

Supporting Information

Directional and ultrafast migrations of excitons/biexcitons in organic polymers by utilizing a local nonuniform electric field

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1. The model description of a polymer in the framework of a tight-binding SSH model

For the polymer, we give it a model description referring to *cis*-polyacetylene, consisting of weakly interacted linear chains of CH units. Along a single *cis*-polyacetylene chain, each carbon atom has three $2sp^2$ hybrid orbitals in a plane and one $2p_z$ orbital orthogonal to this plane. The $2sp^2$ orbitals give rise to three σ -bonds, two of which are formed with neighboring carbons and one with a hydrogen. The electron in the $2p_z$ orbital of one carbon atom will be paired with the electron in the neighboring carbon's $2p_z$ orbital, such that it can be delocalized along the chain, denoted as π -electron. According to the Peierls instability, the one dimensional (1D) chain will be dimerized and form a single-double bond alternation lattice structure.

Here, such a polymer chain can be described by an extended version of the 1D tight-binding Su-Schrieffer-Heeger (SSH) model,¹⁻³ where each CH unit is regarded as a site. The Hamiltonian consists of three parts

$$H_0 = -\sum_n t_{n,n+1} (C_{n+1}^+ C_n + C_n^+ C_{n+1}) + \frac{1}{2} K \sum_n (u_{n+1} - u_n)^2 + \frac{1}{2} M \sum_n \dot{u}_n^2 \quad (1)$$

The first one shows the electronic part, which describes the hopping of π -electrons between the neighboring sites along the polymer chain. $t_{n,n+1}$ shows the transfer integral of a π -electron between sites n and $n+1$, written as

$$t_{n,n+1} = t_0 - \alpha(u_{n+1} - u_n) - (-1)^n t_e \quad (2)$$

It should be stressed that $t_{n,n+1}$ is tightly related to the site displacement u_n , and the correlation extent is determined by the electron-lattice (e-l) interaction constant α . For an organic polymer, the value of α is much larger than the silicon-based inorganic

materials. Therefore, once the electronic states are changed, such as through photoexcitation, the lattice structure will undergo a distortion, which, vice versa, results in a reconstruction of the electronic states (i.e., self-trapping effect).³ t_0 represents the transfer integral between neighboring sites for a uniform lattice structure, and t_e the symmetry-breaking parameter introduced to describe a system with a non-degenerate ground state.

The second and the third terms in eqn (1) show the lattice part of the polymer, which separately describes the elastic potential energy and the kinetic energy of the lattice. K represents the elastic constant between neighboring sites, and M the mass of a site.

Values of the model parameters are separately set as $t_0=2.5$ eV, $\alpha=41$ eV nm⁻¹, $K=2100$ eV nm⁻², $M=1.35\times 10^5$ eV fs² nm⁻², and $t_e=0.05$ eV.

2. Realization of the initial state (exciton or biexciton)

Here, let us clarify how we get the initial state of exciton/biexciton before the dynamical simulations. For the modeled polymer chain consisting of $N=200$ sites, its ground state can be obtained with 200 π -electrons occupying the 100 levels of the valence band. Moving an electron (or two electrons) from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), an exciton (or biexciton) can be created in the polymer by iteratively solving the static electronic eigenequation (eqn (3)) and the lattice balance equation (eqn (4))

$$-t_{n,n+1}\varphi_{\mu}(n+1)-t_{n-1,n}\varphi_{\mu}(n-1)=\varepsilon_{\mu}\varphi_{\mu}(n) \quad (3)$$

$$u_{n+1} - u_n = -\frac{2\alpha}{K} \left(\rho_{n,n+1} - \frac{1}{N-1} \sum_m \rho_{m,m+1} \right) \quad (4)$$

ε_μ is the eigenenergy of an eigenstate $\varphi_\mu(n)$. The lattice balance equation is obtained by minimizing the total energy E of the system (i.e., $\partial E / \partial u_n = 0$), in which we employ a fixed boundary condition. The total energy E is written as

$$E = \sum_{\mu}^{occ} \varepsilon_\mu + \frac{1}{2} K (u_{n+1} - u_n)^2 \quad (5)$$

Here, “*occ*” indicates the sum only for the occupied electronic states.

3. The quantum nonadiabatic evolution method

In dynamical simulations, we assume that an exciton or biexciton has already formed in the polymer chain. Once the nonuniform electric field $E_n^{//}$ is turned on, the initially formed exciton/biexciton will experience dynamical evolutions. By employing a nonadiabatic evolution method, we can separately obtain the temporal evolution of the lattice displacement $u_n(t)$ (i.e., nuclear motion) and the electronic state $|\psi_\mu(t)\rangle$. Here, the nuclear motion is classically described by the Newtonian equation of motion

$$M\ddot{u}_n = -K(2u_n - u_{n+1} - u_{n-1}) + 2\alpha[\rho_{n,n+1}(t) - \rho_{n-1,n}(t)] + eE_n^{//}(t)[\rho_{n,n}(t) - 1] \quad (6)$$

The density matrix $\rho_{n,n'}(n' = n \pm 1)$ is defined as

$$\rho_{n,n'}(t) = \sum_{\mu} \psi_{\mu}^*(n,t) f_{\mu} \psi_{\mu}(n',t) \quad (7)$$

$\psi_{\mu}(n,t) = \langle n | \psi_{\mu}(t) \rangle$ is the projection of electronic state $|\psi_{\mu}(t)\rangle$ on the Wannier state of site n . f_{μ} ($= 0, 1, 2$) is a time-independent distribution function and determined by the initial occupation of the electronic state $|\psi_{\mu}(t)\rangle$. Evolution of $\psi_{\mu}(n,t)$ follows the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \psi_{\mu}(n,t) = -t_{n,n+1} \psi_{\mu}(n+1,t) - t_{n,n-1} \psi_{\mu}(n-1,t) + e r_n E_n(t) \psi_{\mu}(n,t) \quad (8)$$

The coupled differential eqn (6) and (8) are numerically solved by the Runge-Kutta method of order eight with step-size control,⁴ which has been widely used and proven to be an effective approach in the dynamical investigations of polymers.⁵⁻⁸

4. Comparison, definition, and the detailed calculation method for the exciton/biexciton binding energies

Quantitatively, we can introduce the binding energy to describe the binding extent between the excited electron and hole in an exciton (E_B^{ex}) or a biexciton (E_B^{biex}), the values of which are separately calculated to be $E_B^{\text{ex}} = 0.26$ eV and $E_B^{\text{biex}} = 0.89$ eV for the present values of parameters. Compared with the exciton, the larger binding energy of the biexciton should be attributed to the stronger local lattice potential. This result can be reflected by the deeper lattice distortion (see Fig. S1) and gap energy levels (see Fig. S2) of a biexciton than those of an exciton. The definition and the detailed calculation method for the exciton/biexciton binding energies are as follows.

For an exciton in the polymer, the binding energy is defined as the energy difference of the system after and before its dissociation.⁹ Different from the conventional inorganic system, the generated electron and hole after the exciton dissociation will also behave in spatially localized forms,^{10, 11} known as the negative polaron (P^-) and positive polaron (P^+), respectively (see Fig. S3a). So, the exciton binding energy can be obtained by calculating $E_B^{\text{ex}} = E_{P^+P^-} - E_{\text{ex}}$, where $E_{P^+P^-}$ is the

system energy with free negative and positive polarons existed, and E_{ex} the system energy with an exciton generated.

Similarly, for a biexciton in the polymer, the binding energy is defined as the energy difference of the system after and before its dissociation. However, the difference is that, after the biexciton dissociation, a negative bipolaron (BP^{2-}) and a positive bipolaron (BP^{2+}) are generated (see Fig. S3b).^{12, 13} Correspondingly, the biexciton binding energy is obtained by $E_{\text{B}}^{\text{biex}} = E_{\text{BP}^{2+}+\text{BP}^{2-}} - E_{\text{biex}}$, where $E_{\text{BP}^{2+}+\text{BP}^{2-}}$ is the system energy with free negative and positive bipolarons existed, and E_{biex} the system energy with a biexciton generated.

5. Model description for two parallelly aligned polymer chains

For the interaction between two interacted polymer chains with a parallel alignment, we can employ the following description

$$H_{\perp} = -\sum_n t_{\perp} (C_{1,n}^+ C_{2,n} + C_{2,n}^+ C_{1,n}) \quad (9)$$

t_{\perp} stands for the interchain transfer integral of a π -electron between the nearest sites of the two chains.

6. Supplementary Figures

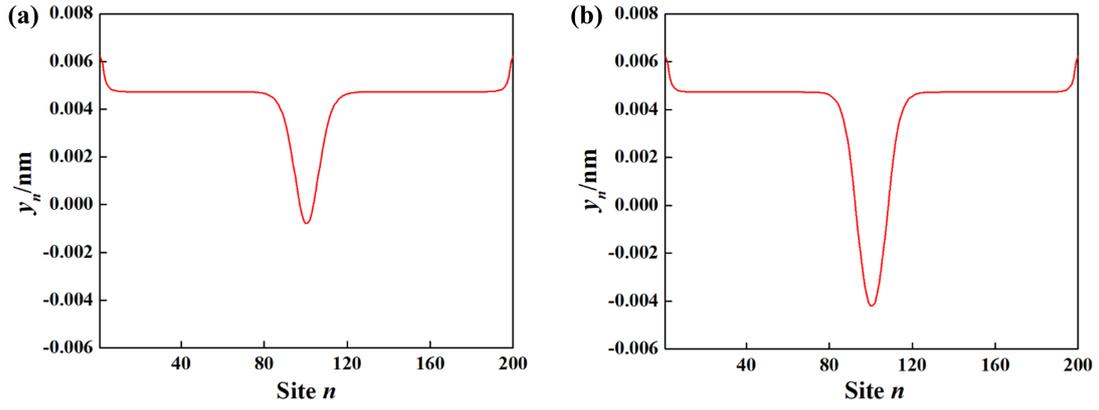


Fig. S1 Lattice structure ($y_n = (-1)^n(u_{n+1} - u_n)$) of a polymer chain, which separately lies in an exciton state (a) and a biexciton state (b).

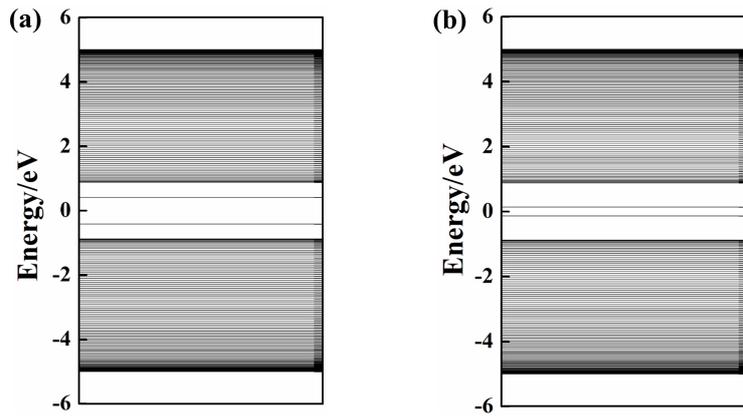


Fig. S2 Energy level structure of a polymer chain, which separately lies in an exciton state (a) and a biexciton state (b).

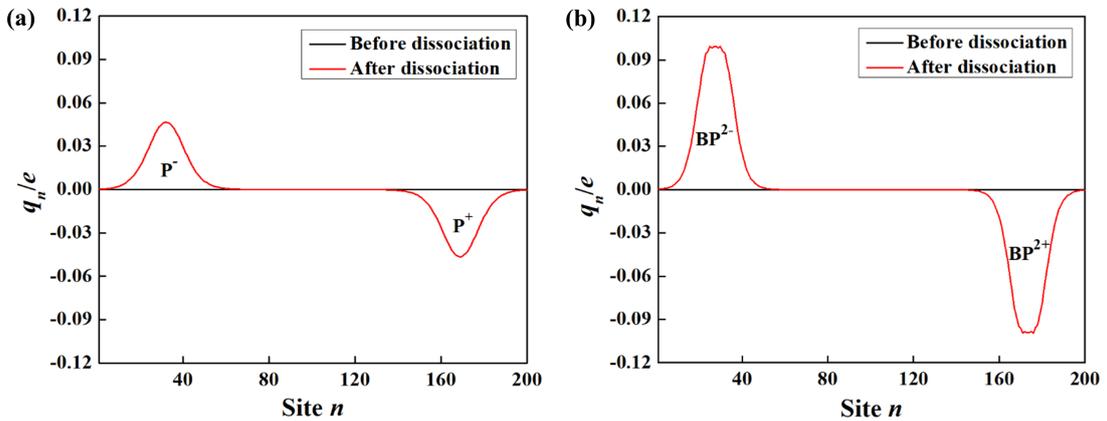


Fig. S3 The net charge distribution ($q_n = e(\rho_{n,n} - 1)$) of an exciton (a) and a biexciton (b) before and after dissociations.

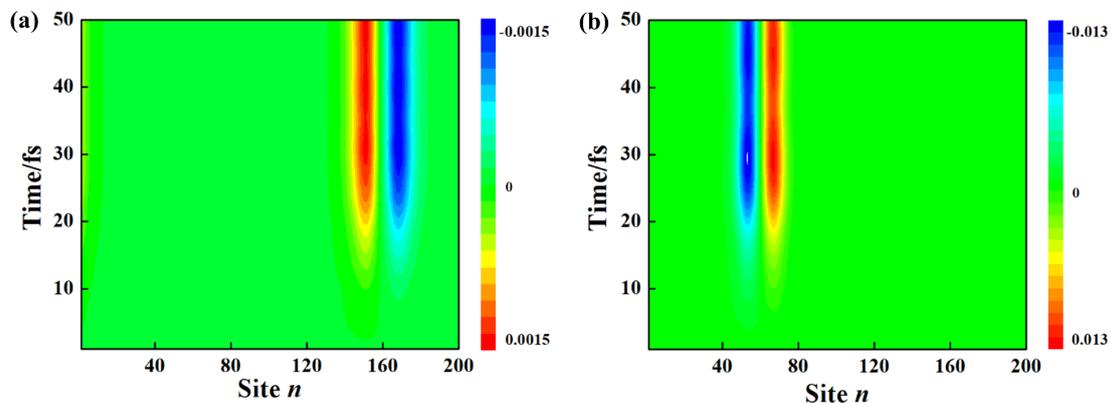


Fig. S4 Initial evolutions ($t \leq 50$ fs) of the net charge distribution $q_n(t)$ (unit: e) during the exciton (a) and biexciton (b) dynamics.

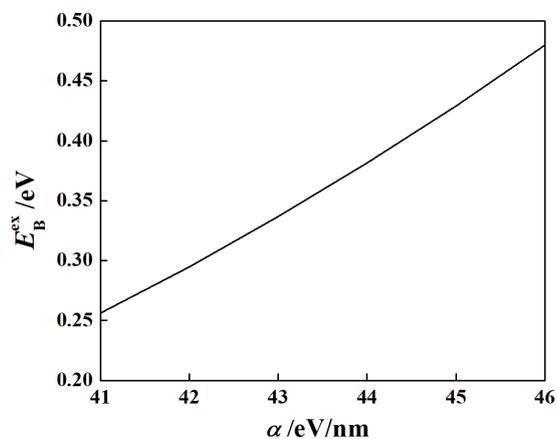


Fig. S5 Dependence of the exciton binding energy E_B^{ex} upon the electron-lattice interactions α in the polymer chain.

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