

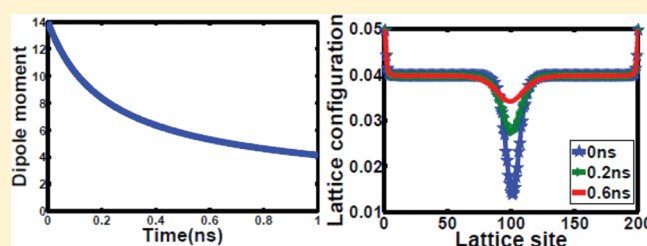
Fluorescence Dynamics and Dipole Moment Evolution of Singlet Exciton Decay in Conjugated Polymers

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ABSTRACT: Both fluorescence dynamics and time-dependent electron transitions are introduced within a previously developed molecule dynamics approach for treating conjugated polymers. This is able to provide a panoramic view of luminescence dynamics during singlet exciton decay, in which the fluorescence dynamics is largely determined by the electron population and the evolution of the dipole moment. The fluorescence intensity is weakened due to a reduced dipole moment and diminished decay rate of the electron, which validates a previous assumption based on experimental studies. The lifetime of the singlet exciton in a conjugated polymer is found to be 1.2 ns, and the calculated time profile of the fluorescence intensity is in agreement with recent experimental results.



I. INTRODUCTION

The prominent one-dimensional nature of a conjugated polymer results in specific optoelectronic and mechanical properties that have been of great interest over the past several decades. Combining photoelectronics with plastics is an interesting topic in regard to both polymer light-emitting diodes (PLEDs) and polymer solar cells.^{1–11} As it turns out, the light emission of a PLED and the photoinduced charge in a polymer solar cell is largely attributed to the dynamic properties of an exciton, that is, the bound electron–hole pair, in the conjugated polymer.

Thus, an understanding of the evolution of excitons in conjugated polymers is of particular importance to discover the mechanism of the dynamical decay of excitons in solar cells as well as PLEDs. In exploring the dynamic process of the exciton over time, time-resolved emission studies, Monte Carlo simulations, and ultrafast transient absorption polarization measurements have been utilized to explore the dynamical evolution of exciton decay,^{12–17} especially based on poly[2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylene vinylene (MEH-PPV) and its derivatives.^{18–21}

Recently, through experimental measurements by femtosecond-resolved fluorescence up-conversion, Banerji et al. demonstrated ultrafast temporal evolution of the emission spectrum of pristine poly(*N*-9-heptadecan-2,7-carbazole-alt-5,5-(4,7-di-2-thienyl-2,1,3-benzothiadiazole)) (PCDTBT) thin film and the solution in chlorobenzene after light absorption, in which the fluorescence dynamics clearly depicts the details of exciton relaxation ranging from about 500 fs to nanoseconds.²² Measuring the time-dependent fluorescence seems to provide a practical approach in experiments to discover the underlying system properties associated with the evolution of a singlet exciton. The conventional molecular dynamics method illustrates the time-dependent aspects

when a polymer undergoes external excitation; however, the difficulty to link the electron transition with the emission spectrum makes it unable to describe the temporal evolution of the emission spectrum during the evolution of exciton. The absence of a valid theoretical method depicting the fluorescence dynamics results in a gap between the experimental and theoretical research. Fortunately, in 2009, Devizis et al. pointed out that both the decay of the exciton and its dynamic relaxation might strongly depend on the dipole moment of the transition.²³ Thus, by embedding the dipole moment of transition within the molecular dynamics, we could have a first step to link theory and experiment. Combining the electron transition and fluorescence dynamics with conventional molecular dynamics in a conjugated polymer makes it possible to exhibit a panoramic view of luminescence dynamics during exciton decay, which is the purpose of this paper.

Here, we report on a molecule dynamics approach that not only involves fluorescence dynamics but also introduces time-dependent electron transitions and the evolution of the lattice configuration into the molecule dynamics. Based on this, the relaxation process of radiative decay of a singlet exciton is exhibited in detail, which provides a full picture of the evolution of exciton decay.

II. HAMILTONIAN, ELECTRONIC TRANSITIONS, AND FLUORESCENCE DYNAMICS

Considering the prominent property, strong electron–phonon coupling, of a conjugated polymer, the Hamiltonian

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for the electron–phonon interaction can be expressed as

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

where t_0 is a hopping constant, α 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 , with displacement u_l , and t_e is the Brazovskii–Kirova term. Including the elastic potential energy of lattice oscillations, the total Hamiltonian describing the polymer chain becomes

$$H = \frac{K}{2} \sum_l (u_{l+1} - u_l)^2 + H_{e-p} \quad (2)$$

namely, the Su–Schreiffer–Heeger Hamiltonian, where K is an elastic constant.

In order to describe the electron's behavior, we have to know its energy spectrum ε_μ and wave function Φ_μ , which are functionals of the lattice displacement u_l , as determined by the following eigenequation:

$$H\Phi_\mu = \varepsilon_\mu \Phi_\mu \quad (3)$$

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

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

where *occ* stands for the occupation or population of electrons. Since 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.^{24–26}

When an external optical pulse/beam is focused on a PLED or polymer solar cell and its photon's energy is resonant with the band gap of the polymer, we have the self-trapping effect, where an electron from the highest-occupied molecular orbital (HOMO) bonds to the hole of the lowest-unoccupied molecular orbital (LUMO). Concurrently, the original HOMO and LUMO move to the center of the gap and form two localized energy levels, Γ_u and Γ_d , leading to a singlet exciton.

To begin, $|u\rangle$ and $|d\rangle$ are taken as the wave functions of the localized energy levels Γ_u and Γ_d whose energies are E_u and E_d ($E_u > E_d$), and the electron population of Γ_u (Γ_d) is P_u (P_d). 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 is the dipole operator. The transition rate γ_{ud} between these states is the following:

$$\gamma_{ud} = \frac{4(E_u - E_d)^3}{3\hbar^4 c^3} p^2 \quad (5)$$

The evolution of the electron populations P_u and P_d during the electron transition are expressed by the decay equation

$$\frac{dP_u}{dt} = -\gamma_{ud} P_u, \quad P_d = n - P_u \quad (6)$$

where n is the total electron number.

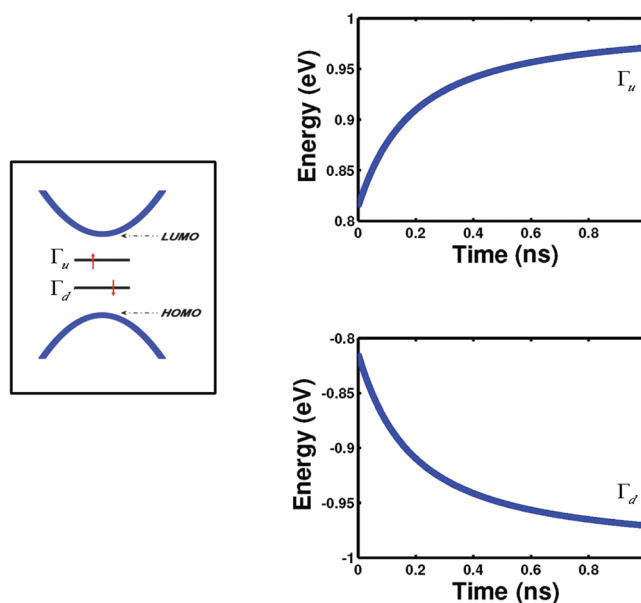


Figure 1. Left side: Electronic structure of a singlet exciton with the state Γ_u (Γ_d) occupied by a spin-up (spin-down) electron. Right side: Evolution of the energy levels Γ_u and Γ_d during the radiative decay of a singlet exciton in a conjugated polymer.

The electronic transition between Γ_u and Γ_d emits light to create the so-called fluorescence, whose intensity, F , is strongly dependent on the electron population in the upper energy level and is expressed as the following:

$$F = P_u \frac{4(E_u - E_d)^4}{3\hbar^4 c^3} p^2 \quad (7)$$

From this expression and using the rate eq 6 with conventional molecular dynamics, we are able to calculate the luminescence dynamics over time. Based on this, we can quantitatively describe the dynamical evolution of not only the fluorescence dynamics but also the lattice structure in a conjugated polymer chain.

III. RESULTS AND DISCUSSION

As mentioned in Section I, Banerji et al. utilized femtosecond-resolved fluorescence up-conversion and demonstrated the ultrafast temporal evolution of the emission spectrum of pristine PCDTBT thin film and in a solution of chlorobenzene after light excitation.²² Due to the weak coupling between polymer chains of PCDTBT in a solution of chlorobenzene, the luminescence properties in this case are largely attributed to intrachain interactions after external optical excitation. Our focus here will be on the single polymer molecule.

When a polymer undergoes excitation by an external optical pulse/beam, as mentioned in Section II, the electron from the HOMO is bound with the hole of the LUMO. This bound electron–hole pair produces two localized energy levels, Γ_u and Γ_d , at the center of the gap, leading to a singlet exciton whose electron structure is shown on the left side of Figure 1.

According to the method in Section II, thanks to the prominent self-trapping effect of the conjugated polymer, the electron transition from Γ_u to Γ_d changes the electron structure as well as the lattice configuration. The experimental data presented for the femtosecond-resolved fluorescence up-conversion for the PCDTBT

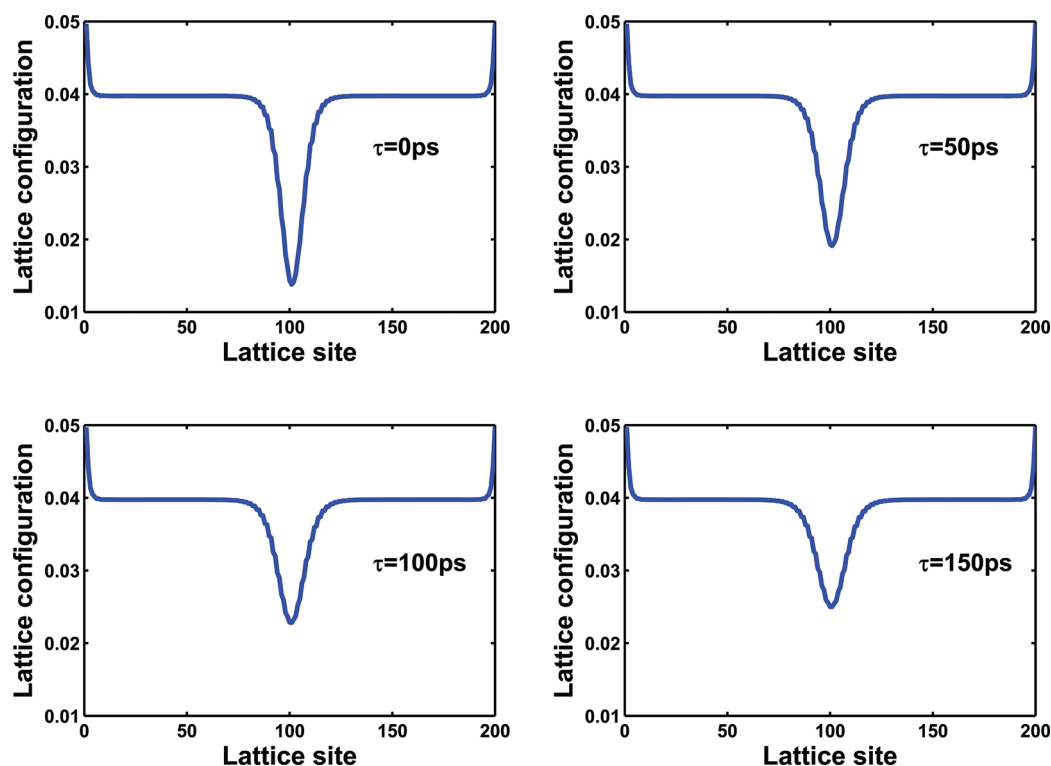


Figure 2. Lattice configuration of the singlet exciton for the first 150 fs of the radiative decay. The vertical axis is the lattice configuration in units of angstroms.

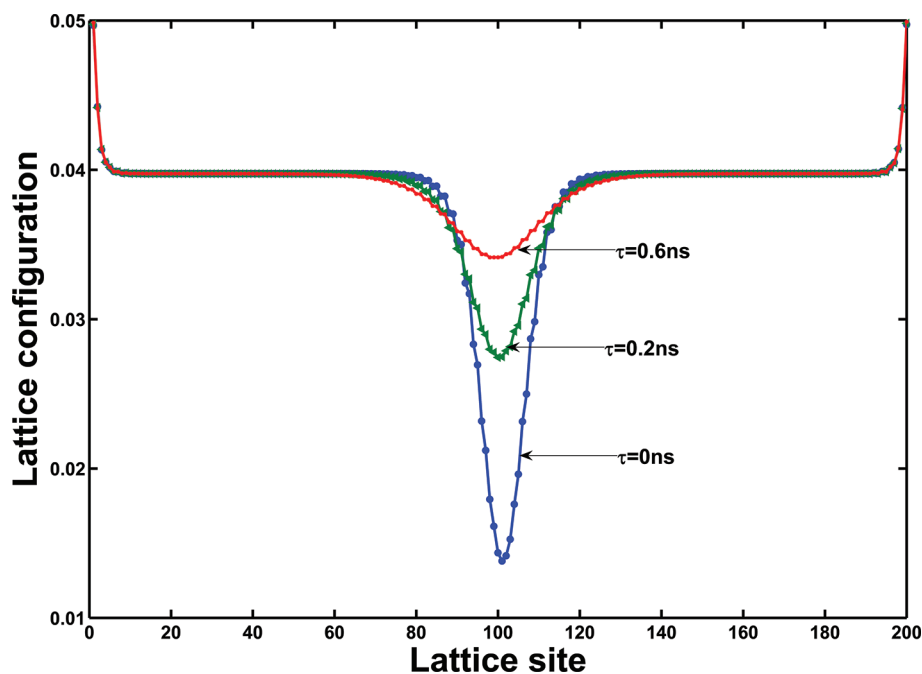


Figure 3. Lattice configuration of the singlet exciton at 0, 0.2, and 0.6 ns of the radiative decay. The vertical axis is the lattice configuration in units of angstroms.

in a solution of chlorobenzene ranges from femtoseconds to nanoseconds.²² For convenience of comparison between the experimental and theoretical results, the time scale of our obtained results is mainly in the nanosecond range. At the beginning of the light emission, the profile of the electron population is depicted

as Figure 1, where each of the two localized energy levels, Γ_u and Γ_d , is occupied by one electron with different spin, leading to the singlet exciton.

During the electronic transition contributing to light emission, the electron in Γ_u transits to Γ_d and emits light, which can be

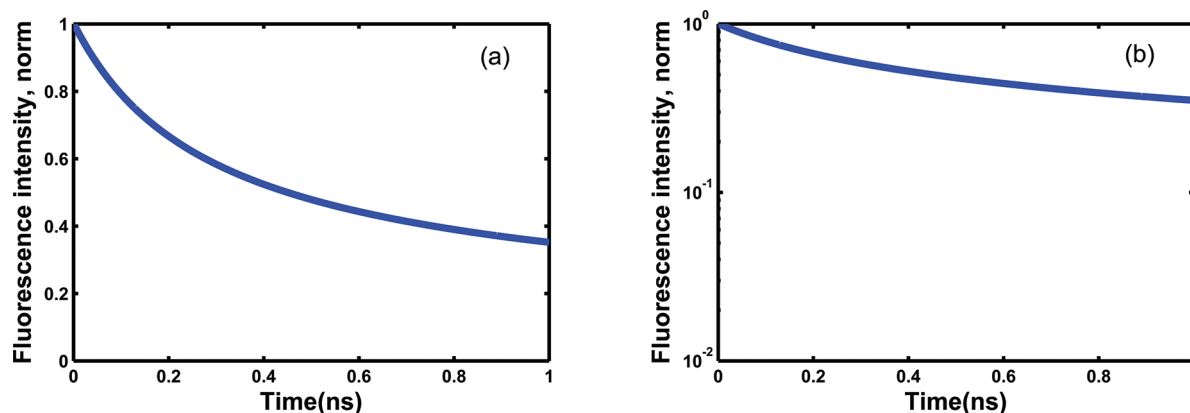


Figure 4. Time-dependent normalized fluorescence during the radiative decay of the singlet exciton. The vertical axis is the normalized fluorescence.

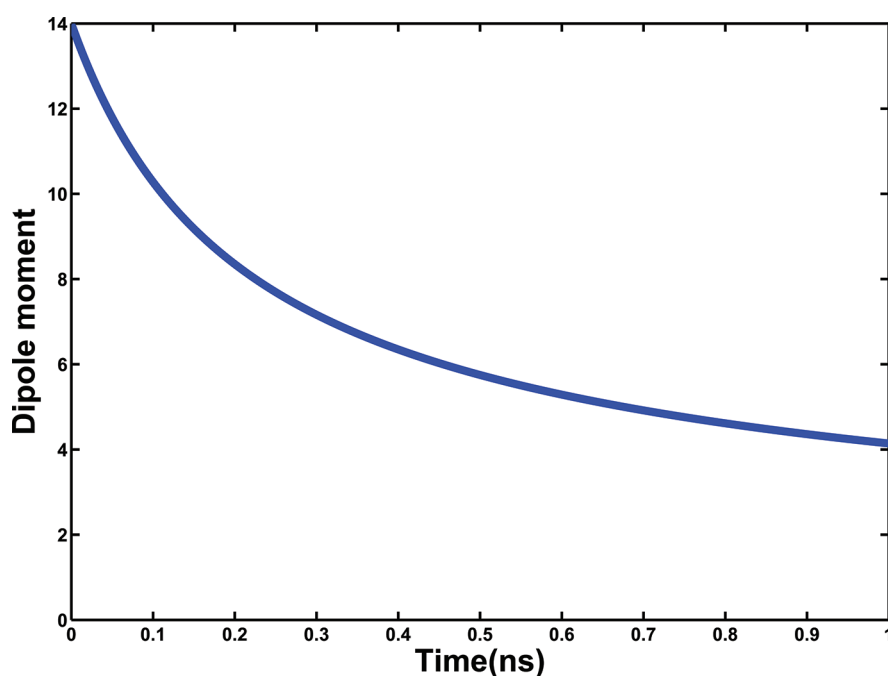


Figure 5. Time profile of the square of the dipole moment, p^2 , between Γ_u and Γ_d during the decay of the singlet exciton. The vertical axis is the square of the dipole moment in the units of $e^2 \text{ \AA}^2$.

called the decay of the exciton. During the decay, the electronic structure starts to change accordingly, where the localized energy level Γ_u moves to the LUMO and the localized energy level Γ_d is driven close to the HOMO from the beginning up to a time of 1 ns, as described on the right side of Figure 1.

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 , the lattice configuration $\phi_l = (-1)^l u_l$ describes the evolution of the lattice structure. As illustrated in Figure 2, at the beginning, the lattice configuration of the singlet exciton is locally distorted at the center of polymer chain, corresponding with its electron structure in Figure 1. Within the first 150 ps, the lattice distortion of the conjugated polymer is gradually reduced along with the change of electronic structure. When time reaches 0.2 and 0.6 ns, the lattice distortion of the conjugated polymer becomes softer than before, which as shown in Figure 3, finally goes back to the homogeneous lattice dimerization during the

decay of the exciton. Once time reaches 1.2 ns, the localized lattice configuration no longer exists.

Along with the electronic transition of the singlet exciton, the polymer emits light. Based on the method indicated in Section II, the time-dependent luminescence is depicted in Figure 4 where the emitted fluorescence has been normalized, which makes it possible to compare with the experimental results for the PCDTBT solution in chlorobenzene.²² In the ultrafast fluorescence time profile, the normalized fluorescence intensity with wavelength 660 nm becomes 0.65 when time reaches 200 ps. The spectrum intensity is 0.52 at 400 ps and 0.41 at 800 ps, which coincides well with the time profile of the experimental fluorescence spectrum.²² The time-dependent fluorescence spectrum disappears until time reaches 1.2 ns, which is the end of the electronic transition, thus indicating the lifetime of the exciton as 1.2 ns.

The agreement with the ultrafast fluorescence measurements indicates that our molecule dynamics approach is a viable means

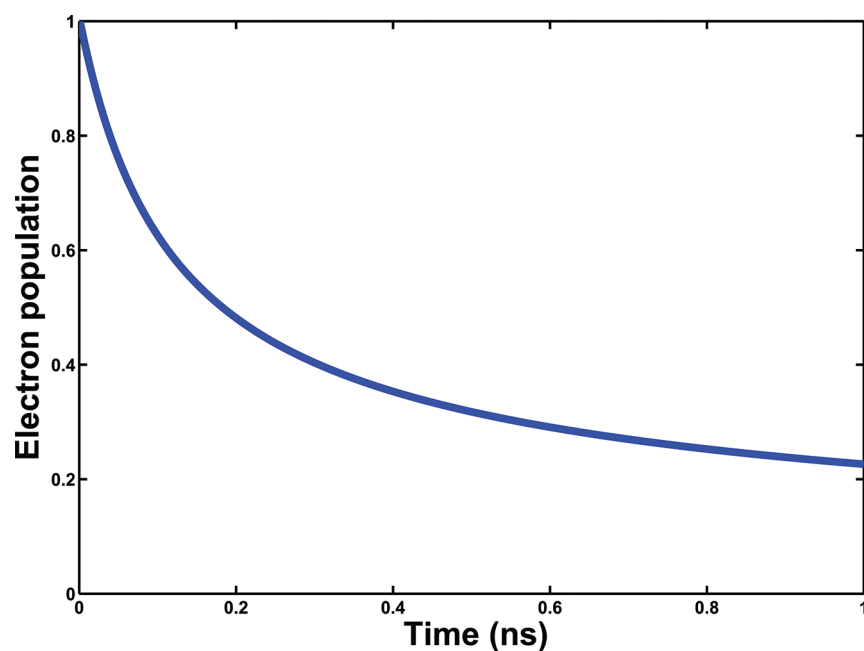


Figure 6. Time-dependent electron population in the state Γ_u of the singlet exciton of a conjugated polymer during the excitonic decay. The vertical axis is the electron population in the state Γ_u .

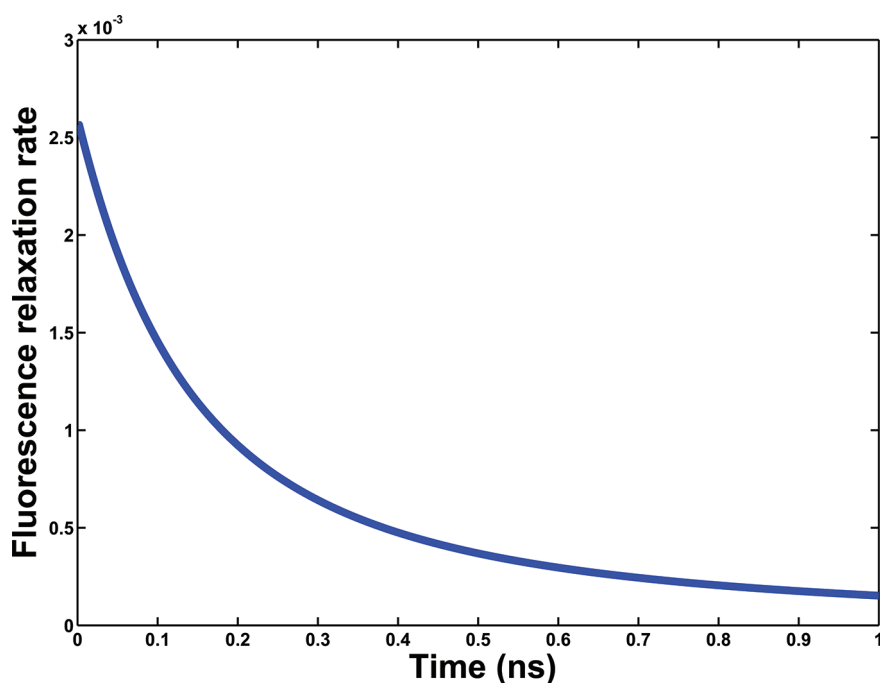


Figure 7. Time-dependent decay rate of the electronic transition from Γ_u to Γ_d during the decay of the singlet exciton. The vertical axis is the decay rate of the electronic transition from Γ_u to Γ_d in the unit of fs^{-1} .

to decipher the underlying mechanism of excitonic decay. As demonstrated experimentally by Devizis et al.,²³ the localization influences largely the property of the excited state and thus changes the transition process. We have assumed that both the decay of the exciton and its dynamic relaxation strongly depend on the dipole moment of the transition. Thus, a description of the evolution of the dipole moment seems necessary to determine the dynamical mechanism of singlet excitonic decay in conjugated polymers.

From eqs 6 and 7 in Section II, it is also found that the fluorescence intensity is proportional to the electron population and the dipole moment between Γ_u and Γ_d . During excitonic decay, the electronic transition from Γ_u to Γ_d results in a decrease of the population in Γ_u . In Figure 5, when time reaches 100 ps, the electron population of Γ_u is 0.76. Within the first 400 ps, the electron population of Γ_u exponentially decreases to 0.35. Up to 1 ns, the electron population of Γ_u becomes 0.23. Simultaneously, as

shown in Figure 1, the energy level of Γ_u moves close to the LUMO, which combined with the evolution of the lattice configuration, also reflects the self-trapping effect in the conjugated polymer.

At the beginning of the singlet excitonic decay, the dipole moment has its maximum value, and the fluorescence intensity is its largest. As we anticipated previously, the dipole moment decreases with time (Figure 6). Especially during the first 100 ps, p^2 decreases rapidly from $14 \text{ e}^2 \text{ \AA}^2$ to $10.2 \text{ e}^2 \text{ \AA}^2$. By 200 ps, the decay of the dipole moment becomes gradual, coinciding with the normalized fluorescence spectrum illustrated in Figure 4. With the reducing dipole moment in Figure 6, the decay rate of the electron transition from Γ_u to Γ_d is also diminished, as shown in Figure 7, both of which weaken the fluorescence intensity (Figure 4).

IV. CONCLUSION

Thanks to our developed method where both the fluorescence dynamics and time-dependent electronic transitions are introduced and embedded within the molecular dynamics, we can exhibit in detail how the electron population and dipole moment determine the fluorescence dynamics of the singlet exciton decay in a conjugated polymer, which validates the previous experimental assumption that the decay of the exciton and its dynamic relaxation might strongly depend on the dipole moment of the transition. Hence, the overall fluorescence dynamics for the conjugated polymer, due to the radiative decay of the singlet exciton, can be described as follows: The fluorescence emission of a conjugated polymer is attributed to the radiative electronic transition for a singlet exciton. In agreement with recent experimental results,^{22,23} during the decay of the exciton, not only is the fluorescence intensity weakened, but also the dipole moment is reduced. Associated with the evolution of the lattice structure, the lattice distortion of the conjugated polymer diminishes during the decay of the exciton, finally going back to the homogeneous lattice dimerization. Also, the time-dependent fluorescence intensity obtained theoretically agrees with recent experimental results, and the lifetime of the singlet exciton in the conjugated polymer is seen to be 1.2 ns, also in agreement with the experiment.^{22,23}

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