \quad (6)$$

It is obvious that only an optical field with a certain frequency  $\omega$  and energy density  $\rho$  can affect the transition between energy levels  $\Gamma_u$  and  $\Gamma_d$ , where the intensity  $I$  of the pump laser can be expressed as  $I = \rho \times c$ . Then,

$$\Delta P_{d \rightarrow u} = W_{d \rightarrow u} P_u \Delta t \quad (7)$$

Another important factor along with stimulated emission is spontaneous emission. The spontaneous transition rate  $\gamma_{ud}$  between these states is

$$\gamma_{u \rightarrow d} = \frac{4(E_u - E_d)^3}{3\hbar^4 c^3} p^2 \quad (8)$$

Also,

$$\Delta P_{u \rightarrow d} = -\gamma_{u \rightarrow d} P_u \Delta t \quad (9)$$

Although the external optical pulse/field with a certain bandwidth determines the transition process, the spontaneous transition rate modifies the transition rate equation of electron population. Thus, the evolution of the electron populations  $P_u$  and  $P_d$  during the electron transition are expressed by the decay equation

$$\lim_{t \rightarrow 0} \frac{\Delta P_u}{\Delta t} = \lim_{t \rightarrow 0} \frac{\Delta P_{d \rightarrow u} + \Delta P_{u \rightarrow d}}{\Delta t}$$

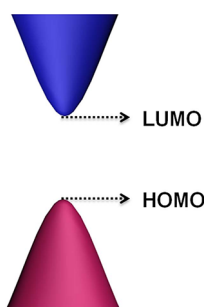
$$= \frac{dP_u}{dt} = (W_{d \rightarrow u} - \gamma_{u \rightarrow d})P_u$$

$$P_d = n - P_u \quad (10)$$

where  $n$  is the total electron number. Combining the above equations, we can quantitatively and dynamically illustrate the whole process of the self-localization of photoexcitation and exciton formation.

### III. RESULTS AND DISCUSSION

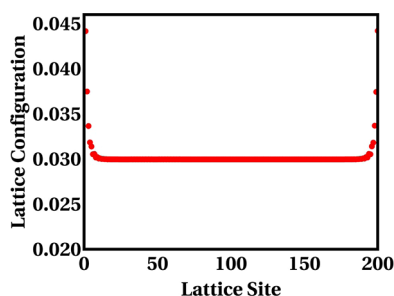
A conjugated polymers is one of the main materials of organic solar cells. Without external photoexcitation, its lattice structure is usually dimerized, which results in an energy band gap between the HOMO and LUMO. The energy spectrum is shown in Figure 1.



**Figure 1.** Electronic structure during dimerization in a conjugated polymer.

The so-called lattice configuration is a parameter to describe the situation of lattice distortion, which is generally defined as  $\phi_n = (-1)^n u_n$ , where  $u_n$  is the displacement of unit cluster/group  $n$  along the polymer chain. For convenience of demonstration, we choose a conjugated polymer consisting of 200 unit cluster/groups. For the ground state of those conjugated polymers mentioned previously, the unit cluster/groups of the conjugated polymer alternates between single and double bonds, forming lattice dimerization, as shown in Figure 2.

**Localization of an Electron–Hole Pair.** Thus, with continuous external photoexcitation or pumping, an electron in HOMO will absorb a photon, whose energy just matches the energy gap, to be excited to LUMO and thus form a singlet exciton. Recently, to examine the formation of excitons, Heeger

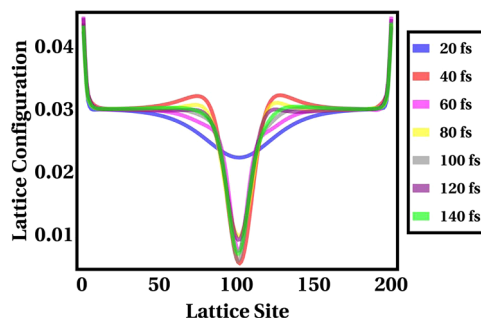


**Figure 2.** Lattice configuration for dimerization in a conjugated polymer. The vertical axis is the lattice configuration in units of Angstroms.

et al. applied an external laser beam with  $30 \mu\text{J}/\text{cm}^2$  intensity to excite conjugated polymers. Here, we apply the method mentioned in section II to depict the singlet formation, and the whole process of the singlet formation will be represented in detail by the evolution of the lattice configuration, change of electron population, and dynamic spatial distribution of electronic states. It has been reported that the dynamic localization of excitation is due to the interaction between the nuclear and electronic degrees of freedom.<sup>29</sup>

Experimentally, the pulse duration of the applied pump laser is typically from several hundred femtoseconds to several picoseconds, so that the pulse duration is longer than the localization of the electron–hole pair. Due to this and for a convenient but reasonable approximation, we have regarded the laser beam with  $30 \mu\text{J}/\text{cm}^2$  intensity as a continuous wave during the localization of the electron–hole pair.

Based on recent experimental observations, our theoretical simulation uses  $30 \mu\text{J}/\text{cm}^2$  for the external optical intensity to exhibit the excitation process of the conjugated polymer. Along with the photoexcitation of the polymer, the evolution of the lattice distortion is also different from the lattice dimerization corresponding to the ground state, as illustrated in Figure 3. As



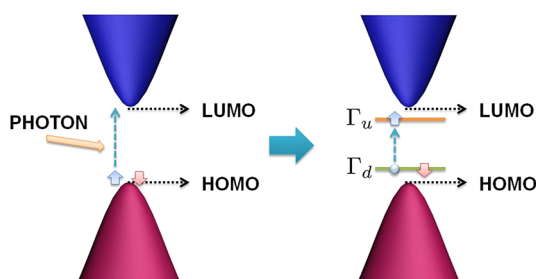
**Figure 3.** Variation of the lattice configuration for the first 140 fs.

shown in this figure, once the conjugated polymer, such as MEH-PPV or poly(3-hexylthiophene) (P3HT), is excited by the external laser beam with  $30 \mu\text{J}/\text{cm}^2$ , at 20 ps there is a shallow dent in the background where the lattice configuration of the ground state is uniformly dimerized. As time progresses, the dent grows deeper, and upon reaching 140 fs, at the center of conjugated polymer chain, the lattice structure of polymer chain is locally distorted.

Along with the lattice distortion of polymer chain, the electron transition takes place in the conjugated polymer due to photoexcitation of the external laser beam of  $30 \mu\text{J}/\text{cm}^2$ . Once the photon energy matches the energy gap between the HOMO and LUMO, the electron in the HOMO can “accept” the photon energy to jump to LUMO, thus changing the electron populations in the HOMO and LUMO. This raises a new puzzle as to what are the details of the related electron states during the photoexcitation.

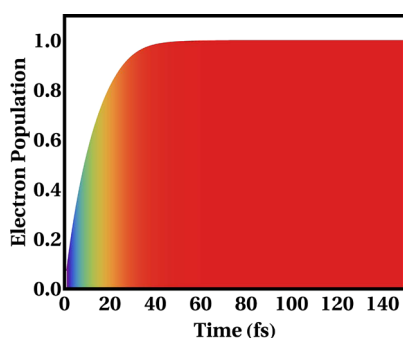
To clarify this, we turn to the spatial behavior of related electrons, concentrating on the evolution of the electronic spectra after the polymer undergoes the photoexcitation. By virtue of the strong electron–lattice coupling, the distorted lattice concurrently induces a change of electron state, including the electronic spatial distribution. Along with the distortion of the lattice configuration, the strong electron–lattice coupling induces a change in the electronic spectrum of the conjugated polymer change due to the photoexcitation.

After the electron in the HOMO accepts the photon energy to jump to the LUMO within 64 fs, the localized lattice distortion of the lattice drives the HOMO and LUMO to move to the center of energy gap, as depicted in Figure 4, forming the new state of the electron–hole pair, denoted by  $\Gamma_u$  and  $\Gamma_d$ .



**Figure 4.** Left side: electronic structure of the conjugated polymer with both electrons in the HOMO before stimulation by an external light field. Right side: electronic structure of an electron–hole pair with the state  $\Gamma_u/\Gamma_d$  occupied by a spin-up/spin-down electron.

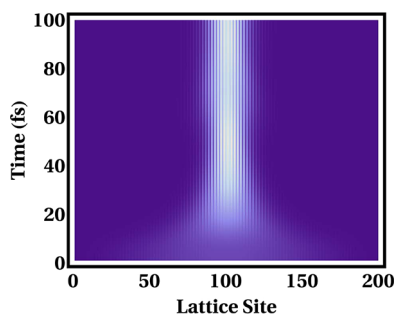
As exhibited in Figure 5, during the first 25 fs of photoexcitation, the electron population at  $\Gamma_u$  increases quickly



**Figure 5.** Time-dependent electron population during the first 150 fs. The vertical axis is the electron population in the state  $\Gamma_u$ .

and then grows more slowly in the next 25 fs. Up to 64 fs, the electron population at  $\Gamma_u$  approaches the certain value of 1. After that, the electron transition of  $\Gamma_u$  has become stable.

Furthermore, Figure 6 records the evolution of the electronic spatial distribution of the electron–hole pair on the polymer chain. At the beginning of the photoexcitation, the electron of the electron–hole pair exists over the whole chain, but after 20 fs the electron begins to be localized in the middle of the chain. Up to 40 fs, the localized electron of the electron–hole pair is



**Figure 6.** Time profile of the electron cloud of the electron–hole pair for the first 100 fs during photoexcitation.

established. Corresponding with the evolution of the lattice structure in Figure 3, we discover that the localization of the lattice structure actually maps the localization of the electron and contributes to the localized exciton as well. By combination of the results from Figures 4, 5, and 6, the electron transition evolves along with the lattice distortion and the electronic spatial distribution of the electron–hole pair, within the first 64 fs, which is in accordance with recent experiments.<sup>23</sup>

On the basis of the evolution of the lattice configuration and electronic spatial distribution due to the photoexcitation of  $30 \mu\text{J}/\text{cm}^2$ , the electron–hole pair is localized within the first 100 fs. Considering that the singlet exciton is actually an electron–hole pair, we can suggest that the localization of the electron–hole pair should be the formation of the singlet exciton. However, as reported from recent papers, exciton formation finishes at 1000 fs, so another question arises: What is the reason behind this difference?

**Relaxation of the Singlet Exciton.** To answer this question, we must understand the shift of the total energy during the process of exciton formation over a 100 fs time span. In a conjugated polymer, the total energy generally consists of electron energy, lattice kinetic energy, and lattice potential energy. Figure 7 depicts the variation of the total energy under photoexcitation of  $30 \mu\text{J}/\text{cm}^2$  within 1200 fs. In the first 100 fs, due to the photoexcitation, the total energy increases as quickly as the transition of electrons (Figure 5). It can be seen at this point that the total energy still oscillates and has not reached a stable value, which implies a relaxation process. Therefore, on the basis of the evolution of the total energy in Figure 7, the exciton formation can be divided into two parts: photon-induced electron transition and exciton relaxation. During the beginning (64 fs) of the former, the external photoexcitation of  $30 \mu\text{J}/\text{cm}^2$  increases the total energy to a level of  $-648.70 \text{ eV}$ . After this first stage of the electron transition, the total energy begins to oscillate around  $-648.96 \text{ eV}$  from 64 to 200 fs, which moves into the second stage, the relaxation process. If we prolong the time span to 1200 fs, we see that the total energy oscillates around  $-648.963 \text{ eV}$  with a period of 40 fs, as shown in Figure 7b. The oscillation amplitude of the total energy becomes weak along with the relaxation.

Besides the variation of total energy, the lattice energy, including kinetic energy and potential energy, also undergoes similar evolution during the exciton formation. As presented in Figure 8a, within the first 200 fs, the electron transition caused by the photoexcitation causes the lattice energy to decrease to  $12.00 \text{ eV}$  from  $13.50 \text{ eV}$  at the beginning, also breaking the original lattice structure of dimerization, which results in distortion of lattice configuration like in Figure 2. During the relaxation process, the lattice energy also oscillates with a period of 40 fs and gradually becomes stable at about 850 fs.

Actually, just starting from the electron–lattice coupling, the related physical picture can be constructed as: Under photoexcitation, the electron energy rapidly reaches a higher level. However, the system has not reached a stable state. To arrive to a new stable state, the system has to undergo process that involves the nuclear vibrations and reconstruction of the electron levels, namely relaxation from the occurrence of the electron–hole pair to the formation of the singlet exciton. Accompanying the oscillation of the total energy and lattice energy, Figure 9 displays the progress of the electron's energy, showing that the first shift of the oscillation happens within 100 fs, which is the same time when the lattice energy and total energy go over the peak. Soon afterward, the electron's energy



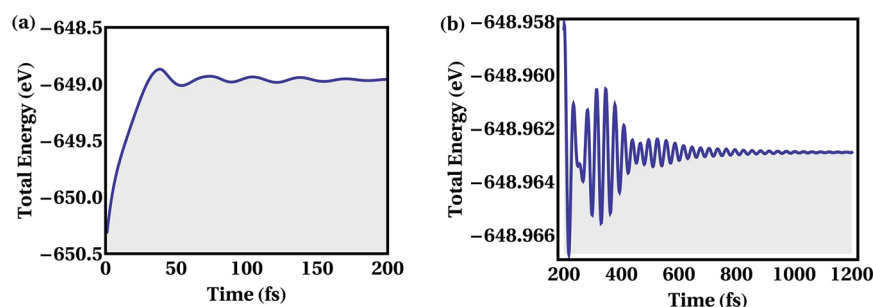


Figure 7. (a) Time-dependent total energy of the polymer chain up to 200 fs. (b) Time-dependent total energy of the polymer chain after 200 fs.

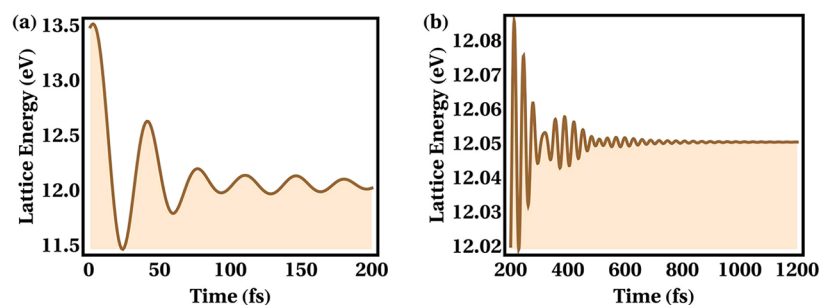


Figure 8. (a) Time-dependent energy of the lattice chain up to 200 fs. (b) Time-dependent energy of the lattice chain after 200 fs.

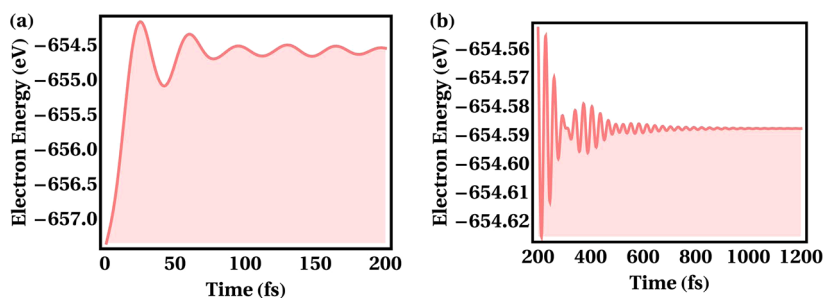


Figure 9. (a) Time-dependent energy carried by all the electrons in the polymer chain up to 200 fs. (b) Time-dependent energy carried by all the electrons in the polymer chain after 200 fs.

tends to become smooth with the original period, coming to a halt at 850 fs. At this time, as shown in Figure 10, the electron

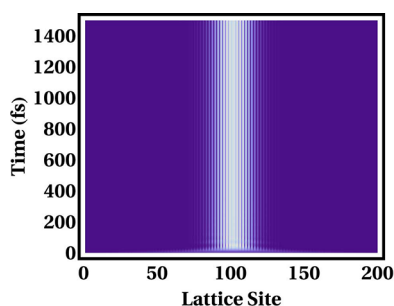


Figure 10. Time profile of the electron cloud in the singlet exciton.

localization becomes stable as well. Thus, the energy of the conjugated polymer, including the lattice and electron parts, lattice configuration and localization of the electron, has the same tendency of heading for a stable value after 850 fs. Mostly, up to 850 fs, the total energy, lattice and electron energies become stable, approaching certain values, as shown in Figures 7–9. This not only is the end of the relaxation process but also means the formation of the singlet exciton.

In the whole process of forming the singlet exciton in a conjugated polymer, the electron transition induces the localization of the electron–hole pair within the first 100 fs, as recently reported in experiment,<sup>22</sup> and the rapid increase of the total energy and electron energy also excites the oscillation of the related energies, which are presented in Figures 7a and 9a. Following this, during the relaxation process of about 800 fs, the oscillation of related energies becomes weak. Finally, at 850 fs, the related energies, such as the total, lattice, and electron energies, approach and reach certain values, and the lattice configuration is stable with local distortion, indicating the formation of the singlet exciton, which is in accord with the latest experimental results.

#### IV. CONCLUSIONS

This paper employs molecular dynamics to reveal that exciton formation can be divided into two stages: the localization of the electron–hole pair and the relaxation process. Under photo-excitation, the electron transition rapidly leads to the electron–hole pair, which also results in localization of the exciton within 100 fs, including the localization of the lattice configuration and the electronic state. In the first stage, the external photo-excitation causes the total energy to shift violently and oscillate

with a period of 40 fs, which then triggers the second stage of the excitation—relaxation. Along with the relaxation process of about 800 fs, the energy oscillates gently while the lattice configuration and electron remain localized. It is also demonstrates that the formation of the electron–hole pair is prior to the relaxation during the formation of singlet exciton. After the relaxation process of about 850 fs, the total energy, lattice energy, and electron energy reach certain values, indicating the formation of a singlet exciton. At 850 fs, the related energies, such as the total, lattice, and electron energies, reach certain values, indicating the formation of the singlet exciton, which is in accord with the latest experimental results.

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### Notes

The authors declare no competing financial interest.

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