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Charge recombination in a poly(para-phenylene vinylene)-fullerene derivative composite film studied by transient, nonresonant, hole-burning spectroscopy

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Transient, nonresonant, hole-burning spectroscopy has been used to study the charge recombination process in poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1-4-phenylene vinylene] (MDMO-PPV): methanofullerene (PCBM) composite films. The position and intensity of the spectral hole in the absorption band of MDMO-PPV have been monitored as a function of time in the 10 ns–10 μs time range. A time-dependent redshift is observed. The intensity of the spectral hole decays with time according to a power law ($\propto t^{-\alpha}$). The exponent $\alpha \approx 0.5$ is found to be nearly independent of the excitation fluence in the range 0.05–2 mJ/cm^2. The depth of the spectral hole depends sublinearly on the excitation fluence (I) and can be described by ($\propto \Gamma^{-\beta}$) with $\beta \sim 0.5$. The time-dependent redshift and the power-law type time decay can be reproduced by numerical simulations. The Monte Carlo method is used to simulate the hopping dynamics of the photoinduced charges in a lattice of energetically disordered sites before they eventually recombine at the MDMO-PPV:PCBM interface. The results indicate that charge separation is assisted by disorder and that, in the 10 ns–10 μs time range, the recombination rate is limited by the detrapping of the cationic charge carriers in MDMO-PPV. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1619946]

I. INTRODUCTION

Following the discovery of photoinduced charge separation between conjugated polymers and fullerene C_{60} (Ref. 1) there has been a large research effort aimed at construction of polymer–fullerene photovoltaic devices.[2] Energy conversion efficiencies of 2.5% in simulated solar light have been obtained by sandwiching a strongly absorbing electron donating conjugated polymer (MDMO-PPV, Fig. 1) and an electron accepting fullerene derivative (PCBM, Fig. 1) into a single bulk heterojunction layer between two electrodes with different work function (usually aluminum and doped indium tin oxide) for charge collection.[3,4] These bulk heterojunctions are spontaneously formed when the two materials are spin cast from a common solution under appropriate conditions. In the active layer, phase separation into bi-continuous fullerene and polymer rich phases occurs with a typical length scale of 50–100 nm. Photogeneration of charge carriers in MDMO-PPV:PCBM blends occurs with a time constant of 45 fs[5] and a quantum yield near unity.

Organic molecular materials are characterized by low values for the relative dielectric constant ϵ_r (typically $\epsilon_r = 3$ to 4). Due to this fact, one expects tight binding between photogenerated electrons and holes. Calculations of the Onsager radius yield values of typically ~15 nm at room temperature (~70 nm at 80 K),[6] i.e., much larger than the molecular dimensions. Based on these considerations, one may expect that the main product of a photoinduced electron transfer reaction in a blend of electron donating and accepting molecular materials is a Coulombically bound electron–hole pair at the interface of the two materials. The energy needed for separation of such pairs is expected to be a few tenths of an electron volt and, hence, considerably larger than kT. Still, measurements of the internal quantum yield of collected charges in a photovoltaic device show high yields (estimated $>85\%$).[2,3,7] A number of papers have dealt with this problem of generation of free charge carriers in organic materials.[8] In an alternative view, the exciton binding energy for the conjugated polymer is estimated to be very low (~0.1 eV) and nearly free charge carriers (positive and negative polarons) on the polymer chains are viewed as primary excitations.[9] The photocarrier quantum efficiency in pure MEH-PPV was estimated at 0.1 in zero applied field,[10] while upon addition of fullerene the yield for carrier generation involving electron transfer to the C_{60} approaches unity.[11]

Here we apply hole-burning spectroscopy to study the dynamical behavior of photogenerated charge carriers in MDMO-PPV:PCBM blends as used in organic solar cells. Transient, nonresonant, hole burning can be applied to conjugated polymers provided that a long-lived ‘‘bottle-neck’’ state is accessible.[12] Here the charge-separated state plays this role.[13] Hole-burning spectroscopy allows for investigation of the dynamical behavior of cationic charge carriers in blends by monitoring the properties of the associated spectral hole in the MDMO-PPV absorption band.

II. EXPERIMENT

Thin films of the MDMO-PPV:PCBM (1:4 w/w) composite material were obtained by spin coating from chlorobenzene solution on a glass substrate. For a film of 170 nm the optical density at 2.76 eV was 0.5.

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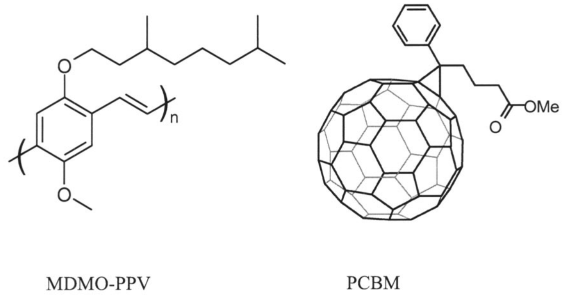

FIG. 1. Compounds used: MDMO-PPV (poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylene vinylene]) and PCBM (1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C_{61}).

Transient hole burning spectra were recorded by exciting the sample with pulses of 2.76 eV photons (pulse width 4 ns, repetition rate 10 Hz) obtained from an optical parametric oscillator, pumped by the third harmonic of a Nd-YAG laser. The excited area was 1.8 mm^2 and the sample was held at 80 K in a vacuum cryostat. An intensified CCD camera was used to record the transmission of a tungsten–halogen probe light through the sample after dispersion by a spectrograph. The signal acquisition by the camera was electronically gated. To obtain differential transmission spectra, the probe light was recorded at the delay time of interest and then the reference transmission at a 25 ms delay. For small acquisition delays, the transmission spectra were corrected for a very small residual fluorescence.

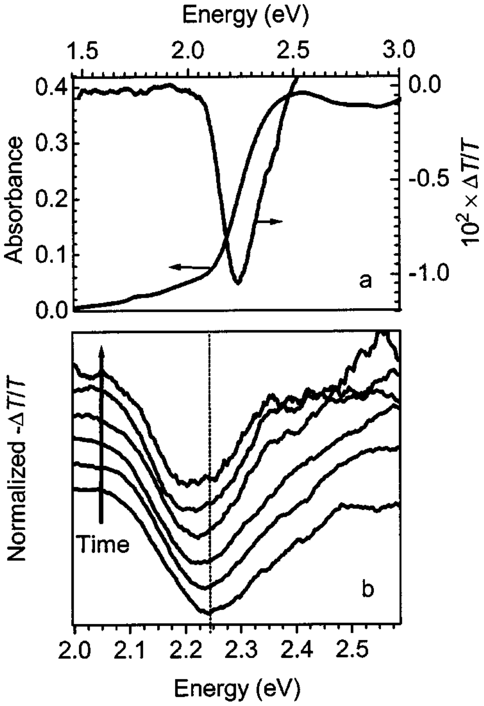

FIG. 2. (a) Absorption spectrum and spectral holes (excitation at 2.76 eV, acquisition delay 33 ns, gate width 10 ns, $T = 80$ K) of a MDMO-PPV:PCBM blend. (b) Time dependence of spectral holes. Spectra were recorded at delay time/gate width combinations of: 10 ns/2 ns; 33 ns/10 ns; 233 ns/30 ns; 1 μs/100 ns, 3 μs/300 ns; and 10 μs/300 ns. Spectra were recorded with excitation at 2.76 eV (fluence 2.0 mJ/cm^2) at $T = 80$ K and are shifted upward in successive steps for clarity.

III. RESULTS AND DISCUSSION

Figure 2(a) shows the absorption spectrum of the MDMO-PPV:PCBM (1:4 w/w) composite film, featuring the lowest energy absorption band of the PPV polymer at around 2.5 eV. Figure 2(a) also shows the nonresonant spectral hole induced by excitation at 2.76 eV photon energy with pulses of 4 ns temporal width from our laser setup. As can be seen from Fig. 2(a), the position of the spectral hole has shifted by about 0.5 eV from the excitation energy. Furthermore, the width of the hole is considerably smaller than the width of the absorption band of MDMO-PPV. This illustrates the inhomogeneous broadening of the polymer band and is consistent with charge transport[14,15] and time-resolved photoluminescence[16,17] studies on PPV polymers. These measurements have provided strong evidence for a disorder model in which quasiparticles such as charge carriers or neutral photoexcitations are localized on chain segments, separated by defects in the polymer structure. The statistical distribution of the length of the segments resulting from the random position of the defects along the chain gives rise to dispersion in the energy of the states available to the particles. The density of states distribution is usually approximated by a Gaussian curve. In the disorder model, the particles move between the chain segments by a hopping type motion. For the data shown in Fig. 2(a), the shift of the hole away from the excitation photon energy can be due several factors. We name relaxation of the initial excitations by intrachain vibrational relaxation and intersegment energy transfer hopping. In addition, migration of the cationic charge carrier (h^+) to chain segments with longer conjugation length can also contribute. From studies on oligomer model compounds it is known that the ionization energy of PV oligomers decreases with increasing conjugation length.[18] Also the energy of the first singlet-excited state decreases with increasing oligomer length,[19] leading to a redshift of the lowest energy absorption band with increasing conjugation length. Explanation in terms of the dynamic Burstein–Moss shift[20] seems unlikely as no changes in hole position could be measured as a function of excitation density.

Figure 2(b) shows the temporal evolution of the spectral holes. A time-dependent redshift of the hole is observed in the ns–ms time window. This can be due to migration of the cationic charge carriers to chain segments of MDMO-PPV with longer conjugation length as explained earlier. An alternative explanation is that recombination, and hence, the lifetime of the charge-separated state, depends on the ionization energy of the chain segment (in its neutral state) occupied by the cationic charge carrier. To explain the experimental observation one then has to assume a slower recombination rate for chain segments with longer effective conjugation length.

To gain more insight into these matters, we have performed numerical simulations of the geminate charge recombination process using a hopping model with energetic disorder and a Gaussian density of states distribution.[14,21] We have included the electrostatic interaction between the geminate charge carriers. In this model, the MDMO-PPV phase is represented by a cubic lattice of 15×15×15 sites with 10 Å lattice constant. The width of the Gaussian distribution of

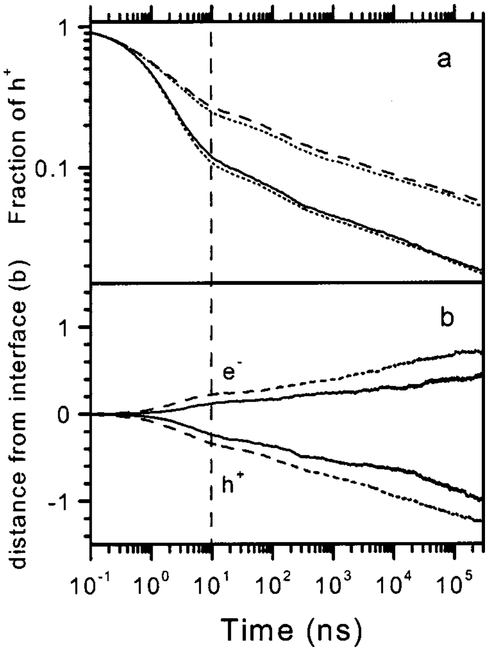

FIG. 3. MC simulations of electron (e^-) and hole (h^+) recombination at the donor:acceptor (MDMO-PPV:PCBM) interface. (a) Fraction of charges that escape recombination. Solid lines correspond to an initial site energy of $E_{\mathrm{start}}=0$ eV, dashed lines to an initial site energy of $E_{\mathrm{start}}=60$ meV for both types of charge carriers. The dotted lines represent a simulations starting with four charge pairs instead of one. (b) Distance of hole (h^+) and electron (e^-) from the interface in units of the lattice constant $b=1$ nm.

states can be obtained from charge transport measurements and from experimental data on pristine MDMO-PPV, $\sigma_{\mathrm{PPV}} \cong 120$ meV has been reported.[22] The PCBM phase is represented by a similar cubic lattice, adjoining the MDMO-PPV. Also for PCBM the width of the Gaussian DOS has been evaluated from transport measurements yielding $\sigma_{\mathrm{PCBM}} = 70$ meV.[23] This value is smaller than for MDMO-PPV, which may reflect the high purity of the material and the limited conformational freedom for chemical bonds involved in the π electron system. At the start of the simulation, a pair of charge carriers is placed at the MDMO-PPV:PCBM interface on opposing lattice positions. The energy of the initially occupied site (E_{start}) is taken as an adjustable parameter. Recombination is allowed only when carriers are directly at the interface on opposing lattice positions. Probabilities for the hopping rates were calculated according to the well-known Miller–Abrahams expression:

$$\nu(r_{ij},\Delta E_{ij},T) = \begin{cases} \nu_0 \exp(-2\gamma r_{ij})\exp(-\Delta E_{ij}/k_B T) & \text{for } \Delta E_{ij}>0 \\ \nu_0 \exp(-2\gamma r_{ij}) & \text{for } \Delta E_{ij}<0\,. \end{cases} \tag{1}$$

In the simulations the following values for the parameters were used: $\nu_0 = 10\,\mathrm{ps}^{-1}$, $\gamma=0.5$ Å^{-1}, and $T=80$ K. Other parameters used are the rate for charge recombination $k_{\mathrm{rec}} = 1.0\,\mathrm{ns}^{-1}$ and the relative dielectric constant of $\epsilon_r=4$. At the interface, the minimal distance between electron and hole is 1 nm. In the simulations we performed we choose to take energy associated with the initial site of the carriers (E_{start}) as an adjustable parameter. The site energy $E=0$ is defined as the center of the Gaussian distribution for both types of carriers.

Typical results of the Monte Carlo (MC) simulations are illustrated in Figs. 3 and 4. In Fig. 3(a) the fraction of charge carriers surviving the (geminate) recombination is shown versus time for two different values of E_{start}. As can be seen a considerable number of recombination events take place at 1 ns and these events can be assigned to recombination of the original charge pair before migration of the carriers away from the interface occurs. A number of carriers survive for a considerable time by hopping away from the interface to a site in the bulk with low site energy. This can be seen in Fig. 3(b) where the average distance of both negatively (e^-) and positively charged carrier (h^+) to the interface are plotted as a function of time. As can be seen, the carriers remain relatively close to the interface and do not escape from their mutual Coulomb attraction. Curiously, the h^+ moves further away from the interface than the e^-, even though the h^+ is expected to be the lowest (bulk) mobility. This can be interpreted as follows: Due to the stronger energetic disorder in MDMO-PPV, the difference in energy between a site at the interface and a neighboring site closer to the bulk can reach more negative values for the MDMO-PPV lattice than for the PCBM grid. The energy gained by jumping of h^+ to a lattice site with lower energy can be used to overcome the Coulomb attraction. As the energetic disorder of the PPV lattice is higher, the probability for the presence of a site slightly away from the interface with sufficiently low energy to compensate for the loss of electrostatic potential energy, is higher for the h^+ than for the e^-. Thus one may expect that, initially,

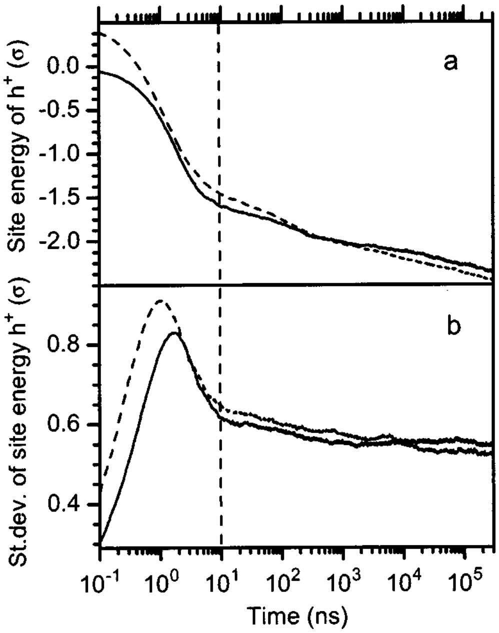

FIG. 4. MC simulations of electron and a hole (h^+) of recombination at the donor:acceptor (MDMO-PPV:PCBM) interface. Solid lines correspond to an initial site energy of $E_{\mathrm{start}}=0$ eV, dashed lines to an initial site energy of $E_{\mathrm{start}}=60$ meV for both types of charge carriers. (a) Energy of the site on which the h^+ resides, expressed in units $\sigma=120$ meV, the standard deviation of the Gaussian density of states for the PPV segments. (b) Standard deviation of the h^+ site energy.

the h^+ can jump away from the interface more easily than the e^-.

In the limit of low temperature and vanishing disorder for the PCBM phase, one could envision the e^- as sort of "image charge" of the h^+. It will be trapped at the interface by the Coulombic attraction, but should be able to "follow" motion of the h^+ in the x, y plane. Once the Coulombic attraction was lowered by diffusion of the h^+ away from the interface, it may be possible for the e^- to escape from the potential well. Once escaped, the e^- can travel over larger distance than h^+ in a certain time interval, due to its higher mobility.

In Fig. 4(a) we have listed the energy of the site on which the h^+ in the PPV phase resides. From the results, it follows that the long-lived charge carriers occupy a low-energy site, which must have been reached by hopping. Apparently, the driving force to jump away from the interface, opposing the Coulomb attraction is the energetic disorder; a number h^+ can jump to a low energy site further away from the interface. Since the width of the Gaussian distribution of the energy of the sites is broader for h^+ than for e^-, it follows that cationic carriers can gain more energy by jumping away from the interface, which gives them more freedom to move in the potential well built up by the Coulomb attraction.

Once the carriers have jumped away from the interface to a low-energy site and have become trapped, the mobility of the charge carrier is strongly reduced and recombination with the opposite charge at the interface now requires thermal activation. Charges at deep traps have the lowest chance per unit time to be detrapped, and therefore these carriers are the more persistent species. When increasing E_{start}, the probability to jump away from the interface is increased and the yield of long-lived charge carriers is enhanced. Interestingly, for the decay of the number of charges with time t, the simulations predict an algebraic law $\propto (1/t)^{\alpha}$ with $\alpha = 0.17$ (when $E_{\text{start}} = 0$). Algebraic behavior has also been predicted for bulk recombination[24] and seems therefore not exclusively related to the presence of the interface but rather to the dispersive nature of the carrier transport.

The numerical results shown in Fig. 4(a) show that the average energy of the sites occupied by the hole decreases with time. This is consistent with the experimentally observed redshift of the spectral hole. Figure 4(b) exhibits the standard deviation of the energy of the states occupied by the h^+ as function of time. At short times, all h^+ occupy the initial site with E_{start} and hence the standard deviation is zero. During the first hopping events, the deviation increases rapidly as the carriers jump to sites that are widely distributed in energy. Curiously, at longer time delays the standard deviation reduces again. Such a time-dependent narrowing has also been observed for the relaxation of neutral photoexcitations in conjugated polymers[25] and can be understood in terms of nonequilibrium dynamics. If quasiparticles with an energy above the average of the ensemble have a faster rate of relaxation or disappearance than the particles with lower energy, such a time-dependent narrowing has to occur. The experimental data show evidence for the occurrence of the dynamical narrowing.

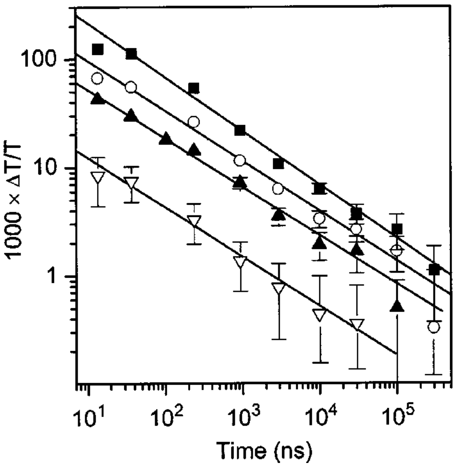

FIG. 5. Decay of the depth of the spectral hole in MDMO-PPV:PCBM as a function of time. Excitation 2.76 eV, pump fluences: (■) ~2 mJ/cm^2; (○) ~1 mJ/cm^2; (▲) ~0.5 mJ/cm^2; and (▽): ~0.05 mJ/cm^2. Solid lines represent fits of $\Delta T \propto (1/t)^{\alpha}$ to the data with (■) $\alpha = 0.50 \pm 0.01$; (○) $\alpha = 0.46 \pm 0.02$; (▲) $\alpha = 0.45 \pm 0.03$; and (▽) $\alpha = 0.46 \pm 0.16$.

As mentioned earlier, the simulations predict an algebraic decay for the number of charges with time. To verify this prediction we have measured the depth of the spectral hole as a function of time. The results are illustrated in Fig. 4 and reveal an algebraic $\propto (1/t)^{\alpha}$ decay, with $\alpha = 0.45$–0.50. The exponent α predicted by the simulations is, however, two to three times smaller than the experimentally observed value and at present we cannot account in detail for this discrepancy. The experimental power-law decay is in agreement with other recent studies of charge recombination, where specific absorption bands of the charge carriers were monitored.[26–29]

Figure 5 also shows the experimental pump fluence dependence of the decay process. Curiously, there is only a limited influence of effect of the pump intensity on the decay. At all fluences investigated (2–0.05 mJ/cm^2), power-law decay is observed. For the highest fluence used, a slightly higher value for the exponent α of the power-law decay is obtained, but the increment is within experimental uncertainty.

The absence of a significant dependence of the decay rate on excitation fluence could be interpreted as an indication that the recombination involves only geminate pairs. Clearly, when recombination occurs exclusively with the geminate carrier of opposite charge, the decay profile will be independent of the excitation density. Conversely for free charge carriers, recombination will be nongeminate in nature and is expected to depend strongly on excitation density. In the case of geminate recombination one expects a linear dependence of the carrier density on the excitation fluence. The latter prediction holds of course as long as no exciton–exciton or exciton–charge[30] annihilation processes become operative.

In Fig. 6, we illustrate the dependence of the intensity of the spectral hole on excitation fluence for several time intervals of detection after the excitation pulse. The data show a sublinear dependence of the photoinduced absorption signal on the excitation fluence. This observation is not consistent

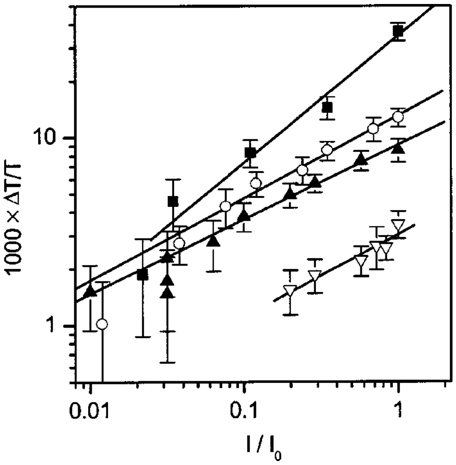

FIG. 6. Fluence dependence of the spectral hole depth. Excitation 2.76 eV, $T=80$ K, $I_0\approx 1$ mJ/cm^2. Data were recorded at delay time/gate width combinations of (■) 33 ns/50 ns; (○) 183 ns/250 ns; (▲) 933 ns/300 ns; (▽) 2933 ns/620 ns. Dashed lines represent a fit of $\Delta T \propto (I/I_0)^\beta$ to the data with: (■) $\beta=0.67\pm0.08$; (○) $\beta=0.44\pm0.06$; (▲) $\beta=0.40\pm0.06$; and (▽) $\beta=0.44\pm0.2$.

with only geminate recombination. Incidentally, we mention that our observations summarized in Fig. 6 differ from those reported by Montanari *et al.*, who observe that the density of photogenerated charge carriers saturates for excitation densities >1 μJ/cm^2 and times >20 ns after excitation at room temperature.

The sublinear dependence of the hole intensity on the excitation fluence can be explained in several ways and we mention the possibility of limitation by trap filling.[31] Before being trapped charges might recombine in either a geminate or nongeminate fashion and the limited number of trap sites will give rise to a sublinear dependence of the number of long-lived charge carriers on the initial carrier density.

Once the charges are trapped, the recombination rate may be controlled by several processes. We name the rate of release from the trap and the rate at which encounters with charge carriers of opposite sign occur at the interface.

To investigate these options further we have again resorted to MC simulations. In Fig. 3(a), we compare the outcome of simulations starting with just one charge pair with simulation starting with four charge pairs. In the latter case the initial positions of the charge pairs was on a horizontal line with just one empty lattice position between like charges. To assess the effect of nongeminate recombination, the carriers were allowed to recombine with all other carriers of opposite sign when at the interface and on opposing lattice positions. The simulations were performed for the same start energies as those with only one charge pair. The results show that in the time range from 10 ns onward, the percentage of surviving holes is smaller for the simulation with four charge pairs when compared to the data for just one charge pair. This means that the density of long-lived carriers depends sublinearly on the initial density of carriers. Qualitatively, this prediction is in agreement with the experimentally observed, $(I/I_0)^{0.5}$ dependence indicating that the disorder model can in principle account for a nonlinear fluence dependence.

Assuming that the microphase separation of the PCBM and the MDMO-PPV takes place with a characteristic length scale of ~100 nm, the internal MDMO-PPV:PCBM surface area can be estimated at 10^6 cm^2/cm^3. Furthermore assuming that all absorbed photons lead to generation of a charge directly at the interface and neglecting recombination events, the distance between two photoinduced charge carriers generated by pulsed illumination of a 100-nm-thick film with ~1 mJ/cm^2 of 2.75 eV photons can be estimated at a few nanometers. Therefore it may be anticipated that under our experimental conditions a significant number of sites at the interface will be occupied after illumination. It seems possible that in the present simulations the number density of charge carriers at the interface is not taken high enough to fully bear out the effect of nongeminate carrier–carrier interactions. Further simulations of multiparticle hopping processes are in preparation. Looking at Fig. 3(a), it appears that the decay of the number of charge carriers for $t>100$ ns is rather insensitive to their initial number density. This observation also holds for simulation at higher temperatures where the yield rate long-lived carriers is higher. Therefore, we favor the interpretation that the recombination in this time window is limited by the rate of release of h^+ from the traps in the MDMO-PPV phase of the mixture. In this case the rate-determining step in the recombination process is a simple mono-molecular reaction, it is expected to be independent of the excitation density.

IV. CONCLUSIONS

By transient, nonresonant, hole-burning spectroscopy it can be shown that recombination of photogenerated charges in the 10 ns–10 μs time range in MDMO-PPV:PCBM blends follows a power law decay with time ($t^{-\alpha}$, with $\alpha=0.45$–0.50). According to MC simulations this behavior is consistent with a hopping model of photogenerated positive and negative charges in energetically disordered Gaussian distributed density of states of donor and acceptor phases, eventually followed by recombination at their interface. In the 10 ns–10 μs time range, the number of charges present depends sublinearly on the excitation fluence. Surprisingly, the power-law exponent α is not affected by the fluence. MC simulations show that this behavior can be rationalized when the recombination is limited by the detrapping of the holes in MDMO-PPV.

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