



Charge carrier recombination in organic solar cells



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ABSTRACT

Solution deposited bulk heterojunction organic solar cells are viewed as one of the most promising alternative energy sources because of their ease of processing and their potential to be produced using large scale techniques such as roll-to-roll, newspaper style, coating. Since organic materials have a relatively low dielectric constant the dissociation of an excited electron–hole pair into free collectable charge carriers is inefficient in many cases. Often the excited electron–hole pairs recombine back to the ground state in a process known as geminate recombination before they ever fully dissociate into free charge carriers. Even after dissociation, free holes and electrons can encounter each other once more and subsequently recombine back to the ground state in a process known as nongeminate recombination. In both cases the incident photon energy is lost and fewer carriers are collected at the electrodes. Hence, charge carrier recombination is one of the key loss mechanisms in organic solar cells. In this review the latest on geminate and nongeminate recombination is discussed.

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1. Introduction

Amid looming concerns over increasing carbon emissions and global climate change, organic solar cells have garnered considerable attention because of their potential to serve as an economically viable, low-carbon source of electricity. After humble beginnings [1], organic solar cells have advanced exponentially with recent reports of power conversion efficiencies (PCE) up to 12% [2,3] with a high of 9% in peer-reviewed literature [4]. This remarkable progress means the PCE of organic photovoltaics (OPVs) are now comparable to inorganic PV technologies such as amorphous silicon [5]. In order to maintain momentum and enable further increases in efficiency [6–11], it is vital that the factors governing the performance of OPV devices are identified and understood.

Although inorganic and organic PV devices both convert photons to electrical power, the underlying physics and device architectures in organic photovoltaics differ significantly from inorganic photovoltaics. Due to the low dielectric constant of organic materials (approximately 2–4) absorbed photons create coulombically bound electron–hole pairs known as excitons that require an additional driving force to separate into free charges. Additionally, while in inorganic semiconductors charges move via band transport, because of the disorder and weak intermolecular forces associated with organic semiconductors their charge transport mechanism is based on localized charge carriers that hop from state to state [12]. Initial organic solar cell development consisted of bilayer device architectures of an electron donating (donor) and an electron accepting (acceptor) material similar to inorganic p–n junctions [13]. The use of donor and acceptor materials facilitates the splitting of excitons by providing an energetic offset between the materials' lowest unoccupied molecular orbitals (LUMO). Due to the limited exciton diffusion length in organic materials (~10 nm) [14], the transition was made to bulk heterojunction (BHJ) solar cells. In a BHJ architecture the photoactive layer consists of a complex network of interpenetrating donor and acceptor phases with average domain sizes on the order of tens of nanometers. A BHJ morphology thereby greatly increases the interfacial area between donor and acceptor, thus increasing the probability an exciton encounters a donor–acceptor interface and separates into free charge carriers before relaxing to the ground state. The most widely studied BHJ systems are blends of conjugated electron donating polymers with electron accepting fullerene derivatives [4,15,16]. However, BHJs consisting of two small molecules deposited either by solution [17–19] or vacuum sublimation [2,20] have also achieved impressive PCEs.

A simplified overview of the photovoltaic process in OPVs is presented in Fig. 1 (for the case of absorption in the donor phase). First, a photon is absorbed creating an exciton. The exciton then transports to an interface with an acceptor. Once at the donor/acceptor (D/A) interface, the electron and hole form a charge transfer (CT) state with the electron on the acceptor and the hole on the donor [21–23]. If the binding energy of the CT state can be overcome the electron will be transferred to the LUMO of the acceptor while the hole is transferred back to the highest occupied molecular orbital (HOMO) of the donor. Due to the internal electric field created by the asymmetry of the electrode work functions, the hole will then drift through the donor domains toward the anode and the electron through the acceptor domains toward the cathode. Ultimately, these photogenerated charges are collected at their respective electrodes thereby creating a measurable photocurrent.

Ideally, every incident photon would be successfully converted into an electron and hole that are collected at the electrodes. However, in reality each step of the above photovoltaic process from absorption to collection is wrought with potential loss mechanisms that limit the overall PCE of OPV devices. Once a photon is absorbed, the exciton only has a few nanoseconds to reach a donor–acceptor interface before it relaxes to the ground state (see a. in Fig. 1). If the domain sizes are larger than the exciton diffusion length the electron–hole pair is more likely to recombine than separate. Those excitons that do make it to a D/A interface to form a CT state still have some probability of recombining rather than dissociating into free charge carriers (see Fig. 1b). These recombination processes involving an electron–hole pair that originated from a single photon event are referred to as *geminate recombination*. The term *geminate* comes from the Latin word *geminus* meaning twins—in this context the electron–hole pair are twins born from the absorption of a single photon. Exactly what influences whether a geminate pair will recombine or dissociate into free carriers remains an area of active research. Much initial research focused on the importance of domain size and energetic offsets between the donor and acceptor [16,24,25]. However recent work suggests that other factors such as the delocalization of CT states, molecular reorganization energies, excess energy from above-gap photons, energy of triplet states, phase purity and the internal electric field may also play a significant role in the competition between geminate recombination and the generation of free charge carriers.

After geminate pairs are successfully dissociated into free carriers, the electrons and holes have to make it to their respective electrodes without recombining with another oppositely charged free carrier. This recombination of free electron and holes is referred to as *nongeminate recombination*. The key distinction from geminate recombination is

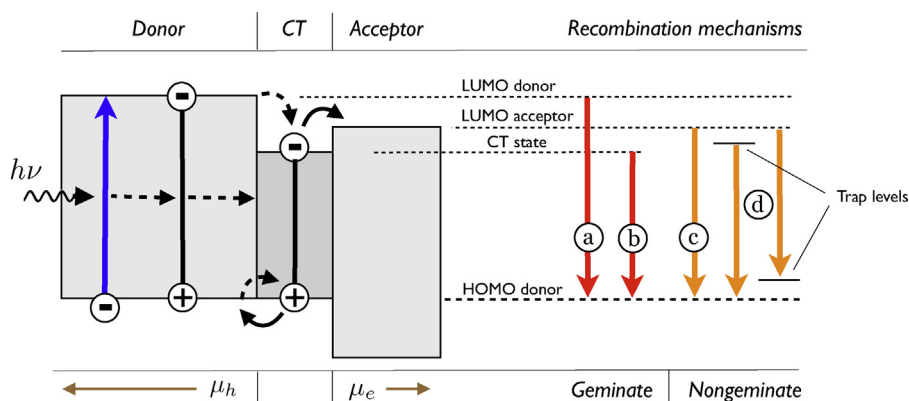


Fig. 1. Left: From left to right. Incoming light is absorbed in the donor material (blue arrow); a bound exciton is formed. The exciton diffuses toward the donor–acceptor interface. The exciton transfers onto the interface state i.e. CT state (dashed arrows), after which the exciton dissociates (solid arrows) and the free hole and electron drift through the donor and acceptor phase respectively, to the extracting contacts (brown arrows). Right: An overview of the four most encountered recombination mechanisms. The geminate mechanisms: (a) exciton decay after excitation, (b) recombination through the CT state, and the nongeminate mechanisms: (c) recombination of free holes and electrons, (d) recombination of free carrier with carrier trapped on sites within the band gap. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

that the hole and electron in nongeminate recombination do not originate from the same photon. As shown in Fig. 1, nongeminate recombination includes the recombination of a free electron and a free hole known as bimolecular recombination (Fig. 1b) and trap-assisted recombination (Fig. 1c) which occurs when a trapped electron (hole) recombines with a free hole (electron). It has been shown that a variety of factors can influence nongeminate recombination in OPV devices including charge carrier mobilities, phase separation, energetic disorder, chemical impurities and active layer thickness. Several noteworthy trends have emerged from the investigation of nongeminate recombination. First and foremost, it is evident that bimolecular recombination is the primary loss mechanism in most efficient OPV systems. Furthermore this recombination can be significantly reduced compared to the Langevin description of bimolecular recombination in disordered materials due to the spatial dependence of carrier density distributions, phase separation, energetic disorder and the re-release of free carriers that form a CT state before recombining. Just as noteworthy is the suggestion that energetic traps may play a significant role in shaping the kinetics of nongeminate recombination not only in systems with known chemical impurities but also in the more efficient OPV systems where bimolecular recombination dominates.

In this review article on recombination mechanisms in organic solar cells we will present the theory and experimental evidence for the various recombination processes described above. The article naturally divides into two parts: (1) geminate recombination and (2) nongeminate recombination. As these topics have been reviewed in the past [26–32], a particular emphasis will be placed on more recent advances and emerging trends. Special attention will also be given to highlighting experimental techniques and relating recombination mechanisms to the basic solar cell metrics (short circuit current (J_{sc}), fill factor (FF) and open circuit voltage (V_{oc})). Finally, we will conclude with a summary of the current understanding of recombination

in organic solar cells while highlighting areas that are still not well understood and that therefore should serve as the focus of future investigations.

2. Geminate recombination

As discussed in the introduction, there exist two distinct processes that must occur in order for a photovoltaic device to work: (1) photogeneration of free charge carriers and (2) collection of photogenerated charge carriers. In OPVs, this first step, the process of going from absorbed photon to free charge carriers, is complicated by the relatively strong Coulomb force between the photo-excited geminate electron–hole pair. In order for a geminate pair to separate into free charges, the Coulomb binding energy must be overcome; otherwise the pair will recombine in a process commonly referred to as geminate recombination. For simplicity, in this article we use the term free charge carriers to describe electron and holes that are not Coulombically bound however, it should be noted that the often used term polaron, which is a charge plus the accompanying lattice distortion, is technically more correct in the context of organic semiconductors.

It is known that some OPV systems convert absorbed photons to free electrons with near 100% efficiency, however, many more systems evidently do not [19,26,27,29]. In such systems, geminate recombination losses can significantly limit the photocurrent (J_{sc}). It has also been shown that the magnitude of geminate recombination can increase with an applied bias thereby also limiting the FF [33–35]. Thus, overcoming geminate recombination losses is essential in order to maximize PCE. In the subsequent sections we will present the theory and terminology associated with geminate recombination and then discuss the implications of recent studies into the basic mechanisms of charge generation.

2.1. Geminate recombination theory and terminology

Geminate recombination occurs when a hole and electron that originate from the same photon recombine before separating into free charges. By definition, this includes the loss of excitons that relax to the ground state before they can diffuse to an interface as well as geminate pairs that recombine at a D/A interface. It is worth noting though, that many reports in the literature limit the use of geminate recombination to describe only the recombination of geminate pairs at a D/A interface. Typically, this interfacial geminate recombination occurs after formation of a CT state where the electron resides in the acceptor and the hole in the donor. In this review, we use the term CT state to describe geminate pairs at the D/A interface however there are multiple synonyms in the literature including exciplex, bound polaron pair, CT complex and CT exciton [36]. Regardless of what processes are involved in separating CT states, geminate recombination is driven by the Coulomb attraction between the geminate electron–hole pair.

Geminate recombination is considered a single body, monomolecular process. The number of geminate pairs that are able to recombine geminately scales linearly with the number of absorbed photons. However, it is important to note that at light intensities comparable to one sun the probability of any given geminate pair recombining is independent of the total density of geminate pairs. The consequence of this is that the *fraction* of geminate pairs lost to geminate recombination is the same at low light intensities as it is at higher light intensities. Thus, the photocurrent of a system limited only by geminate recombination would scale linearly with light intensity. At light intensities exceeding several suns, other recombination processes such as exciton–exciton or exciton–charge annihilation may become significant [37].

2.2. Exciton transport to donor/acceptor interface

Once a singlet exciton is created it must migrate to a D/A interface in order to dissociate into free charge carriers. Until recently it was generally thought that this transport occurs entirely by diffusion. Thus donor and acceptor domain sizes have long been targeted to be similar to the exciton diffusion length—typically 3–30 nm for OPV materials [14,38,39]. However, ultrafast transient absorption studies suggest that a majority of free carriers in efficient OPV systems are photogenerated within 100 fs, far too fast a process to involve exciton diffusion [26,40–45]. Kaake et al. observed photogeneration on sub 100 fs times scales followed by additional generation on picoseconds timescales thought to be from excitons diffusing to charge-separating heterojunctions [46]. The authors posited that the ultrafast transport mechanism is made possible by delocalized excited states consistent with the previous observation of crystalline domains in the same system [47]. Though the precise mechanism of ultrafast migration to the D/A interface remains unclear, it is worth noting that it has been shown that this ultrafast process is also influenced by domain size in a manner similar to that expected for an exciton diffusion process [40]. This may help explain

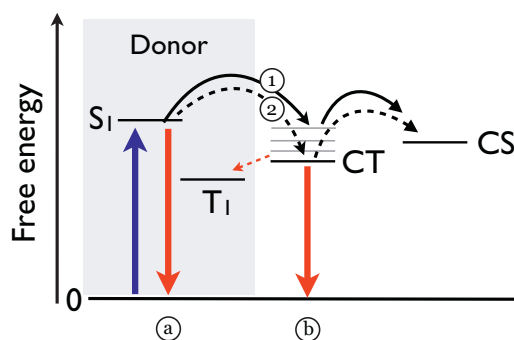


Fig. 2. Jablonski diagram showing the excitation of the donor singlet state and the recombination into the triplet state from the CT state (dashed red arrow). The solid black arrows labeled (1) represents geminate pairs that transfer into higher energy, hot CT states (gray lines) before almost instantaneous separation into the charge-separated state (CS). The black dashed arrows labeled (2) indicate the transfer of electron and hole from the donor singlet state to the CT state with the possibility to relax down to the CT ground state (solid line) where they may need additional energy to dissociate into the charge-separated state (CS). The red arrow labeled (a) indicates decay of an exciton to the ground state before it can make it to the D/A interface while the red arrow labeled (b) represents geminate recombination at the D/A through the CT state. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the strong correlation between domain size and generation efficiency seen in many systems [40,48–50].

Experimentally, the efficiency of exciton transport to the D/A interface is typically gauged by comparing the photoluminescence (PL) of the blend film to the PL of the neat material. Excitons that are not quenched by reaching the D/A interface have some probability of recombining radiatively just as they would in the neat film. Therefore, PL spectrally similar to that of the neat material detected in the blend film is suggestive of excitons that originate in domains larger than the exciton diffusion length. Optimized BHJ OPV systems have been shown to exhibit PL quenching exceeding 99% indicating that nearly every exciton reaches an interface [44]. It is worth noting that this comparison assumes 100% quenching efficiency of the acceptor, which at least has been shown to be the case for fullerene derivative acceptors such as phenyl-C₆₁-butyric acid methyl ester (PCBM) [44].

2.3. Charge separation vs. geminate recombination at the donor–acceptor interface

When an electron–hole pair reaches the D/A interface, charge transfer is initiated by the energetic offset between donor and acceptor. However, the electron–hole pair remains coulombically bound across the D/A interface due to the poorly screened Coulomb potential, forming what is known as a charge transfer state [31,32,36,51–53]. The binding energy of this CT state has been estimated to be a few hundred millielectronvolts [32,54,55]—an order of magnitude higher than the thermal energy at room temperature. As shown in Fig. 2, once electron–hole pairs form a CT state, dissociation into separated charges (CS) is in competition with geminate recombination to the ground state and transfer to a triplet state. If the triplet state is

sufficiently lower in energy than the CT state (<0.1 eV) it can serve as a loss mechanism by providing an efficient pathway to deactivation of CT states [32,56,57]. In the case that transfer to the triplet state is not energetically favorable, geminate recombination directly to the ground state will be the primary loss mechanism for CT states. This recombination can be radiative as evidenced by PL emission that is characteristically red-shifted compared to the pure material film emission [51,58]. Measuring non-radiative geminate recombination from CT states is experimentally challenging as geminate recombination typically occurs on sub-nanosecond timescales. However, geminate losses in a variety of OPV systems have been observed optically and electrically using transient absorption techniques [31,57,59–66] and time delayed collection field experiments (TDCF) [33,67–69]. Multiple reports have also inferred geminate losses based on analysis of device photocurrents and quantum efficiencies [70–73].

There has been much discussion in the literature about what determines whether electron–hole pairs at D/A interfaces will dissociate into free charges or recombine. In principle, electron–hole pairs will only split into free charges if the energy gain in doing so is larger than the Coulombic binding energy. Electron transfer from donor to acceptor and/or hole transfer from acceptor to donor produces an electron or hole, respectively, at a lower potential, thus providing the driving force for exciton dissociation. A distinct trend of increasing D/A energetic offsets (both $\text{LUMO}_D\text{--LUMO}_A$ and $\text{HOMO}_D\text{--HOMO}_A$) corresponding with greater charge separation efficiency has been observed in a variety of OPV material systems [57,74,75]. Several other studies in the literature often cite a 0.3 eV offset between donor and acceptor LUMO levels as a universal prerequisite for efficient exciton separation. However the theoretical basis for this standard is limited [31] and numerous exceptions have been observed [58,76,77]. It is also worth noting that LUMO energy levels measured of single materials by solution cyclic voltametry or optical transitions can only be taken as a rough estimate of the energetics that influence the charge dissociation process in material blends [27,32]. In addition to energy level offsets, other studies have proposed that doping [78], charged defects [79], mixed phases [80] and entropy gains from increased electron and hole separation [31,81] may contribute to the free energy gradient and thereby help charge separation.

The role of electronic delocalization in the charge separation process has also been explored. There is compelling evidence that short lived, (<1 ps) hot, and delocalized CT band states can enable geminate pairs to overcome their Coulombic attraction by increasing the effective electron–hole pair separation [31,32,57,60,64,65,82–84]. For instance, using an electro-optical pump-push experiment, Bakulin et al. found that after exciting a variety of OPV systems either in the visible range or directly into sub-bandgap CT states, a subsequent infrared (IR) push pulse yielded an increase in photogenerated charges [60]. These results are shown in Fig. 3 where $\delta\text{PC}/\text{PC}$ is the percent change in photocurrent after the IR push. The effect of the IR push on photogeneration roughly scaled with the amount of bound charges in localized CT states for each

system. The authors concluded the IR push pulse gives geminate pairs that have relaxed to bound CT states a second chance to dissociate by pushing them back to higher energy states similar to the early time hot states formed directly after the separation of singlet excitons. Further evidence of hot CT states came from Jailaubekov et al. [83]. In this work, transient two-photon photoemission spectroscopy was used to directly measure the photoemission of electrons from hot charge transfer states in films with copper phthalocyanine (CuPc) and C_{60} . They found electrons from hot CT states to be about 0.3 eV higher in energy than electrons from relaxed CT states and conducted simulations to show the interfacial charge distribution for hot CT states is more favorable for charge separation. Other recent studies have observed that in some low bandgap polymer/fullerene systems, the excess energy from absorbing above bandgap photons leads to faster and more efficient generation of free charge carriers consistent with a hot CT state framework [82,84]. In a separate study Bakulin et al. [74] noted that the probability of populating hot CT states favorable for charge separation increases with the energetic offsets between $\text{LUMO}_D\text{--LUMO}_A$ and $\text{HOMO}_D\text{--HOMO}_A$. This may explain why the generation efficiency in systems with large energetic offsets are insensitive to temperature [85,86] and excitation wavelength [87,88] while some systems with small offsets (<0.1 eV) are sensitive [82,84].

The evidence supporting the importance of hot CT states is not, however, ubiquitous. A similar generation efficiency for direct excitation of CT states and above band gap excitations has been reported in several polymer/fullerene systems, implying that at least for the systems considered hot CT states are not essential to the generation process [58,89,90]. Jailaubekov et al. speculated that in these particular systems it may be that the presence of favorable gradients in the interfacial energy landscape that reduces the energy barrier for charge separation to less than the thermal energy. In support of this it was noted that at lower temperatures it's expected that the excess energy of hot CT states may be more important as was observed [89]. Simulations have indicated the difference in ionization potentials and polarizations at the D/A interface compared to the bulk is likely to mitigate the importance of hot CT states in the generation process [91]. The notion that the influence of excess energy would be system dependent is clearly demonstrated in Fig. 3. Depending on the system pushing relaxed CT states back into higher energy hot CT states can have almost no effect or it can almost double the observed photocurrent. In the case of the highly efficient poly[N-9'-hepta-decanyl-2,7-carbazole-*alt*-5,5'-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT):PCBM system [87] it was observed to have a slightly negative influence on the photocurrent which was attributed to increased fast nongeminate recombination. Thus, it stands to reason that in the highly efficient systems like PCDTBT:PCBM the relaxed CT state is sufficiently delocalized negating the need for excess energy to facilitate efficient charge separation. Nonetheless, further investigation is needed to understand why some systems exhibit efficient charge generation from relaxed CT states [58,89,90] while in others it appears that charges in relaxed CT states are most likely to recombine [60].

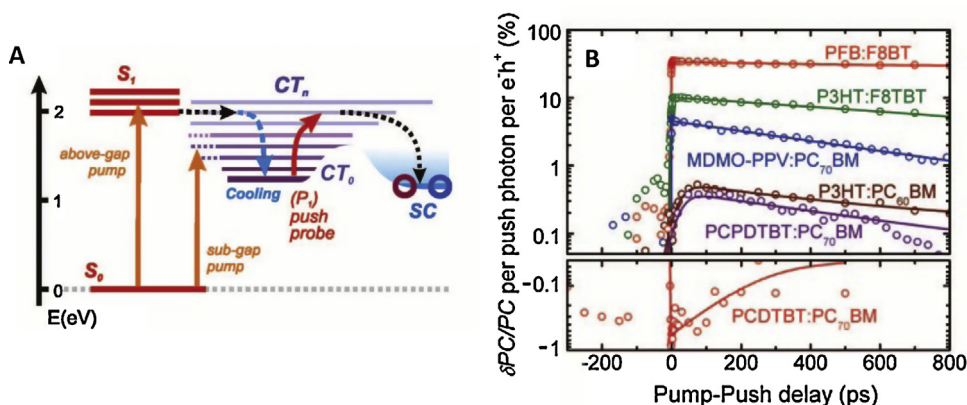


Fig. 3. (A) Free energy state diagram for an OPV system showing the Singlet states (S_1), relaxed CT state (CT_0), higher energy CT band states (CT_n) and separated-charge states (SC). The increasing width of CT_n states is indicative of increasing delocalization. Solid arrows show optical transitions and dashed arrows indicate energy and charge transfer pathways involved in photoconversion. The red arrow represents the IR push pulse in the experiments conducted by Bakulin et al. (B) The results of pump-IR push photocurrent experiments on a set of OPV systems under above-gap excitation. [60], Copyright 2012. Reproduced with permission from the American Association for the Advancement of Science. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Arguments about hot vs. relaxed CT states aside, further evidence for the role of delocalization in the generation process comes from studies that have looked at the influence of aggregated and crystalline domains on the charge separation efficiency. The prevailing theme in these studies is that aggregated and crystalline domains reduce geminate recombination in favor of increased charge separation at the D/A interface [45,48,66,92–96]. Given the established relation between aggregated or crystalline domains and electronic delocalization [60], this trend strongly supports the notion that delocalized states enhance the charge separation efficiency.

Altogether the breadth of work from the literature suggests that the accessibility of delocalized CT states is a function of not only molecular properties (i.e. conjugation length [97], reorganization energy [60,82,83], LUMO degeneracy [92,93], etc.) but also film properties (alignment of donor molecular orbital relative to the acceptor [32,98], degree of crystallinity, etc.). Nonetheless, further study of basic structure-functional relationships is needed in order to better define the general guidelines for the development of new materials and processing techniques that can take advantage of delocalized CT states to allow for near unity charge separation efficiency.

2.4. Electric field dependent geminate recombination

It has been observed that the charge separation efficiency is electric field dependent in some, but not all, OPV systems [34,35,69,99–101]. Though no universal standards have emerged, it does seem that the most efficient OPV systems with FF's exceeding 0.65 generally do not exhibit field dependent geminate recombination losses [26,67,69,102,103]. Interestingly, it has also been observed that the field dependence of generation can be phase dependent—particularly in systems with large PCBM domains [101,104].

In systems known to have field dependent geminate losses, the internal electric field in the device helps dissociate geminate charge pairs into free charges. Thus, the

rate of dissociation and with this the magnitude of geminate recombination changes with applied bias—a reverse bias increases the magnitude of the internal field, thereby increasing the charge separation efficiency, while a forward bias weakens the internal field, thereby increasing the probability of geminate recombination. Due in part to the complexity of differentiating the voltage dependence of dissociation from the voltage dependence of extraction and nongeminate recombination, the issue of field dependent geminate recombination has been the subject of much debate in the literature. Further complicating the matter is the fact that the strength of the field dependence of geminate recombination varies between different materials systems and even processing conditions for the same system [33,99,101]. This phenomenon was well illustrated by the TDCF experiments conducted on a low band gap polymer:fullerene system [33]. In TDCF, a bias is applied to a solar cell device which is then pulsed with a laser. After a delay time as short as 10 ns, a strong collection bias is applied to sweep out all photogenerated charge carriers. Using this technique, the voltage dependence of geminate recombination can be measured directly by observing the total photogenerated charges collected (Q_{tot}) as a function of the initial applied bias. As shown in Fig. 4, Albrecht et al. found that the Q_{tot} from solar cell devices pulsed with a laser depended strongly on the voltage applied within the first ten nanoseconds after absorption. Processing devices with diiodooctane (DIO) solvent additive slightly mitigated this field dependence. However, it is evident that the field dependent geminate recombination still heavily influenced the steady-state current voltage characteristics even in the device with DIO as shown in Fig. 4.

The development of a theory that accurately describes the precise relation between charge separation efficiency and electric field remains an area of active research. Many studies have used the Onsager–Braun formalism [105,106] to model the field dependence in OPVs [27,72,96,107], however, it has since been shown that many systems do not exhibit the electric field or temperature dependencies predicted by the Onsager–Braun model [26,67,102].

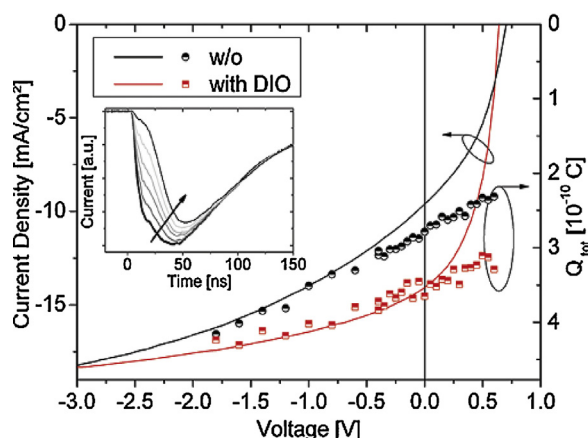


Fig. 4. Current-voltage response of a polymer: fullerene device processed with (red line) and without DIO (black line) plotted along the Q_{tot} measured as a function of voltage in the same devices (red and black symbols, right y-axis) using TDCF. The inset presents the TDCF measured photocurrent transients for an exemplary device with the arrow pointing in the direction of increasing forward bias. [33], Copyright 2012. Reproduced with permission from the American Chemical Soc. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

According to Monte Carlo simulations by Deibel et al., varying degrees of delocalization along conjugated segments could account for differences in field dependent geminate recombination [97]. Other models and experimental evidence further indicate that there is a connection between crystalline phases that form extended, loosely bound CT states and the electric field dependence of charge separation [33,80,99]. Additionally, there is evidence that the molecular geometry at the D/A interface can significantly affect the binding energy of the CT state and thus may also influence the electric field dependence and hence the FF and/or magnitude of the device J_{sc} [91,98,108,109]. Probing the molecular orientation at the D/A interface is experimentally challenging. Nonetheless recent work on model bilayer systems [98,108] and the development of new characterization techniques [110,111] provide a viable path for future experimental investigation and understanding of the role donor–acceptor molecular interfacial geometry plays in the charge generation process.

3. Nongeminate recombination

Once a photogenerated charge carrier successfully separates from its geminate counter charge, the internal electric field in the device drives it toward the electrodes. Holes drift to the anode while electrons drift to the cathode. The maximum photocurrent is achieved when all of these charges are collected at the electrodes. However, even in the best OPV devices, as a forward bias is applied the driving force for charge extraction decreases and so too does the charge collection efficiency [26,27]. How sensitive the charge collection efficiency in a given system is to a change in bias is reflected in the fill factor. A high FF (>0.65) indicates that a forward bias has only a small effect on the collection efficiency up until the maximum power point. Regardless of how high the FF is, when the forward bias is

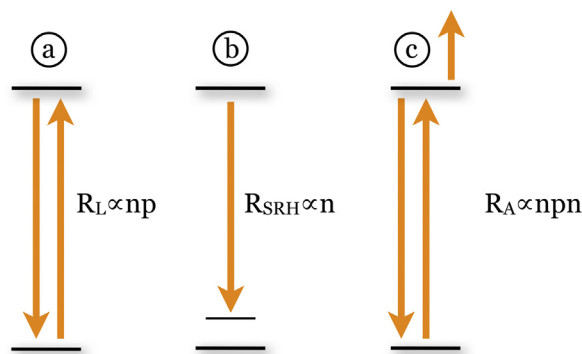


Fig. 5. This figure depicts the nongeminate recombination mechanisms. (a) Represents bimolecular Langevin recombination where the rate is dependent on both hole and electron mobilities and densities. (b) Represents trap-assisted Shockley–Read–Hall recombination where the rate depends on the electron (hole) mobility and density combined with the amount of hole (electron) traps. (c) Depicts Auger recombination wherein the recombination of an electron–hole pair excites an electron from the HOMO back into the LUMO and the rate therefore has a third order dependence on carrier density.

equal to the open circuit voltage, all photogenerated free charge carriers recombine and the net current flowing out of the device is zero. Thus, unlike geminate recombination losses which can be completely overcome, *all* OPV devices are subject to the recombination of free charges—at least at low internal fields (i.e. close to V_{oc}) [26,27]. This recombination is known as *nongeminate recombination*. As we will discuss in the subsequent sections, depending on the system and incident light intensity, nongeminate recombination may limit the J_{sc} , FF and V_{oc} .

3.1. Mechanisms of nongeminate recombination

The term nongeminate recombination encompasses the recombination of any free charge carriers that do not originate from absorption of a single photon. In addition to photogenerated charge carriers, nongeminate recombination may also involve injected charge carriers. The recombination originating from these nongeminate charge carriers can be observed as three fundamentally different mechanisms: trap-assisted (monomolecular, Fig. 5a), bimolecular (Fig. 5a), and auger (trimolecular, Fig. 5c). As we will discuss below these three processes exhibit first, second and third order dependence on charge carrier density respectively.

3.1.1. Bimolecular recombination

The most commonly observed [26] nongeminate recombination in OPV devices is that of the bimolecular mechanism: the recombination of a free electron with a free hole as depicted in Fig. 5a. In a disordered semiconductor with localized charge carriers, bimolecular recombination is limited by the rate at which oppositely charged carriers find one another. The faster charge carriers move, the faster they will find each other; consequently, the rate of bimolecular recombination in OPV is proportional to the charge carrier mobilities. This is

described by the Langevin expression [112] following the relation,

$$R_L = \frac{q}{\varepsilon}(\mu_n + \mu_p)(np - n_i^2) \quad (1)$$

where q is the elementary charge, ε the dielectric constant, μ_n the mobility of the electrons through the LUMO of the acceptor, μ_p the mobility of the holes through the HOMO of the donor, n and p represent the electron and hole charge density respectively and n_i is the intrinsic carrier concentration. This relation describes recombination of two mobile opposing charge carriers attracted to each other in their mutual Coulomb field. Such a behavior is characteristic for materials in which the mean free path of the charge carriers is smaller than the Coulomb capture radius r_c given by

$$r_c = \frac{q^2}{4\pi\varepsilon_0\varepsilon_r k_B T} \quad (2)$$

where T is temperature, at which the Coulomb binding energy between an electron and hole equals the thermal energy $k_B T$. The charge transport in organic semiconductors is of a hopping nature, with a typical hopping distance of 1–2 nm, whereas r_c amounts to about 18.5 nm at $T=300$ K ($\varepsilon_r=3$). Therefore, the manifestation of Langevin recombination in organic semiconductors is expected [113] and observed [114]. Though the rate is often reduced relative to Eq. (1) (see Section 3.1.1.2), Langevin-type recombination has been observed in a large variety of OPV systems [115–119].

Obviously the observation of nongeminate recombination is not restricted to organic solar cells alone; the principle mechanism of organic light emitting diodes is of the nongeminate Langevin-type [120–122]. Being originally derived in 1903 from recombination processes of ions in a gas, the applicability of the Langevin expression in organic semiconductors in general has been an evolving process. Where the recombination in gases is isotropic, the transport, and thus recombination, in organic materials is shown to be of a percolative nature [123] leading to a filamentary transport structure with differences in local current densities that can vary over many orders of magnitude [124–128]. Inconsistencies in the active layer that arise from common film preparation methods such as spin-coating [129] may also contribute to predicted perturbations of Langevin type recombination [130,131].

In particular, an accurate description of the mobility in the Langevin expression for organic solar cells has taken time to develop. In the early years of organic solar cells, mobilities were considered as constant with the argumentation that a solar cell will operate at very low voltages, below V_{oc} , so the possible field dependence of the mobility will not play an important role [72,132]. Later, it was shown that multiple processes (photocurrent, geminate recombination, etc.) exhibit a field dependence thus motivating the inclusion of field dependent mobilities in the Langevin equation [33]. The fact that the active layer in OPV devices is a blend of hole and electron transporting materials further complicates the issue. Since carrier transport has a percolative behavior

the individual carrier transport mechanisms are heavily influenced by the ratio and morphology in the blend [49,133]. For example, pristine poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) comprises a hole mobility of $5 \times 10^{-11} \text{ m}^2/\text{Vs}$. In an optimized blend with 80 wt% PCBM the hole mobility increases 2 orders of magnitude up to $1.4 \times 10^{-8} \text{ m}^2/\text{Vs}$ [134]. Pristine poly(3-hexylthiophene) (P3HT) has a hole mobility of $1.4 \times 10^{-8} \text{ m}^2/\text{Vs}$ [134] and is hardly affected by thermal annealing. In an as cast blend with PCBM the P3HT hole mobility drops almost four orders of magnitude and the PCBM electron mobility drops by 1 order of magnitude with respect to its pristine value of $2 \times 10^{-7} \text{ m}^2/\text{Vs}$. After annealing at 120 °C, favorable phase separation leads back to pristine values for P3HT hole and PCBM electron mobilities [135]. Thus in terms of the Langevin description, it is evident that blend film mobilities are the relevant measure as the pristine film mobility is not necessarily representative of transport in the solar cell device.

3.1.1.1. Implications for mobility. Surveying the Langevin expression one may expect that higher mobility materials would yield solar cell devices with higher recombination rates. However, simulations have shown that the net bimolecular recombination yield in OPV devices generally decreases with increasing mobility [136,137]. This is because increased mobility also reduces the charge carrier density as a result of improved charge extraction. Thus, in the context of organic solar cells, increased mobility is not expected to lead to a net increase in nongeminate recombination. In contrast, if the charge carrier mobility is too low than the inability to efficiently sweep out photogenerated charges will lead to more nongeminate recombination because the charge carrier density within the device will be higher. As shown in Fig. 6, simulations by Wagenpfahl et al. suggest that for an active layer thickness of 100 nm, the FF and J_{sc} will drop off sharply for charge carrier mobilities less than $10^{-8} \text{ V/m}^2 \text{ s}$ [136,137]. Empirical evidence across a wide range of systems presents a similar trend between mobility and FF [137–141] indicating that $10^{-8} \text{ V/m}^2 \text{ s}$ may serve as a rule of thumb for the minimum mobility required for efficient OPV performance. Note that this applies to both hole and electron mobilities. As we will discuss in Section 3.2, imbalanced mobilities can lead to a buildup of space charge that inhibits charge collection.

3.1.1.2. Reduced Langevin recombination. While the presence of Langevin recombination has been satisfyingly confirmed in many organic semiconductors, the strength of this mechanism in OPV devices is often found to be less than that predicted by the Langevin expression [27,28,33,99,102,116,139,142–146] and not higher. This has lead to the addition of another term, ζ , commonly referred to as the Langevin-reduction factor in expressions for the net bimolecular recombination rate, R_{BI} . Neglecting the relatively small n_i and assuming the density of holes and electrons is the same ($n=p$),

$$R_{BI} = \gamma_{BMR} n^2 \quad (3)$$

where γ_{BMR} is bimolecular recombination coefficient defined as $\gamma_{BMR} = \zeta \frac{1}{\varepsilon}(\mu_n + \mu_p)$ Most polymer:fullerene

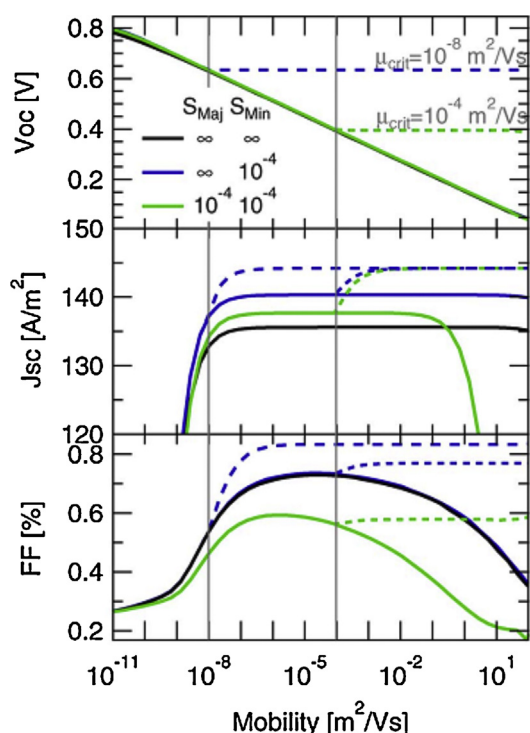


Fig. 6. Calculated dependence of V_{oc} , J_{sc} , and FF on charge carrier mobility assuming reduced Langevin recombination ($\zeta = 0.1$). Solid black, blue, and green lines represent different surface recombination velocity combinations for majority (S_{Maj}) and minority (S_{Min}) carriers; dashed lines are for the case in which the mobilities that determine the recombination rate are capped at $\mu_{crit} = 10^{-8}$ (blue) and 10^{-4} (green) m^2/Vs . [136]. Copyright 2010. Reproduced with permission from IEEE Photonics Soc. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

BHJ systems studied to date seem to have a ζ between 0.01 and 1 [28,99,116,139,142,143,147] with some reports for the P3HT:PCBM system finding ζ as low as 10^{-3} [145,146].

The origin of reduced Langevin recombination (also commonly referred to as non-Langevin recombination) has been explored by several groups. Generally speaking it is expected that the inherent phase separation in BHJ blends would reduce the probability of opposing charge carriers finding one another thereby suppressing the recombination rate compared to a system in which holes and electrons were homogeneously distributed. Multiple studies have observed a correlation between increased phase separation (larger domain sizes) and reduced Langevin recombination [44,45,99,115]. Fig. 7a presents the results of one such study that considered two different polymer:fullerene systems (noted as P-H and P-F in Fig. 7a) as a function of processing with different DIO concentrations (0%, 1% and 3%) [99]. The polymer domain area, estimated from plasmon based energy-filtered transmission electron microscopy (TEM), clearly shows a correlation with the measured Langevin reduction factors across all conditions.

After the first observations of reduced recombination, the presence of phase separation lead to the suggestion that recombination is actually limited by the rate at which the slowest charge carrier can reach a D/A interface instead of

the fastest carrier as would follow from Eq. (1) (which is in most cases is the electron transport through the fullerene [149,150]). This was strengthened by the notion that the mobility should be taken as a spatial average [72,151], as was originally proposed by Langevin [112]. Subsequent investigation however, found that such a model is inconsistent with the observed temperature dependence of ζ and it was proposed that ζ is at least in part due to the spatial variation of electron and hole carrier densities [148] (see Fig. 7b). Combined with the earlier finding that the carrier density in organic LEDs is heavily influenced by carrier diffusion from the contacts [152] this notion is particularly important because most optimized organic solar cells are rather thin, in the 100 nm range, making them very susceptible to this effect [153]. Spatial variation in the carrier density profile may well explain why some systems (such as P-H 0% in Fig. 7a) with an apparently homogeneous mixture of donor and acceptor still exhibit reduced recombination.

Modeling by Groves and Greenham led to the conclusion that the combination of the effect of domain size, electron-hole mobility mismatch, and energetic disorder can only account for reduction factors up to about one order of magnitude. It was then suggested that further reductions in P3HT:PCBM are likely the result of deep carrier trapping [130]. The idea of deep trapping contributing to $\zeta \ll 0.1$ seems to be consistent with other observations of trap-assisted recombination in the highly reduced P3HT:PCBM system but not in other systems with more modest reduction factors (>0.1) [149,154]. This subject remains controversial however as other studies have looked for but not found evidence of deep traps in P3HT:PCBM [155].

Another important consideration in the context of reduced Langevin recombination is that since bimolecular recombination primarily happens at the D/A interface, much like geminate recombination it too likely occurs via CT states. Measurements of electroluminescence from injected charges recombining radiatively through CT states seemingly confirm that this is the case [36,52]. It follows then that once the CT state is formed by two free carriers there may still be some probability that these carriers will separate again [27,105,106]. Therefore the same factors that suppress geminate recombination via CT states (energetic cascades, increased delocalization, etc.) may also contribute to suppressed bimolecular recombination. Recent experimental and theoretical work seems to support this conclusion [92,156–158] which only adds to the imperative to further define exactly how to enhance the charge separation efficiency out of CT states.

3.1.2. Trap-assisted recombination

Trap-assisted recombination is a first order process in which one electron and one hole recombine through a localized energetic trap (Fig. 5b). Though it involves two carriers, it is still considered monomolecular recombination because it involves one carrier at a time; first one carrier is trapped and then the second, oppositely charged, carrier must find the trapped carrier. The recombination rate is ultimately determined by the amount of sites that act as traps and by how quickly the free carrier

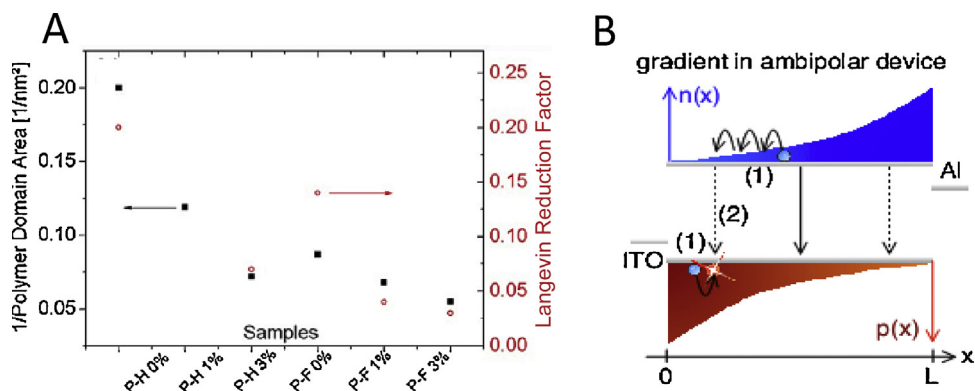


Fig. 7. (A) Comparison of the inverse mean polymer domain area estimated from energy filtered TEM (left scale, black) with the Langevin reduction factor (right scale red) for two different polymer:fullerene systems (P-H and P-F) processed with different concentrations of DIO solvent additive (0%, 1% and 3%). [99], Copyright 2012. Reproduced with permission from the American Chemical Soc. (B) Illustration of expected hole and electron spatial gradients as a function of position (x) in a device of thickness L . [148], Copyright 2009. Reproduced with permission from the American Physical Soc. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

can find the trapped carrier. A model for trap-assisted recombination in inorganic semiconductors, known as Shockley–Read–Hall (SRH) recombination [159,160], was established in 1952 and has recently been applied to organic systems including PLEDs [120–122,161,162] and OPVs [26,141,147,149,154,163–168]. According to SRH, the rate of this trap-assisted recombination process is described by the relation,

$$R_{SRH} = \frac{C_n C_p N_{tr} (np - n_i^2)}{[C_n(n + n_1)C_p(p - p_1)]}, \quad (4)$$

where C_n denotes the probability per unit time that an electron in the conduction band will be captured for the case that the trap is empty and able to capture an electron. Correspondingly, C_p indicates the probability per unit time that a hole will be captured when a trap is filled with an electron and able to capture the hole. N_{tr} is the density of electron traps. And $n_1 p_1 = n_i^2$ their product under equilibrium conditions in the case that the Fermi level coincides with the position of the recombination centers where n_i denotes the intrinsic carrier concentration in the sample.

Application of the Shockley–Read–Hall formalism has led to the introduction of an additional observable: the capture coefficient. Fortunately it has been recently suggested [132], and demonstrated [161], that in organic devices where $n = p$ and $np \gg n_1 p_1$ for the case of electron traps the SRH equation reduces to $R_{SRH} = C_p N_{tr} p$, where the capture coefficient is observed to be thermally activated leading to $C_p = (q/\epsilon)\mu_p$. This essentially implies that trap-assisted recombination in organic semiconductors is governed by the diffusion of the free carrier (hole/electron) toward the trapped carrier (electron/hole), similar to the Langevin recombination for free carriers where both carriers are mobile. As a result, similar to Langevin recombination, trap-assisted recombination is also shown to be thermally activated and dictated by the free carrier transport [161].

In most BHJ solar cells, the electron mobility originates from transport through the LUMO of the acceptor phase (often PCBM) to the cathode, whereas the hole mobility is governed by transport through the HOMO of the donor material toward the anode. The transport through pristine

PCBM is found to be trap free, $\mu_n = 2 \times 10^{-7} \text{ V/m}^2 \text{ s}$, and limited by space charge [150]. Since in most cases fullerene derivatives are known to be trap free, traps in the donor material or general impurities are the origin of most trap-assisted recombination processes observed in organic photovoltaics [163,164,166,169]. It is worth mentioning, the observation of space charge does not rule out the presence of traps and trap-assisted recombination will be present to some degree in presumably any organic bipolar diode simply because organic systems do not comprise ultra clean pristine materials [154,170]. The key issue is that it is the number of traps and their energetics that governs the general trap-free or trap-limited nature of the transport [154,170,171].

Trap-assisted recombination was originally introduced in 2007 by Mandoc et al. in order to explain the behavior of polymer:polymer solar cells where the acceptor polymer was shown to have trap-limited electron transport [141]. It has been observed that many of these systems might suffer from this monomolecular recombination mechanism [172,173]. Notably other recent work seems to indicate that for the vast majority of semiconducting polymers, in a diode configuration, the electron transport is trap-limited [174]. The implication of this finding is that any organic material with a LUMO level above approximately 3.6 eV is predicted to include electron trapping, which will induce trap-assisted recombination in any device where both carriers are present. The consequence for OPVs is that any organic material intended to be used as an acceptor should have a LUMO below this energy level since higher LUMOs may provoke an additional recombination channel which will ultimately limit the OPV device performance [175].

Despite the known presence of traps in common materials used for OPV devices, the majority of efficient OPV systems do not appear to be limited by trap-assisted recombination [26]. For the most part, studies on the trapping in OPV have focused on systems where chemical impurities were intentionally introduced [163,164,169]. It is worth considering whether the intrinsic phase separation in high performing OPV devices may help explain the apparently limited role of trap-assisted recombination [176]. Because

holes and electrons transport through isolated domains trapped carriers must at least be within hopping/tunneling distance of a D/A interface in order to recombine with a free carrier of the opposite charge. Consequently it may be that trapped carriers far from a D/A interface are more likely to be thermally reemitted after some time than they are to recombine. It should be noted though that this also raises the difficult to probe fundamental question as to how pure the D/A domains really are.

3.1.3. Auger recombination

The third possible nongeminate recombination process is that of Auger recombination also known as trimolecular recombination because it is a three-particle process [177] (Fig. 5c). In Auger recombination, an electron in the LUMO recombines with a hole in the HOMO after which the energy is transferred to a third electron which is then excited to a higher energetic state. The Auger recombination rate, R_{Auger} , has been described by the expression

$$R_{Auger} = \Gamma_n n(np - n_i^2) + \Gamma_p p(np - n_i^2) \quad (5)$$

where Γ_n and Γ_p are the Auger coefficients. A requirement for Auger recombination is a high charge density, generally not believed to be present in organic solar cells and as such Auger recombination has not been directly observed in OPV devices [27,178]. Nonetheless, there have been a few reports of a recombination mechanism with a third order dependence on carrier density in P3HT:PCBM solar cell devices [142,179,180] as discussed in the subsequent section.

3.1.4. Carrier density dependence greater than quadratic

The carrier density dependence of the nongeminate recombination rate, often referred to as the order of recombination, has been observed to be higher than that expected for Langevin recombination and temperature dependent for several polymer:fullerene systems [142,153,176,179–185]. Both Deibel et al. and Shuttle et al. suggested that this phenomenon is more likely related to a carrier density dependent recombination rate coefficient rather than a truly trimolecular process. This would not be an entirely unreasonable assumption; Tanase et al., and others, have shown that in pristine organic materials carrier transport at room temperature is mostly governed by carrier density [186–188]. Combined with the previously mentioned finding that carrier density is heavily influenced by carrier diffusion from the contacts [152] this is particularly important because, again, most optimized organic solar cells are rather thin, in the 100 nm range, making them very susceptible to this effect. Kirchartz and Nelson recently modeled the effect of spatial distributions in carrier density originating from the contacts in OPV devices and found that indeed the order of recombination can range from over 8 to 2 when going from an active layer thickness of 50 nm to 300 nm [153]. Likewise it has been shown that for pristine PLEDs the Langevin recombination depends not only on electric field and carrier densities, but also on temperature due to the energetic disorder governing the mobilities in the materials [114,121,131]. Recombination in organic

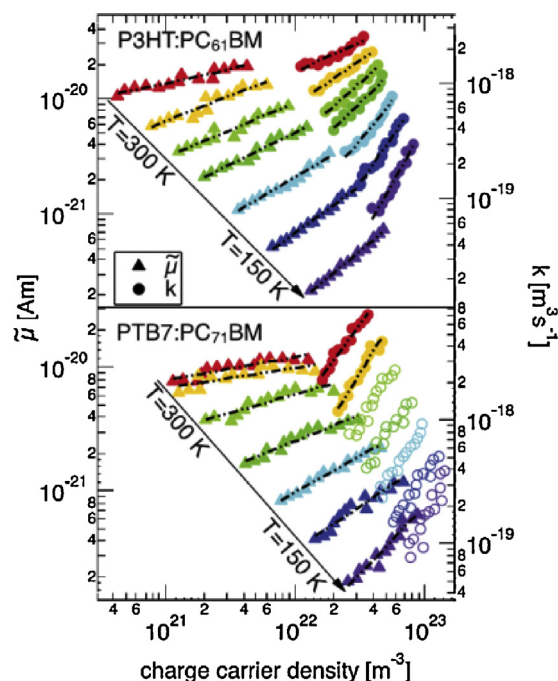


Fig. 8. Charge carrier density dependence of effective mobility (triangles, left axis) and the recombination rate coefficient, k , (circles, right axis) for P3HT:PCBM (top) and PTB7:PCBM (bottom). Solid circles were used for temperatures where the contacts are ohmic and open circles for where the device was limited by injection barriers. [176]. Copyright 2012. Reproduced with permission from John Wiley & Sons Inc.

solar cells has been found to possess similar dependencies [189]. Thus it is clear that higher reaction orders at least in part originate from spatial gradients of the carrier density and the carrier density dependence of the mobility.

What remains an intriguing open question is why the dependence of the bimolecular recombination coefficient in some systems appears to have a stronger temperature dependence than the temperature dependence of the mobilities in the Langevin expression [176,184]. As shown in Fig. 8, Rauh et al., recently found that for two different polymer:fullerene systems, the mobility dependence could only partially explain the temperature dependence of the recombination rate coefficient (shown as k in Fig. 8). They interpret this as evidence in support of previous suggestions that the reemission of trapped carriers can increase the order of recombination [182,190]. This reasoning follows by positing that in an OPV device there are both free and trapped carriers both of which are captured in experimental measures of the total charge carrier density. However, due to the intrinsic phase separation of free electrons and holes, the only trapped carriers that are likely to recombine with an opposing charge carrier are those that are trapped near a D/A interface. Trapped carriers that are far from an interface are more likely to eventually be thermally reemitted back to the transport level. Thus despite the presence of trapped carriers the dominant recombination process is still bimolecular. The rate of which depends only on the density of *free* carriers. Due to the finite number

of trap sites, as the *total* carrier density increases the ratio of free carriers to trapped carriers will increase in favor of more free carriers. Thus the number of free carriers in the device will rise superlinearly with experimentally measured total charge carrier density. Since the recombination order is taken to be the dependence of the recombination rate on the *total* carrier density, this leads to recombination orders in excess of two. Following this reasoning, the carrier density dependence of $k(n)$ in Fig. 8 increases at low temperatures because the ratio of trapped to free carriers increases even more at low temperatures where the probability of thermally activated reemission of trapped carriers is lowered.

With that said, it is worth noting that the stronger dependence observed in the poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl]]-[3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]] (PTB7):PCBM system compared to the P3HT:PCBM system may in part be due to the smaller active layer thickness (105 nm vs. 200 nm) as described above. Furthermore, it has been shown that the temperature dependence of mobility is highly sensitive to the carrier density regime with notable differences in the space charge regime versus the transistor regime [186]. Nonetheless, this intriguing theory certainly warrants further investigation.

3.2. Space charge effects

As mentioned in earlier sections, in most cases the mobility of the electron through the fullerene exceeds that of the hole through the donor. The physical consequence of this is that after dissociation of an exciton the electron will be swept out of the active layer faster than the hole. Goodman and Rose have treated the extraction of photogenerated electrons and holes from a semiconductor in 1971 [191]. They showed that with noninjecting contacts the photocurrent becomes saturated when all photogenerated free electrons and holes are extracted from the semiconductor. This implies that the mean electron and hole drift lengths $w_{e(h)} = \mu_{e(h)}\tau_{e(h)}E$ are equal to or longer than the specimen thickness L : with $\mu_{e(h)}$ the charge carrier mobility of electrons (holes), $\tau_{e(h)}$ the charge carrier lifetime, and E the electric field, respectively. For the case that $w_e < L$ or $w_h < L$ or both are smaller than L , space charge accumulates and the recombination of free charge carriers becomes significant. The most significant implication of this is that a thicker device essentially amplifies a space charge buildup if an imbalance of carrier mobilities is present, increasing bimolecular recombination and lowering the FF [192,193]. It is worth pointing out that, as addressed before, even relatively high pristine hole mobilities in a donor material cannot be held as a guarantee for balanced transport in the blend [135,138,194–196] due to the percolative nature of the transport. Additionally, while the presence of space charge effects has been satisfyingly confirmed for polymer systems with mobility imbalances exceeding a factor of 1000 [138], the lower threshold for how imbalanced mobilities can be without invoking space charge effects is still unclear.

3.3. Surface recombination

Though the topic has not received as much attention in the OPV literature as bulk recombination, recombination losses due to surface recombination may also significantly impact overall device performance [136,151,189,197]. In general surface recombination is governed by the charge injection/extraction behavior of the contacts. The presence of a minority carrier at a contact will govern the recombination. Electrons that diffuse to the anode recombine with injected holes and holes that diffuse to the cathode recombine with injected electrons. Typically the surface recombination velocity of this process is assumed infinite, all minority carriers recombine. Naturally the presence of minority carriers at a contact will reduce the device performance because those charges will not be collected. Since surface recombination is a bimolecular process the fastest carrier governs its rate [197]. Consequently, through modeling high carrier mobility is shown to increase the influence of surface recombination [151] reducing the device performance.

3.4. Experimental probes of nongeminate recombination

A variety of optical and electrical techniques have been used to probe nongeminate recombination losses in OPV devices. These include, but are not limited to, transient absorption [102,198], charge extraction (CE) [199], transient photovoltage (TPV) [179,181], transient photoconductivity [200], light and temperature dependent J - V measurements [102,138], impedance spectroscopy [116,201], time-resolved microwave photoconductivity [156], TDCF [67], and charge extraction from a linear increasing voltage (CELIV) [29,139,143]. In this section, we will highlight how some of these techniques have been used to distinguish nongeminate mechanisms and to measure the charge carrier density and effective charge carrier lifetime in operating OPV devices.

3.4.1. Distinguishing nongeminate mechanism by light intensity dependence of J - V curves

The simplest and most common method to distinguish between bimolecular recombination and trap-assisted recombination is probing the V_{oc} dependence on incident light intensity. For free carrier transport it was proposed by Koster et al. that the dependence of the V_{oc} on light intensity is shaped by the relation:

$$V_{oc} = \frac{E_{gap}}{q} - \frac{k_B T}{q} \ln \left(\frac{N_{cv}^2}{n_e n_h} \right) \quad (6)$$

where E_{gap} represents the effective energy gap between the offset of the LUMO of the acceptor and the HOMO of the donor, N_{cv} is the effective density of states in the donor and acceptor, and n_e and n_h denote the dissociated carrier densities varying with the applied light intensity [202]. Consequently, trap-free carrier recombination is predicted to have a $k_B T/q$ dependence on light intensity. As can also be observed in Fig. 9a, this relation has proven to be universal for trap free transport in organic solar cells

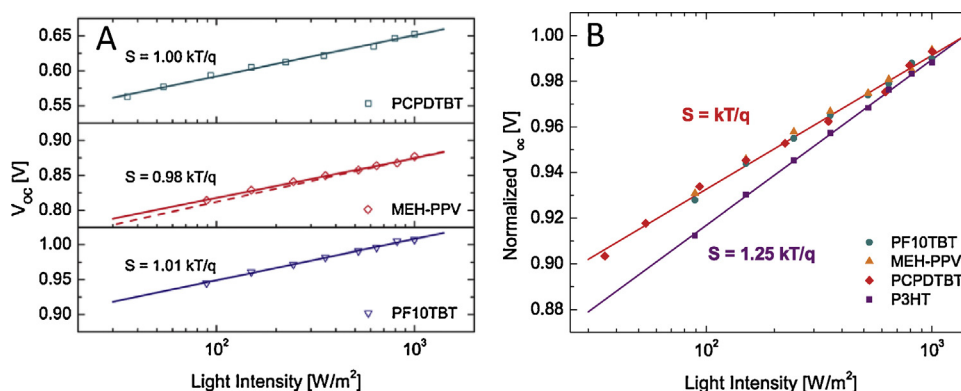


Fig. 9. (A) V_{oc} vs. light intensity for three polymer:fullerene systems that are dominated by bimolecular recombination at the open circuit condition. The solid lines represent best fits to the data for a natural logarithmic dependence of V_{oc} on light with a slope of S . [149], Copyright 2011. Reproduced with permission from the American Institute of Physics. (B) Normalized V_{oc} vs. light intensity for the same three polymer systems in A along with data from a P3HT:PCBM device that exhibits a slope of $S = 1.25$ indicating the presence of both bimolecular and trap-assisted recombination. [154], Copyright 2012. Reproduced with permission from John Wiley & Sons Inc.

[116,147,154,203]. However, when trap assisted recombination is present this relation becomes perturbed and a higher than $k_B T/q$ slope is observed [141,161,163,164] as shown in Fig. 9b for the case of P3HT:PCBM.

It is worth mentioning that this technique requires reasonable quality solar cells where the parasitic leakage current (i.e. injected dark carriers) is low enough such that it does not interfere with the V_{oc} dependence at low light intensities. A simple way to gauge this is by looking at the FF dependence on light. Generally speaking if the FF starts to drop at lower light intensities, then the leakage current is significantly interfering with the photocurrent at those intensities and the slope of the V_{oc} vs. light intensity will be misleadingly inflated.

Determining the nature of nongeminate losses away from the open circuit condition is more challenging. However, measuring the photocurrent as a function of light intensity has proven to be an insightful probe of bimolecular recombination and space charge effects [138,203]. In this case, the photocurrent is taken to be the light current minus the dark current—which is a fair approximation so long as the series resistance is small [204]. Generally a sub-linear dependence of the photocurrent on light intensity is indicative of bimolecular recombination. It should be said though that a linear dependence on light intensity is less insightful. A linear dependence may result from either no recombination or monomolecular recombination and can be especially misleading if at the bias condition considered the photogenerated carrier density is not much larger than the density of injected carriers [205].

3.4.2. Measures of charge carrier density

As nongeminate recombination depends strongly on charge carrier density, reliable measures of the charge carrier density are essential. Techniques such as TDCF, TPC, and CELIV typically use a short laser pulse to create photogenerated charges the density of which can then be determined by integrating the resulting photocurrent transients. While these techniques have proven to be quite insightful they come with the inherent disadvantage that

they do not measure steady state conditions—the consequences of which are not well understood. Alternatively, CE and impedance spectroscopy are two techniques that allow for a direct measure of the charge carrier density at steady state conditions and illumination intensities similar to typical solar cell operating conditions. In the charge extraction technique, a solar cell is held at fixed bias and illumination condition then the light is quickly turned off while the device is simultaneously short circuited. The resulting photocurrent transient can then be integrated to determine the average charge carrier density present in the device at the initial bias and illumination condition [199]. Shuttle et al. used this technique to experimentally show, for the first time, how the carrier density in a P3HT:PCBM device depends on the applied bias [206]. As shown in Fig. 10a, the carrier density increases sharply with forward bias. This is due both to the decreasing driving force for extraction of photogenerated charges and the increasing injection of dark charge carriers. Near open circuit ($V_{cell} \sim 0.55 \text{ V}$) the dark carrier density dominates the total carrier density. For comparison, Shuttle et al. also included the carrier density dependence on voltage expected for conventional doped inorganic semiconductors in which n remains independent of voltage up to within a few $k_B T$ of the V_{oc} and then increases with a Boltzmann-like form (referred to as the Shockley limit) [206]. This stark contrast in carrier density dependence is due largely to charge injection from the contacts well below the built in voltage of the device.

In a recent study published by our group, we demonstrated that impedance spectroscopy can also be used to measure the steady state carrier density in operating OPV devices as a function of bias and light intensity [116]. In this measurement, a solar cell device is illuminated and held at a fixed DC bias condition while the impedance responses from a small (20 mV) AC bias is measured as a function of frequency. In the case of impedance spectra that can be modeled with a simple parallel resistor–capacitor circuit, the active layer capacitance can be directly extracted. The carrier density as a function of bias can then be obtained by measuring and integrating the active layer capacitance

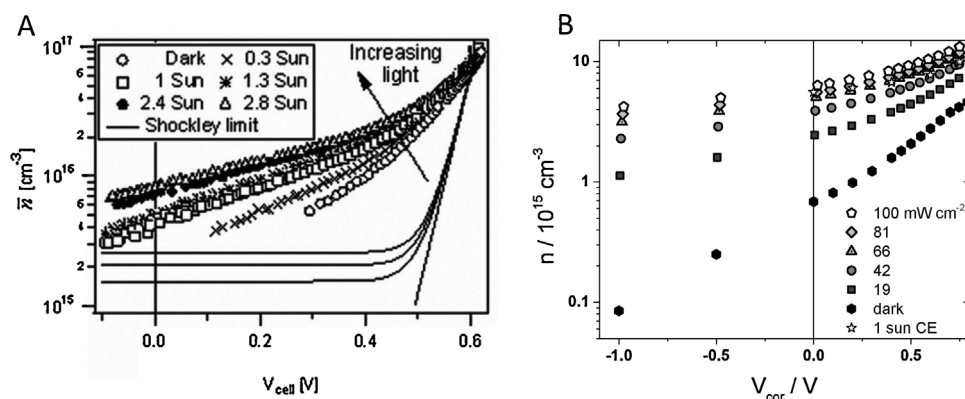


Fig. 10. (A) Bias dependence of the charge carrier density in a P3HT:PCBM solar cell device measured using the CE technique (symbols) and carrier density response expected from Shockley limit (lines). [206], Copyright 2010. Reproduced with permission from the National Academy of Sciences, USA. (B) Bias dependence of the charge carrier density in a small molecule BHJ solar cell device measured using impedance spectroscopy at a range of illumination intensities and a CE technique at one sun equivalent illumination (stay symbols). Both V_{cell} and V_{cor} represent the applied bias corrected for the voltage drop due to the device series resistance. [116], Copyright 2013. Reproduced with permission from John Wiley & Sons Inc.

starting from the voltage where the photocurrent saturates up to the V_{oc} . The carrier density as a function of bias measured using this technique in a small molecule:PCBM BHJ device is presented in Fig. 10b. Once again, it was found that the carrier density rises steadily with forward bias and the dark carrier injection becomes an increasingly significant portion of the total carrier density. We note that the dark carriers do not appear to be as significant in this system as was observed for the P3HT:PCBM system which is consistent with other reports that the strong dark carrier injection in P3HT:PCBM is atypical [156]. For comparison the carrier density for this particular small molecule system was also measured using a CE technique (star symbols). The carrier density from CE agrees well with the impedance measured n within a reasonable variation attributable to device to device variations, deviations from the assumed uniform carrier density profile and limitations in the extraction technique arising from the imbalanced charge carrier mobilities. Though impedance response of organic semiconductors is notoriously difficult to interpret, we posit that this method may prove a useful tool for the characterization of a variety of OPV systems in the future.

3.4.3. Measures of effective charge carrier lifetime

It is sometimes useful to consider a general expression for the nongeminate recombination using an effective charge carrier lifetime, τ , that encapsulates all nongeminate recombination processes. τ is a measure of the average time a free charge carrier lives before recombining nongeminately. The nongeminate recombination rate can then be expressed as

$$R_{NG} = \frac{n}{\tau(n)} \quad (7)$$

where τ may be a function of carrier density. The effective carrier lifetime in an OPV device has been measured experimentally using a variety of optoelectronic techniques including CELIV [142], TPV [179,181] and impedance spectroscopy [116,201]. Systems measured under 1 sun illumination intensity at open circuit typically exhibit

effective carrier lifetimes on the order of microseconds [116,139,181].

Using a combination of CE and TPV, Credington et al. recently measured the effective carrier lifetime at open circuit as a function of carrier density for a large range of OPV systems (Fig. 11) [185]. In TPV, a solar cell is illuminated and held at the open circuit condition and then pumped with a low-intensity nanosecond laser pulse to introduce a small quantity of additional non-equilibrium carriers which subsequently recombine. The transient photovoltage produced by the laser pulse is measured and fit to a mono-exponential decay which allows for direct calculation of τ [207]. All systems that were examined by Credington et al. were observed to have a power-law-like behavior of effective carrier lifetime on carrier density such that $\tau(n) \propto n^{-\lambda}$ with $\lambda < -1$. This is consistent with a bimolecular recombination mechanism in which the

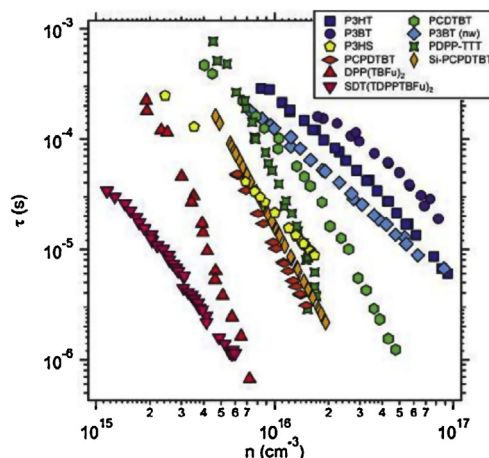


Fig. 11. Effective carrier lifetime (τ) versus average charge carrier density (n) for a variety of polymer and small molecule OPV systems with PCBM as the acceptor measured by a combination TPV and CE techniques. [185], Copyright 2012. Reproduced with permission from the American Chemical Soc.

recombination rate coefficient also depends on carrier density as discussed in Section 3.1.4. Equally noteworthy is that the effective carrier lifetimes measured at the same carrier density vary over several orders of magnitude which illustrates that different OPV systems can exhibit substantially different recombination rate coefficients.

3.5. Summary of how nongeminate recombination affects solar cell metrics

Any nongeminate recombination event is effectively eliminating charge carriers that could otherwise contribute to the photocurrent. Thus generally speaking, the biggest effect of nongeminate recombination is to reduce the photocurrent. Exactly how much nongeminate recombination reduces the photocurrent depends on a number of factors including the carrier mobility, film thickness and degree of phase separation as discussed in the previous sections. Due in large part to the carrier density dependence of the nongeminate recombination, the percentage of photogenerated carriers lost to nongeminate recombination is highly voltage dependent. Near short circuit, the internal field sweeps out most carriers before they can recombine however as a forward bias is applied this driving force decreases leaving more and more carriers in the device. This leads to acceleration in bimolecular recombination particularly as the bias approaches V_{oc} and injection of dark carriers becomes significant. The key to limiting the effects of nongeminate recombination on J_{sc} and FF seems to be first and foremost to establish efficient (see Fig. 6) and balanced charge carrier mobilities. Combined with a strong internal field created by the device's built in voltage, this will enable the efficient collection of photogenerated carriers. Optimizing the device thickness is also essential for the same reason. Generally speaking, it takes longer to extract a charge carrier from a thicker active layer. If the active thickness is too large such that the charge carrier extraction time approaches the effective carrier lifetime than nongeminate recombination losses will become significant.

Nongeminate recombination is known to affect the V_{oc} as well [53,181,185,190]. This can be understood by considering that at the open circuit condition the current flowing out of the device is zero precisely because the photogenerated current is entirely cancelled out by the nongeminate recombination current. It naturally follows then that reducing the rate of nongeminate recombination would allow devices to reach higher voltages before the photocurrent is cancelled completely by recombination. Such gains could be significant. As shown by Credington et al., the V_{oc} of highly intermixed systems with fast recombination may lose up to 300 mV compared to systems with highly phase-segregated domains and thus slower recombination [185].

4. Summary and perspective

In summary, a complex picture of the photogeneration is emerging in which energetic offsets and domain size are not the only factors that determine whether excitons will recombine or separate into free carriers. Once an electron–hole pair reaches a D/A interface, whether the charges can escape their coulomb attraction and avoid

geminate recombination depends on how tightly bound they are. There is compelling evidence that delocalized band states at the D/A interface can reduce this binding energy. The accessibility of delocalized states is a function of not only molecular properties (i.e. conjugation length, energetic offsets, reorganization energy, LUMO degeneracy, etc.) but also film properties (alignment of donor molecular orbital relative to the acceptor, degree of crystallinity, etc.). The fact these properties are both dependent on materials and device processing conditions helps explain long running disagreements in the literature about the roles of the internal electric field and excess excitation energy in suppressing geminate recombination. In the context of overcoming geminate recombination, key issues for further research are to develop a comprehensive quantum mechanical model that encompasses the many processes that contribute to charge separation at the donor–acceptor interface and to better define the general guidelines for material design.

Where it has been shown that with careful choice of materials and processing conditions geminate recombination losses can be almost entirely overcome, nongeminate losses will always be present. This means that the nongeminate recombination processes govern the characteristic solar cell parameters: J_{sc} , V_{oc} and FF. Luckily, it seems that some external variables can potentially reduce nongeminate recombination. The blend morphology is of major influence on both the carrier mobility as well as the recombination process. A favorable phase separation can both reduce bimolecular recombination and enhance charge transport. Moreover, the same factors that help charge separation out of CT states may also reduce nongeminate recombination. Minimizing chemical impurities and choosing the right acceptor material will eliminate the possibility of an additional trap-assisted recombination channel. Optimizing the device thickness is also important. For a thick device charges need more time to reach the contacts rendering them more susceptible to bimolecular recombination, where the most extreme case will result in the buildup of space charge. On the other hand, a thin device will suffer more from contact effects as an increased carrier density or minority carriers enhance bimolecular recombination. Altogether, it is clear that future material design and device fabrication techniques must aim to maintain efficient charge transport properties while encouraging sufficient phase separation in the blend.

Finally we emphasize that while the recent efficiency gains in the OPV field have been remarkable they have generally come along with more complex and expensive materials [208]. Thus, further developing the fundamental understandings of organic photovoltaics may be essential to not only increased efficiencies but also to the design of more cost effective conjugated polymers and small molecules for high performing photovoltaic devices.

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