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Spectroscopic evidence for trap-dominated magnetic field effects in organic semiconductors

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Polaron traps are ubiquitous in organic semiconductors and recent evidence suggests they might be crucial for the large observed magnetic field effects (MFEs) in organic semiconductors. Here we measure MFEs in polymer thin-film devices with engineered, radiative trap sites in order to spectroscopically investigate the influence of the traps. Surprisingly, the luminescence at the trap sites and the polymer backbone is found to have an opposite response to a magnetic field. All our results are compatible with a mechanism in which spin mixing at the traps can create the large MFEs observed on the backbone. This scenario is quantitatively confirmed by numerical drift-diffusion modeling with magnetic-field-dependent exciton densities at the traps. These insights solve an outstanding controversy within the research field.

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I. INTRODUCTION

Traps are localized states with an energy within the band gap and are a virtually inevitable component of organic semiconductor devices, both disordered and crystalline [1,2]. Unfortunately, their ability to capture polarons and quench excitons is detrimental to the performance of, e.g., light-emitting and photovoltaic devices. Understanding [1,3], preventing [4], and disabling [2,5] traps is an active field of research with a significant impact on future applications. However, traps can also be beneficial. Experimental evidence suggests that traps contribute to the magnetoresistive properties of organic semiconductors [6–11]. Damaging organic thin-film devices leads to dramatic increases in the magnetoresistance [7,8], while specifically deactivating the traps completely quenches the magnetoresistance [11]. Nevertheless, most work regarding magnetic field effects (MFEs) in organic semiconductors neglects the ubiquitous traps or dismisses them as device physics, irrelevant for the microscopic spin processes at the origin of the MFEs.

Magnetic fields have long been known to influence molecular reactions [12]. The remarkably large MFEs in organic, electroluminescent devices are seemingly caused by a polaron pair model of electron-hole reactions [13,14]. Such a model describes how the formation kinetics of excitons from electron-hole pairs is altered by a magnetic field, changing the generated ratio of singlet (S) and triplet (T) excitons [15]. In this framework, the MFEs are explained with a change in effective recombination [16] or via the influence of triplets on the polaron transport [9,17,18]. Independent of the exact mechanism, a decrease of the T formation should be accompanied by an increase of the S formation and vice versa. However, all previous attempts to measure these S and T exciton densities suggest that both increase upon application of a magnetic field [19,20], which is in direct conflict with the model.

In our work we resolve this discrepancy via experimental results showing that the luminescence at the electron traps and the polymer backbone has a response of opposite sign to a magnetic field. This indicates that different processes may be occurring on the trap sites. We conjecture that a change in the S/T ratio at the trap sites leads to an increase in both free S and T densities—a mechanism that was overlooked in all former studies. This conjecture is confirmed by detailed device modeling, thereby solving this inconsistency within the research field. Thus we show that traps play an important role in the spin-dependent processes and that they cannot be neglected in the explanation of the MFEs.

The thin-film devices with large MFEs investigated in the literature generally have traps that are nonradiative. This limits the use of sensitive (optical) spectroscopy in their investigation, for which there is a strong call in all organic spintronics-related research [21]. To overcome this predicament, we performed experiments on copolymers designed for white light emission. These copolymers have radiative dyes incorporated in the backbone, which can act as trap sites. We obtained the same polymers as used by Nicolai et al. [22], which were fabricated by Merck (for the chemical structure, see Fig. 1): a blue backbone copolymer, a backbone with green dyes, and a backbone with green and red dyes. Note that the backbone polymer already contains initial electron traps [23], just like many other semiconducting polymers [1], and that their exact nature is still under debate. Here we refer to such traps as the “intrinsic” traps.

II. EXPERIMENTAL RESULTS

The experiments were performed on typical organic light-emitting diode (OLED) structures with the copolymers as active layer. The devices consisted of patterned indium tin oxide glass substrates on which poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PE-DOT: PSS) (50 nm) and the active layer (150 nm) was spin coated. A top electrode consisting of LiF (1 nm)/Al (100 nm) was thermally evaporated in a high-vacuum system inside a nitrogen-filled glove box. After fabrication, the devices are...
always kept in a nitrogen-filled environment. The bias voltage \( V \) and current \( I \) were set and measured using a Keithley 2400 source measure unit (SMU). The magnetic field dependence of the current \( I(B) \) was measured by placing the sample between the poles of an electromagnet and is calculated by \( MC(B) = \frac{I(B) - I(0)}{I(0)} \). The electroluminescence (EL) was measured with a silicon photodiode or with a spectrometer, which consisted of a spectrograph (Newport MS260i) and back-illuminated charge-coupled device (Andor DV420-BV). EL measurements with the spectrometer were performed at constant currents.

### A. Backbone polymer

We first turn attention to the results of the blue backbone polymer, for which the EL and magnetoeloluminescence (MEL) results are shown in Fig. 2. The EL spectrum shown in Fig. 1(a) shows a clear peak around 450 nm, consistent with bimolecular recombination at the backbone. Surprisingly, at low voltages luminescence is also visible at much longer wavelengths. This luminescence seems to peak around 640 nm and it does not increase as rapidly with voltage as the backbone emission. The relative change of this light emission with respect to the backbone emission, shown in Fig. 2(b), is a clear signature of deep trap-assisted Shockley-Read-Hall (SRH) recombination [3]. The bimolecular process occurring on the backbone. The relatively large energy difference between the bimolecular and trap-assisted emission (\( \sim 0.8 \) eV) indicates the traps are positioned deep within the band gap.

The new observation that the initial or “intrinsic” traps are radiative makes it possible to investigate the magnetic field effects occurring on and due to these traps. Results of the spectrally resolved MEL are shown in Fig. 2(c). As expected, the EL around 450 nm increases significantly when a magnetic field is applied. More interestingly, we find a sign change of the MEL at wavelengths that correspond to the trap-assisted recombination. Additionally, it is observed that the bimolecular backbone MEL reduces strongly with voltage [shown in Fig. 2(d)], while the reduction of the trap-assisted MEL seems to be less strong or absent. Note that at higher voltage the EL around 640 nm is mainly dominated by the shoulder of the bimolecular recombination [see Fig. 2(a)]. This may affect the observed weak voltage dependence of the trap-assisted MEL.

To investigate the influence of these traps more closely, electrical stressing experiments were performed. Electrical stress has been shown to enhance the MFEs, which was suggested to be due to the formation of trap sites [7]. Here, two experiments were performed in sequence: first, a voltage of 6.5 V was applied for 1 h and subsequently a voltage of 7.5 V for 1 h. After each run, magnetoconductance (MC), EL, and MEL were measured. The MC was found to increase after each run (not shown here), similar to what was observed in the literature. Because the traps are radiative, we now have access...
to the relative contribution of the trap-assisted recombination increases with electrical stressing, as can be seen in the EL of Figs. 2(a) and 2(b). These results further strengthen the notion that the contribution of traps enhances after device degradation. Furthermore, in Figs. 2(c) and 2(d) it is observed that the MEL arising from the bimolecular recombination increases with electrical stressing; however, the MEL from the trap-assisted recombination remains approximately constant.

B. Incorporating dyes

Besides enhancing the number of traps through electrical stressing, we have investigated the possibility to chemically engineer traps with green and red dyes incorporated into the (blue) backbone [22]. The highest occupied molecular orbital (HOMO) of the dyes aligns perfectly with the HOMO of the backbone, while the lowest unoccupied molecular orbital (LUMO) of the dyes lies lower in energy. Thereby, the dyes only act as electron traps. The EL spectra of the three different copolymers are shown in Fig. 3(a). One can clearly distinguish the different peaks from the dominant dye present in the copolymers, one around 520 nm for the green dye and one around 620 nm for the red dye. Figure 3(b) shows how the strength of the green dye emission remains constant with voltage, while the red dye emission reduces drastically. The reason is that the EL arising from the green dyes can be attributed to energy transfer of excitons, while the red dyes clearly exhibit trap-assisted recombination [22]. This allows us to investigate the effect of these two separate processes on the MFEs.

The MEL measurements for the different devices can be seen in Figs. 3(c) and 3(d). The addition of a green dye does not affect the amplitude of the backbone MEL and its emission has the same MEL as the backbone. The green dye emission obscures the intrinsic trap emission, which can explain the increase of the MEL at wavelengths above 550 nm. Adding a red dye to the copolymer significantly reduces the backbone MEL, while concurrently the MEL of the red dye itself is positive, thereby increasing and changing the sign of the MEL at wavelengths above 600 nm. In Figs. 3(e) and 3(f) we find the same trend with the two dyes at all voltages for both the MC and the MEL. The green dye has virtually no effect on the MFEs, while the red dye significantly reduces both the MC and the MEL.

C. Discussion of experiments

The negative, trap-assisted MEL in the backbone polymer is itself a novel find and suggests that the number of singlet excitons (at the trap sites) can actually reduce when a magnetic field is applied. The central question we wish to address is whether the magnetic field directly changes the S/T ratio on the backbone or the S/T ratio on the traps. The fact that the backbone MEL decreases strongly with voltage and increases with electrical stressing suggests it depends on the number of traps and their contribution to the device. This is difficult to reconcile with an intrinsic change in the backbone S/T ratio, which should not depend on the number of traps. On the other hand, the trap-assisted MEL remains relatively constant under varying voltage and electrical stress, which does point to an intrinsic change of the trapped S/T ratio. Therefore, we conjecture that all the MFEs (MC, bimolecular MEL, and trap-assisted MEL) in these thin-film devices are dominated by microscopic spin-mixing processes occurring on the trap sites.

The experimental results from the BG and BGR polymers suggest that capturing excitons generated from bimolecular recombination with the green dyes has no effect on the MFEs, while adding electron traps with the red dyes can significantly alter the MFEs. These results correspond again with the conjecture that traps are at the origin of the MFEs and not the processes occurring on the backbone. While electrical stressing enhances the MFEs by creating additional traps with the same magnetic response, the red dyes have an opposite MEL compared to the intrinsic traps, which results in a
reduction of the total MC and backbone MEL. These results indicate that the exact physical origin of the traps has a drastic influence on both the strength and the sign of the MFEs.

III. NUMERICAL CALCULATIONS

Our experimental results suggest that a change in recombination at trap sites can lead to an opposite response in the bimolecular recombination and current. Previously, it was assumed that the S/T exciton ratio should change in favor of the singlets on application of $B$ to explain a positive MEL [15]. Now we find the opposite in our experimental results regarding the blue copolymer: a negative trap-assisted MEL indicates a reduction of the S exciton density at the traps with $B$, which suggests an increase of T excitons (at the traps). But how can this cause the observed MFEs at the backbone?

To answer this question we investigated multiple spin-dependent mechanisms at the traps. As illustrated in Fig. 4, trap-assisted recombination consists of multiple steps that could be spin selective. These steps include electron trapping, electron-hole recombination, and exciton formation. Within the framework of a polaron pair model, a magnetic field can influence any of these processes. Magnetic-field-dependent trapping could arise if the ground state of the trap site is a spin radical, such as an oxygen complex. The trap itself would then act as the second particle in a pair. Similar to electron-hole recombination in a bimolecular reaction, a magnetic field can influence the effective recombination rate or the formed singlet/triplet exciton ratio [15]. We note that unlike excitons created in a bimolecular process on the backbone, which are free to move around, the excitons created in a trap-assisted recombination process will most likely occupy the trap on which they were formed.

These mechanisms are investigated quantitatively with a drift-diffusion device model, where the magnetic field effect is incorporated as a change in a material parameter [24], such as the trapping coefficient. We recently exploited such an approach to describe magnetic field effects in polymer-fullerene blends [14] and electrochemical cells [25]. This device model can easily incorporate bimolecular Langevin recombination, trap-assisted SRH recombination, and exciton formation.

The model includes free holes and electrons with densities $p$ and $n$, respectively, and mobility $\mu$. Free electrons are trapped with a coefficient $C_n$ at the available trap sites density $N_t$, resulting in a trapped electron density $n_t$. For simplicity we implemented deep electron traps with a single energy level $E_t$ below the LUMO. Electron trapping only occurs if a trap is empty. The trapping rate thus depends not only on the number of traps, $N_t$, but also on their occupation $f = (n_t + T_t)/N_t$, which includes the trapped electron density $n_t$ and the (optional) trapped exciton density $T_t$. Trapped electrons and free holes undergo trap-assisted recombination with a coefficient $C_p$. In the case of exciton formation, triplet excitons are formed from this process with a magnetic-field-dependent probability $P_T(B)$. We neglect the singlet exciton density because of their short lifetime. The triplets will undergo a monomolecular decay governed by their lifetime $\tau_T$.

Most material parameters are taken from the device characterization of Nicolai et al. [22,23]. The LUMO and HOMO energies are 2.2 and 5.3 eV, respectively. We used $\mu = 1 \times 10^{-10}$ m$^2$ V$^{-1}$ s$^{-1}$, $E_t = 0.8$ eV, and $C_n = C_p = 9 \times 10^{-19}$ m$^3$ s$^{-1}$. Triplet lifetimes can be taken from the literature [26,27]. Monomolecular decay rates of more than 0.5 ms have been found for free triplet excitons [26], while at trap sites triplets have been suggested to live longer than 100 ms at ambient temperature [27]. Here we take a triplet lifetime of $\tau_T = 5$ ms, which still results in significant trap occupation yet manageable calculation times.

A. Field-dependent exciton formation

We first focus on the mechanism that explains the experimental results best: a trap-occupation mechanism based on exciton formation, shown schematically in Fig. 5(a). Trapped electrons will recombine with holes and have a certain probability to become triplet ($P_T$) or singlet ($P_S = 1 - P_T$) excitons. Due to the spin mixing from hyperfine fields, these probabilities depend on the kinetics: a faster S exciton lifetime leads to $P_S > 1/4$ [15]. A magnetic field suppresses the spin mixing and returns $P_S$ towards its statistical value of 1/4. The change in current and the bimolecular EL arise due to the difference in S and T exciton lifetime. The radiative, short-lived S will have a negligible density, while the long-living T can significantly occupy the trap sites, thereby blocking further polaron trapping and recombination. For $k_S > k_T$ a magnetic field thus results in more free charges, which subsequently enhances the current and luminescence. A big difference from previous triplet-based mechanisms is that we no longer assume $k_S < k_T$ and we do not need specific reactions with other particles to account for the MFEs [9,17,18], although such triplet-polaron mechanisms can also be implemented.

Since we wish to focus on the effects of exciton formation at the trap sites on the MFEs, we neglect the influences of free triplet excitons in the model. In previous work we have already shown that interactions of free triplets with polarons do not lead to the correct voltage dependence of the MFEs [24]. Transfer of backbone triplet excitons to the trap sites might actually influence the MFEs; however, our experiments give a good
where $P_{\text{rec}}$ (cannot be measured in the experiments. Trap densities of 1
a magnetic field will increase the $T/S$ ratio on the traps. (b) The calculated ratio between SRH recombination ($R_{\text{SRH}}$) and Langevin recombination ($R_L$). (c) The calculated MC and (d) bimolecular MEL, where $P_S$ is reduced from 0.90 to 0.88. The MEL at low voltages cannot be measured in the experiments. Trap densities of $1 \times 10^{-4}$ (squares), $2 \times 10^{-4}$ (circles), and $4 \times 10^{-4}$ nm$^{-3}$ (triangles) were used.

indication that polaron trapping, and not exciton transfer, is the dominant process at the intrinsic traps. This can be concluded from the voltage dependence of the trap-assisted luminescence [see Fig. 2(b)]. If exciton transfer were the dominant process, the trap-assisted luminescence would scale with the backbone luminescence (similar to the green dye luminescence).

Figures 5(b)–5(d) show an overview of the simulation results for the trap-occupation mechanism, starting with the ratio of trap-assisted SRH recombination $R_{\text{SRH}}$ versus backbone Langevin recombination $R_L$ in Fig. 5(b). As can be seen this ratio reduces strongly with voltage and increases with more traps, similar to the experiments in Fig. 2(b). The MC and bimolecular MEL of the trap-occupation mechanism are shown in Figs. 5(c) and 5(d), respectively. The trap-occupation mechanism can explain the experimental results [in Figs. 3(c) and 3(d)]; we find relatively large, positive MC with an even larger MEL and correct voltage dependencies. The MEL peaks at lower voltages than the MC, which cannot, unfortunately, be confirmed by experiments, since we are unable to measure the MEL at the low light intensities at voltages around the built-in voltage. Furthermore, both the MC and the MEL clearly increase with the trap density in the model.

The exact value $P_S$ is not known (on the traps). In the calculations shown in Fig. 5 we used $P_S = 0.88$, but this could be different in reality. We found that a smaller $P_S$ in the trap-occupation mechanism (due to larger $k_T$) does not significantly alter the MC and MEL, but it will require larger changes to account for the experimental magnitude. Additionally, we investigated the influence of triplet-polaron quenching, which essentially reduces the triplet exciton density. We found that, as long as the triplet-polaron coefficient is relatively small, triplet-polaron reactions do not significantly influence the outcome. We should note that triplet-polaron reactions are generally used to explain high field effects [14,25] and might therefore be required in a complete physical picture of the magnetic field effects.

**B. Other mechanisms**

As mentioned before, other magnetic-field-dependent processes may occur on the trap sites, even in lieu of exciton formation. Using polaron pair models, it could be argued that a magnetic field effectively influences the trap-assisted recombination or polaron trapping. Calculations of such mechanisms are shown in Fig. 6. The first would be similar to an electron-hole pair mechanism proposed in the past for bimolecular recombination [16]. In such a mechanism, the effective e-h pair recombination is spin dependent due to either asymmetric singlet and triplet recombination rates ($k_S \neq k_T$) or dissociation rates ($q_S \neq q_T$). However, in such a mechanism one has to assume that dissociation of the e-h pairs is significant in OLEDs, which can be criticized on the basis of energetic arguments and may only be relevant in organic photovoltaic systems [14]. Nevertheless, this mechanism would result in a reduction of the trap-assisted recombination, which can then enhance the current and backbone luminescence.

The second possibility, magnetic-field-dependent trapping, could arise if the ground state of the trap site is a spin radical, such as an oxygen complex. In that case an electron may only be trapped (or be trapped more favorably) if it has an opposite spin as the trap. Trapping will then depend on the spin mixing and will reduce in an applied magnetic field. These two mechanisms are simulated with a (magnetic-field-dependent) reduction of $C_p$ and $C_n$, respectively. As shown in Fig. 6 both these mechanisms lead to relatively small changes and voltage dependencies different from the experimental results. Therefore, we conclude that the trap-occupation mechanism is the best explanation for the experimentally observed magnetic field effects.

**C. Adding red dyes**

Another question that presents itself is how the inclusion of red dyes could reduce the MC and MEL. As Fig. 3 illustrated, the red dyes show an opposite trap-assisted MEL. When the magnetic field effects are purely dominated by the traps, a
sign change on the traps would result in an opposite (negative) response in the MC and bimolecular MEL. This in itself can explain the experimental results. We note that in order to obtain a positive MEL in the polaron pair model one needs $k_S < k_T$ on the red dyes, while a negative MEL on the “intrinsic” traps implies $k_S > k_T$. This suggests these rates might be strongly material dependent.

The red dyes also distinguish themselves in another manner from the intrinsic traps: they are much more luminescent. Many parameters can influence their luminescent properties, which may also influence the MFEs caused by these dyes. Here we investigate the possibility that the triplet lifetime is negligible on the red dyes, which means the dyes are not occupied by excitons. This can increase the number of trapped electrons and their subsequent SRH recombination with free holes (thus increasing their luminescence). Without triplet excitons the dyes themselves do not lead to any appreciable MC. Nevertheless, in Fig. 7 we show that when we add traps without excitons to the device, we still find that the MC and bimolecular MEL reduce significantly. This is due to the fact that the added traps compete with the intrinsic traps over free electron density. When the traps without excitons dominate the trapping behavior of the device, the MC will be effectively quenched. These results show that to engineer the magnetic field effects in devices one should thus always add traps with favorable parameters, such as a long triplet exciton lifetime.

IV. IMPLICATIONS AND CONCLUSIONS

The experimental and numerical results are crucial for the fundamental understanding of magnetic field effects. A change in $S/T$ ratio at the traps can enhance the current and backbone luminescence. An increase in both singlet and triplet exciton densities, as was measured in the literature [19,20], thus occurs simply because the total electron-hole recombination increases on the backbone. What should be measured instead are the magnetic-field-dependent singlet and triplet densities at the trap sites. Our experimental results provide the verification that the singlet exciton density at the trap sites can indeed decrease. Additionally, our results have implications for predictive OLED models. We find that these should include long-living excitations at the trap sites.

In conclusion, the magnetic-field-dependent current and luminescence in polymer thin films with radiative traps was investigated spectroscopically. Surprisingly, we found an opposite response in the MEL of the traps with respect to the backbone. The MC and MEL can be tuned by creating traps through electrical stressing or incorporation of dyes. The experimental results strongly suggest that magnetic-field-dependent processes at the trap sites affect the MC and MEL in the device. Numerical device calculations further elucidated that a magnetic-field-dependent triplet exciton density at the trap sites can explain the magnetic field effects. An increase in triplet excitons with magnetic field will lead to a reduction in polaron trapping and recombination, which enhances the current and backbone luminescence. These results show that trap sites and their influence on devices cannot be neglected—and might in fact dominate—in the explanation of magnetic field effects and the underlying spin physics in organic semiconductors.

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