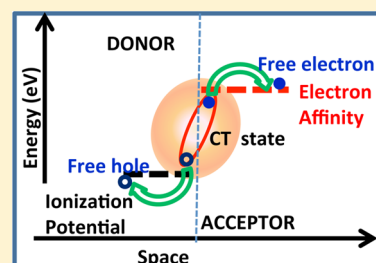


Separating Charges at Organic Interfaces: Effects of Disorder, Hot States, and Electric Field

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S Supporting Information

ABSTRACT: Charge separation at organic–organic (O–O) interfaces is crucial to how many organic-based optoelectronic devices function. However, the mechanism of formation of spatially separated charge carriers and the role of geminate recombination remain topics of discussion and research. We review critically the contributions of the various factors, including electric fields, long-range order, and excess energy (beyond the minimum needed for photoexcitation), to the probability that photogenerated charge carriers will be separated. Understanding the processes occurring at the O/O interface and their relative importance for effective charge separation is crucial to design efficient solar cells and photodetectors. We stress that electron and hole delocalization after photoinduced charge transfer at the interface is important for efficient free carrier generation. Fewer defects at the interface and long-range order in the materials also improve overall current efficiency in solar cells. In efficient organic cells, external electric fields play only a small role for charge separation.



Transfer of electronic charge (charge transfer, CT) at an interface is key to the function of many optoelectronic devices, such as solar cells and detectors. While the process is well understood for inorganic interfaces, especially those of crystalline inorganic semiconductors, the situation is less clear for interfaces that involve organic materials.¹ In organic semiconductors, the exciton binding energy is typically between 0.2 and 1.0 eV (instead of a few meV for common inorganic semiconductors).^{2,3} Therefore, organic semiconductors are efficient light emitters but poor photoconductors. For photovoltaic (PV) applications, organic–organic (O–O) heterojunctions of an electron donor and an electron acceptor are used to promote efficient exciton dissociation.¹

After photoinduced CT, the electron and hole pair can still be bound to each other as organic materials have low dielectric constants. However, many systems show near 100% efficiency in charge separation.⁴ The efficiency in this system is explained by a driving force, which translates in a price in energy, energy that is ultimately lost to the surrounding as heat. The need for excess energy (generally excess photon energy) to drive charge separation has been discussed thoroughly (cf., e.g., refs 5 and 6); the excess energy was thought to be stored in vibronic modes of the organic molecules.⁶ However, it is not well understood how the excess energy is used by the system and why certain systems perform better than others even though the apparently available excess energy is similar. The nature of the process, resulting in free carriers, following exciton dissociation at an O–O interface, is a matter of some controversy. Some authors argue that free carrier generation following exciton dissociation at the O–O interface is facilitated by the electric field in the sample. Others argue for spontaneous

free carrier generation following exciton dissociation at the O–O interface.

The CT state breaks up, not because of the energy content but because of the delocalized nature of its higher energetic states.

A detailed analysis of the CT state that is a precursor to free carriers may improve our understanding of the role of excess energy in charge separation. Such analysis may then also provide (additional) design rules for better materials. It has been shown that material disorder (which implies traps for charge carriers) accounts for loss in achievable voltage in solar cells.⁷ As such, it is of interest to see in what way and to what extent material disorder plays a role in charge separation.

To that end, we provide here a critical view, using the reported experimental results, on the various factors that contribute to efficient free carrier generation, following exciton dissociation at O–O interfaces.

Charge Separation at Organic Heterojunctions. CT state between the donor and acceptor. After photoinduced electron transfer (PIET) between a donor and acceptor molecule at the interface, the electronic charges can still be bound due to the low dielectric constant of the interface-forming materials

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(typical values for the dielectric constant, ϵ_r , of organic materials are 3–4). The state where the hole, h^+ , resides in one material and the electron, e^- , in another material and they are still bound by Coulomb attraction, is termed a CT exciton.⁸

A simple electrostatic model predicts that the dissociation of the CT exciton (also known as a geminate bound polaron pair⁹) state can happen only if the Coulomb radius (e–h pair separation) exceeds 16 nm (i.e., the thermal energy, $k_B T$, with k_B as the Boltzmann constant, at room temperature exceeds the Coulomb potential energy) for a typical organic system with $\epsilon_r \approx 3.5$ (see Figure 1). This requires multiple hopping of carriers

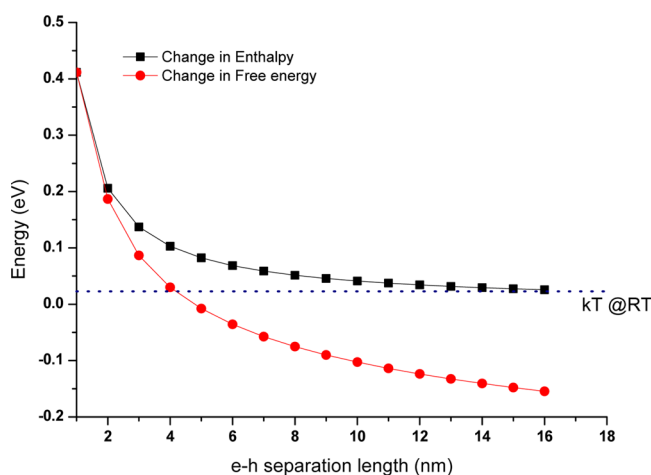


Figure 1. Free energy and enthalpy dependence on the electron–hole separation length. The calculation assumes an effective dielectric constant of 3.5. Black squares show how the enthalpy of an e–h pair changes as a function of separation length; the red dots show the change in free energy (effect of the entropy factor at 298 K). The horizontal blue dashed line shows the thermal energy available at 298 K. With the entropy contribution, the e–h pair can split into free carriers already at 4 nm separation.

(i.e., delocalization of the exciton) before actual separation.¹⁰ Considering all other competing processes that cause recombination from the CT state, one would expect the separation efficiency to be very poor. However, many OPV systems have a CT exciton dissociation efficiency of $\sim 100\%$. This indicates that a simple electrostatic model is insufficient to understand the charge separation process.

Role of Entropy in Charge Separation. A different picture arises if we consider the entropic contribution¹¹ to the free energy (Figure 1). As the distance between the electron and the hole of the bound e^-h^+ pair increases, the hole and electron can be viewed as propagating in two spatially separated regions (see Figure S1 in the Supporting Information (SI)). The entropy increases with the number of available molecular sites to accommodate the electron and the hole that make up the still bound e^-h^+ pair. Typically, the density of states (DOS) for HOMO levels in the donor and for LUMO levels in the acceptor phases is $\sim 10^{21}/\text{cm}^3$ ($\sim 1/\text{nm}^3$). The contribution to the free energy from entropy is given by $k_B T \ln(\Omega)$, where Ω is given by the number of molecular pairs that can accommodate the e^-h^+ pair. The potential energy for the Coulomb interaction is given by $U = e^2/4\pi\epsilon_0\epsilon_r R$. The (free) energy (G) of the system (i.e., with the entropic contribution) is given by $G = U - k_B T \ln(\Omega)$. As there is no change in pressure or volume during the charge separation, the enthalpy change is given by $-e^2/4\pi\epsilon_0\epsilon_r R$. Figure 1 shows the variation of ΔH

(black, top curve) and ΔG (red, bottom curve) with e–h separation length R , assuming 1 state/ nm^3 and $\epsilon_r = 3.5$. A negative value of ΔG leads to spontaneous charge separation, that is, if the entropy contribution more than cancels the Coulomb attraction. We note here that the entropy contribution is calculated assuming delocalization in three dimensions. In actual materials, delocalization may occur in fewer dimensions, in which case the entropic contribution will be less, as pointed out by Gregg.¹²

Though this is not a rigorous analysis, it emphasizes the importance of taking entropy (and delocalization of electrons and holes) into account for charge separation. This analysis also indicates that delocalization of carriers is important in determining charge separation. This analysis holds for equilibrium conditions without any external factors other than temperature. Also, kinetic factors are not considered. However, in practice, the bound e^-h^+ pair has a certain lifetime, and e–h separation must happen within that time limit. In the following, we discuss other factors (mainly kinetics and electric field) that influence charge separation at the interface.

Separation of Charges in a Dielectric Medium: Onsager and Onsager–Braun Models. Onsager was the first to propose a model for charge separation in a dielectric medium. In his model,¹³ the probability (ϕ_0) for spontaneous dissociation of a Coulomb-bound pair (or any geminate pair) in a dielectric medium at zero electric field is given by

$$\phi_0(r_0) = \exp\left(-\frac{r_c}{r_0}\right) \quad (1)$$

where r_0 is the distance at which the geminate pair was created (thermalization distance) and r_c is the Coulomb radius given by $r_c = q^2/\epsilon k_B T$, where q is the electron charge. It follows from eq 1 that a large value of r_0 promotes free carrier generation. Braun¹⁴ showed that eq 1 significantly underestimates the escape probability. In the derivation of eq 1, Onsager assumed that the electron and hole annihilate each other on contact. This is a classical description. In the quantum mechanical description, if the electron and hole approach each other to a distance on the order of the exciton radius, then an exciton will form with a finite lifetime, and the dissociation efficiency is an interplay of various rate constants, shown schematically in Figure 2.

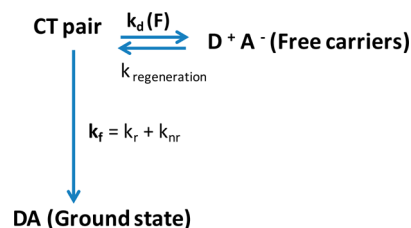


Figure 2. Braun model for charge pair dissociation. The CT state has a finite lifetime. Direct recombination from D^+A^- to the DA ground state is neglected.

In the Onsager–Braun Model, the CT pair recombines with a rate constant of k_t or dissociates into free carriers with an electric field-dependent rate constant of $k_d(F)$.¹⁴ In parallel, free carriers recombine through a Langevin recombination process^{8,15} to regenerate the CT pair.¹⁴ Charge separation competes

with (geminate) recombination. The lifetime, $\tau(F)$, can be written as¹⁴

$$\tau(F) = \{k_f + k_d(F)\}^{-1} \quad (2)$$

where $k_f = k_r + k_{nr}$, that is, the sum of the radiative and nonradiative recombination rate constants, and the dissociation constant $k_d(F)$ can be written as¹⁴

$$k_d(F) = \nu \cdot \exp\left(\frac{-\Delta E}{k_B T}\right) \left\{ 1 + b + \frac{b^2}{3} + \frac{b^3}{18} + \dots \right\} \quad (3)$$

where $b = e^3 F / \{8\pi\epsilon\epsilon_0 k_B^2 T^2\}$ and the zero-field ($F = 0$) value is

$$k_d(0) = \nu \cdot \exp\left(\frac{-\Delta E}{k_B T}\right) \quad (3a)$$

ΔE is the binding energy of the CT pair, and ν is the attempt-to-escape frequency, which depends, in addition to other factors, on the mobility of the carriers. We see from eq 3 that the probability of dissociation of the CT pair, as expressed by the rate, increases with electric field, resulting in a decrease in lifetime and luminescence intensity of the CT state.

Equation 3 also helps to make a simple estimate of the relative importance of rates of ionization, k_d , of the CT pair versus recombination, k_f , in the zero external field limit. Equating $k_d(0)$ to the exciton recombination rate $1/\tau_{ex}$ (where τ_{ex} is the exciton lifetime) provides an estimate as to when dissociation dominates over recombination.¹⁶ If ΔE (in eqs 3) $< k_B T \ln(\nu\tau_{ex})$, dissociation dominates over recombination. Taking $\nu = 10^{13}/s$ and $\tau_{ex} = 10$ ns, Street estimates that ionization dominates over recombination for $\Delta E < 0.25$ eV.¹⁶

Understanding the mechanism of carrier generation is crucial to the interpretation of the current–voltage characteristics of solar cells under illumination. The photocurrent of a solar cell can be written as¹⁷

$$I_p(V) = I_d(V) - qP_R(V)G \quad (4)$$

where $I_d(V)$ is the dark current, G is the carrier generation rate, and $P_R(V)$ is a dimensionless normalization factor, which reflects both carrier collection and free carrier generation. If free carrier generation is governed by geminate recombination, then $P_R(V)$ essentially is determined by the dissociation of CT pairs by the electric field. However, if geminate recombination does not dominate, then free carrier generation does not depend on the applied voltage. In this case, $P_R(V)$ is related to the collection efficiency and the rate at which charge carriers are lost by recombination. Understanding the charge generation mechanism is an important role for the interpretation of solar cell characteristics and for solar cell design, which explains the motivation to understand recombination in solar cell materials.

In the following, we apply our understanding of the photogeneration process and the Braun–Onsager relation to different systems, with emphasis on polymer bulk heterojunctions (BHJs).

Charge Separation in BHJ Solar Cells. A large number of polymer BHJs have been investigated. Some examples are poly(3-hexylthiophene) (P3HT)/[6,6]-phenyl-C61-butyric acid methylester (PCBM) and poly[N-9"-heptadecan-2,7-carbazole-*alt*-5,5-(4',7'-di-2-thienyl-2',1',3' benzothiadiazole) (PCDTBT)/PCBM, where PCBM is the acceptor. The P3HT/PCBM system is studied intensively and used as a test system for understanding BHJs. The PCDTBT/PCBM BHJ has shown 100% internal quantum efficiency (QE), implying

that every absorbed photon gives rise to one electron, flowing in the external circuit.⁴ In a typical BHJ device, most of the light is absorbed by the donor polymer (e.g., P3HT), giving rise to excitons. These excitons diffuse to the DA interface and can dissociate there if the DA interface lies within a diffusion length of where the exciton was generated.

Following CT exciton (=CT pair) formation after PIET, there are at least two possible scenarios, as follows. (a) Exciton dissociation leads to creation of a hot CT state, which subsequently thermalizes to the CT ground state. The excess CT energy, ΔE_{xs} , is given by

$$\Delta E_{xs} = E_x - E_{CT} \quad (5)$$

where E_x is the exciton energy and E_{CT} is the ground state energy of the CT state. At a given temperature, dissociation of the CT pair by an externally applied electric field through the Braun–Onsager mechanism is necessary to create free carriers.¹⁸ A related question that arises is the role of the excess energy (ΔE_{xs} in eq 5), if any, in aiding CT pair dissociation. In parallel, the CT pair can recombine geminately, radiatively or nonradiatively. The role of an electric field is to suppress geminate recombination and enhance free carrier generation. (b) Exciton dissociation at the D–A interface results in generation of free carriers, which are then collected by the electrodes aided by an electric field, giving rise to a photocurrent. The role of the electric field (built-in + applied) in this scenario is to facilitate collection (reducing bimolecular recombination) and has no role in carrier generation.

Depending on the materials system, process (a) or (b) may dominate. Even for a given material system (P3HT/PCBM), it is difficult to resolve if (a) or (b) dominates as conflicting reports exist in the literature.¹¹ We will briefly review our present understanding by way of recent results on the P3HT/PCBM and PCDTBT/PCBM systems as these are relatively well understood. Thus, in the next paragraphs, we discuss various parameters that influence the charge separation process, based on time-resolved transmission measurements (see the SI for a brief summary of time-resolved measurements) on model systems.

Role of Excess Energy in Charge Separation. The CT state is characterized by optical absorption below the band gap, E_G , with a small optical absorption coefficient. However, it is possible to optically excite the CT band and create CT states directly. For the P3HT/PCBM system, the CT states' excitation energy is ~ 1.6 eV. Lee et al.¹⁹ measured the internal QE for P3HT/PCBM solar cells for both directly excited CT states (1.6 eV) and CT states produced from excitons (after $>E_G$ excitation). They found that the internal QE is identical in both cases and concluded that the excess energy, $\delta E = E_x - E_{CT}$, associated with the exciton dissociation is not important for the generation of free carriers in that particular system.

Another way to probe the role of excess energy is to vary the excitation wavelength and measure the polaron yield. Herrmann et al.²⁰ used photoinduced absorption to get a relative polaron yield (0.3 ps after the excitation pulse) as function of excitation wavelength. In a P3HT/Si blend, they note that for $\lambda > 500$ nm excitation, only P3HT aggregates are excited, while P3HT coils are predominantly excited for $\lambda < 500$ nm. The polaron signal peaks 0.3 ps after the excitation pulse. This coincides with the decay of the exciton signal. The polaron yield, measured 300 fs after the excitation pulse, is larger at 600 nm than that at 450 nm (see Figure 3).

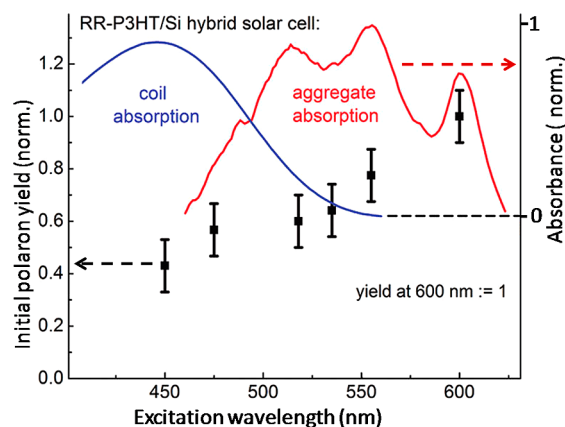


Figure 3. Excitation wavelength dependence of the initial polaron yield in a RR-P3HT/poly-Si solar cell. Initial polaron yield (black squares) 0.3 ps after excitation. A 2× higher efficiency is observed for excitation at 600 nm than that at 450 nm. The difference is due to the presence of two types of domains in the P3HT film, namely, coiled (absorption given by the blue curve) and aggregated (absorption given by the red curve). Adapted from ref 20. Copyright 2011, American Chemical Society.

If only excess photon energy were responsible for the exciton dissociation and subsequent polaron formation, then the polaron yield should have been larger at 450 nm than that at 600 nm.

In contrast to these conclusions, Clarke et al.²¹ and Okhita et al.²² studied CT in P3HT/PCBM and in polythiophene/PCBM blends, respectively. These authors concluded that excess energy is responsible for efficient generation of free carriers in a P3HT/PCBM blend. The arguments are briefly summarized below. In the as-cast blend, the photoluminescence (PL) (of P3HT) is efficiently quenched at >90%. This suggests efficient exciton dissociation at the blend interface. Upon annealing, the short-circuit current of the solar cell increases by a factor of 2, accompanied by an increase in luminescence intensity. The authors argue that an increase in P3HT luminescence implies that annealing does not increase exciton dissociation at the P3HT/PCBM interface. If annealing does not increase the efficiency of exciton dissociation, then it cannot account for the increase in short-circuit current. From transient-induced absorption measurements, they find that there is an increase in the polaron generation yield by a factor of 2 after annealing. The ionization energy of the annealed P3HT was reduced by 50 meV upon annealing. Because the lowest-energy absorption band is unaffected, the authors conclude that the improved current and, hence, the exciton dissociation efficiency upon annealing is due to an excess energy of 50 meV.

Okhita et al.²² reached a similar conclusion from a study of many polythiophene/PCBM blends. They observed efficient PL quenching for all of the blends. The photocurrent for these samples varied, however, by over 2 orders of magnitude. They postulate that the difference in the photocurrent in the different samples is due to different values of excess energy.

Trying to reconcile these different experimental results is difficult, and what follows will, thus, be speculative. Street et al. pointed out¹⁷ that recombination at the PCDTBT/[6,6]-phenyl-C70-butyric acid methyl ester (PC70BM) interface is defect-mediated. Annealing reduces the defects. This, in turn, should reduce the nonradiative recombination. In addition,

annealing also increases the crystallinity and ordering of P3HT. These two factors could be responsible for the increased luminescence seen by Clarke et al. The increasing crystallinity of the P3HT and PCBM and the decreased interface state density after annealing are accompanied by an increase in carrier mobility and can result in an increased number of dissociated pairs and, thus, polarons. We note that PL quenching can only be an indicator of exciton dissociation. PL quenching is a necessary but not a sufficient condition for free carrier generation. If defect-mediated recombination is large, the CT states can recombine geminately or even nonradiatively, accounting for the small photocurrents seen by Okhita and Clarke et al.

Recently, Bakulin et al.²³ presented a mechanism for spontaneous free carrier generation, based on ultrafast time-resolved measurements, involving an excitation pump pulse, a push pulse at 3 μm , and a probe pulse at 3 μm , for a variety of BHJ materials. The neutral polymer has very little absorption at 3 μm . The pump pulse creates excitons, which dissociate at the BHJ interface, creating CT pairs that give rise to positively charged polarons P^+ in the donor. These polarons have energy levels in the gap (0.3–0.5 eV above the HOMO) and can be detected in an optical absorption measurement.

Following the excitation pulse, which created CT states, a push pulse is applied and leads to an increase in the photocurrent. The authors postulate that the push pulse promoted an electron from deep in the HOMO band to the P^+ state, converting it to a P^0 state that is doubly occupied (see the SI). This results in a hot hole deep in the HOMO band, which is more delocalized than a cold one. This delocalization translates in a large r_0 (cf. eq 1) and smaller ΔE (cf. eq 3a), increasing the escape probability for spontaneous dissociation of the CT pair, giving rise to the measured photocurrent. The authors argue that this is essentially the condition before the CT pairs thermalize, a condition that promotes spontaneous free carrier generation.

Proof of the validity of the above picture comes from the fact that the induced absorption, immediately following the push pulse, decreases, implying that the push pulse converted the singly occupied polaron states to doubly occupied states. More recently, Dimitrov et al.²⁴ showed that in a model organic D–A system where the ΔLUMO is small (i.e., small driving force for electron transfer), carrier photogeneration strongly depends on the photon energy used to create the exciton. Similar observations were also reported on other organic heterojunctions,^{25,26} where hot CT states, created by supra-band-gap illumination, give rise to free carriers. In case of the PCPDTBT/PCBM system,²⁵ the peak optical absorption of PCPDTBT is close to 710 nm and corresponds to $\text{S}_0\text{--}\text{S}_1$ (i.e., electronic transition from the ground singlet to first excited singlet state). The absorption at 510 nm corresponds to the $\text{S}_0\text{--}\text{S}_4$ (ground to fourth excited singlet state) transition, much higher in energy and with a lower absorption coefficient. From time-resolved measurements, Grancini et al.²⁵ showed that excitation at 510 nm resulted in higher charge generation efficiency than excitation at 710 nm. The authors argue that at these energies, the hot CT states are delocalized and result in spontaneous free carrier generation. Support for this argument comes from device measurements on a similar PCDTBT/PCBM system.⁴ The internal quantum efficiency (IQE) is close to 100% at 450 nm excitation and close to 90% between 500 and 650 nm for solar cells, using a similar PCDTBT/PCBM⁴ system, where the absorption maximum for the absorber is at

550 nm. The high IQE values can be understood in light of a highly delocalized CT state, in which case the excess photon energy allows high charge generation efficiency and, thus, solar cells of high conversion efficiency. This has been demonstrated for the PCDTBT/PCBM cell, where excitation with 20 mW of 532 nm radiation results in a cell conversion efficiency of 16% as opposed to an efficiency of about 6% with white light irradiation.⁴ This highlights the importance of the role of excess photon energy for efficient charge generation efficiency and high efficiency for solar cells.

Hot CT states need not be vibronically hot states but can also be higher electronic states, formed by direct electron transfer from higher electronic levels of the donor molecule. The hot CT state gives rise to free carriers because of the delocalized nature of the charge pair. Hence, the excess energy that is often taken as being lost as heat to the surrounding is useful for charge separation, in contrast to the case for all inorganic solar cell materials, where excess energy (obtained by supra-band-gap absorption) is lost as heat (see also refs 27 and 28). This suggests that for a molecular absorber, a large absorption cross section in the visible and near-IR, with small energy separation between the S_0 – S_1 and S_0 – S_n ($n > 1$) transitions, is an important design rule for synthesis of a new absorber material for solar cell application. However, it is also possible to have a delocalized CT state without having supra-band-gap optical excitation. For example, for the P3HT/PCBM system, no supra-band-gap excitation is required to separate the hole and electron.^{19,29} This can be explained by formation of a CT state, formed from sub-band-gap absorption (i.e., by direct photoexcitation of the CT state), which has a delocalized character. At the same time, we also note that the state may not be the electronic ground state of the CT pair. If a general mechanism is applicable for all of the efficient systems, then we can say that the CT state breaks up not because of the energy content but because of the delocalized nature of its higher energetic states. The delocalized nature of the CT pair also causes the state to have a lower binding energy than that of the localized CT pair. According to eq 3a, the rate of dissociation (k_d ; cf. eqs 2 and 3) of CT increases with lowering in binding energy of the CT state. Indeed, very fast (subpicosecond) dynamics for charge separation were observed for efficient systems like CuPc/C60²⁶ and PCDTBT/PCBM.³⁰

The rate of dissociation is also affected by the pre-exponential factor (ν ; cf. eqs 3 and 3a) that depends on the carrier mobility. The probability of charge separation depends on $k_d\tau$, where τ is the lifetime of the delocalized state. Charge separation from the delocalized state also competes with thermalization to the localized (ground) state from where geminate recombination can happen.

In efficient systems, the charge separation process dominates because of the lower binding energy of the CT state due to delocalization and high mobility of carriers. For the same reason, no geminate recombination is noticed for efficient systems like PCDTBT/PCBM.³⁰ In less efficient or inefficient systems, the CT pair is formed as a localized one from the beginning or thermalization dominates over dissociation. If the localized CT state decays radiatively, then it is seen in photoluminescence. Many polymeric systems {e.g., (poly(9,9-dioctylfluorene-*co*-benzothiadiazole) (F8BT)/poly(9,9-dioctylfluorene-*co*-bis-*N,N*-(4-butylphenyl)-bis-*N,N*-phenyl-1,4-phenylenediamine) (PFB); F8BT/poly(9,9-dioctylfluorene-*co*-*N*-(4-butylphenyl)diphenylamine) (TFB)} show red-shifted photoluminescence,³¹ which are attributed to CT states

(termed an exciplex in ref 31). CT states always form at type-II (staggered gap) organic–organic interfaces; depending on the delocalization of the CT state and on the mobility of carriers, separation or geminate recombination occurs.

From the above discussion, it is clear that delocalization rather than the excess energy is the central feature for charge generation. Whether excess energy is involved or not is system-specific. In addition, long-range order and crystallinity are important for determining charge separation. In the next paragraphs, we discuss the role of lack of order for charge separation.

Role of Disorder. The role of disorder can be probed by studying the decay of free and bound polarons, using time-resolved photoinduced absorption by (i) comparing blends of regiorandom (RRa)-P3HT and regioregular (RR)-P3HT, (ii) studying nonannealed and annealed RR-P3HT blends, (iii) studying blends of aggregated P3HT, and (iv) studying blends of RR-P3HT with crystalline inorganic semiconductors.

Howard et al.³² estimate that for nonannealed RR-P3HT blend samples, geminate recombination is ~30% and decreases to 15% upon annealing (see Figure 4).

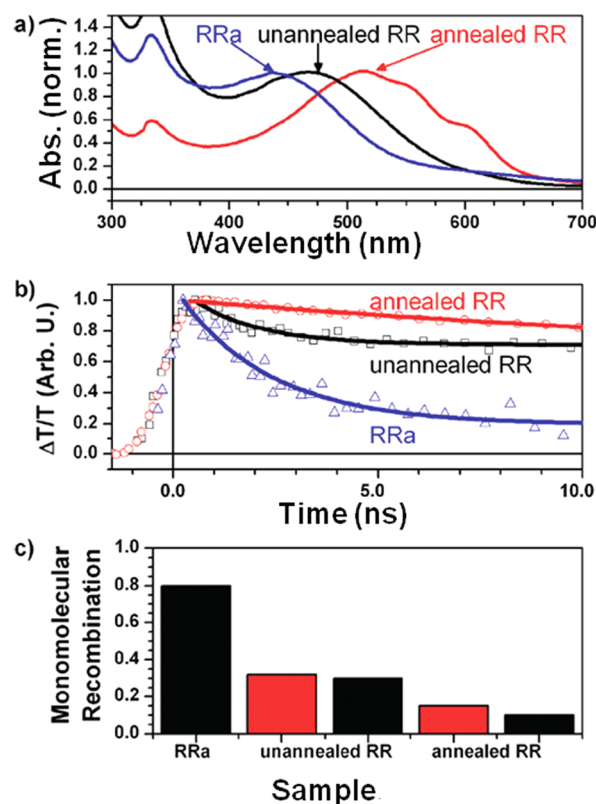


Figure 4. (a) Shift of the absorption spectra between different P3HT/PCBM samples, as result of different interchain ordering; RRa = RRa-P3HT/PCBM, unannealed RR = nonannealed chloroform-cast RR-P3HT/PCBM; annealed RR = annealed chlorobenzene-cast RR-P3HT/PCBM. (b) Kinetics of the charge-induced 750–850 nm absorption shown for the first 10 ns after excitation, plotted as ($\Delta T/T$), the temporal change in the differential transmission measured using a probe pulse after the excitation of the sample with a pump pulse, plotted versus the delay time of the probe pulse. (c) Intensity-independent fraction of recombination in each sample, obtained from low-fluency decay (black bars). Adapted with permission from ref 32. Copyright 2010, American Chemical Society.

This is a consequence of the fact that annealed samples result in improved crystallinity of both P3HT and PCBM. These results highlight the role of disorder.

To specifically address the role of disorder, Hermann et al.²⁰ studied transient absorption spectroscopy of a P3HT/Si nanocrystalline composite BHJ and a P3HT/poly-Si planar heterojunction. The authors noted that P3HT forms two phases, (i) an amorphous coiled phase (which exists in RRA-P3HT), characterized by an absorption peak at 450 nm (2.8 eV) and (ii) an ordered phase (in RR-P3HT), where the polymer chains planarize and form ordered structures with a 0–0 vibronic band at 610 nm.³³ The amount of ordered P3HT can be estimated from the absorption spectrum.²⁰

To study the role of disorder, they measured RR-P3HT/nc-Si (BHJ) and both aggregated, aggRR-P3HT/poly-Si and RRA-P3HT/poly-Si in planar heterojunctions.

The initial yield of polaron formation was found to be largest for aggRR-P3HT and least for RRA-P3HT. The polaron yield for aggRR-P3HT was twice that for the RRA-P3HT blend (also see the preceding paragraphs). The authors hence associated the efficiency of polaron formation with aggregation and extended conjugation. This is directly related to the mobility of carriers. This result is easy to understand as the prefactor (ν) in eq 3a for zero-field dissociation of charged pairs depends on the carrier mobility.

They, furthermore, found that the decay kinetics of polarons, as measured from the induced absorption for RRA-P3HT/poly-Si BHJ samples, is independent of fluence (4–16 μJ), indicating that the recombination is geminate. This agrees with results³⁴ for RRA-P3HT/PCBM blends. In contrast, the decay for aggRR-P3HT/poly-Si is fluence-dependent, indicating bimolecular recombination and, hence, generation of free carriers. The conclusion is that extended conjugation and ordering aid spontaneous free carrier generation. The onset of bimolecular recombination takes place at about 4 $\mu\text{J}/\text{cm}^{-2}$.

Care needs to be exercised in the interpretation of time-resolved experiments. For the RR-P3HT/PCBM system, Marsh et al.³⁵ pointed out that a fluence of $>3 \mu\text{J}/\text{cm}^{-2}$ corresponds to an intensity that results in a decrease in the EQE of the solar cell. In most of the transient measurements reviewed here, the minimum fluence used was $\sim 4 \mu\text{J}/\text{cm}^{-2}$. Hence, the conclusions, based on results obtained with such high fluence, may not always be relevant for solar cells under normal insolation. We conclude that extended conjugation and order play an important role in the efficiency of exciton dissociation into free carriers. In particular, interface defects are very important.

Extended conjugation and order play important roles in the efficiency of exciton dissociation into free carriers.

Because high carrier mobility is key to efficient spontaneous free carrier generation, morphology and ordered regions of the acceptor and donor play crucial roles. Typically, some type of annealing of the PV-active material, at times in the presence of certain solvents, is used to control the morphology. In this context, it is useful to mention that it has been known that using a small amount of an additive like 1,8-diiodooctane improves solar cell efficiency.³⁶ In light-degradation studies, Street et al.³⁷ studied the effect of thermal annealing and light

degradation on PCDTBT/PCBM solar cell parameters. They showed that the presence of defects that give rise to deep states, formed due to illumination and annealing, at the interface degraded the photocurrent. Light-induced states are created in the middle of the band gap. In contrast, thermal annealing gives rise to broader band tails, which can be associated with increased disorder. Because deep states act as recombination centers, control of defects that give rise to them at the interface is also important.

After discussing the role of internal parameters like excess energy, delocalization of the CT state, and disorder upon charge separation, we now review the effect of an external electric field.

Recombination and Role of Electric Field. Marsh et al.³⁵ carried out transient absorption spectroscopy on as-deposited and annealed P3HT/PCBM solar cells as a function of bias. If exciton dissociation leads to creation of a bound CT state (model (a) in the 2nd paragraph, after eq 5, on *charge separation in BHJ solar cells*), then with increasing reverse bias, recombination would be reduced, resulting in a larger lifetime for the carriers. If, however, the excitons dissociated spontaneously to produce free charge carriers (model (b) in the above-mentioned paragraph), then the external field would reduce the lifetime as the carriers will be collected at the electrodes, causing also the bleaching signal intensity to decay due to carrier sweep-out. As the lifetime was found to increase with increasing reverse bias, it was argued that photogenerated carriers are primarily produced by electric-field-aided dissociation of CT pairs, in agreement with the above-mentioned model (a).

These conclusions contradict experimental results obtained by others. For instance, from a study of the temperature dependence of the short-circuit current and the fill factor of P3HT/PCBM solar cells, Mauer et al.³⁴ argue that non-geminate recombination and collection, rather than generation, dominate the fill factor in P3HT/PCBM solar cells. They investigate both RRA-P3HT/PCBM and RR-P3HT/PCBM samples and measure the decay of the integrated transient absorption between 1.3 and 1.5 eV (corresponding to the presence of free and bound charges). The decay of the RRA-P3HT/PCBM blend (see Figure 5) takes place within 2–3 ns, consistent with geminate recombination of excitons, and is independent of temperature between 295 and 77 K. The absorption decay of the RR-P3HT blend is very different and takes up to microseconds at 295 K, with only 20% of the carriers decaying in about 20 ns. The decay rate increases with fluence, suggesting that the decay is bimolecular. The decay also becomes longer at lower (77 K) temperature. The reduced recombination rate at low temperature is consistent with a reduced Langevin recombination probability as the carrier mobility decreases with temperature.

Transient absorption measurements (750–800 nm) reveal that at least 80% of quenched excitons form polarons on a subnanosecond time scale. Because the absorption cross section for free and localized polarons is comparable, these experiments show that the free carrier generation is not field- or temperature-dependent. Hence, the Braun–Onsager mechanism for carrier generation does not dominate the device characteristics. Ezztold et al.³⁸ carried out time-resolved absorption measurements on PCDTBT/PCBM blends. Similar to the results of Mauer et al.,³⁴ they find that after an initial fast decay, the decay of induced absorption is stretched out to microseconds at a fluence of 6.1 $\mu\text{J}/\text{cm}^2$. They show that in the

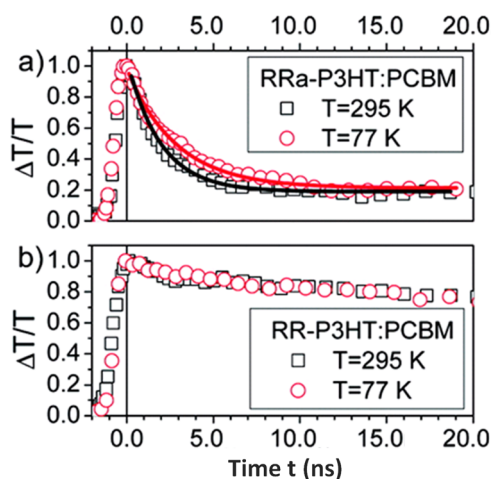


Figure 5. (a) Normalized, induced absorption spectra ($\Delta T/T$ is explained in figure caption for Figure 4b), integrated over the 750–800 nm spectral region, where both free and bound charges absorb equally (isosbestic point), allowing the integrated kinetics to represent the total number of bound plus free charges in an RRa-P3HT/PCBM blend film. The data at room temperature (~ 295 K) and at liquid N_2 temperature (77 K) are given by black squares and red circles, respectively. The excitation pulse (fluence $< 4 \mu J \cdot cm^{-2}$) was at 532 nm. (b) Data for a RR-P3HT/PCBM blend film under similar conditions. Adapted with permission from ref 34. Copyright 2010, American Chemical Society.

initial decay, about 11% of the population decays in a few nanoseconds, which they attribute to geminate recombination. The decay of the rest of the population is bimolecular and, thus, nongeminate. Hence, they argue that optical excitation gives rise spontaneously to free carriers and that the Braun–Onsager mechanism is not relevant for the PCDTBT/PCBM blend system.

An important experiment to determine if geminate recombination is dominant in P3HT/PCBM and PCDTBT/PCBM blends was carried out by Street et al.,³⁹ who measured transient photoconductivity in solar cell structures as a function of an externally applied voltage. If geminate recombination is important, the charge generated at early times (before sweep-out or recombination) should be a function of the applied voltage as exciton dissociation is a field-dependent process. However, if geminate recombination is insignificant, the generated charge will be independent of the applied voltage.

Transient photocurrent measurements allow independent measurement of the initial generated charge and the total collected charge. The transient photocurrent measurement has high sensitivity and can be carried out at low fluence, where space charge effects do not dominate the recombination. It was shown that the initial photoexcited carrier density is independent of applied bias from a -1 V reverse bias to a voltage close to the built-in voltage for both P3HT/PCBM and PCDTBT/PCBM blends, which was found to hold for the PCDTBT/PCBM blend even at 200 K. These results led to the conclusion that for these two systems, geminate recombination is not important. These results are consistent with IQE $> 60\%$ routinely measured in high-quality P3HT/PCBM solar cells and 100% in PCDTBT/PCBM solar cells. These experiments constitute the most direct evidence that geminate recombination is not important in these material systems and that optical excitation spontaneously creates free carriers. Then, the role of

the electric field is primarily one of *collection* rather than *generation*.

Qualitatively, the decay kinetics for P3HT/PCBM at zero bias found by Marsh et al.³⁵ are not very different from the other results^{34,38} reviewed here. However, the conclusions drawn from the two sets of experiments are very different, and this difference needs to be resolved. One plausible explanation for the observations of Marsh et al.³⁵ is that due to formation of trap sites (bad morphology) at the interface, a fraction of the CT states is not very delocalized, which can be because one type of carrier is trapped in shallow traps and makes the CT pair behaves as a bound one, which ultimately undergoes geminate recombination. This argument finds support in an observation by Tvingstedt et al.⁴⁰ where electroluminescence from the CT state at the P3HT/PCBM interface (as-cast film) is suppressed after thermal annealing. *These results also highlight the need for experiments to be carried out on actual device structures to be able to measure the decay both under short-circuit and open-circuit conditions, with dark and light I – V characteristics.* This is important as it is well-known that in P3HT/PCBM-based devices, depending on annealing and substrate conditions, there is a possibility of vertical segregation of P3HT.⁴¹ The short-circuit current and fill factor provide important information regarding the microstructure and the quality of the samples. In this respect, the sweep-out experiments of Street et al.³⁹ that are performed on actual device structures provide clear evidence that in good cells, geminate recombination does not dominate the recombination.

In efficient solar cell materials, the recombination is nongeminate, and the electric field does not dominate the overall charge separation process.

From all of the above discussions, we find that in efficient solar cell materials, the recombination is nongeminate, and the electric field does not dominate the overall charge separation process. In ordered RR-P3HT/PCBM and PCDTBT/PCBM blends, there is experimental evidence that the recombination is non-geminate even at 77 K.³⁴ The dominant mechanism is material-system-dependent and also depends on the microstructure; for example, in regions of high disorder (RRa-P3HT blend), the carriers recombine geminately.

The Braun–Onsager mechanism is not really applicable to efficient solar cells because there delocalization of the geminate pair reduces the binding energy and allows spontaneous charge separation without the help of an electric field.

However, not all of the O–O heterojunctions can behave this way, and there are certain junctions where an electric field helps to dissociate the CT pair efficiently. In the next paragraphs, we illustrate such O–O heterojunctions, to which the Braun–Onsager mechanism for geminate recombination is applicable.

Geminate Recombination at Organic–Organic Junctions. To illustrate the case of dominant geminate recombination, we consider junctions with 3,6-*p*-cyanophenyl-*N*-hexylcarbazole (CNHC) and *N,N'*-diphenyl-*N,N'*-(bis(3-methylphenyl))-1,1'-biphenyl-4,4' diamine (TPD). The PL of the CNHC/TPD (1:1) blend is red-shifted with respect to the films of TPD and CNHC and is identified with the formation of an exciplex (see

the SI).⁴² The photoresponse at 370 nm (peak absorbance) for ITO/CNHC(100 nm)/Al and ITO/CNHC/TPD (100 nm)/Al devices is symmetric with respect to applied bias, suggesting that the photoresponse is a bulk effect.⁴³

The photocurrent could arise from electric field quenching of the exciton by the Braun–Onsager mechanism.¹⁴

The PL quenching efficiency, η_F , can be written as

$$\eta_F = \frac{(PL_0 - PL_F)}{PL_0} \quad (6)$$

where PL_0 , PL_F are the photoluminescence intensities at electric fields 0 (V/m) and F , respectively.

If k_d is the rate constant for exciton dissociation in an external field F (eq 3), then η_F can also be written as (cf. also eq 2)

$$\eta_F = \frac{\{k_d(F)\}}{\{k_d(F) + k_r + k_{nr}\}} \quad (7)$$

where $(k_r + k_{nr})^{-1}$ is the measured fluorescence lifetime for the sample. Figure 6 is a plot of the measured η_F versus F .

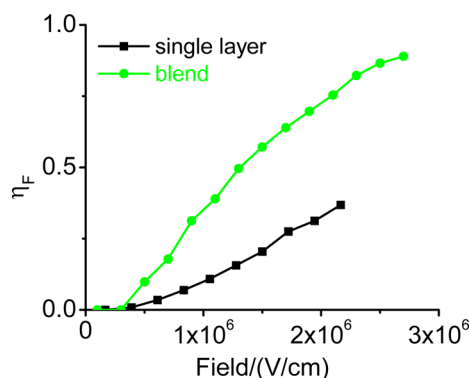


Figure 6. PL quenching efficiency versus applied electric field for a pristine film of CNHC and a blend film of TPD and CNHC. Adapted with permission from ref 43. Copyright 2012, American Chemical Society.

The solid lines show the fit to eq 3 and allow one to extract $k_d(0)$. Making reasonable assumptions for ν in eq 3 provides an estimate for the exciton binding energies,⁴³ 330 meV for CNHC and \sim 300 meV for the blend. Substituting the cyano with an acetyl group reduces the binding energy to 290 meV, while this energy strongly increases when the cyano group is replaced by pyrene. Pyrenyl carbazole is, in fact, an efficient blue emitter.⁴⁴ It can be seen that just by changing a functional group, the binding energy changes significantly.

Studies relating the photocurrent (yield of free charge carriers) and luminescence quenching have been made in many systems both in small molecules^{45–47} and polymers.⁴⁸ Gonzalez-Rabade et al.⁴⁹ studied the relation between luminescence quenching and photocurrent in blends of F8BT/PFB as the blend concentration was varied. In these systems also, they showed that nongeminate recombination is negligible and collection is close to 100%, independent of blend composition. Veldman et al.⁴⁸ show the formation of CT bands in a polyfluorene copolymer/PCBM blend. By monitoring the PL quenching of the blend, they show that the photocarrier generation can be understood using the Braun–Onsager model. Inal et al.⁵⁰ report on photocurrent and luminescence quenching in a blend of a polymer donor poly[2,5-

dimethoxy-1,4-phenylene-1,2-ethynylene-2-methoxy-5-(2-ethyl-hexyloxy)-(1,4-phenylenevinylene-1,2-ethynylene)] (M3EH-PPV) and a small-molecule acceptor 4,7-bis[2-(1-hexyl-4,5-dicyano-imidazol-2-yl)vinyl]benzo[c]-[1,2,5]-thiadiazole (HV-BT). In their experiments, they report on the field quenching of luminescence of a CT state in this system. However, the measured photocurrent did not quantitatively relate to the CT pair dissociation, and they concluded that there is a nonemissive precursor that dissociates in the electric field, which is responsible for the photocurrent. A similar conclusion was reached from experiments with blends, using as the donor the APFO-3, APFO Green-9, or HXS-1 polymers and PCBM as the acceptor molecules.⁵¹ The photocurrent was found to correlate with the PL quenching for the neat polymers, but in the case of blend films, the PL quenching of the CT state there was not in quantitative agreement. These studies point to nonluminescent CT states that act as precursors for free carrier generation. These states are expected to have a smaller binding energy and, hence, to act as efficient precursors for PC generation (see also ref 52).

Issues and Future Outlook. A basic electrostatic model predicts formation of CT states at the interface with localized carriers, and indeed, CT states prevail at most type-II organic–organic interfaces. From recent experimental results for exciton dissociation and charge separation in several organic semiconductor donor–acceptor systems, we conclude that the formation of spatially separated carriers (free carrier generation) versus bound CT pairs depends critically on ordering of both the acceptor and donor and also on the order at their interface. It appears that delocalization of carriers in the CT state plays a central role for free carrier generation. The role of excess energy in charge separation is still a matter of debate, though the majority of DA systems show that excess energy aids charge separation. It is also important to consider if it is possible to design D–A pairs that have strong delocalized CT character. In the case of transition-metal oxides, it is known that carriers move in a band or by hopping, depending on the energy gain of the system by polarization (polaron formation) or by carrier delocalization (bandwidth). Stabilization energy due to delocalization in a band is given by $W/2$, where W is the bandwidth. If the magnitude of polarization (mainly determined by the dielectric constant and the dielectric sphere that contains the carrier) is $<W/2$, the carrier becomes delocalized.⁵³ The CT state can be thought of as a pair of opposite charges. By similar logic, whether a CT state becomes localized or delocalized depends on the polarization energy and the bandwidth of the charge pair, where the CT polarization energy \approx hole polarization energy + electron polarization energy. For rigid molecules (such as pentacene, fullerenes, phthalocyanines, discotic molecules), the hole polaron binding energy is found to be lower (by approximately at least a factor of 2) than that for molecules with many internal degrees of freedom.⁵⁴ For the polarization energy of electrons in organic films, for which no experimental data are available, DFT computations show a similar trend (i.e., rigid molecules have low polarization energy).⁵⁵ If indeed low polaron binding energy is essential for delocalization, then the rigid molecules are more likely to form a delocalized CT than their nonrigid counterparts. At the same time, due to better overlap of electronic wave functions, the bandwidth may also increase. Rigid molecules also convey other benefits such as smaller reorganization energies, which translate into higher carrier mobility. All of the D–A pairs discussed in this Perspective give

very high (sometimes $\sim 100\%$) photon to current conversion efficiency and have fullerene derivatives as acceptors. In these types of acceptor materials, the molecule is rigid, and electron transport (or delocalization) can happen in three dimensions. This could be one of the reasons for the dominance of fullerene derivatives as electron acceptors.

The role of an electric field seems to be system-specific. In some cases, it only serves to sweep out the charges from the interfaces to the electrodes/contacts, while in other cases, it also helps to increase the efficiency of exciton splitting.

We found that the role of morphology, long-range order, and delocalization are all intimately connected and are system-dependent. In the area of material design and preparation, the focus should be on preparing materials with as much long-range order as possible and with extended conjugation while preserving a large interface area (for efficient charge separation). In addition to the high carrier mobility, the quality of the donor/acceptor interface also plays an important role. Development of interfaces with fewer defects is a necessary requirement. Generally, mutually compatible (mixable) materials provide interfaces with fewer defects. However, a balance between defect-free interfaces and large interfacial area is required for these types of solar cells.

In this context, it does appear to be relevant to recall the history of a-Si/H solar cells. The early a-Si/H literature contained many experimental results, the conclusions of which were in conflict with each other. It was later recognized that this was due to use of materials of widely varying electronic quality. Many conflicting results were resolved once experiments were conducted on what *really* were the same materials (in terms of purity, structure), which allowed the samples to be well-characterized.

We can learn from a-Si/H, where many conflicting results were resolved once experiments were conducted on what really were the same materials.

Furthermore, use of device structures played an important role in the characterization of samples and arriving at relevant conclusions. Therefore, we posit that, *in the context of organic solar cells, it is useful if, wherever possible, experiments are done with actual device structures because of our limitation in reproducing identical morphologies and defect profiles in different samples.* As an example, P3HT/PCBM blends are heterogeneous blends. There is vertical segregation depending on heat treatment, aggregate formation depending on solvents, and doping that depends on the atmosphere to which the sample is/was exposed. All of these effects will manifest themselves readily in devices, remain hidden in the absence of good characterization, and sometimes lead to conflicting results in different measurements.

■ ASSOCIATED CONTENT

■ Supporting Information

A brief summary of time-resolved experiments, Langevin recombination, and some useful definitions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(52) In passing, we note that while the existence of CT states at the type-II interface is beyond doubt, their role in determining the open-circuit voltage (V_{oc}) is not agreed upon, particularly if the CT states give rise to free carriers. After creation of free carriers, these states are no longer relevant, and the cell parameters are determined by other factors. If the photon energy is lost via the CT state (due to geminate recombination), then, yes, the CT state adds another loss pathway, and V_{oc} of the cell will be lower than expected. Strongly bound CT states always add a loss mechanism as the photon energy is lost via emission or heat.

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