Dangling Bond Defects: The Critical Roadblock to Efficient Photoconversion in Hybrid Quantum Dot Solar Cells

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Supporting Information

ABSTRACT: Inorganic–organic hybrid materials based on silicon quantum dots (SiQDs) have been utilized for photovoltaic applications but suffer from rapid charge recombination and low carrier mobility. We present an ab initio investigation of charge dynamics to pinpoint the source of this severe problem, and our results indicate that such devices show great promise provided that dangling bond (DB) defects can be sufficiently removed. Without DBs, the predicted charge transfer (CT) rate is much higher than that of photoluminescence (PL), while the electron hopping (EH) proceeds more quickly than interfacial charge recombination (CR). In contrast, one DB in a SiQD leads to a dramatic enhancement, by 10 orders of magnitude, in the CR rate and a reduction of the EH rate by 4 orders of magnitude, so that the diffusion of carriers to electrodes becomes extremely difficult. Although other factors, such as dot size distribution and oxidation, also play a deleterious role in device performance, their effects are deemed much less important than the critical role played by dangling bonds.

INTRODUCTION

SiQD-based inorganic–organic hybrid solar cells are an attractive candidate for photovoltaic applications as they combine the advantages of their constituents. While the conjugated polymers have strong absorption in the visible range,1 SiQDs offer tunable energy levels, high stability2,3 and the potential for multiple exciton generation and hot carrier collection.4 Unfortunately, the solar conversion efficiency of the current SiQD/P3HT blend devices is only 1.1%,3 much lower than the typical value of 5% for their purely organic counterparts.2,3

To understand the origin of such limited performance, a novel broadband (UVVisNIR) transient absorption spectroscopy was recently employed to probe the relevant charge dynamics. The results indicate that in regioregular P3HT/SiQD films, the inherent photovoltaic conversion process is photoexcitation on P3HT followed by an ultrafast electron transfer from P3HT to the SiQD. Such exciton dissociation would primarily result in free charge carriers, but in reality only a small proportion of these carriers are able to diffuse to the electrode because of overwhelming nonradiative recombination at the interface.6 Although the charge transfer (CT) rate of \(7 \times 10^{12} \text{s}^{-1}\) is extremely high, the ultrafast charge recombination (CR), with a rate of \(1 \times 10^{12} \text{s}^{-1}\), along with the low electron mobility \((10^{-6} \sim 10^{-5} \text{cm}^2 \text{V}^{-1} \text{s}^{-1})\) causes the poor performance of the SiQD/P3HT solar cells.6 It is widely believed that a more precise control of the dot size distribution and a lower density of trap states are required, but their influences on the charge dynamics are still unclear,2,3,8 in particular, which factor is most critical to the deteriorated photoconversion?

This has motivated our ab initio investigation to identify the main source responsible for the observed rapid recombination and low electron mobility, which would allow attention to be focused on the key roadblock to device performance. Four possible reasons for the low photoconversion efficiency have been postulated: (1) vibronically induced transitions to the ground state due to conical intersection at the degenerate points of the potential energy surfaces;6 (2) dot size distribution; (3) oxidation; (4) surface dangling bonds. However, quantitative support for these possibilities is lacking, motivating the current analysis. As detailed in the subsequent section, the associated computational methodology calls for phonon-assisted transport theory beyond the standard Marcus and MJL (Marcus, Levich, and Jortner) theories, and excited-state electronic structure beyond those estimated from density functional theory (DFT) are required. The development of a successful computational approach is itself an important aspect of our investigation.

Four rate estimates, depicted in Figure 1, are carried out using first-principles analysis: (Figure 1a) CT of singlet exciton; (Figure 1b) photoluminescence (PL) from P3HT; (Figure 1c) CR at the interface; (Figure 1d) electron hopping (EH) between two dots. Since phonon-assisted hopping is the
incoherent nonadiabatic quantum tunneling scenario is thereby reasonable. The full quantum treatment, based on perturbation theory, gives the charge transport rate as \( k_{\text{fullQTM}} = \frac{1}{\hbar^2} |V_{\text{DA}}|^2 \int_{-\infty}^{+\infty} dt \exp \left\{ \frac{\Delta G}{\hbar} t - \sum_j S_j (2n_j + 1) - n_j e^{-\omega_j t} - (n_j + 1) \right\} e^{i\omega_j t} \)

Here \( -\Delta G \) is the driving force, \( V_{\text{DA}} \) is the electron coupling between donor and acceptor, and the phonon occupation number is

\[ n_j = \frac{1}{\exp(\hbar\omega_j/k_B T) - 1} \]

The Huang–Rhys factor \( S_j \) is defined as

\[ S_j = \lambda_j / \hbar\omega_j \]

where \( \lambda_j \) is the reorganization energy for vibrational mode \( j \).

In the high-temperature limit, i.e., when \( k_B T \gg \hbar\omega \), holds for all vibrational modes \( j \), the full quantum treatment reduces to that of Marcus theory

\[ k_{\text{Marcus}} = |V_{\text{DA}}|^2 \frac{\pi}{\hbar^2 k_B T \lambda} \exp \left\{ - \frac{(\Delta G + \lambda)^2}{4\hbar k_B T} \right\} \]

with \( \lambda \) the total reorganization energy.

For lower temperatures, CT may be coupled to both high-frequency intramolecular modes and low-frequency solvent modes: \( \hbar\omega_j \approx k_B T \approx \hbar\omega \). In this regime it is appropriate to use the MJL equation provided that the phonon spectrum in the high frequency range is narrow enough to be represented by one effective mode. Under these conditions, the transport rate is given by

\[ k_{\text{MJL}} = \frac{2\pi}{\hbar} |V_{\text{DA}}|^2 \frac{1}{4\pi^2 \lambda} \sum_i e^{-S_i} \frac{\Delta G + \lambda + i(\hbar\omega_{\text{eff}})^2}{4\lambda^2 \hbar^2 T} \]

Here \( \lambda_i \) is the reorganization energy related to solvent or surrounding matrix, and \( \omega_{\text{eff}} \) is the frequency of the effective molecular mode. For our system, the calculated molecular modes with energies lower than thermal fluctuations (24 meV) were merged into the \( \lambda_i \) term, and \( \omega_{\text{eff}} \) was taken to be the weighted average over molecular modes with energies higher than 24 meV.

In all of these methods, there exists an implicit assumption that the phonon-assisted charge transport is slower than vibrational relaxation, making it reasonable to employ an equilibrium phonon occupation. Although the frequencies of both molecular and solvent phonon modes exceed 10 cm\(^{-1}\), some of our calculated rates turned out to violate this assumption. For those cases, we employed a self-consistent correction procedure wherein a cutoff phonon frequency is set to the original transfer rate. By excluding the contribution of the phonon modes with frequencies lower than this cutoff, a new rate and a corresponding new cutoff frequency were obtained. Such iterations were continued until self-consistency was reached.

The driving forces were computed as the energy changes of isolated donor and acceptor, plus the Coulomb interaction between pairwise charges localized on each atom obtained by Mulliken population analysis. The reorganization energy \( \lambda \) was divided into an inner part \( \lambda_{\text{int}} \) and an external (solvent) part \( \lambda_{\text{ext}} \), corresponding to donor/acceptor and P3HT matrix, respectively. Within the harmonic approximation, the reorganization energy spectrum was obtained by modal decomposition.

The driving force and inner reorganization energy were calculated from density functional theory (DFT) as implemented in the DMOL package. The conductor-like screening model (COSMO) was used to account for the dielectric effect of the solvent. An all-electron approach was used with exchange and correlation effects accounted for by the generalized gradient approximation (GGA) parametrized by Perdew, Burke, and Ernzerhof (PBE). A real-space, double numeric plus polarization (DNP) basis was used along with an octupole expansion to specify the maximum angular momentum function. One exception was the optical gap, which was set to be 2.0 eV as observed in experiments because of the incapability of our calculation to capture the \( \pi-\pi \) stacking.

**Figure 1.** Initial states and final states: (a) charge transfer (CT); (b) photoluminescence (PL); (c) nonradiative charge recombination (CR); (d) electron hopping (EH); (e) polaron dissociation (PD). Tan spheres depict SiQDs and red wavy lines are P3HT. Yellow ellipses represent exciton binding in parts b, c, and e.
effect.\textsuperscript{13} Besides, an empirical formula was used for the external reorganization energy,\textsuperscript{13} and we verified that the transition rates were quite insensitive to both the frequencies and the reorganization energies of the solvent modes.

The electronic coupling $V_{DA}$ for CT and CR between the dot and molecule were calculated using a two-state model\textsuperscript{17} at the Hartree–Fock (HF) level\textsuperscript{18} as implemented in the NWChem Package.\textsuperscript{19} The anticrossing methodology\textsuperscript{9,20} was employed to compute $V_{DA}$ for EH by taking advantage of the similar energy levels of initial and final states. Once the charge hopping rate is obtained, the drift mobility can be evaluated as\textsuperscript{21}

$$\mu = \frac{e}{k_B T} \frac{1}{2N} r^2 k_{EH}$$

where $N = 3$ is the dimensionality and $r$ is the distance between the center of the neighboring SiQDs.

This computationally intense approach restricts our explicit calculations to dots with diameters less than 2 nm, while CT and CR rates for larger dots might be estimated via extrapolation. In particular, the lowest unoccupied molecular orbital (LUMO) shifts of large dots are estimated to be half of the optical gap changes,\textsuperscript{22} and the solvent reorganization energy can be computed by fixing the face-to-face distance between the dot and the P3HT. In addition, the spectrally resolved reorganization energy can be taken to be that of a computationally tractable but rescaled dot.\textsuperscript{9} A similar approach was applied to estimate the electronic hopping rates between two dots with different diameters along with an additional assumption that only the wave functions within the prescribed distance of the dot surfaces contribute to the electronic coupling.

In addition to the CT, CR, and CH rates associated with nonradiative processes, the photoluminescence (PL) rate at room temperature was calculated via Fermi’s golden rule,\textsuperscript{4,23}

$$k_{PL} = \sum_i p(i) \frac{4e^2}{\hbar} \frac{f_{eff}^2 (r_{mol}) E_i^3}{3c^2 \hbar^2} |M|^2$$

Here $p(i)$ is the room-temperature Boltzmann occupation, $E_i$ is the excitonic energy of excited state $i$, $f_{eff}$ is the local field factor derived from the effective dielectric constant, and $M$ is the dipole matrix element between excitonic state $i$ and the ground state. The excitonic state is described as a linear combination of pairwise electron–hole wave functions. Both the coefficients and the excitonic energies were obtained by solving the Bethe–Salpeter equation (BSE) using the RGWBS suite\textsuperscript{24} while dipole moments were computed using the MX code.\textsuperscript{25}

It is also worth noting that the energy-level alignment and the charge transfer rates are determined by the quasi-Fermi level and thus depend on the device working conditions.\textsuperscript{26} However, it is very difficult to obtain the interaction between the electrolyte and the SiQD/P3HT blend via quantum chemistry calculations, which is beyond the scope of our analysis. In this work, we focus on the rates in the limit of isolated dots without connection to the electrodes.

More details on the computational method are available in the Supporting Information.

## RESULTS AND DISCUSSION

**Four Essential Rates to Determine Charge Dynamics.** Four rates, CT, CR, PL, and EH, were quantified to elucidate the complex charge dynamics carried out in SiQD/P3HT films. Three related processes were not considered because: (1) no triplet exciton is detected during the ultrafast charge transfer, ruling out intersystem crossing as a source of efficiency loss;\textsuperscript{6} (2) hole mobility through P3HT is measured to be much higher than electron mobility among the dots;\textsuperscript{27} and, (3) the dissociation rate of the interfacial charge transfer state (polarons) bound by Coulomb attraction is known to be extremely fast\textsuperscript{6} even though the relevant binding energies can be as large as 0.1–0.5 eV.\textsuperscript{28}

To elucidate the efficiency of polaron dissociation (Figure 1e)—i.e., why holes can easily escape from deep Coulomb traps and create free carriers in the film—we consider hole hopping from a nearest neighbor (NN) P3HT to a next NN P3HT in the vicinity of a 4 nm SiQD. Regioregular P3HT (rrP3HT) exhibits lamellar aggregation,\textsuperscript{29} so it is reasonable to assume a π-stacking separation distance of 3.8 Å. In addition, our DFT calculations indicate that the separation distance between the dot surface and a NN P3HT is 4 Å. Adopting an effective dielectric constant of $\varepsilon = 3$ results in an estimated Coulomb well of 27 meV. This implies that the Coulomb well does not block polaron from dissociation at room temperature, and it is actually an upper bound since the NN P3HT may not wrap tightly around the dot.

Such Coulomb attraction is expected to be stronger for smaller dots, however. In particular, dots of the optimal size for providing the largest open circuit voltage are predicted by our analysis to be 17.4 Å in diameter, and the associated Coulomb well depth for a hole to hop from a NN P3HT to a next NN P3HT increases to 87 meV. We argue that this should be largely offset by a larger energy gradient related to the stoner quantum confinement in more disordered P3HT closer to the interface of such small dots. For instance, previous computational analysis has shown that the highest occupied molecular orbital (HOMO) of the P3HT around the PCBM (with diameters of 1–2 nm) is 150 meV lower than that of the P3HT far away.\textsuperscript{30} As a result of this mitigating influence of the energy gradient, we expect that holes can efficiently leave the interface at room temperature.

In addition, wave function delocalization associated with the crystalline environment should also mitigate the influence of any Coulomb trap. Specifically, delocalization of the hole wave function in crystallized P3HT favors polaron dissociation due to the significantly enhanced effective distance between the hole and electron. This is illustrated in Figure 2 where the HOMO in the P3HT close to the SiQD has a nearly homogeneous distribution over all of the three layers included in our calculation.

![Figure 2. Isosurfaces of HOMO (blue) and LUMO (red) at a Si$_4$H$_6$/P3HT interface. The isosurfaces are plotted at electron densities of 0.02 Å$^{-3/2}$.](image-url)
Charge Transfer, Recombination, and Photoluminescence on Defect-free Interface. The HOMO and LUMO levels of a SiQD depend on its size, and the construction of a type-II junction, in which not only HOMOs and LUMOs form a staggered level alignment but also the local excited-state energy is higher than the CT state energy, requires that the dots be sufficiently large. This is summarized in Figure 3a, obtained by idealizing the P3HT to a 6-unit oligomer as in previous works13 as shown in Figure 3b,c. However, photoconversion efficiency decreases for sizes beyond this threshold value.2,3 A hydrogen-passivated Si147 dot with a diameter of 1.7 nm was found to be optimal with minimum magnitude of driving force and was utilized here for the following rate analyses.

Our calculated phonon-assisted CT/CR rates for defect-free SiQD/P3HT interface and the EH rate employing three approaches are summarized in Table 1, with the phonon spectrum shown in Figure 4. For the CT at the Si147H100/P3HT interface and EH between two dots at the Marcus normal region, the three approaches gave similar rates. In contrast, within the Marcus inverted region, the CR rates predicted by the Marcus and MJL formulas were many orders of magnitude lower than the more accurate prediction of the full quantum mechanical treatment.

This observation could be explained within the scenario of phonon-assisted quantum tunneling. The major contributions to the transport rates come from the resonance channels between the vibronic levels of initial and final states. In the Marcus normal range, the magnitude of driving force $\Delta G$ is close to the reorganization energy $\lambda$, and the resonance channels correspond to the molecular phonon modes. The low frequency modes in P3HT solvent are dominant so that both Marcus and MJL theories give reasonable estimates of the rates. However, in the Marcus inverted range, the high-frequency modes that are ignored in Marcus theory play a critical role, while using one effective mode in the MJL equation reduces the possibility to achieve resonance. A full quantum treatment is therefore necessary in this range, which requires a substantial computational investment.31

In our analysis of the influence of dot size distribution and surface defect on charge dynamics, CT, CR, and CH may all be in the Marcus inverted region as the driving forces far exceed the reorganization energies, so the full quantum treatment is necessary and has been carried out to obtain all associated rates.

As illustrated in Figure 5, our calculated CT ($1.5 \times 10^{12} \text{ s}^{-1}$) and PL ($7.9 \times 10^8 \text{ s}^{-1}$) rates are in good agreement with experiments6,32 demonstrating that our model accurately captures the key dynamics. Crucially, though, the predicted CR rate ($1.5 \times 10^7 \text{ s}^{-1}$) is lower by 10 orders while the electron mobility ($2.9 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) is higher by 3–4 orders than the reported experimental values of $10^{12} \text{ s}^{-1}$ and $10^{-6} \sim 10^{-5}$.
respect to dot size. As shown in Figure 7, the change in driving reorganization energies and electron couplings were scaled with molecules. Extremely fast charge recombination of many organic coupling. This has been shown to be responsible for the nonadiabatic transition channel rises due to strong vibronic breaks down, and a large surface-hopping rate within the nonadiabatic transition channel rises due to strong vibronic coupling. This has been shown to be responsible for the extremely fast charge recombination of many organic molecules.

For our interface, the scenario of conical intersection is photoexcitation from the ground state (GS) to the local exciton (LE) manifold followed by a vertical transition to the CT manifold at the point B in Figure 6. Subsequent relaxation brings the system to the conical intersection from which an efficient, nonradiative surface hop to the GS manifold is possible. The conical intersection cannot be reached by thermal excitation from point C though. Suppose that this mechanism is responsible to the ultrafast charge recombination at our Si$_{147}$H$_{100}$/P3HT interface, then, during the relaxation of the CT state from the LE structure, the energy surface of the GS happens to intersect that of the CT state. So the prerequisite of this process is that the energy of the GS in the lowest energy CT geometry (point C) should be higher than the energy of the CT state from the LE structure, the energy surface of the GS happens to intersect that of the CT state. Therefore, this nonradiative process cannot be the reason for the observed ultrafast CR.

A second postulated source for rapid CR and slow EH is that assemblies of SiQDs have a substantial size distribution. To examine this, we used the computed CT and CR rates for the Si$_{147}$H$_{100}$/P3HT interface to estimate analogous rates for dots of differing sizes. Driving forces were estimated using optical gaps obtained from previous theoretical studies, and the reorganization energies and electron couplings were scaled with respect to dot size. As shown in Figure 7, the change in driving force is about 0.8 eV when the dot diameter increases from 1.7 to 8 nm. This leads to a decrease of the CT rate and an increase in the CR rate (Figure 7a). However, even for 8 nm dots, the calculated CR rate is still lower by 7 orders than the experimental value, suggesting that there must exist other ultrafast CR channels.

An accompanying analysis was carried out for EH between two SiQDs over a range of size mismatches (Figure 7b). The rates between two identical dots with different sizes are similar, varying within only two orders when diameter increases from 1.7 to 8 nm, and electrons can hop efficiently from smaller dots to larger dots provided that the size difference is not too large. However, hopping from larger dots to smaller dots is energetically unfavorable so electrons should tend to get trapped in larger dots. Thus, QD size fluctuation would be a plausible explanation for low electron mobilities, but it alone cannot explain the ultrafast CR, and our subsequent analysis indicates that the dangling bond defects offer even stronger trapping to electrons.

The third possible source is surface oxidation, which was investigated by inserting 12 OH ligands (Figure 8b) and 12 backbond O atoms (Figure 8c) into the dot surface (Figure 8a). Our computations suggest that the OH ligand has a negligible impact on either the HOMO/LUMO levels (Figure 9) or the wave function localization. In contrast, while the shape of the LUMO remains similar to that of the nonoxidized dot, a high density of backbond O atoms (12 O/per dot) reduces the
Dangling Bonds: The Primary Source of Fast Charge Recombination and Slow Electron Hopping. After ruling out the above possibilities, we now demonstrate that DBs are the most likely source of high CR rates and low EH rates. A single DB defect was therefore created on the surface of the Si147H100 dot (Figure 10, parts c and d) and both CR and EH rates were then calculated. In the presence of the DB, the LUMO energy level of the dot decreases while the HOMO level increases significantly due to the generation of surface states inside the gap, leading to a much larger driving force (from 0.06 to 1.32 eV) for CT and a reduced driving force (from 1.84 to 0.58 eV) for CR (Figure 10a). In addition, a much larger distortion of the SiQD with a DB present than without a DB is induced by excitation, consequently the reorganization energy ($\lambda$) for the dot increases by a factor of 6 (Figure 10b). The LUMO is localized around the DB (Figure 10, parts c and d) and now becomes closer to the HOMO which itself tends to be localized on the P3HT. As a result, the electronic coupling increases for both CT and CR (Table S4 in the Supporting Information).

Combining all these together, our calculations suggest that the introduction of only one DB on the Si147H100 dot only slightly decreases the CT rate, but increases the CR rate by 10 orders of magnitude and decreases the EH rate by 4 orders of magnitude. With the DB accounted for, both CR and EH rates are in reasonable agreement with experiment as shown in Table 2. Moreover, the ratio of these rates asserts that electrons are very unlikely to diffuse to the electrode prior to recombining.

Table 2. Charge Transfer (CT) and Charge Recombination (CR) Rates at Si147H100/P3HT Interface along with Electron Hopping (EH) Rate between Two Dots with and without One Dangling Bond (DB) on Each Dot$^{a, b}$

<table>
<thead>
<tr>
<th>no DBs</th>
<th>DBs</th>
<th>experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{CT}$</td>
<td>$4.0 \times 10^{12}$</td>
<td>$2.8 \times 10^{11}$</td>
</tr>
<tr>
<td>$k_{CR}$</td>
<td>$1.5 \times 10^{10}$</td>
<td>$2.7 \times 10^{12}$</td>
</tr>
<tr>
<td>$k_{EH}$</td>
<td>$1.3 \times 10^{12}$</td>
<td>$1.3 \times 10^{7}$</td>
</tr>
</tbody>
</table>

$^{a}$All rates are in unit of s.

As has been pointed out previously,$^{26}$ the charge transfer rate could be sensitive to the driving force in the inverted Marcus range. In our case, introducing an 0.15 eV uncertainty in $\Delta G$, which is the estimated upper bound for errors in our computed driving forces, leads to a fluctuation of 1–2 orders of magnitude on transition rates (Figure 11). For instance, the inaccuracy of

\[ \Delta G \]


Figure 10. (a) Energy level alignment between P3HT and Si147H100 without and with one dangling bond (DB). (b) Reorganization energy spectrum of Si147H100 neutral dot relaxed from anion structure without and with one DB. The inset shows the large excitation-induced distortion around a DB. (c, d) Side and top views of localized HOMO and LUMO (red) of the interface between P3HT and Si147H100 with one DB. The Si atom with a DB is highlighted in green. The isosurfaces are plotted for an electron density of 0.015 Å$^{-3}$. The LUMO energy by 0.4 eV. However, such high backbond O density is highly unlikely; however, this is still much smaller than the change of 1.2 eV caused by the same density of DBs, and even smaller than the 0.9 eV caused by only one DB on a SiQD, indicating that although the O backbonds could serve as shallow electron trap to reduce the device performance, their effect is much less important than the DB.

CONCLUSION

Our analysis suggests that the charge dynamics plays out in the thin film as follows. After photoexcitation of P3HT, charge transfer occurs at the dot/polymer interface. The resulting polarons are quickly dissociated into free charge carriers, and the electrons subsequently diffuse efficiently through the film.
before getting trapped at the DBs. As a result, electrons and holes eventually recombine on DBs.

In order to extract free carriers to the external circuit, the carriers must drift to the electrodes before CR occurs. The efficiency of this process is determined by a comparison between the carrier sweep out time and the CT state lifetime, where the carrier sweep out time is taken to be the period required by the carrier to drift from the center of the active layer to the electrode. Elimination of DB defects would improve the CR hopping rate and reduce the CR rate, making it possible for the CT state lifetime to be much longer than the characteristic sweep-out time of the carriers drifting in the internal field.

In summary, the charge dynamics of SiQD/P3HT solar cells have been investigated from first-principles using a phonon-assisted full quantum treatment, which accurately captures the CT and PL rates and, with dangling bonds accounted for, recovers the CR and EH rates observed experimentally. We conclude that the dangling bond defects are the critical reason for the deleterious ultrafast CR and low electron mobility measured in these hybrid materials. Thus, the mitigation of such defects is expected to dramatically improve the performance of hybrid solar cells.

## ASSOCIATED CONTENT

### Supporting Information

Detailed computational methods, accuracy and sensitivity analysis, and electron coupling with dangling bonds. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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Computational Methods

Non-Radiative Charge Transfer Rate

The full quantum treatment, based on perturbation theory, gives the charge transport rate as

$$k_{\text{fullQM}} = \frac{1}{\hbar^2} |V_{DA}|^2 \int_{-\infty}^{+\infty} dt \exp \left\{ \frac{\Delta G}{\hbar} t - \sum_j S_j [(2n_j + 1) - n_j e^{-i\omega_j t} - (n_j + 1) e^{i\omega_j t}] \right\}, \quad (1)$$

Here $-\Delta G$ is the driving force, $|V_{DA}|$ is the electron coupling between donor and acceptor, $n_j$ is the phonon occupation number and $S_j$ is the Huang-Rhys factor.

Energies released by the system following charge transfer (CT), charge recombination (CR), or electron hopping (EH) are written as

$$\Delta G_{\text{CT}} = E_D^+ + E_A^- + E_c - E_D^0 - E_A^0 - E_g^{\text{opt}}$$

$$\Delta G_{\text{CR}} = E_D^0 + E_A^0 - E_D^- - E_A^+ - E_c$$

$$\Delta G_{\text{EH}} = E_A^{\text{LUMO}} - E_D^{\text{LUMO}}$$

$E_D^{+/0}, E_A^{-/0}$ are ionic/ground state energy of donor and acceptor, $E_c$ is the Coulomb stabilization energy, $E_g^{\text{opt}}$ is the optical gap of the donor, and $E_A^{\text{LUMO}}/E_D^{\text{LUMO}}$ are the LUMO levels of donor/acceptor.

The reorganization energy, $\lambda$, is divided into an inner part, $\lambda_{in}$, and an external part, $\lambda_e$, corresponding to the donor/acceptor and the P3HT matrix respectively so that

$$\lambda_{in}^{\text{CT}} = E_D^{ca/le} + E_A^{an/gs} - E_D^{ca/ca} - E_A^{an/an}$$

$$\lambda_{in}^{\text{CR}} = E_D^{gs/ca} + E_A^{gs/an} - E_D^{gs/gs} - E_A^{gs/gs}$$

$$\lambda_{in}^{\text{EH}} = E_D^{an/gs} + E_A^{gs/an} - E_D^{an/an} - E_A^{gs/gs}$$

Here subscripts $ca$, $an$, $le$ and $gs$ represent cation, anion, local exiton and ground states, respec-
tively, while $E^{x/y}$ denotes the energy of state $x$ in $y$ configuration, obtained by relaxation of state $y$ followed by energy calculation of state $x$ occupation. Within the harmonic approximation, the reorganization energy spectrum is obtained via a modal decomposition routine in which

$$\lambda_{j}^{EH} = \frac{1}{2} \omega_{j}^{2} \Delta Q_{j}^{2}$$

(8)

The amplitude of the $j$th vibrational mode, $\Delta Q_{j}$, is calculated as

$$\Delta Q_{j} = \Delta \vec{Q} \cdot \hat{e}_{j}$$

(9)

where $\Delta \vec{Q}$ is the total displacement of the structure during the charge transfer. The vector, $\hat{e}_{j}$, is the eigenvector of the $j^{th}$ vibrational mode.

Nearly all the above quantities were calculated from the density functional theory (DFT) as implemented in the DMOL package. The Conductor-like Screening Model (COSMO) was used to account for the dielectric screening of the solvent. An all-electron approach (no pseudopotential) was used with exchange and correlation effects accounted for by the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE). A real-space, double numeric plus polarization (DNP) basis was used along with an octupole expansion to specify the maximum angular momentum function.

Optical gaps cannot be reliably calculated using DFT, so we used the many-body perturbation theory with the GW approximation to account for quasi-particle effects. This was followed by solving the Bethe Salpeter Equation (BSE) to correctly obtain both energies and wave functions for excitonic effects. Both quasi-particle and excitonic corrections were carried out using the package including the RGWBS and Parsec code sets.

As a previously employed computational expedient, P3HT was idealized as a $P3(C_{3}H_{7})T$ oligomer. Since it has comparable size to the dot, it is generally thought to preserve the essential character of dot/polymer interaction. However, our calculated optical gap of P3HT is 2.4 eV, much higher than the 2.0 eV observed in experiments due to the neglect of the $\pi - \pi$ stacking effect.
order to obtain accurate energy level alignments, the experimental value of the optical gap is used along with the computational wave functions.

The following empirical formula is used for the external reorganization energy:\(^3\)

\[
\lambda_s = \frac{(\Delta q)^2}{2} \left( \frac{1}{\sqrt{(R_xR_yR_z)_D}} + \frac{1}{\sqrt{(R_xR_yR_z)_A}} - \frac{2}{l_{DA}} \right) \left( \frac{1}{\varepsilon_{opt}} - \frac{1}{\varepsilon_s} \right) \tag{10}
\]

Here \(\Delta q\) is the transferred charge, \(R_i\) are the semi-axes of the ellipses that separately encompass the donor and acceptor: (9.7,8.8,9.4) Å for \(\text{Si}_{147}\)H\(_{100}\) and (12.6,2.8,6.6) Å for \(\text{P3(C}_3\text{H}_7\text{T)}\). The parameter, \(l_{DA} = 10.7\) Å is the center-to-center distance between donor and acceptor, and \(\varepsilon_{opt/s}\) are the optical/static dielectric constants of the surrounding P3HT matrix.\(^9\) Because the evaluation of these dielectric constants via ab initio methods is daunting, requiring an account of a linear response to the electric field for an the ensemble average of molecule arrangements, we chose to use experimental the experimental values of \(\varepsilon_{opt} = 1.96\) and \(\varepsilon_s = 3.3\).\(^3\)

The electronic coupling, \(V_{DA}\), for CT and CR between the dot and molecule are calculated using a two-state model\(^10\) at the Hartree Fock (HF) level\(^11\) as implemented in the NWChem Package:\(^12\)

\[
V_{DA} = \frac{|H_{fi} - S_{fi}(H_{ii} + H_{ff})/2|}{1 - S_{fi}^2} \tag{11}
\]

Here \(S_{fi}\) is the overlap between initial and final wavefunctions,

\[
S_{fi} = \langle \Psi_f | \Psi_i \rangle \tag{12}
\]

and the matrix elements of the total electron Hamiltonian are defined as

\[
H_{fi} = \langle \Psi_f | H | \Psi_i \rangle, \quad H_{ff} = \langle \Psi_f | H | \Psi_f \rangle, \quad H_{ii} = \langle \Psi_i | H | \Psi_i \rangle \tag{13}
\]

The electronic coupling associated with EH between two dots must also be calculated, but the HF method is a computationally expensive proposition in this case. By taking advantage of the similar
energy levels of initial and final states, an anticrossing methodology is employed instead. This method forces the eigenvalue of one SiQD to cross the associated eigenvalues of the other dot by applying a very small external electric field on the system. Minimizing the difference between these two eigenvalues provides good estimation of $2V_{DA}$.

Once the charge hopping rate is obtained, the drift mobility can be evaluated as

$$\mu = \frac{e}{k_B T} \frac{1}{2N} r^2 k_{EH}$$

where $N = 3$ is the dimensionality and $r$ is the distance between the center of the neighboring SiQDs.

### Photoluminescence Rate

Starting from Fermi’s golden rule, the photoluminescence (PL) rate at room temperature is

$$k_{PL} = \sum_i p(i) \frac{4e^2 f_i^2 (\varepsilon_{mol} E_i^3)}{3c^3 \hbar^3} |\vec{M}_i|^2$$

Here $p(i)$ is the room-temperature Boltzmann occupation, $E_i$ is the excitonic energy of excited state $i$, $f_i$ is the local field factor derived from the effective dielectric constant, and $M_i$ is the dipole matrix element between excitonic state $i$ and the ground state.

For the P3HT polymer film, the dielectric constant inside the molecule is similar to that of the environment, so the local field factor for all multi-pole expansions reduces to

$$f_i(x) = \frac{2l + 1}{(\varepsilon_{mol} / \varepsilon_s + 1)l + 1} \approx 1$$

The dipole matrix elements are calculated as the sum over pairwise electron-hole states,

$$\vec{M}_i = \sum_{h,e} C_{h,e}^i \langle \psi_h | \vec{r} | \psi_e \rangle$$
where $\psi_{h/e}$ are single-particle wave functions and $C_{h,e}^i$ are coefficients that used to describe the ith excitonic state as a linear combination of these wave functions. Both $C_{h,e}^i$ and the associated energies, $E_i$, are obtained from a combined GW-BSE analysis with the RGWBS suite, while dipole moments are computed using the MX code.

Sensitivity of Charge Transfer Rates to Solvent Modes

The main difficulty associated with the full quantum mechanical treatment lies on the computational challenge of using ab initio methods to quantitatively characterize the solvent modes. Fortunately, our computational results demonstrate that when the frequency of the solvent mode is much less than that of thermal fluctuations, the calculated rate is extremely insensitive to the solvent phonon frequency. To verify this, a number of effective solvent frequencies ($\omega_s$) between 10 and 100 cm$^{-1}$, a range typically associated with organic polymers, were tested and the corresponding change of CT, CR and EH rates are less than 4% (Table S1). For convenience, the values corresponding to the 10 cm$^{-1}$ frequency are used for discussions in the manuscript.

Table S1: CS and CR rates at the Si$_{147}$H$_{100}$/P3HT interface and the EH rate between two Si$_{147}$H$_{100}$ dots calculated using the full quantum mechanical treatment with varying effective frequencies for the solvent modes.

<table>
<thead>
<tr>
<th>$\omega_s$(cm$^{-1}$)</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{CT}$ (s$^{-1}$)</td>
<td>1.52E12</td>
<td>1.53E12</td>
<td>1.53E12</td>
<td>1.53E12</td>
<td>1.53E12</td>
</tr>
<tr>
<td>$k_{CR}$ (s$^{-1}$)</td>
<td>1.49E2</td>
<td>1.49E2</td>
<td>1.49E2</td>
<td>1.50E2</td>
<td>1.50E2</td>
</tr>
<tr>
<td>$k_{EH}$ (s$^{-1}$)</td>
<td>1.32E11</td>
<td>1.32E11</td>
<td>1.32E11</td>
<td>1.33E11</td>
<td>1.33E11</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$\omega_s$(cm$^{-1}$)</th>
<th>60</th>
<th>70</th>
<th>80</th>
<th>90</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{CT}$ (s$^{-1}$)</td>
<td>1.53E12</td>
<td>1.53E12</td>
<td>1.53E12</td>
<td>1.53E12</td>
<td>1.54E12</td>
</tr>
<tr>
<td>$k_{CR}$ (s$^{-1}$)</td>
<td>1.51E2</td>
<td>1.51E2</td>
<td>1.52E2</td>
<td>1.53E2</td>
<td>1.54E2</td>
</tr>
<tr>
<td>$k_{EH}$ (s$^{-1}$)</td>
<td>1.33E11</td>
<td>1.33E11</td>
<td>1.33E11</td>
<td>1.33E11</td>
<td>1.34E11</td>
</tr>
</tbody>
</table>

Another potential arises from the possible inaccuracy of the empirical formula for solvent reorganization energy ($\lambda_s$). We did observe a non-negligible variation of the CT, CR and EH rates with varying values of $\lambda_s$, and this implies that a much more delicate solvent model should be used in the future in order to quantitatively predict the rates. However, even if the error of $\lambda_s$ is as large
as 30%, the rate inequalities that we obtained, $CT \gg PL$ and $EH \gg CR$, do not change (Table S2).

**Table S2:** CS and CR rates at the $\text{Si}_{147}\text{H}_{100}/\text{P3HT}$ interface and the EH rate between two $\text{Si}_{147}\text{H}_{100}$ dots calculated by full mechanical quantum treatment with varying reorganization energies for the solvent modes.

<table>
<thead>
<tr>
<th>Change in $\lambda_s$ (%)</th>
<th>-30</th>
<th>-20</th>
<th>-10</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{CT}$ (s$^{-1}$)</td>
<td>2.20E12</td>
<td>1.94E12</td>
<td>1.72E12</td>
<td>1.52E12</td>
<td>1.35E12</td>
<td>1.20E12</td>
<td>1.06E12</td>
</tr>
<tr>
<td>$k_{CR}$ (s$^{-1}$)</td>
<td>6.33E1</td>
<td>8.43E1</td>
<td>1.12E2</td>
<td>1.49E2</td>
<td>1.97E2</td>
<td>2.62E2</td>
<td>3.46E2</td>
</tr>
<tr>
<td>$k_{EH}$ (s$^{-1}$)</td>
<td>2.15E11</td>
<td>1.82E11</td>
<td>1.55E11</td>
<td>1.32E11</td>
<td>1.13E11</td>
<td>9.67E10</td>
<td>8.28E10</td>
</tr>
</tbody>
</table>

**Use of an Oligomer to Represent the P3HT Polymer**

In our calculations, the large P3HT polymer is idealized as a small molecule containing 6 thiophene rings in the main chain and 3 carbon units in the side chains. This is computationally motivated and is based on the measured effective conjugation length of polythiophene as being between 6 and 12 thiophene rings. In addition, the effect of the side alkyl chains on the electronic structure and optical properties of the polymer are expected to be negligible. A similar approach was used to represent P3HT in previous ab initio calculations that successfully reproduced the energy level alignment, CT and CR rates at P3HT-PCBM interfaces when compared with experiment measurements. A longer side chain in our molecule, as compared with that study, was adopted in order to accommodate the larger sizes of the SiQDs as compared with PCBM. This idealization may slightly change the energy level alignment at the interface, but this is not deemed to be too important because the data is only used to identify an optimal dot size to match the experimental energy levels of the P3HT, the goal being to find a dot size for which the driving force for CT is positive but nearly zero. Because of this, our conclusions that the energy loss is small, the exciton dissociation is fast, and the interfacial CR are not deemed to rest on the idealization of the P3HT.
Anti-crossing Method

The anti-crossing method is a computationally efficient means of calculating the electronic coupling between two nearly degenerate states. For the Si$_{147}$H$_{100}$ dimer, relaxed in a face-to-face configuration, the LUMO and LUMO+1 orbitals (Figure S1) are localized on different dots. From the energy profile of the LUMO and LUMO+1 in the presence of a small electric field (Figure S2), we can determine the minimal splitting of these two states that can be shown to be a reasonable estimate of twice of the electron coupling for electron hopping.

Extrapolation of Charge Transfer Rates to Larger dots

To extrapolate the CT and CR rates from the Si$_{147}$H$_{100}$/P3HT interface with dot diameter of 1.7 nm to that associated with larger dot sizes (2-8 nm), the LUMO shifts of the dots are estimated as being half of the optical gap change obtained from previous computational studies. The solvent reorganization energy, as a function of dot size, is computed by preserving the face-to-face distance between the dot and the P3HT, namely for the dot with radius R, donor-acceptor distance in

Figure S1: LUMO (blue) and LUMO+1 (red) of an Si$_{147}$H$_{100}$ dimer. The values of the isosurfaces are 0.015 Å$^{-3/2}$.
Figure S2: Energy profile of the LUMO (blue) and LUMO+1 (red) in the presence of a small electric field. The green dashed line guides the eye to the point of minimal splitting of the two states.

Equation (14) is estimated by

\[ l^R_{da} = l^{Si_{147}}_{da} - 2R_{Si_{147}} + 2R \]  

(18)

In addition, the spectrally resolved reorganization energy is taken to be that of Si_{147}H_{100} but re-scaled so as to match the total reorganization energy of each dot: ²

\[ \lambda_{dot} \propto \frac{1}{\Omega} \propto \frac{1}{D^3} \]  

(19)

where \( \Omega \) is the volume and D is the diameter of the SiQD. Furthermore, as the LUMO extends over the entire dot, the wave function on the surface should scale as

\[ \psi_{dot} \propto \sqrt{\frac{1}{\Omega}} \propto D^{-3/2} \]  

(20)

In order to satisfy wave function normalization. Since the P3HT polymer conforms to the dot, the electron coupling is taken to have the following scaling:

\[ V^{CS/CR}_{DA} \propto S \times \psi_{dot} \propto D^2 \times D^{-3/2} \propto \sqrt{D} \]  

(21)
where $S$ is the surface area of the dot. We used a similar approach to estimate the electron hopping rates between two dots with diameters $D_1$ and $D_2$. As illustrated in Figure S3, we assume that the two dots are circles, and only the wave functions within distance, $h$, of the dot surfaces contribute to the electronic coupling so that the scaling of $V_{DA}$ can be approximated as

$$V_{DA}^{EH} \propto \min(S_1, S_2) \times \psi_{\text{dot}1} \times \psi_{\text{dot}2} \propto \min(D_1, D_2) \times D_1^{-3/2} \times D_2^{-3/2}$$

(22)

Here

$$S_1 = \pi r_1^2 \approx \pi D_1 h, \quad S_2 = \pi r_2^2 \approx \pi D_2 h$$

(23)

provided that $h \ll D$.

**Influence of Dangling Bonds on Electronic Coupling**

In contrast to the delocalized wave function of defect-free dots, the LUMO becomes localized on the surface of the dot in the presence of a dangling bond (DB). The result is that it becomes closer
Figure S4: Three configurations of the Si$_{147}$H$_{100}$/P3HT interfaces with one dangling bond (green).

to the HOMO of the surrounding P3HT and this significantly enhances the electronic coupling for both CT and CR (Table S3). Since the wave function of the dot with DB is spatially inhomogeneous, the electronic coupling depends strongly on the interfacial configuration. Three representative configurations (Figure S4) of Si$_{147}$H$_{100}$/P3HT interfaces are considered in our calculation, and the average value is used in the rate expression of CT and CR. For the electron hopping between two dots, we assumed that the electron coupling for all three DB configurations is the same as that without DBs.

Table S3: Electronic coupling of charge transfer and recombination at the Si$_{147}$H$_{100}$/P3HT interface without any dangling bonds and with one dangling bond. Three different configurations are considered.

<table>
<thead>
<tr>
<th></th>
<th>No DB</th>
<th>DB: config1</th>
<th>DB: config2</th>
<th>DB: config3</th>
</tr>
</thead>
<tbody>
<tr>
<td>CT (meV)</td>
<td>9.8</td>
<td>29.6</td>
<td>60.6</td>
<td>46.2</td>
</tr>
<tr>
<td>CR (meV)</td>
<td>4.0</td>
<td>4.6</td>
<td>18.1</td>
<td>13.0</td>
</tr>
</tbody>
</table>

Performance of the Device without Dangling Bonds

The current density in an electric field $E$ is

$$ J = nev_d = ne\mu E \propto \mu $$

(24)
where \( n \) is the carrier concentration and \( \mu \) is the carrier mobility. Enhancement of the mobility therefore leads to the same order of improvement in the current provided the internal voltage drop does not change. In order to extract free carriers to the external circuit, the carriers must drift to the electrodes before CR occurs. The efficiency of this process is determined by a comparison between the carrier sweep out time and the CT state lifetime, where the carrier sweep out time is taken to be the period required by the carrier to drift from the center of the active layer to the electrode:

\[
\tau_s = \frac{d^2}{2\mu V_{in}}
\]  

Here \( d \) is the distance between the electrodes and \( V_{in} \) is the internal potential drop.

As an example, we consider a set of typical solar cell parameters, with \( V_{in} = 0.2 \) V and \( d = 120 \) nm.\(^{24}\) For the Si\(_{147}/P3HT\) blend with a DB on the dot surface,

\[
\tau^{DB}_{s} = \frac{d^2}{2\mu^{DB} V_{in}} = \frac{(120 \times 10^{-9})^2}{2 \times (2.8 \times 10^{-10}) \times 0.2} = 1.2 \times 10^{-4} s \gg \tau^{DB}_{CT} = \frac{1}{k_{DB}^{CR}} = \frac{1}{2.5 \times 10^{12}} = 4.0 \times 10^{-13} s
\]  

implying a noticeable proportion of carriers would be lost to CR. In contrast, for the assemblies without a DB,

\[
\tau^{Perfect}_{s} = \frac{d^2}{2\mu^{Perfect} V_{in}} = \frac{(120 \times 10^{-9})^2}{2 \times (2.9 \times 10^{-6}) \times 0.2} = 1.2 \times 10^{-8} s \ll \tau^{Perfect}_{CT} = \frac{1}{k_{Perfect}^{CR}} = \frac{1}{1.5 \times 10^{2}} = 6.7 \times 10^{-3} s
\]  

indicating that most of the carriers will contribute to the photocurrent.
References


