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Investigating the influence of traps on organic magnetoresistance by molecular doping

M. Cox, E. H. M. van der Heijden, P. Janssen, and B. Koopmans
Department of Applied Physics, Center for Nano Materials and COBRA Research Institute, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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Traps are localized, deep lying energetic states and are generally considered detrimental for organic semiconducting devices. In this work, we investigate their influence on the magnetic field sensitive current in organic devices, an effect often called organic magnetoresistance. Polymer thin films were doped with materials well known to influence trap characteristics in such devices. We analyzed the observed trends in the intrinsic magnetic field effects in terms of a trapped trion model, which incorporates the spin dependent formation of excitations at these trap sites. The results provide strong evidence that the intrinsic traps in the polymer material are indeed at the origin of these magnetic field effects. This shows that traps have beneficial properties and that their control may provide an appealing route for the engineering of efficient organic magnetic field sensors.

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I. INTRODUCTION

Organic electronics is considered to be a field of untold possibilities [1]. However, whereas the spin degree of freedom of electrons is utilized to its fullest in inorganic "spintronic" devices [2], organic materials are still lagging behind. This limits the use of organic materials in conjunction with many conventional memory and sensing applications. However, in the past decade, the young field of organic spintronics has been catching up [3,4]. Beside the realization of state-of-the-art spin injecting devices [5–8], which try to mimic spin valve technology, another development piqued tremendous interest. It was found that a small magnetic field can have a large effect on the current in organic semiconductors—an effect that was referred to as organic magnetoresistance (OMAR) [9–32]. OMAR is an intrinsic effect that manifests itself at room temperature and magnetic fields of only a few millitesla. The changes in current can become as large as 25% in thin-film devices [14], while very recent work even reports on ultrahigh magnetoresistance values of over 2000% in perfectly one-dimensional molecular systems [21]. Cheap plastic sensor applications have already been suggested as an example of its application potential [33].

The desire to unravel the underlying physics of this intrinsic magnetoresistance effect in organic semiconductors has initiated intense experimental [9–24] and theoretical [24–32] research. Multiple mechanisms have been proposed for OMAR and recent work shows these can all become dominant under specific conditions [23]. Additionally, there is a growing awareness of the role of defects and polaron traps in the explanation of the large reported OMAR values [12,14,20–22,24]. In this manuscript, we investigate the influence of traps on OMAR more closely with molecular dopants known from previous trap related research. Our results further strengthen the notion that traps are crucial for the large magnetic field effects observed in organic semiconductors.

Although the exact influence of traps is still under debate, the origin of OMAR is believed to lie in the spin physics occurring in organic semiconductors. Nowadays, it is well established that a magnetic field can change reactions and interactions of spin carrying particles, such as polarons and excitons, created in semiconducting polymers and molecules [23–30,34]. When a pair of particles meets, the spin of these individual particles evolves in time, leading to mixing of the pair's total spin state—a process in which hyperfine fields are involved [15], although in certain materials spin orbit coupling might also play a role [31]. A large applied magnetic field can then suppress the spin mixing and thereby influence the outcome of spin dependent reactions [29,30]. We note that the organic spintronics community has already been preceded by spin chemistry, where magnetic field dependent reactions are well-known [34]. For example, such mechanisms have been suggested to play a role in how birds orient in magnetic fields, using specialized photoreceptors [35].

Much experimental work has focused on finding the exact particle reactions at the origin of OMAR. Large effects were initially observed in organic light emitting devices (OLEDs) consisting of thin films of organic material sandwiched between two nonmagnetic electrodes [9]. In such devices, many different spin dependent particle reactions are occurring. Electron and hole polarons can react and form excitons with either a singlet or triplet state [26,29]. These excitons can react with other polarons again or, alternatively, with other excitons [10,27,30]. Furthermore, reactions of polarons with the same charge into (short living) bipolarons can be considered [25]. Additionally, polarons can become trapped and this will influence their reactions and interactions with the free particles in the organic semiconductor.

A considerable amount of research on OLEDs made of pristine polymers suggests that, out of the many possibilities, in particular, the reactions of triplet excitons and polarons play an important role in the origin of organic magnetoresistance [10,16–18,23,24]. In recent work we investigated these triplet-polaron reactions more closely and validated the possibility of a trapped trion mechanism for OMAR [24]. Trions are quasiparticles created from the reaction of excitons and polarons and are only considered to be metastable when formed at a trap site [36]. We were able to successfully model the change in current with magnetic field, or magnetoconductance (MC), by solving the rate equations for all the relevant (magnetic field dependent) particle reactions. The experimentally found magnetic field and voltage dependence of the MC of several OLEDs could be described perfectly by a trion mechanism, but only when the excitons and subsequent trions were indeed formed at trap sites.

The fact that traps have a profound influence on the polaron transport through organic materials is well known in the literature [40] and their involvement in OMAR is also starting to become apparent [12,14,20]. Recently, an experimental study suggested that OMAR was enhanced by increasing the amount of trap sites in a small molecule OLED [20]. Although the authors used a somewhat crude manner by exposing devices to highly energetic electrons generated by x rays, this seems as strong experimental evidence of the importance of traps (or at least material defects) for OMAR. In order to investigate the effects of traps on the polaron transport and recombination in organic semiconductors, the field of organic electronics has developed pioneering and reliable methods in recent years [37,38], but these techniques have not been utilized for the study of OMAR yet.

The above considerations motivated the research in the current manuscript, in which we investigate the influence of traps on the magnetoconductance more closely. We examine devices where the active layer is comprised of the phenyl-substituted poly(p-phenylene vinylene) copolymer (PPV) also known as "super yellow" PPV, which is known to exhibit large magnetic field effects [14]. PPV derivatives are known to have an abundance of electron traps [39], although their exact nature is still under debate [40]. In this work, we aim to both add electron traps and deactivate the traps relevant for the MC, which are already present in the device. To the latter traps we will in the remainder of the manuscript refer to as the intrinsic traps. To examine the effect of adding *strong extrinsic electron traps* the PPV devices are doped with tetrafluorotetracyanoquinodimethane (F4TCNQ) [37]. In a parallel study, the electron donor decamethylcobaltocene (DMC) is used to *deactivate the intrinsic electron traps* of PPV [38]. See Fig. 1(a) for the chemical structure of these dopants and Fig. 1(b) for the energy levels of the materials which are taken from the literature [38,41]. Super yellow PPV is bought from Merck and known to have HOMO and LUMO energy levels of −5.2 and −2.8 eV, respectively. The energy level of the electron traps in PPV derivatives is estimated at approximately 0.7–0.8 eV below the LUMO [40]. By doping the PPV devices with these well studied materials, we will unambiguously show that the intrinsic PPV traps are at the origin of organic magnetoresistance. Moreover, it is shown that the trends can be explained by the trion model.

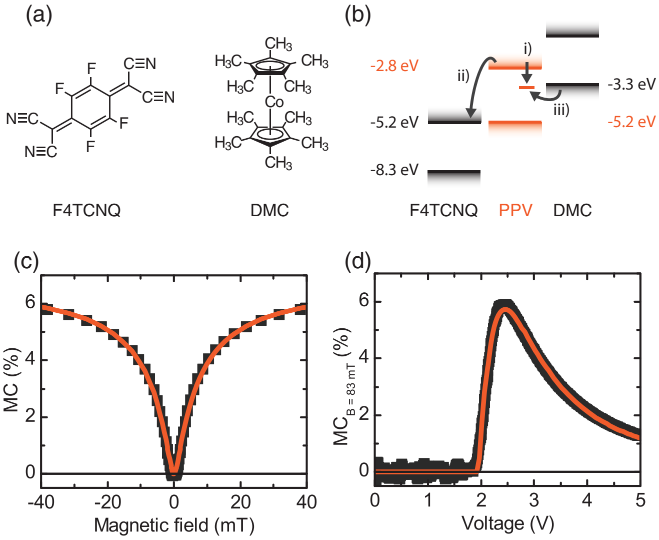

FIG. 1. (Color online) (a) The chemical structure of the used dopants. (b) An energy level diagram showing the HOMO and LUMO of F4TCNQ, super yellow PPV and DMC, where PPV has an electron trap level below the LUMO. The LUMO of DMC is not mentioned in the literature as far as we know. The electron transport in PPV is influenced by (i) initial trapping of electrons at intrinsic trap sites, (ii) by trapping at extrinsic F4TCNQ, and (iii) by filling the intrinsic traps with DMC. The lower panels show typical results of an undoped PPV device for the magnetoconductance (MC) as a function of (c) magnetic field at a fixed voltage of 2.5 V and (d) as a function of voltage at a fixed magnetic field of approximately 83 mT. The solid line in (c) is a non-Lorentzian fit and the one in (d) is a fit from the trion model.

II. EXPERIMENTAL RESULTS

Typical OLED device structures were used in the experiments, in which the active PPV layer is sandwiched between two electrodes. The PPV:F4TCNQ layers were created from a chlorobenzene (CB) solution and the PPV:DMC layers from a CB:N-methylpyrrolidon solution (9:1). The dopants were added from a stock solution (F4TCNQ in CB, DMC in N-methylpyrrolidon) to the PPV. The PPV concentration was kept constant at 6 mg/ml in all solutions. The bottom contact of the devices consists of pre-patterned indium tin oxide (ITO) on which we spincoated 40 nm of poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT:PSS) from aqueous suspension. The active layer of was spin-coated at 1200 rpm (90 nm) on the samples inside a nitrogen filled glove box. The top contact consisting of LiF (1 nm)/Al (100 nm) was thermally evaporated inside a high-vacuum system in another glovebox. Unipolar devices were fabricated with a similar method. For the hole-only devices, a gold top electrode was evaporated instead of LiF/Al, while for the electron-only devices, a zinc oxide layer was spincoated instead of PEDOT:PSS. After fabrication the samples were transported to another glove box, where they were electrically characterized with a Keithley 2400 series. All transport between glove boxes took place inside a nitrogen filled container. The magnetic field dependence of the current J is measured by placing a sample between the poles of an electromagnet and sweeping the magnetic field and is calculated with $\mathrm{MC}(B) = [J(B) - J(0)]/J(0)$. The MC as a function of voltage V is measured using a method in which a disk with permanent magnets is rotated over the sample while measuring the J-V curve, for more details see Ref. [45].

A typical shape of the MC(B) of PPV is shown in Fig. 1(c), which can be fitted with a so-called "non-Lorentzian" [9], in which the width of the curve depends on the strength of the spin mixing mechanism. Numerical simulations of a two-particle spin system are able to reproduce such line shapes [25,30]. Figure 1(d) shows a typical measurement of the MC(V). In recent work we have shown that the trend, a rapid incline—starting at the built-in voltage around 2 V—up to a maximum and followed by a slower decline, can be fitted with the trapped

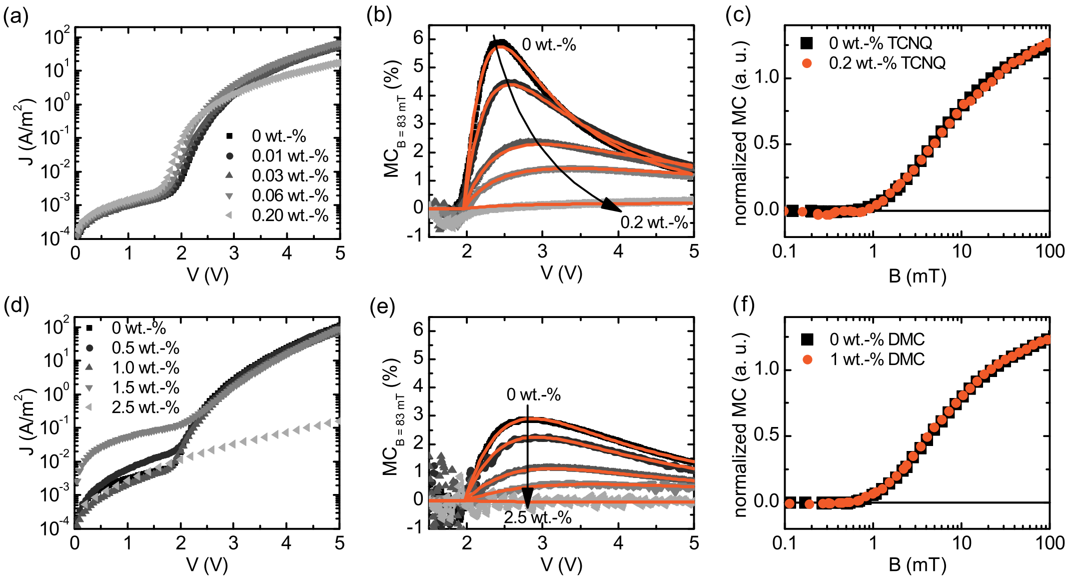

FIG. 2. (Color online) The results of adding extrinsic traps (F4TCNQ) are shown in the top panels and for the trap filling study (DMC) in the bottom panels. (a) and (d) show the J-V curves, while (b) and (e) show the MC(V) curves at different dopant concentrations. The solid lines are fits with the trion model. The normalized line shape of the MC as a function of magnetic field for devices with and without dopant are shown in (c) and (f), which illustrates the fact that the shape of the MC(B) does not change when adding a dopant.

trion model [24]. In this model, the triplet-polaron reactions are limited to trap sites, which leads to the eventual decrease of the MC(V).

In the remainder of this paper, we will first investigate the effect of adding the dopants to the "super yellow" PPV devices with a detailed experimental study. This will be followed by a concise overview of the spin dependent reactions occurring in such devices, including those of relevance for the trion model. The observed experimental results will then be addressed within the framework of this model.

An overview of the general results in the doped PPV devices can be seen in Fig. 2. We first describe the results of the F4TCNQ study, where the goal was to investigate the influence of *creating extrinsic traps* by adding a strong electron acceptor. The PPV devices were doped with relatively small concentrations of no more than 0.20 wt.% F4TCNQ. These concentrations seem to have no distinct effect on the J-V characteristics of the devices [Fig. 2(a)], while the MC is found to greatly diminish with increasing F4TCNQ concentration [Fig. 2(b)]. Adding only 0.01 wt.% of F4TCNQ to PPV already leads to an observable drop of the MC, and at a concentration of 0.20 wt.%, the MC is reduced by more than one order of magnitude. Clearly, adding a strong electron acceptor to a device with electron traps does not benefit the MC. However, there is a very specific way in which the MC(V) decays with F4TCNQ concentration: while the maximum MC decreases it simultaneously shifts to higher voltages. Assuming electrons trapped on F4TCNQ do not contribute to the MC, the results can be explained by a shift of electron trapping from the intrinsic trap sites to the extrinsic F4TCNQ trap sites. This means the J-V characteristics do not change significantly, because the total amount of trapping is conserved. On the other hand, the MC is affected drastically, because the intrinsic trap sites no longer contribute to the current and its spin-dependent processes.

When doping PPV devices with DMC, in order to *deactivate the intrinsic traps*, different effects than in the F4TCNQ study are observed, as can be seen in Figs. 2(d)–2(e). What is similar is that the changes in current are small at low DMC concentration, while the MC reduces dramatically. We first address the differences in the current. Clearly some devices have a larger leakage current at low voltages (0–2 V), but a more pronounced effect is that after a certain DMC concentration (>2 wt.%) the current reduces rapidly. Although DMC is known to deactivate electron traps [38] it also acts as a deep hole trap [43], eventually leading to a significant reduction of the current in bipolar devices. With respect to the MC, the changes are visible in Fig. 2(e). The effect of adding DMC is quite clear, the total MC reduces with concentration and the shift in voltage of the maximum is insignificant compared to the F4TCNQ study. In principle, this corresponds well with the notion that the intrinsic traps contribute directly to the MC and that DMC deactivates these traps. In passing, we note that without adding any DMC, the MC is already diminished by the use of the polar cosolvent N-methylpyrrolidon (NMP). Solvents are known to have a profound effect on chain orientation and film morphology [44], which can affect material parameters such as the trapping or the triplet-polaron interaction coefficient.

In contrast to the reduction of the total MC when adding the dopants, we observed no changes in the actual shape of the MC as a function of magnetic field B, as can be seen in Figs. 2(c) and 2(f) for significant dopant concentrations. We argue that this is not a completely trivial result. For instance, DMC contains cobalt, which has a high Z number and could therefore induce spin-orbit coupling leading to enhanced spin dephasing [31]. In the past this has been suggested to diminish the MC [11]. Deviations in the spin mixing mechanism should lead to identifiable changes in the line shape of the MC(B). Since these are absent, one can conclude that for neither dopant

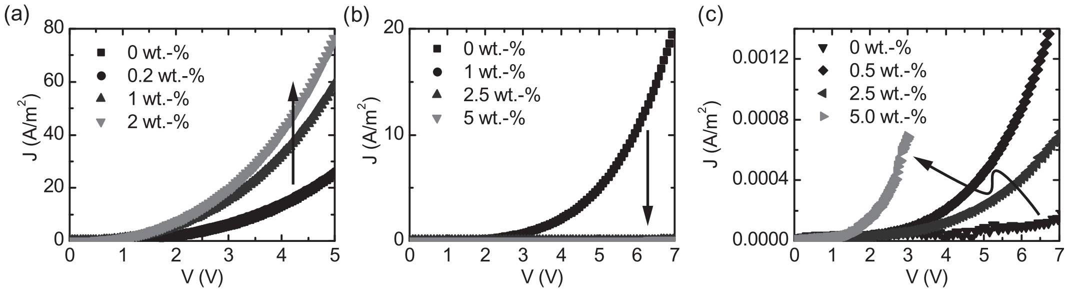

FIG. 3. The J-V characteristics of (a) hole only PPV:F4TCNQ devices, (b) hole only PPV:DMC devices and (c) electron only PPV:DMC devices.

there are changes occurring in the spin mixing at the polaron pair level and that all MC trends must be due to device physics, i.e., the answer lies in the change in particle reactions and transport.

Some discussion is required with respect to our hypotheses regarding the dopants. Besides being a strong electron trap it is known that F4TCNQ, as a p-type dopant, can enhance the hole density and mobility [42]. This in itself could have effects on the MC, but it also implies that some of the F4TCNQ sites are ionized, which means they can no longer act as trap sites. In order to check the effectiveness as a p-type dopant, hole only devices PPV:F4TCNQ devices were created. The results shown in Fig. 3(a) suggest this effect is only noteworthy at much higher dopant concentrations than used in the bipolar devices (>0.2 wt.%). Therefore this is excluded as a possible explanation for the MC decay. Although some F4TCNQ sites may be thermally ionized, due to the relatively small energy difference in PPV HOMO and F4TCNQ LUMO, at least a significant fraction of F4TCNQ sites will be available to trap electrons. We tried to check the effectiveness of F4TCNQ as an electron trap by making electron-only devices. Unfortunately, the undoped electron-only device already has a current density at the detection limit of our setup. Doping with F4TCNQ lowers the current below the detection limit, so we were unable to verify its true effectiveness as an electron trap.

Additionally, an electron donor such as DMC may act as a hole trap. Therefore, hole only and electron only PPV:DMC devices were fabricated. From the results shown in Figs. 3(b) and 3(c), it is found that both the hole and electron current change significantly in the investigated doping regime. This suggests that the creation of hole traps might also be a cause of the reduction of the MC in the bipolar study shown in Fig. 2. However, in the hole-only devices the current is already quenched after the addition of 1 wt.% of DMC, while in the bipolar devices [Fig. 2(d)] this occurs at much higher concentrations. The difference with the latter case is that recombination with electrons can empty the DMC sites again, thereby stalling this effect. The filling of electron traps by DMC cannot be countered in a similar fashion by hole recombination in a bipolar device, because the remaining hole on the nearby DMC will shield the charge of the trapped electron, thereby completely deactivating the trap. Therefore, in the remainder of the paper, we assume that the deactivation of the intrinsic electron traps is the underlying cause of the MC reduction.

III. ANALYSIS

As stated before, there is strong evidence that triplet exciton-polaron reactions are at the heart of the MC in OLEDs. In the following part of the paper, we will show that the trends in the magnetic field dependent results as discussed above can be explained within the framework of the trion model; a triplet-polaron interaction model that incorporates traps sites. The observed changes in the MC(V) curves will be assigned to specific changes in parameters in the model. However, first, we will give a concise overview of the model.

The initial assumption of a triplet-based OMAR mechanism is that triplet-polaron reactions can be considered to hinder the polaron transport [27]. By reducing the number of triplet excitons with a magnetic field as described in the introduction, the current can thus be increased. Key steps of such a process are shown in Fig. 4(a). Without spin mixing the state of an electron and hole that meet in space is defined by statistics; 1/4 chance to be a singlet (S) and 3/4 chance to be a triplet (T). However, due to the spin mixing the singlet and triplet state evolve in time. If the rate to form a T exciton is larger than the S exciton formation rate, the T exciton yield will be larger than 3/4, which is in agreement with experimental studies [29]. When a large magnetic field is applied, the degeneracy of two of the three triplet pair states is lifted, blocking mixing to and from these states. This lowers the probability to form T excitons and thus reduces the number of triplet-polaron (TP) reactions.

In the trion model, it is assumed that these TP reactions are most efficient at trap sites and might even form a metastable particle: the trion [24,36]. We have given an overview of all the relevant processes of trion formation at a trap site in Fig. 4, which are explained in more detail in Ref. [24]. The model describes a cascade of particle reactions, starting at the trapping of electrons. These trapped electrons can react with free holes to form (triplet) excitons at the trap sites, which subsequently react with other free polarons to form trions. Trions can be argued to have a long lifetime, thereby significantly affecting the charge transport as polarons are temporarily captured by them until they recombine or dissociate. Such a trion model is able to describe the MC(V) with an analytical fit function [see Fig. 1(d)]. The initial increase of MC as a function of V is due to the progressive formation of excitations (T excitons and trions) from trapped electrons, while the subsequent decline is caused by filling of the traps by these excitations.

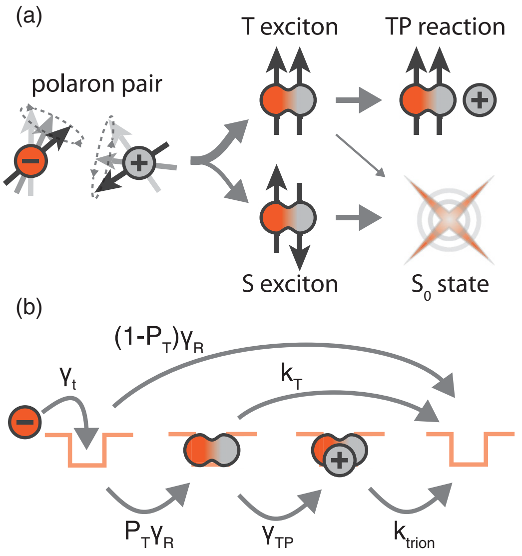

FIG. 4. (Color online) (a) The process of spin mixing makes the pair's spin state evolve in time from singlet to triplet. This means the probability to either form a singlet (S) or triplet (T) exciton is no longer only based on spin statistics, but also on their separate formation rates. When a large magnetic field is applied, the degeneracy of two of the three triplet pair states is lifted, blocking mixing to and from these states. This can reduce the probability to form T excitons and thus reduce the number of triplet-polaron (TP) reactions. The TP reactions are the dominant exciton-polaron interaction as T excitons live much longer than S excitons before recombining to the ground state. (b) In our trion model, we use this notion by assuming that electrons which are trapped (with a coefficient γ_t) and recombine with holes (with a coefficient γ_R) have a magnetic field dependent probability to form a triplet exciton (PT). Singlet excitons are neglected due to their short lifetime. The triplets can then recombine directly to the ground state with a rate k_T or form a trion (with a coefficient γ_{TP}) by interacting with another polaron. This trion can recombine again while releasing a free polaron with a rate k_{trion}. A magnetic field can thus reduce the number of triplet excitons, leading to less trions and more free polarons.

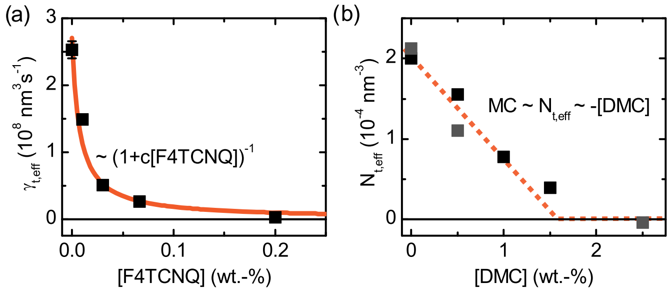

FIG. 5. (Color online) The changes in fit parameters with dopant concentration for TCNQ on the left and DMC on the right. For the DMC study, we show the results of two separate batches of samples (black and grey). The solid line in (a) is a fit described in the text and the dotted line in (b) is a linear guide to the eye.

We now apply this knowledge to analyze our experimental data. For the F4TCNQ study we observed that creating deep electron traps in PPV by adding a strong electron acceptor reduces and shifts the MC(V). We conjectured that this happens because the intrinsic PPV trap sites have to compete for the free electrons with the F4TCNQ molecules. It can be argued that an exciton or trion can only form on an intrinsic trap and not on F4TCNQ, where only a loosely bound charge transfer state can be formed with a hole in PPV. This means the number of trions reduces through an effective reduction of the intrinsic trapping (because the electron trapping shifts to the F4TCNQ). The trion model then allows to assign the change in MC to the reduction of a single parameter: the trapping coefficient γ_t of the electrons at the trap sites. All fits in Fig. 2(b) can be attained by only varying this parameter, including the shift of the maximum MC to higher voltages. Due to the competition with F4TCNQ, one can take an effective trapping coefficient $\gamma_{t,\text{eff}}$ from γ_t by taking a weighted average of γ_t and the dopant trapping coefficient γ_{dop} as

$$\gamma_{t,\text{eff}} = \gamma_t \frac{\gamma_t N_t}{\gamma_t N_t + \gamma_{\text{dop}} N_{\text{dop}}}, \tag{1}$$

in which it is naturally assumed that the number of dopant sites N_{dop} scales linearly with the F4TCNQ concentration. As can be seen in Fig. 5(a) the effective trapping coefficient taken from the fits indeed follows this trend.

We now turn to the DMC study. The reduction of the MC(V) with DMC observed in Fig. 2(e) can, in principle, be explained with the deactivation of the intrinsic electron traps. We find that the MC actually reduces linearly with DMC concentration. This can be expected from the trion model, since the MC scales linearly with the number of traps available for trion formation [24]. Therefore the MC(V) is fitted with a varying trap site density N_t, although we also had to allow the voltage dependence of the polaron density parameter a to change slightly as well. As can be seen in Fig. 5(b) the effective trap density taken from the fits indeed follows this linear trend. At some concentration, all the electron traps will be filled and the MC reduces to zero. We note that different batches of devices created on separate days show a slightly different decline of the MC with DMC concentration. This could be due to the low solubility of DMC, leading to deviations in the concentrations. However, the trend is always the same among devices created from the same solvent batch.

Not only does this study show that traps do indeed play a major role in these magnetic field effects, more generally, it shows that molecular doping methods from the field of organic electronics can be used successfully in the field of organic spintronics as well. Vice versa, the analysis of the magnetic field effects may provide novel information about the processes occurring in organic semiconductors. Even at dopant concentrations where the changes in the current are still insignificant, the magnetic field effects can already respond greatly to changes in the polaron reactions and transport. As such, the research of magnetic field effect could play an important role in unravelling the exact nature of trap sites in organic semiconductors. Models incorporating spin dependent reactions, such as the trapped trion model, are now beginning to have clear predictive value, not only at the microscopic polaron pair level, but also in terms of device physics.

We will end this section with a discussion of our current view regarding the nature and role of the "intrinsic" traps at the origin of the magnetic field effects. Recent work suggests that the traps are most likely impurities in the form of oxygen complexes [40]. Although these are probably present, oxygen seems difficult to reconcile with the traps at the origin of the MC. In the literature, it is shown that radiative damage [20] and electrical stress [14] enhances the MC. This would suggest traps created through structural changes or ionization [46] are at the origin of the MC. Finally, we also suggested that an exciton or trion can form on an intrinsic trap, but not on F4TCNQ. This puts a single criterion on the intrinsic traps. Its HOMO should not lie much lower in energy than the HOMO of the host material, i.e., PPV, so that the energy cost of creating an excitation on the trap by transferring a hole from PPV is not too high.

IV. CONCLUSION

In conclusion, using well known dopants we have investigated the influence of traps on magnetic field effects in the semiconducting polymer "super yellow" PPV. We used the strong electron acceptor F4TCNQ and found that the magnetoconductance (MC) declines rapidly with F4TCNQ concentration in a manner that can be assigned to a reduction in the effective electron trapping at the intrinsic trap sites. This result shows that while the intrinsic electron traps of PPV lead to a large MC, the traps induced by the dopant do not, and competition of the latter with the intrinsic traps leads to an eventual decline. Additionally, we used the electron donor DMC that is known to fill and deactivate the PPV traps. This latter study showed a linear decline of the MC as the traps become filled, although we cannot entirely exclude that creating hole traps has no similar effect. Both studies clearly indicate that traps play a crucial role in the large MC observed in thin film PPV devices. Not only are these results highly relevant for the fundamental understanding of spin physics and magnetic field effects in organic semiconductors, they also suggest that traps—which are generally considered detrimental for device performance—can be beneficially utilized in organic magnetic field sensors.

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