Traps and trions as origin of magnetoresistance in organic semiconductors

M. Cox, P. Janssen, F. Zhu, and B. Koopmans
Department of Applied Physics, Center for NanoMaterials and COBRA Research Institute, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands
(Received 11 October 2012; published 2 July 2013)

The large effect of a small magnetic field on the current, magnetoconductance (MC), in organic semiconductors—so-called organic magnetoresistance—has puzzled the field of organic spintronics during the last decade. Although the microscopic mechanisms regarding spin mixing are well understood by now, it is still unknown which pairs of spin carrying particles are influencing the current in such a drastic manner. Here, a model for the MC is presented based on the spin selective formation of metastable trions from triplet exciton-polaron pairs. Additionally, the magnetic-field and voltage dependence of the MC are experimentally investigated in materials showing large effects. Using a combination of analytical and numerical calculations, it is shown that the MC is perfectly described by a process in which trions are created at polaron trap sites.

DOI: 10.1103/PhysRevB.88.035202 PACS number(s): 72.80.Le, 75.47.Pq, 85.30.De

I. INTRODUCTION

Large room-temperature magnetoresistance effects dubbed organic magnetoresistance (OMAR) have been found in many organic semiconductor devices during the last decade.[1–9] All contemporary models explaining OMAR rely on magnetic-field dependent reactions of the spin carrying particles. One competing model proposes reactions between polaronic electron and hole pairs,[2] whereas another relies on the reaction between triplet excitons and (trapped) polarons.[3,4] Conversely, the reactions of equal charges are described by a third (bipolaron) model.[5] These models have been used to explain low-field effects (LFEs), which are visible on a relatively small field scale of a few mT, as well as high-field effects (HFEs) on much broader field scales. However, there is still no consensus on which exact mechanism dominates OMAR under which conditions in devices.

The suggested models are all based on mixing of the spin states of pairs of excitations prior to the formation of subsequent (quasi)particles from these pairs. It has been demonstrated that hyperfine fields are involved in the spin mixing.[9] However, there is still on-going debate as to whether spin-orbit coupling might play a role in certain materials.[10] Regardless of the exact underlying nature, an external magnetic field suppresses this mixing and can consequently adjust the spin ratio of the subsequent particles. In the case of polaronic electron-hole pairs this results in an increased fraction of singlet (S) excitons compared to triplet (T) excitons, if the formation of triplet excitons from the polaronic pairs is faster than for singlets. This has been used to successfully simulate magnetic-field effects in the electroluminescence of organic semiconductors using a density-matrix approach.[11] A similar theoretical framework has been applied to account for other microscopic mechanisms and their effect on the magnetic-field dependent current, i.e., magnetoconductance (MC).[12]

In recent work[13] we have shown that the dominant mechanism for OMAR in a real device depends on the operating conditions and morphology. Inspired by pioneering work from Wang *et al.*,[8] we blended a polymer and a fullerene and showed that the MC and the underlying spin-based reactions could be tuned. We also integrated microscopic mechanisms into numerical device simulations in order to calculate and understand the experimental voltage dependence of the MC. However, no quantitative analysis of the reactions between triplet excitons and polarons was readily available for incorporation in a device model. Nevertheless, our experimental results did strongly suggest that a triplet-polaron interaction is the dominant MC mechanism of the pure polymer devices. Using magnetic-resonance techniques Baker *et al.* have also come to a similar conclusion.[14] This provided a strong motivation to extend the investigation of spin-based triplet exciton-polaron reactions, as we do in the present manuscript.

The reactions of triplet excitons and polarons have been studied extensively in the past.[15–20] The effect of a magnetic field on these reactions was already considered by Ern and Merrifield in molecular crystals.[15] Desai *et al.*[3] were the first to qualitatively describe how this can give rise to large room-temperature MC in disordered organic semiconductors. The authors consider the triplet excitons to momentarily capture polarons in states they recently referred to as charged excitons,[21] thereby reducing the polaron transport. Since the formation of triplet excitons as well as their reactions with polarons[12,15] can be considered magnetic-field dependent,[11,22] a change in current can be explained.

Charged excitons are generally not considered to live very long[16,21] and their actual impact on the current is thus debatable. However, Kadashchuk *et al.*[23] have recently shown that charged excitons can be metastable if they are created at a polaron trap site, and in this form they refer to them as trions. A trion can have a lifetime on the order of milliseconds, after which it releases the polaron again via a dissociation or recombination process. Because trions are immobile and long living, they can hinder the transport of polarons through an organic semiconductor significantly. Therefore, we conjecture that trions are at the origin of organic magnetoresistance.

As stated before, previous work on magnetic-field effects has investigated the trapping of polarons on triplet excitons.[3,21] Additionally, the magnetic-field dependent quenching of triplet excitons at trapped charges has been considered, which can lead to the release of these charges.[15,24] The trapping of triplet excitons themselves, which can then lead to the formation of metastable trions,[23] has as far as we know not been investigated with respect to magnetic-field effects.

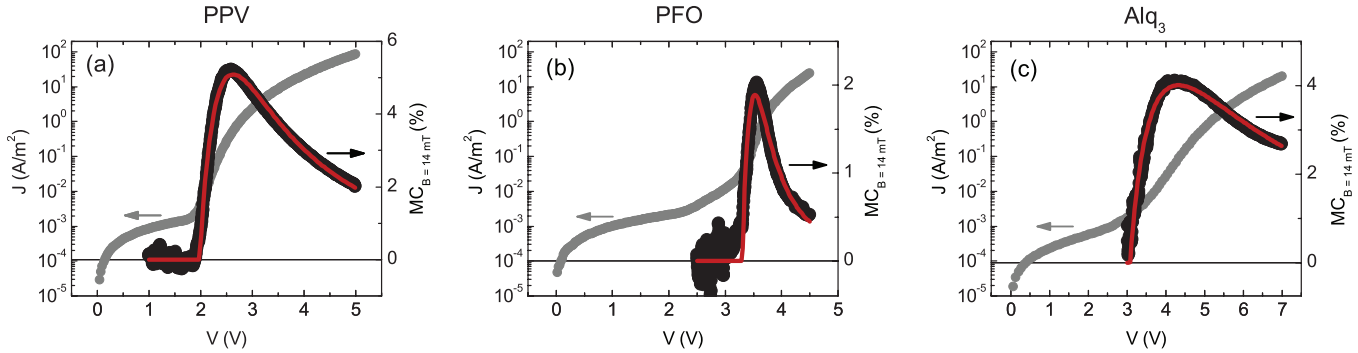

FIG. 1. (Color online) (a–c) The current density J and the magnetic-field effect on the current (MC) as a function of bias voltage V for (a) PPV, (b) PFO, and (c) Alq_3. The MC is measured at a fixed magnetic field of $B = 14$ mT. The solid red line is a fit with the analytical function derived in the text.

Additionally, accurate voltage dependent calculations of the MC have never been performed for such mechanisms.

In the remainder of this manuscript we experimentally investigate the MC of several materials exhibiting large room-temperature effects and we show that the MC in these materials can indeed be explained with a model based on the formation of trions from triplet exciton-polaron reactions at trap sites. Solving a set of elementary rate equations describing the relevant reactions, we derive an elegant analytical expression which fits the experimental voltage dependence of the MC perfectly. This voltage dependence is also supported by numerical device calculations. Furthermore, we show that the trap sites—and more specifically which particles occupy them—are imperative for understanding the observed nonmonotonic trend of the MC as a function of voltage.

II. EXPERIMENTAL RESULTS

All our experiments were performed on devices with a typical organic light emitting diode (OLED) structure. We have chosen three different materials that are known to exhibit large MC:[7,25] the polymer superyellow poly(p-phenylene vinylene) (PPV), the polymer poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO), and the small molecule tris(8-hydroxyquinoline)aluminium (Alq_3). The devices are fabricated on patterned indium tin oxide glass substrates, on which poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) was spincoated (40 nm). PPV was dispersed in chlorobenzene and PFO was dispersed in toluene, and both were spincoated on substrates (90 nm). Alq_3 (100 nm) was thermally evaporated onto substrates in a high-vacuum system inside a nitrogen filled glovebox. After this a top electrode consisting of LiF (1 nm) and Al (100 nm) was thermally evaporated onto all samples in another vacuum system inside the same glovebox. All devices (active area 3×3 mm) were then transported inside a nitrogen environment to another glovebox, where they were electrically and magnetically characterized. A Keithley 2400 source meter is used to set a bias voltage V and measure the current density J.

The J-V characteristics of the three different devices are shown in Fig. 1 together with MC(V) curves at a fixed magnetic field of $B = 14$ mT. The MC(V) curves are measured using a method where a fixed magnet is rotated over the sample while sweeping the bias voltage.[26] At low voltages we always observe an Ohmic leakage current, which does not exhibit any observable MC. Due to the built-in voltage caused by the different work function of the electrodes, the devices act like a diode and suddenly turn on after a certain voltage. This turn on voltage also seems to correspond with the observation of a finite MC. Figure 1 also show the results of the low-field analytical MC(V) fit function that we will derive from in the remainder of this manuscript. At high voltages and correspondingly large current densities, all devices suffer from severe degradation and/or significant conditioning of the MC,[7] which is why this region is not investigated.

We have also investigated the MC as a function of applied magnetic field B. Inside the same glovebox the samples can be placed between the poles of two electromagnets. This allows us to measure the current while sweeping the magnetic field. The magnetic-field dependence of the current density $J(B)$ is then calculated with $\mathrm{MC}(B) = [J(B) - J(0)]/J(0)$. In order to separate the LFE and HFE, we fit the resulting MC with the sum of two empirical "non-Lorentzian" fitting functions: $\mathrm{MC}(B) = a_{\mathrm{LFE}}B^2/(|B| + B_{\mathrm{LFE}})^2 + a_{\mathrm{HFE}}B^2/(|B| + B_{\mathrm{HFE}})^2$, which incorporates the amplitudes a_{LFE} and a_{HFE} and widths B_{LFE} and B_{HFE} for the LFE and HFE, respectively. For each specific material the widths are taken independent of the bias voltage, allowing us to focus on the V dependency of the amplitude of the magnetic-field effects. In the past, these non-Lorentzian functions have been found to accurately describe the LFE in various materials.[1] Additionally, numerical calculations using a density-matrix approach of a two particle spin system can account for this function.[5,12]

The results of the MC(B) curves of Alq_3, PFO, and PPV are shown in Fig. 2(a). The double non-Lorentzian describes the data well, although there is a slight mismatch at small magnetic fields. We found that a more intricate empirical function[24] can fit the low-field data better but results in similar voltage trends.[27] Therefore, for the sake of simplicity we stick to the double non-Lorentzian to extract the behavior of the LFE and HFE amplitude as a function of voltage. The latter trends can be seen in Figs. 2(b)–2(d), where the three different materials clearly show the same tendency. As far as we know this particular MC(V) behavior has only been reported in the literature for the LFE in PPV[28] and Alq_3.[29] Figures 2(b)–2(d) also show the results of the analytical MC(V) fit functions that

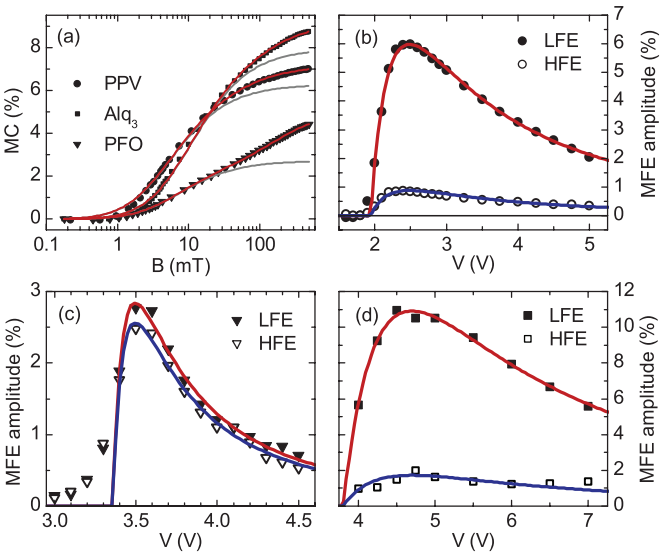

FIG. 2. (Color online) (a) The magnetic-field effect on the current (MC) as a function the magnetic field B for Alq_3, PFO, and PPV. The red lines are the result of the double non-Lorentzian fit function, and the gray lines show the shape of only the low-field effect (LFE) non-Lorentzian. (b–d) The fitted magnitude of the low- and high-field effect as a function of the bias voltage for (b) PPV, (c) PFO, and (d) Alq_3. The solid lines in (b–d) are analytical fits from the model derived in the text.

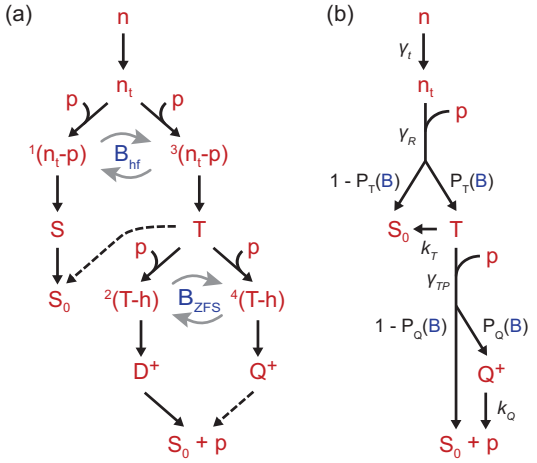

FIG. 3. (Color online) (a) A schematic overview of all relevant particles and reactions of the trion model. The spin state of polaronic electron-hole pairs is mixed at the field scale of the hyperfine interaction B_{HF}, while that of the triplet exciton-polaron pairs is mixed at the zero-field splitting field scale B_{ZFS}. (b) Rate equations are derived from a simplified picture where spin mixing is replaced with a magnetic-field dependent formation probability, and singlet excitons and doublet trions are not considered due to their negligible lifetimes. See the text for a more detailed description.

we will derive from our proposed model in the remainder of this manuscript.

III. TRION MODEL

Before we begin with a detailed description of the model, some general discussion about the background of the devices is in order. The devices with the three different materials, Alq_3, PFO, and PPV, are well-known organic light emitting diodes (OLEDs), and light emission was also clearly visible during characterization. Effects of exciton-polaron reactions on the polaron transport in OLEDs have been reported numerously in the literature.[17–19] Additionally, it is well known that for materials such as PPV or Alq_3 traps are explicitly present in the polaron transport,[30,31] which as we mentioned before is required for metastable trions. It is also known that these traps are mainly present in either the electron or hole transport. For Alq3 the transport is described with only hole traps, while for polymers such as PPV and PFO only electron traps are considered. Recent experimental work has shown that these traps are primarily responsible for the often observed difference in effective mobility between electrons and holes.[32]

Most experimental and theoretical work on OMAR has neglected the existence of traps and their pronounced influence on the polaron transport. Additionally, contemporary OMAR models have not been able to explain the positive LFE and HFE in the MC with a single mechanism. With respect to the origin of the MC(V) trend, multiple suggestions have been made,[6,28,33,34] but none have succeeded in giving a full quantitative description. Therefore, we have constructed a quantitative trion model with all previous reasoning in mind. The relevant reactions are shown schematically in Fig. 3(a) for the formation of positive trions. The actual calculations will be done with a simplified model shown in Fig. 3(b). In this manuscript we will also discuss the results of other possible exciton-polaron reaction mechanisms to show that *our proposed implementation of trions is not only the most physically feasible but it is also the only one to yield the results observed in our experiments*.

The model describes a device with free electrons and holes with densities n and p, respectively. As described above, we assume similar mobilities where one type of polaron (electrons or holes) gets trapped. We discuss the case of the polymers, where the trapped electron density n_t is created with a coefficient γ_t at the available trap site density N_t. The trapped electrons can form polaronic pairs with free holes with a coefficient γ_R, where spin mixing takes place at the hyperfine field scale. The S and T excitons are created from the recombination of these pairs and here we assume that strong on-site exchange interactions prevent spin mixing. Triplet excitons can either recombine directly to the ground state with a rate k_T or react with free polarons with a coefficient γ_{TP}.

Spin mixing also occurs between triplet exciton-polaron pairs.[12] Doublet (D) trions with total spin $1/2$ and quartet (Q) trions with total spin $3/2$ are then created in a different fraction when spin mixing is suppressed by a magnetic field, similar to the case of S and T excitons. The recombination of a doublet trion into a free polaron is spin allowed, while that of a quartet trion is not. Therefore, it is evident that the doublet trion has a much shorter lifetime than the quartet trion. As a consequence, the quartet trion is more efficient in capturing free polarons and hinders the charge transport more severely. Moreover, it is shown from calculations that a magnetic field suppresses the spin mixing of triplet exciton-polaron pairs not on the hyperfine field scale but on a much larger field scale

related to the zero-field splitting (ZFS) of the triplet exciton.[12] Trions can thus perfectly explain both the LFE and HFE of the MC(B).

Following the analysis of the LFE, the HFE will only be positive if the fraction of long living trions reduces with magnetic field. This is the case if the Q trions are created at a higher rate from their precursor pairs than the D trions. Such rates are still under discussion for S and T excitons as well, as they have not been measured directly. Furthermore, we assume that exchange splitting prevents spin mixing between D and Q trions, similar to S and T excitons.[11] Finally, we note that our analysis can in principle also be used to model trapping of triplet-polaron pairs without significant spin coupling.

In the simplified model we skip the pair states and create excitons and trions directly from their precursor particles with magnetic-field dependent formation probabilities $P_T(B)$ and $P_Q(B)$, respectively. Additionally, singlet excitons and doublet trions are neglected due to their relatively short lifetimes. A magnetic field will thus release free polarons captured in the quartet trion state through a decrease in the triplet or quartet formation probability. We neglect the short living singlet excitons and doublet quartets. Additionally, we only consider the case of deeply trapped electrons, i.e., the case in which the trap energy is much larger than the thermal energy, and we thus neglect thermally assisted release from traps. The trion model can accordingly be described with the following rate equations:

$$\frac{\partial n_t}{\partial t} = \gamma_t n N_t (1 - f_t) - \gamma_R n_t p, \tag{1}$$

$$\frac{\partial T}{\partial t} = P_T(B)\gamma_R n_t p - [\gamma_{TP}(n + p) + k_T]T, \tag{2}$$

$$\frac{\partial Q^+}{\partial t} = P_Q(B)\gamma_{TP} T p - k_Q Q^+, \tag{3}$$

$$\frac{\partial Q^-}{\partial t} = P_Q(B)\gamma_{TP} T n - k_Q Q^-. \tag{4}$$

Here we differentiate between positive Q^+ and negative Q^- quartet trions. In our central analysis the occupation of the trap sites is $f_t = (n_t + T + Q^+ + Q^-)/N_t$. However, the case that excitons and trions are themselves free is also considered, which can be calculated with $f_t = n_t/N_t$. Additionally, we considered the case that excitons and trions are created from free electrons and holes. This means that the trapped electrons are neglected in Eq. (1) and that n_t is substituted by n in Eq. (2). For all cases the above equations can easily be solved for an equilibrium situation.

IV. ANALYTICAL CALCULATIONS

To do a full analysis one should not only determine the local particle densities but also take the polaron transport through the device into account. This can be done by solving the continuity equations of the electron and hole densities. For a device with a current flow of electrons J_n and a current flow of holes J_p in opposite direction, one would find

$$\frac{\partial n}{\partial t} = \frac{1}{q}\frac{\partial J_n}{\partial x} - R - \gamma_t n N_t (1 - f_t) - \gamma_{TP} T n + k_Q Q^-, \tag{5}$$

$$\frac{\partial p}{\partial t} = -\frac{1}{q}\frac{\partial J_p}{\partial x} - R - \gamma_R n_t p - \gamma_{TP} T p + k_Q Q^+, \tag{6}$$

where q is the elementary charge and R is the intrinsic recombination of electrons and holes. The latter is generally given by a Langevin recombination process, where $R = \gamma np$ with γ being the bimolecular recombination coefficient. However, the entire system of Eqs. (1)–(6) together with a drift and diffusion approach for the current can only be solved numerically. Therefore, we first try an analytical approach by assuming that the influence of the trions on the electron and hole densities is relatively small and we thus only solve Eqs. (1)–(4).

Additionally, one needs an approximation for how the current (and voltage) scales with polaron density. We do this for a bipolar space-charge limited device, for which it is well known that current density $J(V)$ is given by[35]

$$J = \frac{9}{8}\varepsilon\sqrt{2\pi\mu_p\mu_n}\frac{V^2}{L^3}, \tag{7}$$

if the device has Ohmic contacts and the polarons recombine via a Langevin process. Here μ_p and μ_n are the mobilities of the hole and electron polarons, respectively, and L is the thickness of the organic semiconductor. The electrical permittivity ε of organic semiconductors is generally about three times the permittivity of free space.

The polaron densities p and n are related to the current by the drift equation:

$$J = (\mu_n n + \mu_p p)eF, \tag{8}$$

where e is the elementary charge. We assume that the device is quasineutral ($n \approx p$) and that the electric field F is given by the applied voltage V over the contacts as $F = V/L$. Then we find a linear relation between the polaron density and the applied voltage:

$$p = \frac{9\varepsilon}{8eL}\left(1 + \frac{\mu_n}{\mu_p}\right)^{-1}\sqrt{2\pi\frac{\mu_n}{\mu_p}}V = aV, \tag{9}$$

where a is largest when $\mu_n = \mu_p$. For a 100-nm-thick device we thus find $a \leqslant 2.3 \times 10^{-5}$ nm^3 V^{-1}. This linear approximation is supported by the numerical calculations performed in the next section.

The current through a space-charge limited device thus scales proportionally with the free polaron density in first-order approximation, while at the same time the free polaron density scales linearly with voltage. If one assumes that the transport of one of the polarons is severely trap limited then its effective mobility will be relatively small and the current will mainly be carried by the other polaron, e.g., $J \approx \mu_p peF$ if the electrons are trapped. Therefore, we assume that the holes contribute to most of the current and state that the current will change with magnetic field for the LFE according to

$$\frac{\Delta J}{J} \propto \frac{\Delta p}{p} \sim -\frac{1}{p}\frac{\partial p}{\partial P_T}\Delta P_T \sim \frac{1}{p}\frac{\partial Q^+}{\partial P_T}\Delta P_T, \tag{10}$$

where ΔP_T is the change in P_T with magnetic field. This results in the following MC:

$$\begin{aligned}\mathrm{MC}(n,p) = {} & k_Q P_Q N_t \gamma_t \gamma_R \gamma_{TP} np(\gamma_t n + \gamma_R p) \\ & \times [k_T + \gamma_{TP}(n + p)]/\{\gamma_t k_Q n(k_T + \gamma_R P_T p) \\ & + \gamma_R k_Q k_T p + \gamma_{TP}(n + p)[\gamma_t n(k_Q + \gamma_R P_Q P_T p) \\ & + \gamma_R k_Q p]\}^2. \end{aligned} \tag{11}$$

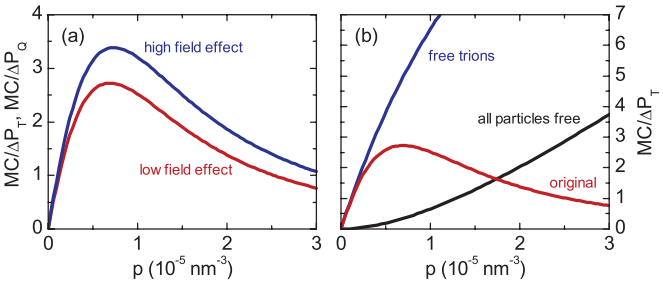

FIG. 4. (Color online) (a) The LFE and HFE as functions of the polaron density. (b) The LFE as a function of the polaron density for three different cases of the trion model: the original from (a), the case that trions and excitons are considered as free particles, and the case that all particles are free. The parameters used here are $k_T = 2 \times 10^4$ s^{-1}, $k_Q = 1.3 \times 10^3$ s^{-1}, $N_t = 2 \times 10^{-4}$ nm^3, $\gamma_t = \gamma_R = 9 \times 10^8$ nm^3 s^{-1}, $\gamma_{TP} = 4 \times 10^8$ nm^3 s^{-1}, $P_T = 0.75$, and $P_Q = 0.66$.

When we consider that a general LED is quasineutral ($n \approx p$), we find the general shape of the MC of the LFE as a function of the polaron density:

$$\mathrm{MC}(p) = \Delta P_T C p \frac{k_T + 2\gamma_{TP} p}{(b_0 + b_1 p + b_2 p^2)^2}, \tag{12}$$

where $C = k_Q P_Q N_t \gamma_t \gamma_R \gamma_{TP}(\gamma_t + \gamma_R)$, $b_0 = k_T k_Q(\gamma_t + \gamma_R)$, $b_1 = k_Q[P_T \gamma_t \gamma_R + 2\gamma_{TP}(\gamma_t + \gamma_R)]$, and $b_2 = 2P_T P_Q \gamma_t \gamma_R \gamma_{TP}$. Almost all parameters can be taken from the literature.[19,23,30,36–39] The only unknown parameter is ΔP_T, although it should be on the order of a few percent at large magnetic fields.[11] We can also derive the MC of the HFE with

$$\mathrm{MC} \propto \frac{1}{p} \frac{\partial Q^+}{\partial P_Q} \Delta P_Q \tag{13}$$

and find a similar shape for the MC(p):

$$\mathrm{MC}(p) = \Delta P_Q \frac{P_T}{P_Q} C p \frac{c_0 + c_1 p}{(b_0 + b_1 p + b_2 p^2)^2}, \tag{14}$$

where $c_0 = k_T(\gamma_R + \gamma_t)$ and $c_1 = P_T \gamma_R \gamma_t + 2(\gamma_R + \gamma_t)\gamma_{TP}$. The LFE and HFE corresponding to a respective change in P_T and P_Q both show the same trend, as can be seen in Fig. 4(a). Additionally, more features can be added to the trion model, such as shallow traps or trion dissociation, but we have found that these modifications make little difference.

Next we will discuss several alternative scenarios. As described before, the MC can also be derived for different cases, e.g., when excitons and trions are created from free electrons and holes, which is similar to the suggestion of charged excitons. This leads to the following simple solution:

$$\mathrm{MC}(n,p) = \frac{P_Q \gamma_R \gamma_{TP} np}{k_Q(k_T + (n+p)\gamma_{TP})}. \tag{15}$$

Another possibility would be that the excitons and trions created from the trapped electrons are free themselves and do not occupy the trap sites. In that case we find that

$$\mathrm{MC}(n,p) = \frac{P_Q N_t \gamma_t \gamma_R \gamma_{TP} np}{k_Q(\gamma_R p + \gamma_t n)[k_T + (n+p)\gamma_{TP}]}. \tag{16}$$

Both of these considerations lead to a monotonic increase of the MC(p), as can be seen in Fig. 4(b). It is clear that only our original concept of trions results in a nonmonotonic trend of the MC(p) in agreement with the experimentally found MC(V). Additionally, another process has been considered in the literature, where free triplet excitons are able to release trapped polarons.[24] However, the sign of the LFE would be negative for this mechanism, as a reduced fraction of triplet excitons results in less free polarons. We conclude that only the original scenario, in which trions are created at the trap sites, results in a nonmonotonic positive MC as seen in the experiment.

To finalize the analysis and find a function for the MC(V) we now only need to implement the relation between the voltage and polaron density. As stated before, for the most trivial situation of a space-charge limited device with a homogeneous electric-field distribution one finds that $p = a \times (V - V_{\mathrm{on}})$, where a is a constant on the order of 10^{-5} nm^3/V. For completeness we have added an onset voltage V_{on} for bipolar charge transport. We end up with an analytical function $\mathrm{MC}(V, V_{\mathrm{on}}, a, \Delta P_T)$ that fits our experimental data well, as can be seen in Figs. 2(b)–2(d). Some deviations can be observed, most clearly for PFO at low voltages. A possible explanation for this will be discussed in the next section.

V. NUMERICAL CALCULATIONS

In order to put some of the previous approximations on more solid ground, we have performed finite element drift-diffusion calculations. Such a method can also be used to model the voltage dependence of magnetic-field effects by altering parameters that are presumed to be magnetic-field dependent.[40] In addition, the trion rate Eqs. (1)–(4) and trion densities can readily be implemented in the simulation method. Here we investigate such an implementation with the altered continuity equations as described by Eqs. (5) and (6). Furthermore, the Poisson equation has to incorporate the charge of the trapped electron and trion densities:

$$\varepsilon \frac{\partial^2 \psi}{\partial x^2} = q(n - p + n_t + Q^- - Q^+), \tag{17}$$

where ψ is the electrostatic potential.

We investigated a low-mobility semiconducting device with a PPV inspired band gap of 2.8 eV.[41] Contact barriers with metal electrodes of 0.1 eV are assumed, which results in Ohmic contacts at room temperature.[42] We investigate the current and polaron density as a function of voltage for three different cases: (i) a trivial device without traps and trions, (ii) a device with electron traps with an energetic trapping depth of 0.4 eV, and (iii) a device with said traps and the complete trion formalism as described in this manuscript. The results of these simulations are shown in Fig. 5.

As can be seen in Figs. 5(a) and 5(b), the addition of electron traps has relatively little effect on the free hole density but has a significant effect on the free-electron density as can be expected. The addition of trions actually has an opposite effect, as they trap holes as well, thereby rebalancing some of the charge transport. It is clear that the addition of both traps and trions lead to a reduction of the current in the space-charge limited region after the built-in voltage, as can be seen in Fig. 5(c).

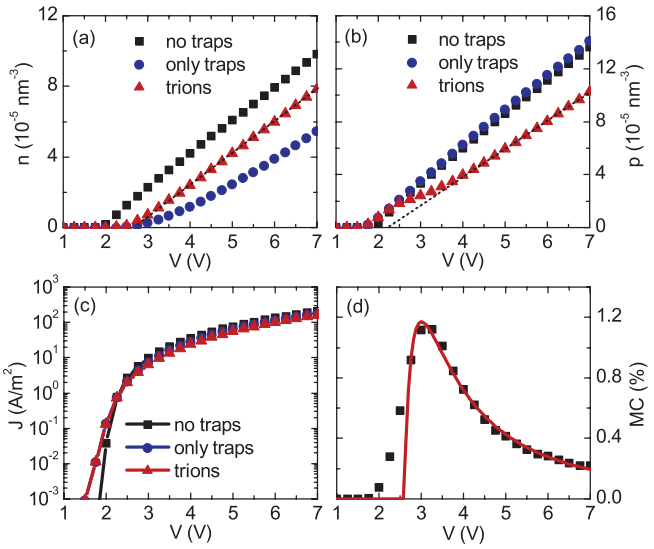

FIG. 5. (Color online) Finite element drift-diffusion device simulations performed for three different cases: a device without traps, one with traps, and one with trions. The free-electron and hole polaron densities in the center of our device are shown in (a) and (b), respectively, for the three cases as functions of voltage. As shown by the dotted linear guide to the eye, the polaron density scales approximately linearly with voltage with some deviations close to the built-in voltage. (c) The J-V curves for the three cases. (d) The calculated MC(V) for the trion simulation for a reduction in the triplet exciton formation of $\Delta P_T = -0.05$. The solid red line is a fit with the trion function. For the calculations we used $k_T = 1.66 \times 10^4$ s^{-1}, $k_Q = 1 \times 10^3$ s^{-1}, $N_t = 2 \times 10^{-4}$ nm^3, $\gamma_t = 2 \times 10^8$ nm^3 s^{-1}, $\gamma_R = 4 \times 10^8$ nm^3 s^{-1}, $\gamma_{TP} = 1 \times 10^9$ nm^3 s^{-1}, $P_T = 0.8$, $P_Q = 0.66$, $\mu_n = 6 \times 10^{-11}$ m^2/V s, and $\mu_p = 1 \times 10^{-10}$ m^2/V s.

The calculations suggest that a linear voltage dependence of the polaron density as assumed in our analytical approach can be considered fairly reasonable. Some deviations are observed at low voltages around 2–3 V. This also leads to changes in the shape of the MC(V) with respect to the analytical function in this same region, as can be seen in Fig. 5(d). Although such deviations are also observed in some of the experimental results, primarily for PFO [see Fig. 2(c)], they are less dramatic then in our simulations. This suggests that some effect that is currently not considered in the numerical simulations suppresses these nonlinearities in the real devices.

An aspect of organic materials that has not been incorporated in the device simulations is the energetic (and spatial) disorder. State-of-the-art drift-diffusion OLED simulations consider the Gaussian disorder of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the organic material, by implementing electric-field and polaron density dependent mobilities.[43] Additionally, the energetic distribution of traps is also known to be Gaussian.[44,45] Electric-field dependent mobilities can assist in pushing the polarons faster into the bulk of the device, since the highest electric fields are present at the edges of the devices. This might help to overcome the small nonlinearities at lower voltages.

Finally, we note that numerical calculations involve more parameters than our analytical derivation of the trion model, which complicates their interpretation. Nevertheless, these results suggest that our analytical approximations are realistic. This helps to identify the relevant underlying physics of the observed magnetic-field effects. The advantage of numerical calculations is that they can relatively easily be applied to a diverse range of devices. Additionally, this work can help to improve predictive OLED models which do not yet incorporate the combination of triplet-polaron interactions, trions, and traps.

VI. DISCUSSION

With the trion model in mind we are now able to intuitively explain the trend of the MC(V). The initial rise of the MC with voltage is, quite straightforwardly, due to the progressive formation of trions. Because they are created from a trap-assisted recombination mechanism, the incline is relatively steep at low voltages and scales linearly with $V - V_{\text{on}}$. The eventual decline is on account of trap filling by the triplet excitons and trions. With their increasing presence they are impeding the trapping of polarons and their own subsequent formation. As a result the number of trions stabilizes with voltage, while the free polaron density continues to rise. The relative effect of the trions on the total current will diminish while the MC drops at higher voltages with $(V - V_{\text{on}})^{-2}$.

We note that the reported weak temperature dependence of the MC[1] does not directly interfere with the trion model, because the temperature dependences of many processes may cancel out. For example, when it comes to the actual formation of the trion, the (monomolecular) triplet exciton lifetime will reduce with temperature, leading to less chance of forming a trion. At the same time the polaron mobility will increase, leading to a larger triplet-polaron interaction chance and thus more chances of forming a trion. The possible temperature dependence of a triplet-based magnetoresistance model has also been discussed by Zhang *et al.*,[46] while for an electron-hole pair recombination mechanism this has been done by Bagnich *et al.*[28]

In experimental studies it should be possible to enhance the MC by adding more trap sites and thereby open the way to the engineering of efficient organic magnetic-field sensors. Interestingly, a first step on this road was recently taken in Alq_3 devices by exposing them to x rays, leading to an enhancement of the MC.[47] Whether this same process could be applied to other devices is debatable as the exact nature of traps is still under investigation. Recently, an elaborate study suggested that hydrated oxygen complexes can explain the electron traps in most semiconducting polymers.[48] Therefore, we are currently investigating how different kind of traps can influence the MC, both experimentally and theoretically. As a final comment it should be noted that trions and their effect on the current have been greatly overlooked in organic devices so far.

VII. CONCLUSION

In conclusion, we have investigated the magnetic-field dependence of the current in several organic light emitting devices. A high-field contribution in the MC(B) was observed in all measured devices, the width of which can be attributed to the zero-field splitting of triplet excitons. We also found nonmonotonic trends in the MC with applied voltage in

all devices, which can be explained with a magnetic-field dependent formation of long living excitations at trap sites. We can model all our experimental data well with our proposed trion mechanism: the spin dependent formation of triplet excitons at trap sites and their subsequent spin selective reaction with free polarons into metastable trions. An analytical function was derived that fits the data well and can be used to analyze and better understand the MC in OLEDs. The trion model was also implemented into numerical device simulations, which not only confirmed our analytical derivations but can ultimately be used in a broad range of predictive device simulations.

ACKNOWLEDGMENTS

This research is supported by the Dutch Technology Foundation (STW), which is part of the Netherlands Organization for Scientific Research (NWO).

[1] Ö. Mermer, G. Veeraraghavan, T. L. Francis, Y. Sheng, D. T. Nguyen, M. Wohlgenannt, A. Köhler, M. K. Al-Suti, and M. S. Khan, Phys. Rev. B **72**, 205202 (2005).
[2] V. N. Prigodin, J. D. Bergesona, D. M. Lincoln, and A. J. Epstein, Synth. Met. **156**, 757 (2006).
[3] P. Desai, P. Shakya, T. Kreouzis, W. P. Gillin, N. A. Morley, and M. R. J. Gibbs, Phys. Rev. B **75**, 094423 (2007).
[4] B. Hu and Y. Wu, Nat. Mater. **6**, 985 (2007).
[5] P. A. Bobbert, T. D. Nguyen, F. W. A. van Oost, B. Koopmans, and M. Wohlgenannt, Phys. Rev. Lett. **99**, 216801 (2007).
[6] F. L. Bloom, W. Wagemans, M. Kemerink, and B. Koopmans, Phys. Rev. Lett. **99**, 257201 (2007).
[7] U. Niedermeier, M. Vieth, R. Pätzold, W. Sarfert, and H. von Seggern, Appl. Phys. Lett. **92**, 193309 (2008).
[8] F. J. Wang, H. Bassler, and Z. ValyVardeny, Phys. Rev. Lett. **101**, 236805 (2008).
[9] T. D. Nguyen, G. Hukic-Markosian, F. Wang, L. Wojcik, X. Li, E. Ehrenfreund, and Z. V. Vardeny, Nat. Mater. **9**, 345 (2010).
[10] Z. G. Yu, Phys. Rev. Lett. **106**, 106602 (2011).
[11] S. P. Kersten, A. J. Schellekens, B. Koopmans, and P. A. Bobbert, Phys. Rev. Lett. **106**, 197402 (2011).
[12] A. J. Schellekens, W. Wagemans, S. P. Kersten, P. A. Bobbert, and B. Koopmans, Phys. Rev. B **84**, 075204 (2011).
[13] P. Janssen, M. Cox, M. Kemerink, M. M. Wienk, and B. Koopmans, Nature Communications (to be published).
[14] W. J. Baker, D. R. McCamey, K. J. van Schooten, J. M. Lupton, and C. Boehme, Phys. Rev. B **84**, 165205 (2011).
[15] V. Ern and R. E. Merrifield, Phys. Rev. Lett. **21**, 609 (1968).
[16] V. M. Agranovich, D. M. Basko, K. Schmidt, G. C. LaRocca, F. Bassani, S. Forrest, K. Leo, and D. Lidzey, Chem. Phys. **272**, 159 (2001).
[17] J. Kalinowski, W. Stampor, J. Mezyk, M. Cocchi, D. Virgili, V. Fattori, and P. Di Marco, Phys. Rev. B **66**, 235321 (2002).
[18] S. Reineke, K. Walzer, and K. Leo, Phys. Rev. B **75**, 125328 (2007).
[19] D. Hertel and K. Meerholz, J. Phys. Chem. B **111**, 12075 (2007).
[20] Y. Meng, X. J. Liu, B. Di, and Z. An, J. Chem. Phys. **131**, 244502 (2009).
[21] J. Y. Song, N. Stingelin, A. J. Drew, T. Kreouzis, and W. P. Gillin, Phys. Rev. B **82**, 085205 (2010).
[22] E. L. Frankevich, A. A. Lymarev, I. Sokolik, F. E. Karasz, S. Blumstengel, R. H. Baughman, and H. H. Hörhold, Phys. Rev. B **46**, 9320 (1992).
[23] A. Kadashchuk, V. I. Arkhipov, C.-H. Kim, J. Shinar, D.-W. Lee, Y.-R. Hong, J.-I. Jin, P. Heremans, and H. Bässler, Phys. Rev. B **76**, 235205 (2007).
[24] W. W. Wagemans, P. Janssen, A. J. Schellekens, F. L. Bloom, P. A. Bobbert, and B. Koopmans, SPIN **1**, 93 (2011).
[25] T. L. Francis, Ö. Mermer, G. Veeraraghavan, and M. Wohlgenannt, New. J. Phys. **6**, 185 (2004).
[26] W. Wagemans, W. J. Engelen, F. L. Bloom, and B. Koopmans, Synth. Met. **160**, 266 (2010).
[27] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.88.035202 for technical details.
[28] S. A. Bagnich, U. Niedermeier, C. Melzer, W. Sarfert, and H. von Seggern, J. Appl. Phys. **106**, 113702 (2009).
[29] W. Wagemans, P. Janssen, E. H. M. van der Heijden, M. Kemerink, and B. Koopmans, Appl. Phys. Lett. **97**, 123301 (2010).
[30] M. Kuik, L. J. A. Koster, G. A. H. Wetzelaer, and P. W. M. Blom, Phys. Rev. Lett. **107**, 256805 (2011).
[31] P. E. Burrows, Z. Shen, V. Bulovic, D. M. McCarty, S. R. Forrest, J. A. Cronin, and M. E. Thompson, J. Appl. Phys. **79**, 7991 (1996).
[32] Y. Zhang, B. de Boer, and P. W. M. Blom, Phys. Rev. B **81**, 085201 (2010).
[33] J. D. Bergeson, V. N. Prigodin, D. M. Lincoln, and A. J. Epstein, Phys. Rev. Lett. **100**, 067201 (2008).
[34] J. Kalinowski, J. Szmytkowski, and W. Stampor, Chem. Phys. Lett. **378**, 380 (2003).
[35] R. H. Parmenter and W. Ruppel, Jour. Appl. Phys. **30**, 1548 (1959).
[36] G. A. H. Wetzelaer, M. Kuik, H. T. Nicolai, and P. W. M. Blom, Phys. Rev. B **83**, 165204 (2011).
[37] M. A. Baldo and S. R. Forrest, Phys. Rev. B **64**, 085201 (2001).
[38] J. Partee, E. L. Frankevich, B. Uhlhorn, J. Shinar, Y. Ding, and T. J. Barton, Phys. Rev. Lett. **82**, 3673 (1999).
[39] H. H. Liao, H. F. Meng, S. F. Horng, J. T. Shy, K. Chen, and C. S. Hsu, Phys. Rev. B **72**, 113203 (2005).
[40] M. Cox, P. Janssen, S. H. W. Wouters, E. H. M. van der Heijden, M. Kemerink, and B. Koopmans, Synth. Met. **173**, 10 (2013).
[41] P. Gomes da Costa, and E. M. Conwell, Phys. Rev. B **48**, 1993 (1993).
[42] G. G. Malliaras and J. C. Scott, J. Appl. Phys. **83**, 5399 (1998).
[43] R. Coehoorn and P. A. Bobbert, Phys. Status Solidi A **209**, 2354 (2012).
[44] H. T. Nicolai, M. M. Mandoc, and P. W. M. Blom, Phys. Rev. B **83**, 195204 (2011).
[45] M. Kuik, J. Vandenbergh, L. Goris, E. J. Begemann, L. Lutsen, D. J. M. Vanderzande, J. V. Manca, and P. W. M. Blom, Appl. Phys. Lett. **99**, 183305 (2011).
[46] S. Zhang, A. J. Drew, T. Kreouzis, and W. P. Gillin, Synth. Met. **161**, 628 (2011).
[47] J. Rybicki, R. Lin, F. Wang, M. Wohlgenannt, C. He, T. Sanders, and Y. Suzuki, Phys. Rev. Lett. **109**, 076603 (2012).
[48] H. T. Nicolai, M. Kuik, G. A. H. Wetzelaer, B. de Boer, C. Campbell, C. Risko, J. L. Brédas, and P. W. M. Blom, Nat. Mater. **11**, 882 (2012).