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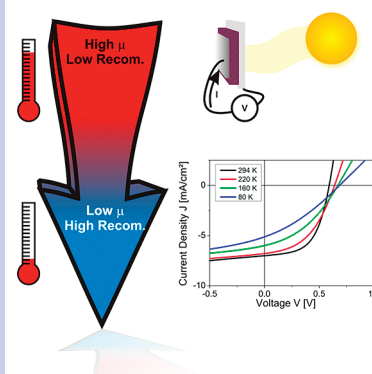
# Effect of Nongeminate Recombination on Fill Factor in Polythiophene/Methanofullerene Organic Solar Cells

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**ABSTRACT** A key factor in solar cell efficiency is the dependence of the photocurrent on applied bias. With respect to organic solar cells, it is often suggested that this factor is governed by the field dependence of charge-transfer state separation. Here, we demonstrate that this is not the case in benchmark polythiophene/methanofullerene solar cells. By examining the temperature and light intensity dependence of the current–voltage characteristics, we determine that (1) the majority of free charge generation is not dependent on the field or temperature and (2) the competition between extraction and recombination of free charges principally determines the dependence of photocurrent on bias. These results are confirmed by direct observation of the temperature dependence of charge separation and recombination using transient absorption spectroscopy and highlight that in order to achieve optimal fill factors in organic solar cells, minimizing free carrier recombination is an important consideration.

**SECTION** Kinetics, Spectroscopy



Organic solar cells with power conversion efficiencies exceeding 7% have recently been demonstrated.<sup>1</sup> However, there is still a debate over the physical mechanisms that limit the figures of merit in organic solar cells and over the directions that should be pursued to further improve device efficiency and stability toward the regime required for commercial relevance.<sup>2</sup> In particular, several contradictory explanations have been proposed for the process that determines the bias dependence of the photocurrent. This is an important issue to resolve because the bias dependence of the photocurrent has a large influence on the solar cell's fill factor, which directly affects its power conversion efficiency (power conversion efficiency is equal to the product of open-circuit voltage, short-circuit current, and fill factor). In this Letter, we provide evidence that, contrary to popular models, it is the bias dependence of separated charge sweep-out rather than the bias dependence of charge-transfer state separation that determines the bias dependence of the photocurrent.

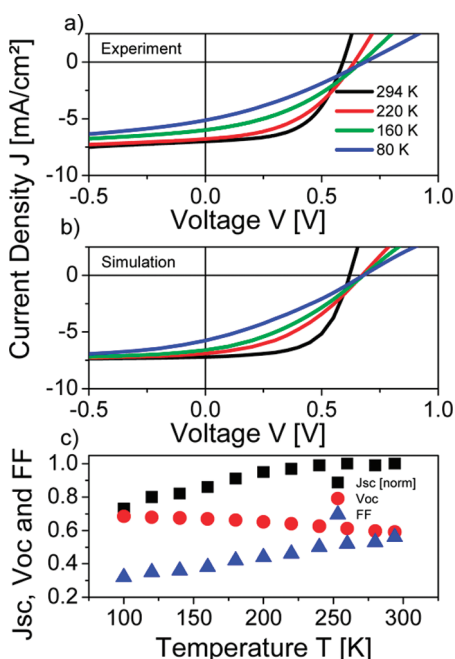
A common explanation of the bias dependence of the photocurrent is that it is determined by the field dependence of the separation of charge-transfer states.<sup>3–7</sup> The photo-physical processes involved in this explanation run as follows. Tightly bound excitons created by photon absorption diffuse to a donor–acceptor interface, at which point a charge-transfer state (or bound charge pair) is created across the heterojunction. This charge-transfer state can then either separate to yield photocurrent or can recombine, causing a loss of quantum efficiency. The branching ratio of the charge-transfer state population between separation and recombination depends on, among other factors, field and temperature

in a manner theoretically approximated by Braun's extension of Onsager theory<sup>8</sup> and further refined by Tachiya.<sup>9</sup> This is asserted to cause the bias dependence of the photocurrent. Importantly, in this explanation, charge recombination occurs between an electron and hole generated by the same photon, termed geminate recombination, and therefore is a monomolecular process (it occurs at the same rate irrespective of the charge density). Recently, such a mechanism has been proposed to explain the bias-dependent transient absorption of a polythiophene/methanofullerene blend.<sup>6</sup> However, other recent results show that the majority (> 80%) of excitons in such a blend form separated free charges directly after they are quenched at the interface even in the absence of field,<sup>10–12</sup> suggesting that the field-dependent suppression of geminate recombination is unlikely to account for the bias dependence of the photocurrent, a position that is also supported by device-based measurements and charge extraction techniques.<sup>13–15</sup> These latter experiments suggest that the bias dependence of the photocurrent is determined by a process that occurs after photo-generated electron–hole pairs have become spatially separated, such as the process of nongeminate recombination (wherein a free charge captures an opposite charge and recombines).<sup>16</sup> This process occurs in competition with the field-dependent sweep out of the photogenerated charges and therefore can cause field dependence in the photocurrent.

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**Figure 1.** (a)  $IV$  characteristics of a P3HT/PCBM photovoltaic device at various temperatures under illumination equivalent to  $0.8 \times \text{AM1.5G}$  (see Methods section). (b) Simulations of the  $IV$  characteristics at the various temperatures demonstrating nongeminate recombination can describe the bias dependence of the photocurrent. The mobility is decreased at lower temperatures. See text for details. (c) Experimentally observed short-circuit current, open-circuit voltage, and fill factor as a function of temperature.

Furthermore, in contrast to geminate recombination, the rate of nongeminate recombination depends on the charge density, and therefore, its effect increases at higher carrier densities caused by higher light intensity, lower carrier mobilities, or low internal fields. Nongeminate recombination has already been observed to be important close to the open-circuit voltage.<sup>17,18</sup>

In order to experimentally clarify the cause of the field dependence of the photocurrent and the underlying charge recombination mechanism, we study devices based on the highly optimized poly(3-hexylthiophene)/methanofullerene (P3HT/PCBM) and combine an investigation of the temperature dependence of the solar cell's current–voltage characteristics with transient absorption measurements. These experiments reveal that ultrafast, temperature- and field-independent charge separation followed by competition between charge extraction and nongeminate recombination explain the device characteristics.

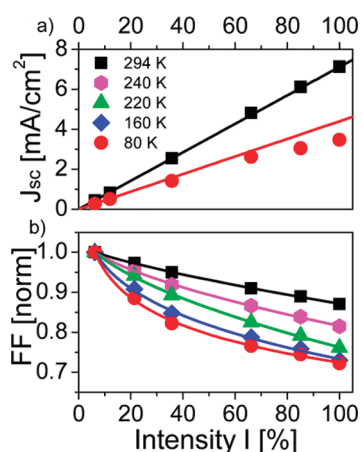
**Temperature and Intensity Dependence of Device Characteristics.** In Figure 1, we present the temperature dependence of the  $IV$  characteristics of the solar cells. All parameters that describe the power conversion efficiency change with temperature. The open-circuit voltage increases with decreasing temperature. This increase is mainly caused by a decrease in the dark current (Supporting Information) at lower temperatures that is compatible with a reduced thermionic injection<sup>19</sup> and lower mobility<sup>20</sup> of the charge carriers. High dark current reduces the net amount of extracted charge carriers and

simultaneously increases nongeminate recombination, thus leading to a decrease in open-circuit voltage.<sup>18,21</sup> Once the dark current is negligibly small, the open-circuit voltage saturates at 0.7 V, a value which corresponds with the work function difference of the ITO/PEDOT:PSS and aluminum electrodes and is roughly 0.3 V smaller than the energy of the charge-transfer state at the P3HT/PCBM interface.<sup>22</sup>

The fill factor, which is affected by the field dependence of the extraction of photogenerated charge carriers, decreases almost linearly over the temperature range studied. This eventually also leads to a reduction of the short-circuit current at temperatures below 250 K (once the fill factor drops below 50%). There are two possible explanations of why at lower temperature for a fixed electric field fewer charges are extracted from the device. If charge separation were described by the temperature- and field-activated dissociation of charge-transfer states as assumed by Onsager–Braun type models, then at low temperatures, more charge-transfer states would recombine geminately, and fewer would lead to separated charges. To compensate for the reduction in thermally activated splitting at low temperatures, higher fields would be required to generate free charges. Alternatively, if charge separation were unaffected by field and temperature, then an increased nongeminate recombination due to higher charge densities caused by lower mobility at lower temperatures would lead to a reduction in extraction efficiency. In the latter process, the bias dependence of the photocurrent is determined by a competition between nongeminate recombination and charge extraction in accordance with a recently developed model for the open-circuit voltage by Maurano et al.<sup>18</sup> In this context, the charge carrier mobility is the main parameter influencing the bias dependence of the photocurrent as a lower mobility will lead to reduced extraction rates and thus to an increased charge carrier density in the device. As the extraction rate also varies with field, the charge carrier density also increases with the positive applied voltage. A higher charge carrier density in turn leads to a higher nongeminate recombination rate, and thus, the ratio of charge extraction to nongeminate recombination will be shifted in favor of nongeminate recombination. Figure 1b shows the results of numerical simulations (see Methods for details) based on this model of field-independent charge separation followed by nongeminate recombination. The change in the bias dependence of the photocurrent caused by nongeminate recombination causes a fill factor reduction, and the increased probability of nongeminate recombination at higher charge densities caused by more intense illumination or lower mobility recreates the trends observed in the data. It will be shown in the further discussion that only this second model is consistent with all features of the data.

In summary, the central question is whether geminate or nongeminate recombination is the dominating loss mechanism in the devices under study. In the following considerations, we make use of the fact that geminate recombination is independent of the charge carrier density (and, therefore, also excitation intensity) while nongeminate recombination does depend on the density.<sup>23</sup>

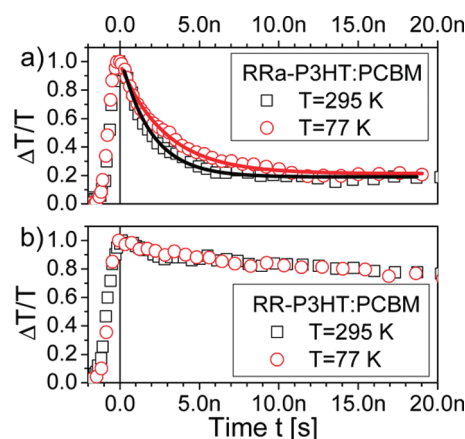
In Figure 2a, the excitation intensity dependence of the short-circuit current density is shown for measurements



**Figure 2.** (a) Short-circuit current density  $J_{sc}$  as a function of excitation intensity  $I$  at 294 and 80 K. The lines represent a linear fit through the origin and the first two data points. (b) Fill factor (FF) as a function of excitation intensity for the series of temperatures indicated in (a). Lines serve as guides to the eye. 100% intensity corresponds to the equivalent of  $0.8 \times \text{AM1.5G}$  illumination (see Methods for details).

performed at room temperature and 80 K. The straight lines are fits through the first two points of the data series plus the origin and represent a linear dependence of  $J_{sc}$  on the intensity. At room temperature,  $J_{sc}$  follows the linear trend up to intensities equivalent to 1 sun conditions. However, at 80 K, the higher-intensity data points systematically deviate from the linear trend, with  $J_{sc}$  lying further below the linear trend with increasing intensity. This suggests that nongeminate recombination at short-circuit conditions is negligible at room temperature (all separated charges can be extracted) but is important at lower temperatures. This is further supported by Figure 2b, in which the intensity dependence of the fill factor is presented. For all temperatures, the fill factor decreases toward higher intensities, with a stronger dependence at lower temperatures. The fill factor is best (64%) at high temperatures and low excitation intensities, that is, at the lowest charge carrier density in the device, and it is worst (33%) at low temperatures and high excitation intensities when the charge carrier density is the highest. Critically, while smaller fill factors at lower temperatures can be expected from a temperature- and field-dependent charge separation model, as mentioned above, a change in the intensity dependence cannot.<sup>24</sup> In contrast, it is completely consistent with nongeminate recombination being the process that determines the fill factor.

**Temperature Independence of Charge Separation.** To further elucidate whether geminate or nongeminate recombination is responsible for the observed changes, we have conducted transient absorption spectroscopy measurements of P3HT/PCBM blend films on quartz substrates (representative of the kinetics in a device at zero internal field) at room and liquid nitrogen temperature. We wished to monitor the total population of bound charges (which can recombine geminately) and free charges (which recombine nongeminately). Therefore, we searched for an isosbestic point, where the absorption of these two bound and free charges is equal and therefore the induced absorption is proportional to the total number of

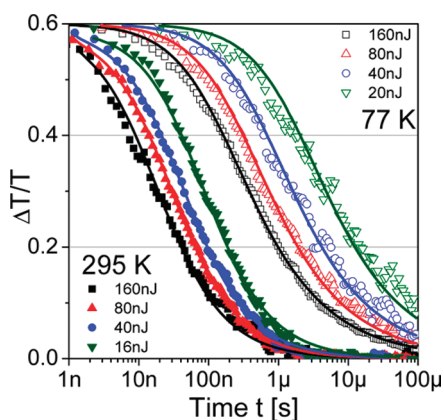


**Figure 3.** (a) Normalized induced absorption of free and bound charges integrated over the spectral region of 750–800 nm as a function of time in a RRa-P3HT/PCBM blend film measured at room temperature (black squares) and at liquid nitrogen temperature (red circles) after a  $< 4 \mu\text{J cm}^{-2}$  excitation pulse at 532 nm. (b) Same data for a RR-P3HT/PCBM blend film.

bound plus free charges. In earlier work,<sup>11</sup> we identified that when integrated between 750 and 800 nm, the absorptions of the bound and free charges are equal, allowing the integrated kinetics in this region to be interpreted as representing the total number of bound plus free charges. The difference between geminate and nongeminate recombination lies in the kinetics of their decay. Charge carriers bound in a charge-transfer state recombine geminately in less than 2 ns in the absence of field,<sup>10,11</sup> while separated charges recombine on time scales from nanoseconds up to micro- to milliseconds at room temperature.<sup>10,11,25</sup> The ratio of bound to separated charges depends strongly on morphology,<sup>11,26</sup> with about 80% charge-transfer state formation in amorphous blends containing regiorandom (RRa) P3HT but almost no ( $< 20\%$ ) charge-transfer state formation in well-ordered blends with highly regioregular (RR) P3HT. Figure 3 shows transient absorption data at room and liquid nitrogen temperature for both RRa-P3HT/PCBM and annealed RR-P3HT/PCBM blends taken at very low fluence in order to highlight monomolecular recombination of charge-transfer states. The data reveal that the formation of spatially separated charges is not temperature-dependent and remains close to unity in RR-P3HT even in the absence of field and at low temperature. The recombination dynamics for RRa-P3HT are shown in Figure 3a. In this amorphous blend, the short-lived decay typical of geminate recombination of charge-transfer states reduces the signal by 80% within the first 10 ns at both temperatures. As shown in the Supporting Information, this decay does not depend on the excitation intensity, supporting its assignment to geminate charge-transfer state recombination. The residual 20% long-lived absorption at both temperatures is caused by the longer-lived free charges. As the branching ratio of 4:1 between bound and free charges is not changed by a decrease in temperature of over 200 K, we conclude that the spatial separation of charges is not temperature-activated in RRa-P3HT.

Figure 3b presents the recombination dynamics for RR-P3HT. We have previously found that in this annealed blend at room temperature, there is no geminate decay





**Figure 4.** Kinetics of the normalized charge-induced absorption in RR-P3HT/PCBM integrated over the spectral region of 750–800 nm at room and liquid nitrogen temperature, starting when the signals have decayed to 60% of their initial value. The symbols correspond to various excitation pulse energies.

caused by charge-transfer states.<sup>11</sup> Here, we observe that the dynamics of the decay over the first 10 ns are the same at 295 and 77 K, indicating that again the branching ratio is unaffected by the over 200 K change in temperature. The small fraction of monomolecular decay in this case occurs on a time scale longer than charge-transfer state recombination and is assigned to recombination of a small fraction of charges that become trapped near an interface,<sup>11</sup> and therefore, at low temperature as at room temperature, the yield of free charges even in the absence of applied field is found to be close to unity.

**Temperature Dependence of Nongeminate Recombination.** Our examination of the transient absorption over the first 10 ns revealed that the formation of free charges does not depend on temperature. In Figure 4, we extend our observation of the transient absorption to longer time scales to examine the effect of temperature on nongeminate recombination. The rate of nongeminate recombination can be described by  $(dn/dt) = -k\mu(n,T)n^2$ , where  $n$  is the charge carrier density,  $k$  is a constant, and  $\mu(n,T)$  is the charge-carrier-density- and temperature-dependent mobility. If the density dependence of the mobility can be expressed for a given temperature,  $T$ , as  $\mu(n,T) = \mu_0(T)n^{\beta(T)}$ ,<sup>27</sup> then the nongeminate recombination rate can be expressed as  $(dn/dt) = -\gamma(T)n^{2+\beta(T)}$ , where  $\gamma$  is the temperature-dependent rate prefactor. Many recent reports observe that the nongeminate (bimolecular) recombination at room temperature depends on density with an order greater than 2, indicating that the density dependence of the charge mobility does affect the recombination kinetics of free charges.<sup>11,28,29</sup> At lower temperatures, the mobility will decrease ( $\mu_0$  becomes smaller), and the density dependence of the mobility will increase ( $\beta$  becomes larger). The cause of the increased density dependence of mobility at low temperature is related to the broad density of states (DOS) caused by disorder.<sup>30</sup> It can be understood qualitatively in the following manner: when the temperature is high, charges occupying sites in the low-energy tail of the DOS can still make a thermally assisted hop to a site higher in the DOS and thereby retain a reasonable mobility;

however, at low temperature, the thermal assistance is lost, and the mobility of the tail states becomes significantly lower than that of states higher in the DOS, leading to a strongly density-dependent mobility. Therefore, as we decrease the temperature, we expect the rate of free charge recombination to decrease due to the lower mobility, and we also expect that the stronger density dependence of mobility at lower temperature<sup>31</sup> will mean that the decay rate changes more significantly with excitation fluence. This is what we observe in Figure 4, wherein we investigate the effect of temperature on free charge recombination. In order to present a qualitative comparison between the rates of free charge recombination for a series of excitation fluences at the two temperatures, we focus on the decay of the last 60% of the signal in each case that is exclusively caused by free carrier recombination. All signals were normalized and shifted so that they decayed to 60% at zero time. Comparing the decay of the free charges, it is clear that at both room and low temperature, the decay is density-dependent, with the decay occurring at different rates for the different excitation fluences. The first striking difference is that the recombination is much slower at low temperature, occurring with rates almost two orders of magnitude slower than recombination at room temperature. This indicates that the mobility also decreases by roughly 2 orders of magnitude between room temperature and 77 K. This reduction in mobility agrees well with that used in our simulations (see Methods for details) and that obtained from previous time-of-flight experiments.<sup>32</sup> The second difference between the decays at room and low temperature is the increased density dependence of mobility at lower temperature, as evidenced by the wider spread of recombination rates over the same range of excitation fluences.

In summary, transient absorption experiments reveal that the majority (at least 80%) of quenched excitons form spatially separated carriers on a subnanosecond time scale irrespective of field and temperature. The transient absorption experiments also show that the carrier mobility is strongly reduced at lower temperatures. Measurements of device characteristics at a variety of light intensities for a wide temperature range were collected, and a decrease in fill factor and short-circuit current with decreasing temperature and increasing intensity were observed. Qualitatively, the measurements at low temperature immediately reveal that the bias dependence of the photocurrent cannot be accounted for by bias-dependent charge-transfer state separation because the light intensity dependence is strongly nonlinear. The device characteristics can be described by a model (consistent with the transient absorption results) in which temperature- and field-independent free charge generation is followed by kinetic competition between nongeminate recombination and charge extraction. Implementation of this model in a numerical simulation (see Methods for details and parameters) led to the simulated  $IV$  curves shown in Figure 1b that reproduce well all of the trends observed in the experimental data. These results provide strong direct evidence that the device performance of annealed P3HT/PCBM solar cells is attributable to fast, field-independent charge separation followed by a competition between nongeminate recombination and charge extraction.

In order to relate our findings to device characteristics at room temperature, we make the following observations. The IQE of high-performance polythiophene/methanofullerene solar cells is approximately 80 % at short-circuit,<sup>33,34</sup> which corresponds well to the approximately 20 % total of monomolecular losses observed at the zero field in ultrafast measurements of annealed blends.<sup>10,11</sup> Although we note that monomolecular loss processes can be highly morphology-dependent, this rough equality of monomolecular loss at short- and open-circuit conditions supports our assertion that the monomolecular loss mechanisms do not account for the field dependence of the photocurrent. Instead, our results suggest that at room temperature, as at low temperature, it is competition between carrier extraction and nongeminate recombination that determines the bias dependence of the photocurrent. We approximately estimate the theoretical maximum fill factor by subtracting a bias-independent (recombination-free) photocurrent from the measured dark current (see Supporting Information). This results in an approximation for the maximum obtainable fill factor of about 0.7, while that observed is 0.6. Thus, we can roughly estimate that the fill factor reduction due to nongeminate recombination at low biases reduces the efficiency of devices by approximately 15 % and therefore has a similar effect on the net power conversion efficiency as the nonunity IQE caused by geminate processes. Therefore, we suggest that an opportunity to increase the power conversion efficiency of organic solar cells by reducing nongeminate recombination at low internal fields exists in parallel to those currently pursued to minimize monomolecular losses related to charge-transfer states.<sup>35</sup>

## METHODS

Regioregular (RR) P3HT (Sepiolid P200, MW = 25 000 g mol<sup>-1</sup>, PDI = 1.6, regioregularity, ~98 %) and regiorandom (RRa) P3HT were supplied by BASF SE. PCBM (~99 %) was purchased from Sigma Aldrich. All materials were used as received. The polymers and PCBM were dissolved separately in chlorobenzene at 70 °C, and the solutions were mixed and then spin-cast onto precleaned quartz substrates in a nitrogen-filled glovebox. The RR-P3HT samples were annealed on a hot plate at 120 °C for 20 min in a nitrogen-filled glovebox. Solar cells were prepared in the same way by spin-casting the mixed solutions on a PEDOT:PSS (Clevios P VPAI 4083, H.C. Starck) coated ITO substrate with subsequent evaporation of a 100 nm thick layer of aluminum followed by annealing. The power conversion efficiency of the devices measured was 2.9 %, with a peak short-circuit external quantum efficiency of 65 % between 500 and 530 nm. The discrepancy in efficiency between our device and 4 % efficient devices commonly reported in the literature<sup>36</sup> lies in slightly suboptimal layer thicknesses reducing the photon absorption, as supported by optical transfer matrix simulation of our rather thin device. Our results are therefore also applicable to devices with the standard 4 % efficiency.

The pump–probe setup used for the transient absorption measurements has been described in great detail elsewhere.<sup>11</sup> In short, a commercial titanium:sapphire laser (Coherent

LIBRA HE) was used to pump a home-built noncollinear optical parametric amplifier for white light probe generation in the visible and near-infrared spectral range. As pump, either the output of an optical parametric amplifier (Coherent OPerA Solo) or an actively Q-switched Nd:YVO<sub>4</sub> laser (AOT Ltd. MOPA) was used. The delay between the pump and probe pulses for the two pump sources was realized by using a mechanical delay stage and an electronic delay generator, respectively. The measurements were performed in a home-built cryostat at room temperature and 77 K under dynamic vacuum at pressures < 10<sup>-5</sup> mbar.

Solar cell devices were first measured using a solar simulator (K.H. Steuernagel Lichttechnik GmbH, Germany) with a 80 mW cm<sup>-2</sup> AM1.5G illumination spectrum inside of a nitrogen-filled glovebox. Then, they were transferred to a temperature-controlled cryostat, where they were kept in dynamic vacuum at pressures < 10<sup>-5</sup> mbar. As an illumination source for the temperature-dependent measurements, a green LED (center wavelength 530 nm) was used. The intensity of the LED was tuned to reproduce the current–voltage characteristics as measured with the solar simulator inside of the glovebox at room temperature. For the intensity-dependent measurements, various neutral density filters were used to adjust the excitation.

Fully coupled optical and electronic simulations were performed using the commercial simulation software setfos 3 by Fluxim AG. For details, see ref 37. The model under study uses an ultrafast, temperature- and field-independent charge generation with an internal quantum efficiency (IQE) that is adjusted to match the IQE of the experimental devices at room temperature (~80 %). Recombination is assumed to be bimolecular, following the Langevin recombination formalism. Charge carrier mobilities at each temperature are set to 1.3 × 10<sup>-4</sup>, 1.3 × 10<sup>-5</sup>, 7.5 × 10<sup>-6</sup>, and 3.5 × 10<sup>-6</sup> cm<sup>2</sup>/(V s) for the temperatures of 294, 220, 160, and 80 K, respectively, and are assumed to be independent of the electric field or charge carrier density. The mobility of electrons and holes is assumed to be equal. While the neglect of the electric field dependence should not have a pronounced influence on the results,<sup>32</sup> the neglect of the carrier density dependence is likely a cause of slight error in the calculated current–voltage characteristics.<sup>27,38</sup> However, the calculated curves reproduce well the qualitative form of the data, even neglecting this second-order effect, and as the density dependence of the mobility affects both recombination and extraction, the influence of this omission is expected to be minor. The only parameters varied between the simulations are the temperature, which mainly influences the dark current via a thermionic injection model, and the charge carrier mobility. It should be noted that as the charge carrier mobility is well-known over a broad range of temperatures<sup>32</sup> and the temperatures are easily accessible during experiment, there is no completely free parameter contained in the model.

**SUPPORTING INFORMATION AVAILABLE** Dark current as a function of temperature, fluence dependence of transient absorption data, mobility and temperature dependence of simulated device characteristics, and approximation of maximum fill factor. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## REFERENCES

- Liang, Y.; Xu, Z.; Xia, J.; Tsai, S.-T.; Wu, Y.; Li, G.; Ray, C.; Yu, L. *Adv. Mater.* **2010**, *22*, E135.
- Dennler, G.; Scharber, M. C.; Brabec, C. J. *Adv. Mater.* **2009**, *21*, 1323.
- Mihailetchi, V. D.; Koster, L. J. A.; Hummelen, J. C.; Blom, P. W. M. *Phys. Rev. Lett.* **2004**, *93*, 216601.
- De, S.; Pascher, T.; Maiti, M.; Jespersen, K. G.; Kesti, T.; Zhang, F. L.; Inganas, O.; Yartsev, A.; Sundstrom, V. *J. Am. Chem. Soc.* **2007**, *129*, 8466.
- Marsh, R. A.; McNeill, C. R.; Abrusci, A.; Campbell, A. R.; Friend, R. H. *Nano Lett.* **2008**, *8*, 1393.
- Marsh, R. A.; Hodgkiss, J. M.; Friend, R. H. *Adv. Mater.* **2010**, *22*, 3672.
- Veldman, D.; Ipek, O.; Meskers, S. C. J.; Sweelssen, J.; Koetse, M. M.; Veenstra, S. C.; Kroon, J. M.; van Bavel, S. S.; Loos, J.; Janssen, R. A. J. *J. Am. Chem. Soc.* **2008**, *130*, 7721.
- Braun, C. L. *J. Chem. Phys.* **1984**, *80*, 4157.
- Wojcik, M.; Michalak, P.; Tachiya, M. *Appl. Phys. Lett.* **2010**, *96*, 162102.
- Guo, J. M.; Ohkita, H.; Benten, H.; Ito, S. *J. Am. Chem. Soc.* **2010**, *132*, 6154.
- Howard, I. A.; Mauer, R.; Meister, M.; Laquai, F. *J. Am. Chem. Soc.* **2010**, *132*, 14866.
- Pensack, R. D.; Asbury, J. B. *J. Phys. Chem. Lett.* **2010**, *1*, 2255.
- Inal, S.; Schubert, M.; Sellinger, A.; Neher, D. *J. Phys. Chem. Lett.* **2010**, *1*, 982.
- Street, R. A.; Cowan, S.; Heeger, A. J. *Phys. Rev. B* **2010**, *82*, 121301.
- Hamilton, R.; Shuttle, C. G.; O'Regan, B.; Hammant, T. C.; Nelson, J.; Durrant, J. R. *J. Phys. Chem. Lett.* **2010**, *1*, 1432.
- These measurements also suggest that nongeminate recombination dominates recombination on the time scales shown to have a field dependence in ref 6.
- Shuttle, C. G.; O'Regan, B.; Ballantyne, A. M.; Nelson, J.; Bradley, D. D. C.; Durrant, J. R. *Phys. Rev. B* **2008**, *78*, 113201.
- Maurano, A.; Hamilton, R.; Shuttle, C. G.; Ballantyne, A. M.; Nelson, J.; O'Regan, B.; Zhang, W.; McCulloch, I.; Azimi, H.; Morana, M.; Brabec, C. J.; Durrant, J. R. *Adv. Mater.* **2010**, *22*, 4987–4992.
- Scott, J. C.; Malliaras, G. G. *Chem. Phys. Lett.* **1999**, *299*, 115.
- Shen, Y. L.; Klein, M. W.; Jacobs, D. B.; Scott, J. C.; Malliaras, G. G. *Phys. Rev. Lett.* **2001**, *86*, 3867.
- Shuttle, C. G.; Maurano, A.; Hamilton, R.; O'Regan, B.; de Mello, J. C.; Durrant, J. R. *Appl. Phys. Lett.* **2008**, *93*, 3.
- Vandewal, K.; Tvingstedt, K.; Gadisa, A.; Inganas, O.; Manca, J. V. *Phys. Rev. B* **2010**, *81*, 125204.
- We note that monomolecular nongeminate kinetics can be caused by interface trap recombination. Our results at low temperature show that a density-dependent nongeminate recombination mechanism occurs in our devices, and we therefore approximate that all nongeminate recombination occurs between mobile charges.
- A change in separation yield caused by space-charge effects reducing the efficiency of charge separation is ruled out by the almost quantitative yield of separated charges at zero field observed in the transient absorption experiments.
- Howard, I. A.; Hodgkiss, J. M.; Zhang, X.; Kirov, K. R.; Bronstein, H. A.; Williams, C. K.; Friend, R. H.; Westenhoff, S.; Greenham, N. C. *J. Am. Chem. Soc.* **2009**, *132*, 328.
- Keivanidis, P. E.; Clarke, T. M.; Lilliu, S.; Agostinelli, T.; Macdonald, J. E.; Durrant, J. R.; Bradley, D. D. C.; Nelson, J. *J. Phys. Chem. Lett.* **2010**, *1*, 734.
- Shuttle, C. G.; Hamilton, R.; Nelson, J.; O'Regan, B. C.; Durrant, J. R. *Adv. Funct. Mater.* **2010**, *20*, 698.
- Clarke, T. M.; Jamieson, F. C.; Durrant, J. R. *J. Phys. Chem. C* **2009**, *113*, 20934.
- Shuttle, C. G.; O'Regan, B.; Ballantyne, A. M.; Nelson, J.; Bradley, D. D. C.; de Mello, J.; Durrant, J. R. *Appl. Phys. Lett.* **2008**, *92*, 093311.
- Nelson, J.; Choulis, S. A.; Durrant, J. R. *Thin Solid Films* **2004**, *451–452*, 508.
- Pasveer, W. F.; Cottaar, J.; Tanase, C.; Coehoorn, R.; Bobbert, P. A.; Blom, P. W. M.; de Leeuw, D. M.; Michels, M. A. J. *Phys. Rev. Lett.* **2005**, *94*, 206601.
- Mauer, R.; Kastler, M.; Laquai, F. *Adv. Funct. Mater.* **2010**, *20*, 2085.
- Burkhard, G. F.; Hoke, E. T.; Scully, S. R.; McGehee, M. D. *Nano Lett.* **2009**, *9*, 4037.
- Street, R. A. *Phys. Rev. B* **2010**, *82*, 207302.
- Deibel, C.; Strobel, T.; Dyakonov, V. *Adv. Mater.* **2010**, *22*, 4097.
- Li, G.; Shrotriya, V.; Huang, J.; Yao, Y.; Moriarty, T.; Emery, K.; Yang, Y. *Nat. Mater.* **2005**, *4*, 864.
- Hausermann, R.; Knapp, E.; Moos, M.; Reinke, N. A.; Flatz, T.; Ruhstaller, B. *J. Appl. Phys.* **2009**, *106*, 104507.
- Eng, M. P.; Barnes, P. R. F.; Durrant, J. R. *J. Phys. Chem. Lett.* **2010**, *1*, 3096.