Exciton fission via ultrafast long-range resonant tunnelling in organic photovoltaic diodes

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We present an exciton/lattice model of the electronic dynamics of primary photoexcitations in a polymeric semiconductor heterojunction which includes both polymer \(\pi\)-stacking, energetic disorder, and phonon relaxation. Results from our model are consistent with a wide range of recent experimental evidence that excitons decay directly to well-defined polarons on a sub-100 fs timescale, which is substantially faster than exciton relaxation processes. Averaging over multiple samples, we find that as the interfacial offset is increased, a substantial fraction of the density of electronic states in the energy region about the initial exciton carries significant charge-transfer character with two charges separated in the outer regions of the model lattice. The results indicate a slight increase in the density of such current-producing states if the region close to the interface is more disordered. However, since their density of states overlaps the excitation line-shape of the primary exciton, we show that it is possible that the exciton can decay directly into current-producing states via tunneling on an ultrafast time-scale. We find this process to be \textit{independent} of the location of energetic disorder in the system, and hence we expect exciton fission via resonant tunnelling to be a ubiquitous feature of these systems.

Subject Areas: Chemical Physics, Condensed Matter Physics, Materials Science

\section{I. INTRODUCTION}

Photovoltaic diodes based on blends of semiconductor polymers and fullerene derivatives now produce power conversion efficiencies exceeding 10\% under standard solar illumination \cite{1}. This indicates that photocarriers can be generated efficiently in well-optimized organic heterostructures, but the mechanism for converting highly-bound Frenkel excitons to photocarriers is not understood in spite of vigorous, multidisciplinary research activity. A detailed mechanistic understanding of primary charge generation dynamics is of key fundamental importance in the development of organic solar cells, and we propose it to be generally important in photoinduced charge-transfer processes in condensed matter. Recent spectroscopic measurements on organic photovoltaic systems have reported that charged photoexcitations can be generated on \(\leq 100\)-fs timescales \cite{2,10} but full charge separation to produce photocarriers is expected to be energetically expensive given strong Coulombic barriers due to the low dielectric constant in molecular semiconductors. Nonetheless, experiments by Gélinas et al., in which Stark-effect signatures in transient absorption spectra were analyzed to probe the local electric field as charge separation proceeds, indicate that electrons and holes separate by \(~40\AA\) over the first 100 fs and evolve further on picosecond timescales to produce unbound charge pairs \cite{11}. Concurrently, Provencher \textit{et al.} have demonstrated, via transient resonance-Raman measurements, clear polaronic vibrational signatures on sub-100-fs on the polymer backbone, with very limited molecular reorganization or vibrational relaxation following the ultrafast step \cite{12}. Such spectacularly and apparently universally rapid through-space charge transfer between excitons on the polymer backbone and acceptors across the heterojunction would be difficult to rationalize within Marcus theory within a localized basis without invoking unphysical distance dependence of tunnelling rate constants \cite{13}. We focus here on the role that quantum coherence dynamics in a disordered \(\pi\)-stacked polymer lattice, which are correlated to the dynamical motion of the molecular framework \cite{14}, and that of energetic disorder in promoting the asymptotic separation of mobile charge pairs following photoexcitation. The significant element in the context of ultrafast charge separation in the system considered here is the involvement of delocalized charge-transfer states in the early quantum dynamics of the exciton. Our model is based upon a Frenkel exciton lattice model parameterized to describe the \(\pi\)-electronic states of a polymeric-semiconductor type-II heterojunction \cite{15,18}.

We introduce energetic disorder by randomizing the local site energies in the region about the heterojunction interface or in the region away from the interface and analyze the resulting electron-hole eigenstates. Polymer microstructural probes have revealed general relationships between disorder, aggregation and electronic properties in polymeric semiconductors \cite{19}. Moreover, aggregation (ordering) can be perturbed by varying the blend-ratio and composition of donor and acceptor polymers \cite{20}. On one hand, energetic disorder at the interface would provide a free-energy gradient for localized charge-transfer
states to escape to the asymptotic regions. In essence, the localized polarons in the interfacial region could escape into band of highly mobile polarons away from the heterojunction region [21]. On the other, energetic disorder in the regions away from the interface would provide an entropic driving force by increasing the density of localized polaron states away from the interfacial region, allowing the polarons to hop or diffuse away from the interface before recombination could take place [22]. Finally, a report by Bakulin et al. indicates that if relaxed charge-transfer-excitons are pushed with an infrared pulse, they increase photocurrent via delocalized states rather than by energy gradient-driven hopping [23].

II. LATTICE EXCITON MODEL

We employ a two-band exciton/phonon model we described previously modified as to include both stacking and a band-offset to define a heterojunction domain [15–18]. Each site contributes a valance and conduction band Wannier orbital and the ground state consists of each site being doubly occupied. A sketch of our model system is shown Fig.1h. The blue sites have an energy band offset relative to the red-sites of $\Delta E$ which provides the necessary driving force for charge-separation at the interface between the two domains. The important distinction between the present model and that for a single chain is that we estimate the interchain hopping term is an order of magnitude smaller than the intrachain hopping term $t_{\perp} \approx t_{\parallel}/10$. Single electron/hole excitations from the ground-state are considered within configuration interaction (CI) theory which includes all singlet electron/hole configurations.

Each local site also contributes two localized phonon modes which modulate the energy gap at each site and give rise to optical phonon bands that are delocalized across each chain. No explicit interchain vibronic coupling was included in our model. The two bands included correspond to the Franck-Condon active modes that contribute to the absorption and fluorescence spectra of conjugated polymer containing phenylene groups such as poly-phenylen-vinylene (PPV). Specifically, these correspond to low frequency torsional modes with frequencies $\omega_\parallel$ and the higher frequency C=C stretching modes which are well-known to be coupled to the $\pi$-electronic states in poly-phenylene type conjugated polymer systems. With exception as noted above, the electronic couplings and electron/phonon couplings used here are the same as reported in our earlier works on exciton dissociation at interfaces [21][22]. A complete listing of the interaction terms and parameters is given in Ref. [10].

A. The role of interfacial disorder

To explore the role of interfacial disorder, we include a small amount of gaussian noise ($\sigma/t_{\parallel} = 0.2$) in the local HOMO–LUMO gaps in either the region close to the interface or in the regions away from the interface. We shall refer to the two as the “ordered-disordered-ordered” model (ODO) and “disordered-ordered-disordered” model (DOD) respectively. In Fig. 1, we show the average density of states produced by our model as the energy off-set between the donor and acceptor region is increased. By and large, the total density of states produced by the ODO and DOD models are indistinguishable. Increasing the interfacial bias generally produces a shift towards lower energy states composed primarily of charge-transfer states pinned to the donor-acceptor interface. The averaged density of states appears to be insensitive to whether or not the interface is disordered or ordered within the context of our model.

In the presence of an energy off-set at the interface, the lowest energy single-excitations are composed of electron/hole configurations pinned along the interface (i.e. exciplex states). Even though charge separation has occurred, little or no photocurrent can be produced since the binding energy of the exciplex is greater than the thermal energy. In order to produce current, the electron and hole must overcome their mutual Coulombic attraction and be separated at a distance $R > 2e^2/(3\varepsilon k_B T)$ (assuming a homogeneous 3D medium with dielectric constant $\varepsilon$). Within our model we define current-producing states as any elementary configuration with the positive hole on the outer-most donor chain and the negative electron on the outer-most acceptor chain. Such states serve as gateway states for charges to escape from the local heterojunction region [27].

Fig. 2 shows three types of singlet states produced by our ODO lattice model with $\Delta E = 0.5eV$ with their relative energetic ordering. Shown are the charge densities on each site. State (a) typifies the lowest energy excited state of our model with positive charge (hole density) shown in red and negative charge (electron density) shown in blue. The lowest energy state produced by our model is an interracially pinned charge-transfer state that is delocalized over the entire length of the interface. Such states are typically $300meV$ lower in energy than the primary exciton shown in (b) and carry some oscillator strength to the ground-state due to mixing between purely charge-transfer and neutral electron/hole configurations and may be referred to as a charge-transfer exciton or an exciplex. This excitonic state (b) is primarily composed of neutral electron/hole configurations and is delocalized over three of the polymer chains on the “acceptor” side of the heterojunction. State (c) typifies the charge-transfer/polaron states that lie very close in energy to the primary exciton. In the case shown here, the hole (red) has been transferred across the heterojunction and is separated from the electronic by 3-5 polymer chains. Such states lie 80-100 meV above the primary exciton. The oscillations in the electron/hole density indicate that the state has kinetic energy perpendicular to the interface and as such are likely channels for direct
fission of the excitation into states capable of producing photocurrent.

In Fig. 2, we show the absorption line-shapes for both the ODO and DOD cases along with the density of “current-producing” states as defined by requiring the states to have a threshold density of 10% of their electron/hole configurations on two outermost polymer chains corresponding to states with maximal charge separation. Clearly, increasing the interfacial bias shifts the fraction of states capable of directly producing current towards lower energies to the extent that they begin to overlap the absorption spectrum of the system. It should also be noted that the energetic onset for producing current is somewhat higher for the DOD cases suggesting that disorder at the interfacial region may facilitate efficient charge separation as suggested by Forrest. [21] [23] [24]

### B. Couplings due to phonon fluctuations

We now consider the couplings and state-to-state transition rates between the primary exciton and its neighboring states due to fluctuations and noise in the phonon degrees of freedom included our model. For this, we first obtain the full set of diagonal and off-diagonal exciton/phonon couplings and then transform the Hamiltonian into a dressed representation using a non-adiabatic polaron transformation described by Pereverzev and Bittner. [29] We refer the reader to Ref. [29] for explicit derivations and expressions. We then use this to construct time correlation functions of the exciton/phonon coupling operator and compute the spectral density \( \nu \).

\[
S_{nm}(\omega) = \int_{-\infty}^{\infty} dt \langle \hat{V}_{nm}(-t)\hat{V}_{mn}(t) \rangle e^{-i\omega t},
\]

where \( \hat{V}_{nm}(t) \) is the polaron-transformed electron/phonon operator written in the Heisenberg representation and \( \langle \cdots \rangle \) is the thermal average over phonon degrees of freedom

\[
\langle V_{nm}V_{mn}(t) \rangle = \text{Tr} \left[ \sum_{ij} (V_{nm}V_{mnj}(t)\rho_{eq}^{ij}) \right], \tag{1}
\]

and \( \rho_{eq}^{ij} \) is the equilibrium density operator for the oscillator degrees of freedom. It is important to note that in the perturbative regime, \( S_{nm}(\omega_{nm}) \) is the Fermi’s “golden rule” transition rate between states \( n \rightarrow m \). Integrating the spectral density over frequencies gives a phonon-averaged coupling between states

\[
W^2 = \int \frac{d\omega}{2\pi} S(\omega). \tag{2}
\]

When \( \sqrt{W^2} \) is comparable to the energy gap between states \( n \) and \( m \), phonon fluctuations can induce resonant tunneling between the two states. [30]
In Figure 2, we show the distribution of noise-averaged interstate couplings between the primary exciton and each of its neighboring states for the ODO polymer model with a $\Delta E = 0.5 \text{eV}$ offset (sampled over multiple realizations of the lattice). States with $E < E_{\text{ex}}$ are predominantly interfacially bound electron-hole pairs (exciplex states). On average, these lower-lying states are coupled very weakly to the primary exciton indicating that relaxation to the lower-lying pinned CT state proceeds via a sequence of micro-states. It is surprising, however, that in many cases, the coupling between the exciton to states that are immediately higher in energy are on the order
of the energy difference between the primary exciton and the final state. This puts initial (primary exciton) and final state into the strong coupling or resonant tunneling regime. Since the majority of the states with large couplings correspond to current-producing states as defined above, Comparing this plot to the density of current producing states one can conclude that the primary exciton can decay directly into the current producing states by resonant tunneling.

In Fig.3b we show the distribution of golden-rule rate constants for transitions originating from the primary exciton (again sampled over multiple realizations of the lattice). Defining \( k_+ \) as the average rate to all nearby higher energy states and \( k_- \) as the average rate to all lower energy states, we can estimate the time-scale for exciton fission into current producing states as \( 1/k_+ = 35 \text{ fs} \) and the time-scale for exciton fission into pinned charge transfer states as \( 1/k_- = 43 \text{ ps} \). Both of these estimates are consistent with a wide-range of recent experimental evidence indicating that excitons decay into current producing states on time-scales of \(< 100 \text{ fs} \).

III. CONCLUSION

We presented here a lattice model for the inter-facial electronic states of a polymer-polymer bulk-heterojunction interface. With increasing band off-set, a sizable density of “gate-way” states is brought into a resonance with the primary photo-excitation. As the energy difference decreases couplings due to phonon fluctuations become equivalent the energy difference between the states, leading to long-range resonant tunneling of charges away from the initial excitation on an average time-scale of \( 35 \text{ fs} \). Taking the spacing between polymer chains to be \( \approx 4 \text{ Å} \) over this timescale, the electron or hole would tunnel 12-15 Å away from the site of the initial excitation within \( 35 \text{ fs} \) following excitation. Moreover, given the universal nature of our model, we propose that direct resonant tunneling to current producing states plays a ubiquitous role in the ultrafast dissociation of excitons in organic BHJ cells.

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