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Why is exciton dissociation so efficient at the interface between a conjugated polymer and an electron acceptor?

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Although doping of a conjugated polymer by electron acceptors strongly facilitates exciton dissociation into geminate pairs of carriers, the yield of free carrier photogeneration can be high only at high doping levels, that is, in polymer/acceptor blends. We suggest a model that explains how excitons can efficiently dissociate into free carriers at an intrinsic polymer/acceptor interface despite the Coulomb interaction between the charges within precursor geminate pairs. © 2003 American Institute of Physics. [DOI: 10.1063/1.1586456]

The discovery of efficient charge transfer across a conjugated polymer/fullerene interface¹ paved the way for technological breakthrough in the design of organic photovoltaic devices.^{2,3} Strong electron acceptors have long been known to be efficient quenching centers for excitons in conjugated polymers such that practically all optical excitations are quenched at the acceptor molecules even if their concentration is less than 1%.⁴ The probable quenching mechanism was identified as dissociation of a vibrationally relaxed exciton into a short geminate pair of a hole at the donor and an electron at a nearby acceptor.^{4,5} Nevertheless, the efficiency of free carrier photogeneration remains very low, $\approx 10^{-3}$, at acceptor concentrations less than 5%.⁵ At higher concentrations, that is, in polymer/acceptor blends, the yield of intrinsic charge carrier photogeneration can increase up to 60%–70% provided that the morphological demands are met.^{3,6} This implies that the mechanisms of geminate pair dissociation are different at small and large concentrations of electron acceptors. This notion is supported by the fact that strongly bound short geminate pairs of photogenerated charge carriers can be detected at small concentrations of acceptors, while in polymer/acceptor blends, free charges and/or loosely bound long pairs have been observed.⁷

It is generally believed that dissociation of relaxed excitons into free charge carriers occurs upon electron trapping at a charge transfer center. If so, a short geminate pair of charge carriers must be formed as a first step of the dissociation, with the electron being localized in an acceptor molecule and the hole occupying an adjacent conjugated segment. Since low dielectric constants of 3–4 are typical for conjugated polymers, such short pairs must be strongly bound by the Coulomb interaction with a binding energy of several tenths of an electron volt. However, experimentally observed activation energies of carrier photogeneration at charge transfer centers and at polymer/acceptor interfaces are typically less than 0.1 eV at room temperature, and tend to vanish at lower temperatures. This anomalously weak temperature depen-

dence indicates that, in excess of the equilibrium phonon bath, some sort of energy assists separation of short geminate pairs into free carriers. Since relaxed excitons can also dissociate into free carriers, this cannot be the excess energy an initially hot exciton might supply.^{8,9} Vibrational energy, released from electron trapping, will be rapidly dissipated, and it can hardly assist hopping of the localized electron.

However, there is another way for making profitable use of the energy gained from carrier trapping. It is based on the notion that the Coulomb electric field of the trapped electron together with the external electric field forms both a potential well and a potential barrier for the on-chain hole. The kinetic energy of zero-point oscillations of the hole within the potential well effectively reduces the energy required for crossing of the barrier and thus facilitates dissociation of geminate pairs. In qualitative agreement with experimental data, obtained on pristine^{10,11} and weakly doped⁵ polymers, this model predicts a relatively low carrier photogeneration yield that depends only weakly upon temperature.¹² However, this mechanism cannot explain the much higher yield in some polymer/acceptor blends with appropriate composition/morphology.¹³ The fact that the intrinsic dissociation yield can even exceed 50% at moderate electric fields indicates that Coulomb attraction between carriers within short geminate pairs must be effectively screened or counterbalanced. In the present letter, we suggest a model of interfacial exciton dissociation in donor–acceptor blends that shows how the repulsive potential barrier can be formed at a polymer/acceptor interface.

The model rests on the notion that a dipolar layer can be formed at a polymer/acceptor interface, as testified by the observation of a vacuum level shift of 0.25 eV at the interface between the five-ring conjugated oligomer *p*-bis[(*p*-styryl)styryl]benzene and C_{60} .¹⁴ The associated dipole moment is 4.7 D and the partial charge of 10% of the elementary charge for the dipole size of 1 nm. An optical excitation, generated in a conjugated polymer, can diffuse towards the interface and dissociate into a short geminate pair. Immediately after dissociation, the electron will be localized at the electron acceptor molecule, while the hole re-

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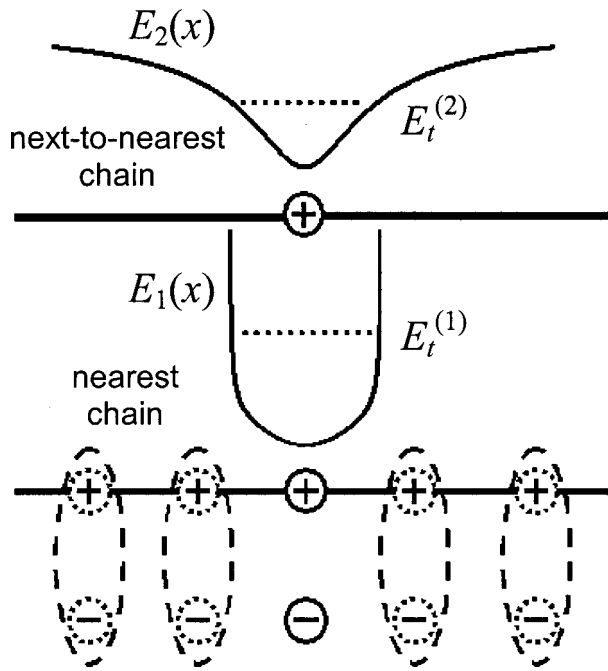


FIG. 1. Potential energy distribution and total energy of a hole occupying a polymer chain either nearest or next-to-nearest to a polymer/acceptor interface. The potential distributions are caused by dark interfacial dipoles and the sibling electron trapped at an acceptor next to the interface.

mains on the polymer chain next to the interface. The potential energy of the on-chain hole, E_p , is determined by its interaction with the negatively charged nearest electron acceptor and partial charges of dark dipoles, as shown in Fig. 1. The following consideration is based on the existence of an internal interface between donors and acceptors in the blend, in which the polymer chains are parallel to the interface and the acceptors form a regular array. By neglecting contributions of all partial charges except for four nearest ones, the

coordinate dependence of the potential energy along the chain can be evaluated as

$$E_p(x) = \frac{e^2}{4\pi\epsilon_0\epsilon} \left(-\frac{1}{\sqrt{x^2+b^2}} + \frac{\alpha}{a+x} + \frac{\alpha}{a-x} - \frac{\alpha}{\sqrt{(a+x)^2+b^2}} - \frac{\alpha}{\sqrt{(a-x)^2+b^2}} \right), \quad (1)$$

where a is the distance between electron acceptors and, therefore, between on-chain partial charges of the interfacial dipoles, b is the distance between the chain and electron acceptors, and αe is the partial charge transferred from the chain to an acceptor in the dark.

Although an on-chain hole is supposed to be in extended state, it cannot move freely along the chain, mainly because of positive partial dipole charges residing on the same chain to the right and to the left of the hole. Together with negatively charged acceptors, these charges form an on-chain potential well for the hole and restrict its otherwise free motion along the chain. In order to estimate the energy of zero-point oscillations within this potential well, E_{osc} , one can approximate the real potential distribution given by Eq. (1) by the oscillatory potential as

$$E(x) \approx \frac{e^2}{4\pi\epsilon_0\epsilon} \left(-\frac{1}{b} + \frac{2\alpha}{a} - \frac{2\alpha}{\sqrt{a^2+b^2}} \right) + \frac{e^2}{8\pi\epsilon_0\epsilon} \left[\frac{1}{b^3} + \frac{4\alpha}{a^3} - \frac{6\alpha a^2}{(a^2+b^2)^{5/2}} \right] x^2. \quad (2)$$

The total energy $E_t^{(1)}$ of a hole, occupying the ground state on the chain nearest to the interface, is a sum of the minimum potential energy $E_p(0)$ and the kinetic energy of zero-point oscillations:

$$E_t^{(1)} = \frac{e^2}{4\pi\epsilon_0\epsilon} \left(-\frac{1}{b} + \frac{2\alpha}{a} - \frac{2\alpha}{\sqrt{a^2+b^2}} \right) + \frac{\hbar}{2} \sqrt{\frac{e^2}{4\pi\epsilon_0\epsilon m_{\text{eff}}}} \left[\frac{1}{b^3} + \frac{4\alpha}{a^3} - \frac{2\alpha}{(a^2+b^2)^{3/2}} - \frac{6\alpha a^2}{(a^2+b^2)^{5/2}} \right], \quad (3)$$

where m_{eff} is the on-chain carrier effective mass. If the hole has been transferred from the chain nearest to the interface to the next-to-nearest one, its Coulombic potential energy increases but, at the same time, its kinetic energy drops significantly because the caging effect is eroded. The calculation, similar to the described earlier, leads to the following expression for the total energy $E_t^{(2)}$ of such a hole:

$$E_t^{(2)} = \frac{e^2}{4\pi\epsilon_0\epsilon} \left[-\frac{1}{(b+c)} + \frac{2\alpha}{\sqrt{a^2+c^2}} - \frac{2\alpha}{\sqrt{a^2+(b+c)^2}} \right] + \frac{\hbar}{2} \sqrt{\frac{e^2}{4\pi\epsilon_0\epsilon m_{\text{eff}}}} \left\{ \frac{1}{(b+c)^3} - \frac{2\alpha}{(a^2+c^2)^{3/2}} + \frac{6\alpha a^2}{(a^2+c^2)^{5/2}} + \frac{2\alpha}{[a^2+(b+c)^2]^{3/2}} - \frac{6\alpha a^2}{[a^2+(b+c)^2]^{5/2}} \right\}, \quad (4)$$

where c is the distance between polymer chains. The energy difference $E_t^{(1)} - E_t^{(2)}$ is shown in Fig. 2 as a function of the effective carrier mass for different values of the parameter α . Remarkably, this energy difference is positive at sufficiently small values of the effective carrier mass, that is, a repulsive potential barrier separating a negatively charged acceptor

and a hole occupying a segment of a chain next nearest to the interface is established. This prevents geminate recombination and stabilizes the interfacial geminate pairs provided that the effective mass is ≤ 0.1 free electron mass.

Since the model requires polymer chains being fully parallel to the interface within, at least, two molecular layers

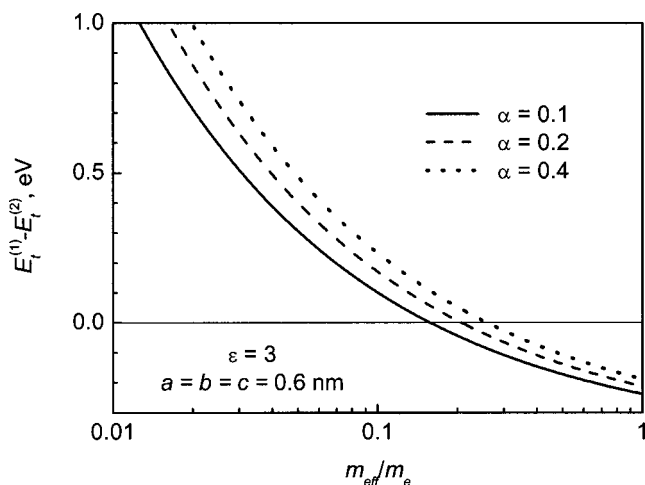


FIG. 2. Dependence of the repulsive barrier height upon the effective on-chain carrier mass for different values of the dark-charge-transfer parameter α .

nearest to the interface and the array of acceptor molecules being ordered, it readily explains why (i) the molecular ordering near the internal donor/acceptor interface and (ii) a sufficiently high concentration of acceptors is crucial for attaining a high photovoltaic efficiency. Because of the importance of zero-point oscillations of one of the carriers comprising the initial geminate pair, it is also obvious why polymeric photovoltaic cells are more efficient than small molecular devices. The only exception from the rule we are aware of are cells containing a discotic donor, such as derivatives of benzocoronene.¹⁵ In the context of the present theory, this is remarkable because it is known that their lowest excited states are excitons with efficient charge oscillations within a pair of molecules. This is equivalent to a low effective mass of the charge.

The suggested model explains the increase of the photo-generation efficiency at higher acceptor concentrations in terms of the increase of the dissociation rates rather than a decrease of the rate of monomolecular decay of the geminate pair. Alternatively, one could invoke the onset of percolative motion of the electron across the array of acceptor molecules. However, any change of the carrier diffusivity without an independent increase of the dissociation rate constant could not affect the trade-off between dissociation and recombination of geminate pairs.

The present model has several practically important implications. (i) The morphology of the interface separating a conjugated polymer and an electron acceptor must strongly affect the exciton dissociation yield, as experimentally verified. Any structural disorder at the interface is counterproductive because it will diminish the energy of zero-point oscillations and, therefore, destroy the barrier for geminate recombination. (ii) The existence of a dipolar layer at the

donor/acceptor interface facilitates dissociation. Partial charges, existing prior to photoexcitation, narrow the on-chain potential well and thus increase both the energy of zero-point oscillations and the height of the barrier, which can act as a bottleneck against interfacial geminate pair recombination. (iii) Efficient dissociation of excitons is possible at moderate external electric fields only if carriers within geminate pairs are separated by potential barriers, which prevents geminate recombination. This is not the case for so-called "double-cable" polymers.¹⁶ Therefore, the present model of interfacial dissociation predicts a relatively low efficiency of photovoltaic devices based on double cables.

In conclusion, we suggest a model explaining efficient exciton dissociation at an interface between a conjugated polymer and an electron acceptor. We show that, due to zero-point oscillation of an on-chain hole, an effective energy barrier for the hole can be formed on the chain nearest to the interface. When the hole is transferred to the next-nearest chain, this barrier separates the twins within the geminate pair and prevents them from geminate recombination. The model emphasizes the importance of the molecular ordering at the interface and the existence of a dipolar layer at internal interface due to different electronegativities of donor and acceptor materials.

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