Effect of disorder on exciton dissociation in conjugated polymers*

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By using a multi-configurational time-dependent Hartree–Fock (MCTDHF) method for the time-dependent Schrödinger equation and a Newtonian equation of motion for lattice, we investigate the disorder effects on the dissociation process of excitons in conjugated polymer chains. The simulations are performed within the framework of an extended version of the Su–Schrieffer–Heeger model modified to include on-site disorder, off-diagonal, electron–electron interaction, and an external electric field. Our results show that Coulomb correlation effects play an important role in determining the exciton dissociation process. The electric field required to dissociate an exciton can practically impossibly occur in a pure polymer chain, especially in the case of triplet exciton. However, when the on-site disorder effects are taken into account, this leads to a reduction in mean dissociation electric fields. As the disorder strength increases, the dissociation field decreases effectively. On the contrary, the effects of off-diagonal disorder are negative in most cases. Moreover, the dependence of exciton dissociation on the conjugated length is also discussed.

Keywords: polymer, exciton, electron–electron correlation, dynamical evolution

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1. Introduction

In recent years, optoelectronic devices based upon conjugated polymers, for instance, organic light-emitting diodes (OLEDs),[1] field-effect transistors (FETs),[2] and photovoltaic cells,[3] have attracted sustained attention in global society.[4] Specifically, organic photovoltaic cells (OPVs) are particularly attractive because of their outstanding advantages such as low cost, light weight, easy fabrication, and flexible features, which are emerging as as a promising solution to the energy crisis and environmental pollution.

The photovoltaic effect involves the generation of electron and hole pairs and their subsequent collection at the opposite electrodes. In inorganic materials, free charges are produced by the photon absorption directly, while in organic materials, due to the strong electron–phonon interactions, photoexcitations will induce a generation of an electron-hole pair bound by lattice distortion, i.e., the exciton.[5] Therefore, the dissociation of excitons is considered to be one of the most important processes for photovoltaic conversion in polymer-based solar cells, and is a key influencing factor in determining the strength of the photocurrent.[6]

The generation of separated charges in photovoltaic materials generally results from the dissociation of these strongly bound excitons through the assistance of bulk trap sites, interface of materials with different electron affinities, or a high electric field. Based on these properties, a considerable amount of both experimental and theoretical research works has been done to effectively improve the charge generation efficiency of organic photovoltaic devices,[7–14] in which, the dissociation field of the exciton is a primary measure for photovoltaic conversion. However, studies have shown that it is practically impossibly to expect the theoretical predicted dissociation fields could occur in the electric fields usually encountered in organic solar devices.[15,16] Moreover, disorder commonly occurs in organic materials, and considerable research has indicated that the disorder effects are crucial for improving organic devices.[17–20] For example, theoretically, Yuan *et al.* simulated the polaron dynamics in a system of two randomly coupled polymer chains, and suggested that the inter-chain coupling disorder can achieve higher charge transport depending on the coupling strength and the electric field. Moreover, they also indicated that the diagonal disorder depresses polaron motion in most cases while off-diagonal disorder can open energetically easier pathways for charge transport.[21,22] Böhlin, *et al.* studied the effect of dynamic disorder on charge transport along a pentacene chain, and given the picture that the evolution of charge transport process may vary from an adiabatic polaron drift process to a combination of sequences of adiabatic drift and non-adiabatic hopping events depending on the degree of disorder.[23] Experimentally, Menon *et al.* studied the controlling polydispersity and demonstrated that energetic disorder has a negative effect on the device efficiency.[24] However, Konezny *et al.* indicated with experimental and numerical model results that increasing the energetic disorder in the active layer can lead to an increase in the device efficiency depending on the device parameters.[25] Clearly, the structural disorder is an im-

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portant factor in determining the charge transport for polymer-based devices, and the disorder can be controlled but not eliminated. In this work, we focus on the effects of disordered structure on exciton dissociation under the influence of electric field in polymer chains. Two kinds of disorder, on-site disorder and off-diagonal disorder, are under consideration in this work, which are introduced into the simulations by randomly chosen on-site energies and hopping integrals between nearest-neighbor sites, respectively. In additional, the electron–electron correlation effects also play an important role in transport/recombination/dissociation processes,[26–32] which are taken into consideration in our simulations by employing the multi-configurational time-dependent Hartree–Fock (MCTDHF) method.[33,34]

This paper is arranged as follows. The model and method are present in Section 2 and the results and discussions are shown in Section 3. Finally, a summary is given in the last section.

2. Model and method

We consider a polymer chain with structural disorder, which can be well modelled by Hubbard extension of a Su–Schrieffer–Heeger (SSH)-type Hamiltonian.[35–38] The Hamiltonian is given as follows:

$$H = H_{\text{latt}} + H_{\text{elec}}. \tag{1}$$

The first part is to describe the lattice elastic potential energy and kinetic energy, respectively,

$$H_{\text{latt}} = \frac{K}{2}\sum_i (u_{i+1} - u_i)^2 + \frac{M}{2}\sum_i \dot{u}_i^2, \tag{2}$$

where K denotes the force constant originating from the σ-bond between carbon atoms, M is the mass of a CH group, and u_{i} is the monomer displacement of site i from its undimerized equilibrium position.

The second part in Eq. (1) is to describe the Hamiltonian of the electronic part of the system

$$H_{\text{elec}} = H_{\text{el}} + H_{\text{E}}, \tag{3}$$

which includes both the on-site energy of π-electrons, electron transfer integral, and electron–electron interaction:

$$H_{\text{el}} = \sum_{i,s} \varepsilon_i c_{i,s}^{\dagger} c_{i,s} - \sum_{i,s} t(i)[c_{i,s}^{\dagger} c_{i+1,s} + \text{H.c.}] + U\sum_i n_{i,\uparrow} n_{i,\downarrow}, \tag{4}$$

where $t(i)[\equiv t_i - \alpha(u_{i+1} - u_i) + (-1)^i t_e]$ is the hopping integral between sites i and $i+1$ with α being electron–lattice coupling constant; t_e is the Brazovskii–Kirova symmetry-breaking term introduced for non-degenerate polymers,[39] U presents on-site repulsive interaction. $c_{i,s}^{\dagger}$ and $c_{i,s}$ are electron creation and annihilation operators at site i with spin s, respectively. $n_{i,s}$=$c_{i,s}^{\dagger} c_{i,s}$ is the electron occupation operator. ε_i is the on-site energy of π-electrons of the i-th site, and t_i is the transfer integral of π electrons for an undimerized lattice. In our simulations, ε_i and t_i are considered as random variables which satisfy a probability distribution. There are many types of disordered distribution and we choose the most commonly used Gaussian distribution:

$$\rho(\varepsilon_i) = \frac{1}{\sigma_\varepsilon\sqrt{2}} \exp[-\varepsilon_i^2/2\sigma_\varepsilon^2], \tag{5}$$

and

$$\rho(t_i) = \frac{1}{\sigma_t\sqrt{2}} \exp[-(t_i - t_0)^2/2\sigma_t^2], \tag{6}$$

where the standard deviation σ_ε and σ_t describe the degree of disorder, corresponding to on-site disorder and off-diagonal disorder, respectively. Thus, structural disorder can be introduced into the simulation in an easy and controlled way. It should be noted that the disorder considered here is static and uncorrelated.

The electric field $E(t)$ is included in the Hamiltonian as a scalar potential. This gives the following contribution to the Hamiltonian:

$$H_{\text{E}} = E(t)|e|\sum_{i,s}(\text{i}a + u_i)\left(c_{i,s}^{\dagger} c_{i,s} - \frac{1}{2}\right), \tag{7}$$

where e is the electron charge, and a is the lattice constant. The model parameters we use in this work are those generally chosen for trans-polyacetylene:[40] $t_0 = 2.5$ eV, $t_e = 0.05$ eV, $K = 21.0$ eV/Å, $\alpha = 1.22$ Å, $M = 1349.14$ eV$\cdot$fs^2/Å^2, and a bare optical phonon energy $\hbar\omega_Q = \hbar\sqrt{4K/M} = 0.16$ eV.

Now, we briefly describe the numerical method in our simulations. The static structure is determined by the minimization of the system energy in the absence of an external electric field. In the non-adiabatic evolution processes, the atoms are considered as classical particles, governed by the Newtonian equation of motion, and move under the effects of lattice and electronic contributions:

$$M\ddot{u}_i = -\nabla_i\langle\psi|H|\psi\rangle. \tag{8}$$

The electrons, on the other hand, are treated quantum-mechanically and evolve according to the time-dependent Schrödinger equation

$$\text{i}\hbar|\dot{\psi}\rangle = H|\psi\rangle. \tag{9}$$

If the electronic part of the Hamiltonian only contains one-body operators, the solution is trivial. But when two-body operators occur as well as the electron–electron interactions, the solution of the full many-body problem given in Eq. (9) is generally not possible and approximate methods are necessary. As mentioned above, we use the MCTDHF method to solve this Schrödinger equation.[33,34] Within this method, the

electronic wave function can be written in terms of the linear combination of atomic orbitals (LCAO) coefficients, C_{ik_μ}

$$\mathrm{i}\hbar\dot{C}_{ik_\mu} = \sum_j R_{ij} C_{jk_\mu} \tag{10}$$

with

$$R_{ij} = \sum_{\mu,\nu(n^\mu \neq n^\nu)} \sum_{k,l} P^\nu_{ik} \frac{n^\nu F^\nu_{kl} - n^\mu F^\mu_{kl}}{n^\nu - n^\mu} P^\mu_{lj}. \tag{11}$$

The Fock operator for shell μ is expressed in the atomic orbitals basis set as

$$\begin{aligned} F^\mu_{ij} = &-\left[\frac{U}{2} + \sum_{k\neq i} v_{ik}\right]\delta_{ij} - t_i\delta_{i+1,j} - t_{i-1}\delta_{i-1,j} \\ &+ \left[\sum_\nu \sum_k n^\nu a^{\mu\nu} P^\nu_{kk} v_{ik}\right]\delta_{ij} - \frac{1}{2}\sum_\nu n^\nu b^{\mu\nu} P^\nu_{ij} v_{ij} \\ &+ eE(t)(\mathrm{i}a + u_i)\left[1 - \sum_\mu P^\mu_{ij}\right]\delta_{ij}, \end{aligned} \tag{12}$$

where $P^\mu_{ij} = \sum_{k_\mu} C_{ik_\mu} C^*_{jk_\mu}$ denotes an element of the projector onto shell μ in the atomic orbitals basis set, $n^\mu = 0, 1, 2$ is its occupation number and $a^{\mu\nu}$, $b^{\mu\nu}$ are state parameters specific to the particular form of the wave function. The evolution of the lattice is determined by the equations of motion

$$\begin{aligned} M\ddot{u}_i(t) = &-K(2u_i - u_{i+1} - u_{i-1}) + 2\alpha(\mathrm{Re}\rho_{i,i+1} - \mathrm{Re}\rho_{i,i-1}) \\ &+ |e|E(t)(1 - \rho_{i,i}), \end{aligned} \tag{13}$$

where the density matrix is

$$\rho_{ij} = \sum_\mu n^\mu P^\mu_{ij} = \sum_\mu \sum_{k_\mu} n^\mu C_{ik_\mu} C_{jk^*_\mu}. \tag{14}$$

The coupled differential Eqs. (10) and (13) can be solved numerically by using the Runge–Kutta method of order 8 with step-size control.

3. Results

Our numerical simulations are mainly performed on a conjugated polymer chain of length $N = 100$. As is known, charge injection or photo-excitation generates an electron–hole pair, i.e., the exciton, which is trapped by lattice distortion because of the strong electron–lattice interactions in organic materials. For convenience, a pre-existing exciton is deliberately situated around the middle of the chain. The initial geometry is acquired by minimizing the total energy of the chain with static disorder before dynamic evolution. Because we simulate a chain including structural disorder, the exciton should adjust the position to ensure the system energy reaches its minimum. When the external electric field is applied, but in order to avoid abrupt changes and reduce the lattice vibration, the electric field is turned on smoothly in the form of Gaussian function, that is, the field strength changes as $E(t) = E_0 \exp[-(t - t_c^2/t_\omega^2)]$ when $0 < t < t_c$, $E(t) = E_0$ when $t_c < t$ with t_c being a smooth turn-on period, t_ω the width. Here, we choose $t_\omega = 25$ fs, $t_c = 75$ fs.

The disorder is introduced according to a Gaussian distribution, and the larger the standard deviation σ_ε (σ_t), the more disordered the system. When the σ_ε (σ_t) is fixed, the random seeds produce a set of random sequence, $\{\varepsilon_i\}$ ($\{t_i\}$), which determines the on-site energies (hopping integrals). The dynamical process of dissociation should be different under diverse disordered configurations. Theoretically, more seeds lead to less random error. However, numerical simulations are finite and time-consuming, especially involving electron–electron correlation effects. As described in Ref. [22], most of the simulations are performed repeatedly with 16–20 random seeds. For some regions of strong disorder, more than 32 samples are analyzed to ensure the convergence of results.

At first, it should be stated that we find the field required to dissociate a singlet exciton reduces with the increasing of on-site Coulomb repulsion in present Su–Schrieffer–Heeger + Hubbard model, which is contrary to the results of Su–Schrieffer–Heeger + Pariser–Parr–Pople (PPP) model.[41] In the PPP model including long-range Coulomb attraction, the electron and hole are not easily separated under the presence of an electric field, such that eventually an over-large field is required to dissociate the exciton. Furthermore, the Hubbard model can be regarded as an infinite shielding factor limit of the PPP model. As illustrated in Fig. 6 of Ref. [41], the critical dissociation electric field decreases quickly with an increase in shielding factor β. For the case of singlet exciton, the net electron charge density (defined by $\rho(n) = \sum_s \rho_s(n), \rho_s(n) = \langle c^\dagger_{n,s} c_{n,s}\rangle - 0.5$) for spin-up and spin-down electrons are equal, and the width of exciton is broadened by the Hubbard U because the Coulomb repulsive does not favor two antiparallel electrons to occupy the same site. In general, the wider the exciton width, the smaller its binding energy. Along with the reducing of binding energy, the exciton becomes unstable, resulting in a decrease of dissociation field. In contrast, the net charge distributions are opposite for opposite spins in triplet excitons. Therefore, the exciton states become more localized whith the increasing of Coulomb interactions and result in a narrower exciton width. Furthermore, the charges in lattice deformation are polarized by applied external electric field before the exciton dissociation. As qualitatively described above, the singlet exciton polarizability can be much larger than that of triplet excitons (not shown here). As a result, the dissociation of triplet exciton is much harder than that for singlet exciton. Therefore, the on-site Coulomb interaction U should exert opposite effects on the dissociation of singlet and triplet excitons in the present SSH+Hubbard model. The correctness of the above mentioned is also confirmed by our time-dependent density matrix renormalization group (t-DMRG) calculation.

We are now investigating the dynamic evolution of excitons under the influence of an external electric field. We consider first the dynamic process of singlet excitons with on-site disorder. Figure 1 shows the contrast between ordered and disordered systems by plotting the time-dependence of staggered bond order parameter $\delta_i = (-1)^i(u_{i+1} - u_i)/2$ for $U = 2.0$ eV with different electric field strengths. When the electric field strength is below the critical dissociation field, e.g., $E_0 = 5.0$ mV/Å, the lattice deformations exhibit an amplitude oscillation with time, and the electron and hole are confined in one lattice deformation during the overall process, as shown in Fig. 1(a). With the increasing of electric field, the electronic polarization in lattice deformation becomes stronger, the excitons have a tendency to dissociate if the energy provided by the electric field is high enough to overcome the constraint of the lattice. When the external electric field reaches a critical value of about $E_0 = 5.8$ mV/Å, as shown in Fig. 1(b), the width of the exciton becomes wider initially. Soon afterwards, the electron and hole separate and move toward opposite ends of the chain about 180 fs. The situation is quite different when the on-site disorder effects are taken into account. In Fig. 1(c), we show the dynamical evolution of staggered bond order parameter for the case of $E_0 = 5.0$ mV/Å but with $\sigma_\varepsilon = 0.1$ eV. And of course, the simulations should give somewhat different results with different sets of disorder configurations. One should note that the electron–hole symmetry and space-inversion symmetry are broken by introducing the disorder, and more importantly, the dissociation electric field strength, which reduces obviously compared to the ordered system.

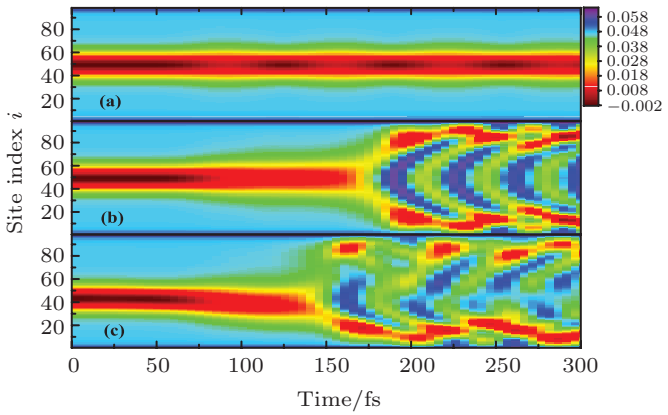


Fig. 1. (color online) Dynamical evolution of the staggered bond order parameter $\delta_i = (-1)^i(u_{i+1} - u_i)/2$ with time for singlet excitons. (a) $U = 2.0$ eV, $E_0 = 5.0$ mV/Å, $\sigma_\varepsilon = 0$ eV; (b) $U = 2.0$ eV, $E_0 = 5.8$ mV/Å, $\sigma_\varepsilon = 0$ eV; (c) $U = 2.0$ eV, $E_0 = 5.0$ mV/Å, $\sigma_\varepsilon = 0.1$ eV.

In the following, we analyze the dominant mechanism of exciton dissociation process under different Coulomb interactions and on-site disorder degree. Since different disorder configuration of $\{\varepsilon_i\}$ may cause fluctuations in the potential gradient, it is clear that a saturated or constant critical electric field strength is no longer expected when a system with static disorder is considered. Generally, the stronger the disorder, the larger the standard deviation(variance) is. In Fig. 2(a), we give the relation of mean critical fields $\langle E \rangle$ of singlet excitons, along with the standard deviations (plotted as error bar), to the degree of disorder σ_ε for several values of on-site Coulomb repulsion. Although the dominating contribution to the exciton dissociation comes from the electron–electron correlation effect, the importance of disorder may also be significant. When the interaction between the electrons is not too strong, our simulation results suggest that the increased on-site disorder leads to a reduction in mean dissociation electric fields and an increase in standard deviations. Take $U = 2.0$ eV as an example, it is found that the critical fields exhibit a random amplitude fluctuation around the critical value of a system without disorder, as shown in the inset of Fig. 3. The maximum and minimum dissociation fields are $E_0 = 6.4$ mV/Å and $E_0 = 4.0$ mV/Å for $\sigma_\varepsilon = 0.1$ eV, respectively. After a statistical average over the fluctuations of fields, compared with an ordered system, more than 11% reduction in critical field is achieved when the degree of disorder σ_ε equals 0.14 eV. As in the case of strongly correlated electrons, such as $U = 4.1$ eV, the mean critical field increases slightly first, and then decreases with increasing of disorder strength. Besides an increasing dependence on on-site Coulomb repulsion, the disorder effect on dissociation of triplet excitons is qualitatively similar to that of singlet excitons, as shown in Fig. 2(b).

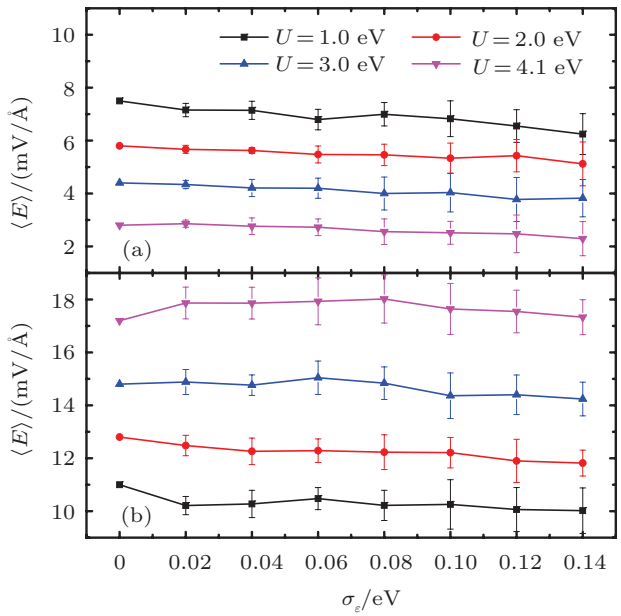


Fig. 2. (color online) The mean critical dissociation electric field $\langle E \rangle$ and the standard deviations (plotted as error bar) as a function of the degree of on-site disorder σ_ε for different on-site Coulomb repulsion U: (a) single exciton; (b) triplet exciton.

Since the conjugation length of polymers also plays a vital role in determining the dissociation of exciton states, it is necessary to study the relationship of static disorder to conjugated length. In the inset of Fig. 3, we give a comparison

of critical electric fields between the chain length of $N = 100$ and $N = 140$ for $U = 2.0$ eV, $\sigma_\varepsilon = 0.1$ eV. One can find that the strengths of critical field are almost all less than that in an ordered chain of length $N = 140$. This behavior is different from that in a short chain, in which the critical fields fluctuate around a value of without including disorder. As a result, the mean critical dissociation electric fields show an even more decreasing trend with increasing the conjugated chain length.

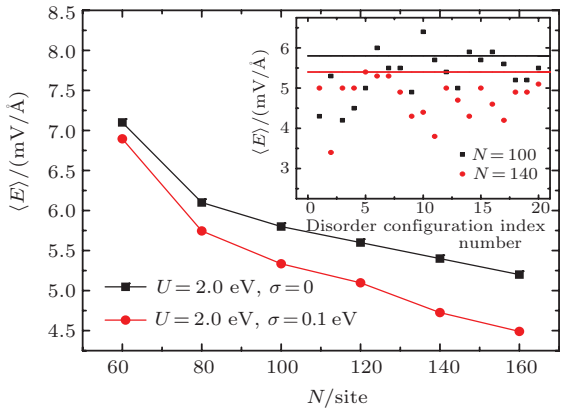


Fig. 3. (color online) The mean critical dissociation electric fields $\langle E\rangle$ as a function of conjugated length. The inset shows critical fields with different disorder configurations for the case $N = 100$ (black dots) and $N = 140$ (red dots) compared with the corresponding ordered systems (black line and red line).

Finally, for the case of off-diagonal disorder, because the hopping integrals determine the charge hopping rate most directly, the mean critical dissociation electric fields should be quite sensitive to the off-diagonal disorder, as shown in Fig. 4 (note the different scale as compared to Fig. 2). But unfortunately, we find that the off-diagonal disorder does not favor the exciton dissociation process in most cases. The mean critical dissociation electric field only exhibits a small decrease in the very weak disorder region ($\sigma_t < 0.004$ eV).

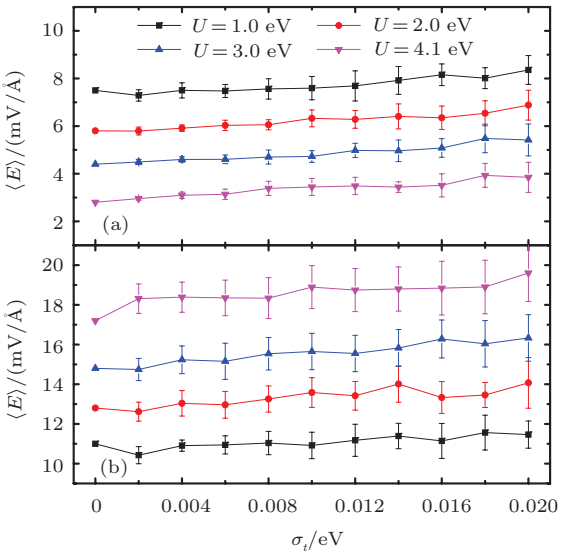


Fig. 4. (color online) The mean critical dissociation electric field $\langle E\rangle$ and the standard deviations (plotted as error bar) as a function of the degree of off-diagonal disorder σ_t for different on-site Coulomb repulsion U: (a) single exciton; (b) triplet exciton.

4. Conclusion

Within a Su–Schriffer–Heeger model modified to include disorder effect, electron–electron interaction, and an external electric field, we have investigated the dependence of exciton dissociation on the Coulomb interaction strength, degree of disorder, and the conjugated length. The simulations are performed using a multi-configurational time-dependent Hartree–Fock method for the time-dependent Schrödinger equation and a Newtonian equation of motion for lattice. Our results suggest that the on-site disorder effects contribute to the dissociation of exciton, thereby leading to a distinct lower mean critical dissociation field compared to an ordered system. However, the off-diagonal disorder does not favor the exciton dissociation process in most cases. We hope the theoretical results are able to provide productive guidance for organic solar cells.

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