

# Increases in the Charge Separation Barrier in Organic Solar Cells Due to Delocalization

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ABSTRACT: Because of the low dielectric constant, charges in organic solar cells must overcome a strong Coulomb attraction in order to separate. It has been widely argued that intermolecular delocalization would assist charge separation by increasing the effective initial electron-hole separation in a charge-transfer state, thus decreasing their barrier to separation. Here we show that this is not the case: including more than a small amount of delocalization in models of organic solar cells leads to an increase in the free-energy barrier to charge separation. Therefore, if delocalization were to improve the charge separation efficiency, it would have to do so through nonequilibrium kinetic effects that are not captured by a thermodynamic treatment of the barrier height.



rganic solar cells (OSCs) are promising candidates for renewable energy generation because of their flexibility, low weight, chemical tuneability, and potential low cost. Efforts to improve OSC performance would benefit from a deeper understanding of the fundamental processes of energy and charge transport in these devices, some of which remain incompletely understood.

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OSCs consist of electron donor and electron acceptor materials that are usually blended into an interpenetrating network to form a bulk heterojunction. The absorption of a photon creates an exciton that diffuses through the material until it reaches a donor-acceptor interface. Because of an energetic offset between the two materials, the electron can move into the acceptor (or the hole into the donor). After this charge transfer, the electron and the hole experience a Coulomb attraction

$$U(r) = -\frac{e^2}{4\pi\varepsilon_0\varepsilon_r r} \tag{1}$$

where e is the elementary charge, r the electron-hole separation,  $\varepsilon_0$  the vacuum permittivity, and  $\varepsilon_r$  the dielectric constant. Assuming that the electron and hole are initially separated by 1 nm,<sup>1</sup> they would experience a Coulomb binding energy of about 500 meV, forming a bound charge-transfer (CT) state. The binding energy far exceeds the thermal energy  $(k_{\rm B}T = 25 \text{ meV})$  because of the low dielectric constant of organic semiconductors ( $\varepsilon_r \approx 3-4$ ).

How the Coulomb attraction is overcome to yield free charges, sometimes with near-unit efficiency,<sup>2</sup> has been a longstanding question.<sup>1,3-5</sup> As a result, several mechanisms have been proposed that would lower the effective barrier the charges experience. In particular, charge delocalization is

thought to lower the barrier by allowing the charges that constitute the initial CT state to be effectively farther apart.<sup>6-13</sup>

However, Hood and Kassal showed that the assumption of a large barrier to charge separation is incorrect and that highefficiency separation can be obtained even from thermalized, localized charges.<sup>14</sup> This is because charge separation is governed not by the Coulomb potential energy but by the free energy, and a calculation that includes entropy and modest amounts of energetic disorder results in a free-energy barrier to separation comparable to  $k_{\rm B}T$  or absent altogether.

Nevertheless, although localized charges experience only a modest free-energy barrier to separation, it remains possible that adding delocalization would decrease the barrier even further. Indeed, several groups have included delocalization effects into dynamical models of charge separation (e.g., kinetic Monte Carlo or more complete quantum-dynamical theories), generally finding that delocalization, even in modest amounts, facilitates the dissociation of CT states.<sup>6-9,15-17</sup>

Here, our goal is to determine whether the delocalizationdependent charge separation enhancements seen in kinetic theories can be reconciled with the widespread view that delocalization is beneficial because it lowers the energetic barrier to charge separation. As we noted in the classical case,<sup>1</sup> arguments about barrier heights are essentially thermodynamic, because they do not rely on any kinetic properties of the system, most notably the attempt frequency of crossing the barrier. As a result, thermodynamic interpretations can be assessed using conceptually simple approaches. Here, we extend

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**Figure 1.** Schematic of the donor—acceptor interface model. The red spheres represent the donor molecules, which could correspond to a polymer chain perpendicular to the interface. The blue spheres are hexagonally close-packed sites representing the electron acceptor, such as a fullerene. The hole is localized in the donor (it can be on one of the sites shown), and the electron can be delocalized in the acceptor phase. The yellow spherical shell encloses the acceptor sites a distance *r* from the donor site closest to the interface.

our model of the free-energy barrier<sup>14</sup> to include delocalization, finding, contrary to the common view, that delocalization does *not* decrease the free-energy barrier. Therefore, conclusions about the role of delocalization in charge generation cannot be drawn on the basis of purely energetic arguments, without considering the influence of delocalization on nonequilibrium dynamic properties such as hopping attempt frequencies.<sup>18</sup>

The first choice in modeling delocalized charges at donoracceptor interfaces is the dimensionality of the system. Of course, the most realistic representation would be threedimensional. However, quantum-mechanical calculations needed to obtain electronic wave functions are computationally expensive, and even a small lattice of  $10 \times 10 \times 10$  sites would give 500 possible donor states and 500 possible acceptor states, requiring the diagonalization of a  $250\,000 \times 250\,000$ Hamiltonian. As a result, previous groups have used either two-dimensional lattices<sup>7,16</sup> or allowed delocalization in only the donor or the acceptor.<sup>6,15</sup> Here, we follow the latter approach, because changing the dimensionality can have dramatic effects on delocalization. In particular, it is known from the theory of Anderson localization<sup>19-21</sup> that in one and two dimensions all states are localized for any nonzero disorder (although only logarithmically so in two dimensions). In three dimensions and with modest disorder, there is a mobility edge above which states remain delocalized. Furthermore, if all other parameters are held fixed, states in three dimensions are considerably larger than in lower dimensions, which would significantly alter the Coulomb interaction. Finally, in this work it is important to capture the entropic contributions to charge separation, which are substantially larger in higher dimensions, where there are more ways to arrange the particles.<sup>7,14,22,23</sup>

Figure 1 depicts the lattice used to model charge separation. The acceptor, which is treated quantum-mechanically, is a three-dimensional, hexagonal-close-packed lattice with density  $1 \text{ nm}^{-3}$ . The classical donor can, because of translational invariance,<sup>14</sup> be represented as a chain of sites perpendicular to the acceptor. (The same conclusions would hold if the identities of donor and acceptor were reversed to describe hole transfer.) To reduce the computational cost, we restricted ourselves to a donor chain of 10 sites and a 12 × 12 × 12 acceptor lattice, which is the typical size of donor and acceptor phases in bulk-heterojunction OSCs.

We use a tight-binding Hamiltonian to model on-site energetic disorder in both materials and nearest-neighbor coupling within the acceptor:

$$H = \sum_{i,k} (U(r_{ki}) + E_k^{h} + E_i^{e})|k, i\rangle\langle k, i|$$
  
+  $\mathbb{I}_h \otimes \sum_{i \neq j} J_{ij}(|i\rangle\langle j| + |j\rangle\langle i|)$  (2)

where  $|k, i\rangle$  is the state of the hole localized on site k in the donor and the electron on site *i* in the acceptor; U(r) is the Coulomb binding between the charges (eq 1), and  $E_i^h$  and  $E_i^e$ are the site energies, drawn from independent Gaussian distributions with standard deviation  $\sigma$ .<sup>24<sup>-</sup></sup> In principle, the Gaussian distributions should be centered at the donor and acceptor lowest unoccupied molecular orbital energies; however, because this would result only in an overall shift in the zero of energy, the distributions were assumed centered at zero.  $I_{ii}$  are the electronic couplings between acceptor sites, which we assume are equal for all nearest-neighbor sites  $(J_{ij} = J)$ and zero otherwise.  $\mathbb{I}_h$  is the identity operator for the donor sites; the absence of couplings between donor sites ensures that H is block-diagonal and can be diagonalized for each value of kseparately, with the hole remaining localized on the kth donor site.

For simplicity, eq 2 does not include vibrational degrees of freedom and therefore cannot describe polaron formation. However, the reduction in delocalization due to polaron formation can often be described using an effective coupling that is smaller than the bare J.<sup>25</sup> Therefore, if polaron formation were considered, the effects described below would mostly be the same, although somewhat weaker.

The electronic states are the eigenstates of *H*. In the absence of a Coulomb interaction, the delocalization of the states would be governed by the ratio of the electronic coupling and the strength of the energetic disorder: the larger the  $J/\sigma$ , the larger the states.<sup>19–21</sup> The presence of the Coulomb interaction changes this analysis, but  $J/\sigma$  remains a useful guide for states far from the interface. We characterize the extent of delocalization of state  $\psi$  using the inverse participation ratio (IPR)

$$IPR(\psi) = \left(\sum_{n} |\langle n|\psi\rangle|^4\right)^{-1}$$
(3)

which roughly corresponds to how many sites appreciably contribute to  $\psi$ . Figure 2 shows the difference between a relatively localized state and a more delocalized one.

Another important feature of a state is the expectation value of the distance between the electron and the hole, which we refer to as the separation  $r(\psi)$ . The two example states in Figure 2 illustrate the fact that an electron closer to the hole, i.e., deeper in the Coulomb well, will be more localized than one farther away.

Properties of the electronic states are shown in Figure 3 for a single, representative realization of the energetic disorder ( $\sigma = 125 \text{ meV}$ ) with J = 10 meV. The resulting value of  $J/\sigma = 0.08$  is typical, because  $\sigma$  is generally on the order of 100 meV or more,<sup>1</sup> while *J* for small molecules ranges from 1 to 30 meV in PCBM<sup>6</sup> and up to 100 meV in high-purity organic crystals.

The three panels of Figure 3 show the pairwise relationships between the energies of the states, their IPRs, and their electron-hole separations, revealing several important proper-



**Figure 2.** Two representative electronic states, with size and opacity representing the probability of finding the electron on a particular site. In both cases, the hole is localized adjacent to the donor–acceptor interface (red sphere). The state in green is a low-lying and tightly localized charge-transfer (CT) state (energy E = -491 meV; expected value of the electron–hole separation r = 1.1 nm; inverse participation ratio IPR = 1.2). The state in blue is a higher-lying, delocalized state far from the interface (E = -107 meV; r = 9.7 nm; IPR = 7.2).

ties. Figure 3a shows the large spread in eigenstate energies due to the energetic disorder, especially at large electron—hole separations. However, those states with  $r \leq 4$  nm are substantially lower in energy than the rest, stabilized by the attractive interaction with the hole. Figure 3b shows that those states are also much more localized than the more separated states; in fact, every state with  $r \leq 4$  nm has IPR < 20, and most of them are much less than that. This agrees with the examples in Figure 2, where the bound interfacial state is much more localized than the separated state. Finally, Figure 3c confirms that the states at more extreme energies are more localized, being confined in deep traps.

Figure 3b confirms that our lattice was large enough to rule out finite-size effects. The largest state in this realization had an IPR < 60, much less than our lattice of 1728 sites.

In simulations with  $J/\sigma > 0.08$ , some states became large enough that the maximum IPR plateaued with increasing  $J/\sigma$ , meaning that states began to be affected by the edges of the lattice. As a result, a larger lattice would be needed to accurately describe all the states at  $J/\sigma > 0.08$ . However, because we are concerned only with charge separation, we were able to carry out simulations at larger values of  $J/\sigma$ , because the only states relevant to the determination of the charge separation barrier are those with small r (as we show below, the barrier to charge separation almost always occurs around r = 2 nm). Therefore, we carried out simulations up to  $J/\sigma = 0.3$ , at which point some states with  $r \approx 4$  nm began to have IPRs exceeding 20.

The key results of this work are the free-energy barrier heights for a range of J and  $\sigma$ , shown in Figure 4. As in previous work,<sup>14</sup> the free energy (in the absence of *PV* work, the Helmholtz and Gibbs free energies are equal) at a particular separation r is

$$\Delta G(r) = -\langle k_{\rm B} T \ln Z(r) \rangle \tag{4}$$

where  $\langle \cdot \rangle$  denotes averaging over an ensemble of 1000 realizations of disorder. The partition function is



**Figure 3.** Relationships between the expectation value of the electron-hole separation (r), energies, and inverse participation ratios (IPRs) of the electronic states, for a typical realization of energetic disorder, with disorder  $\sigma = 125$  meV and intersite coupling J = 10 meV. Each point corresponds to one eigenstate of the Hamiltonian. (a) State energies as a function of r. At  $r \leq 4$  nm, the states are stabilized by the Coulomb attraction. The red line illustrates the Coulomb potential U(r). (b) IPR of states as a function of r. The IPR remains under 20 for all states with  $r \leq 4$  nm, indicating small finite-size errors for states in this region. (c) IPRs compared to the energies. States at lowest energies are highly localized.

$$Z(r) = \sum_{\psi \in r \pm 0.5 \text{ nm}} e^{-E_{\psi}/k_{\text{B}}T}$$
(5)

where  $E_{\psi}$  is the energy of state  $\psi$  and the sum goes over all states with electron-hole separation within 0.5 nm of *r*. In other words, the states are grouped into bins of width 1 nm according to their electron-hole separations.

The charge separation barrier for particular J and  $\sigma$  is the difference between the maximum of  $\Delta G(r)$  and the value  $\Delta G(1 \text{ nm})$ , being the free energy of a thermalized CT state formed by the jump of an electron from the donor to one of the close-lying states in the acceptor. To facilitate comparison between different scenarios, and because only differences in



**Figure 4.** Free energies of charge separation, averaged over 1000 realizations of disorder, and relative to the free energy at r = 1 nm. (a) At fixed intersite coupling J = 10 meV, increasing the disorder  $\sigma$  reduces the free energy. In particular, there is no barrier to charge separation beyond  $\sigma \approx 140$  meV. (b) At fixed  $\sigma = 125$  meV, a free-energy barrier occurs at r = 2 nm. Increasing *J* has a complex effect on its magnitude. (c) Free-energy barrier height as a function of *J* and  $\sigma$ . After decreasing slightly, the barrier increases for  $J \gtrsim 10$  meV. Barrier heights less than zero indicate the absence of a barrier. (d) Plotted against the mean IPR of the electronic states, the barrier starts to increase when *J* becomes large enough that IPR  $\approx 5$ .



**Figure 5.** Influence of delocalization on factors determining the barrier height to charge separation. (a) Distribution of states with increasing coupling *J*. Each panel shows the energies and electron—hole separations *r* of states for the same realization of energetic disorder ( $\sigma = 125 \text{ meV}$ ), but with different *J*. The red line and the shaded region denote the Coulomb potential  $\pm 2\sigma$ . As *J* increases, most states become more delocalized and therefore move out to larger electron—hole separations. However, energetically low-lying sites are unlikely to have near-resonant neighbors, instead remaining as localized traps. Therefore, as the higher-lying states move away with increasing *J*, the free energy is dominated by the low-lying states. (b) As the coupling increases, the lowest-lying interfacial state becomes slightly delocalized but also more stabilized in energy.

energy matter, the results in Figure 4 are displayed with  $\Delta G(1 \text{ nm})$  set to zero.

Figure 4a shows that increasing  $\sigma$  at constant *J* lowers the barrier to separation so that, at large  $\sigma$ , there is no barrier at all. This is consistent with the previous work by Hood and Kassal, which can be considered as the case with J = 0.<sup>14</sup> As  $\sigma$  increases, the free energy becomes dominated by the lowest-lying states in the tails of the disorder distribution. It is more likely to find particularly low-lying states at larger *r*, where there are more sites available. Therefore, as  $\sigma$  increases, it becomes more likely to find a state at r = 2 nm whose energy is sufficiently lower

than the energy of the initial state at r = 1 nm to overcome the Coulombic penalty.

On the other hand, increasing J at constant  $\sigma$  (Figure 4b) leads to no obvious trend. However,  $\Delta G(r)$  is always largest at r = 2 nm, indicating that charge separation would be thermodynamically spontaneous once the charges are only a small distance away from the interface. Indeed, a charge separation barrier at 2 nm may be practically irrelevant in many blends, because experiments suggest the formation of CT pairs at 3–4 nm separation on ultrafast time scales.<sup>13,26</sup>

To clarify the effect of delocalization, Figure 4c shows the barrier height  $[\Delta G(2 \text{ nm}) - \Delta G(1 \text{ nm})]$  for additional values

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of *J*. For each  $\sigma$ , a small amount of coupling (and therefore delocalization), up to  $J \approx 10$  meV, decreases the barrier slightly. However, increasing coupling beyond  $J \approx 10$  meV leads to significant *increases* in barrier height. The direct relationship between delocalization, expressed as the mean IPR of all the states, and barrier height is shown in Figure 4d, with the minimum barrier occurring at mean IPR  $\approx 5$ .

Figure 5 explains why the charge separation barrier increases beyond  $J \approx 10$  meV. As J increases, most states become so delocalized that their centers of charge move away from the interface to larger separations, so that they are no longer caught in the r = 1 nm and r = 2 nm bins that determine the barrier height (Figure 5a). Instead, the states that remain at r = 1 nm and r = 2 nm are the localized trap states in the tails of the disorder distribution, which come to dominate the changes in the barrier height. Although these states do delocalize somewhat at larger J, their energies in fact decrease in most cases (including the example in Figure 5b), contrary to the expectation that a larger separation would result in a higher energy.

Whether the energy of a state increases or decreases with larger coupling depends on its initial energy relative to its neighbors. In particular, trap sites adjacent to the interface are likely to be lower in energy then their neighbors in the second layer of sites, because they experience a stronger Coulomb potential. Therefore, when coupling is introduced, level repulsion will tend to stabilize the interfacial traps even further, and this stabilization can easily exceed the Coulombic destabilization due to delocalization (Figure 5b). As a result, because the states in the r = 1 nm bin are usually stabilized more than those in the r = 2 nm bin, the ensemble-averaged barrier height increases with larger *J*.

In summary, delocalization is not helpful in lowering the charge separation barrier as previously thought and is indeed deleterious if it is large enough. Indeed, interfacial CT-state traps are further stabilized by level repulsion when coupling is introduced. Therefore, the observation from previous kinetic studies that delocalization can enhance the charge separation efficiency<sup>6,7,15,16</sup> cannot be attributed to a lowering of the Coulomb attraction between interfacially adjacent charges. In other words, the widespread conceptualization of charge separation in organic solar cells as requiring ways to overcome a large thermodynamic Coulomb barrier draws attention from the kinetic factors that truly determine the efficiency.<sup>14,18</sup>

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# Notes

The authors declare no competing financial interest.

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