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Anisotropic magnetoconductance in polymer thin films

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The dependence of the magnetic field sensitive current on the orientation of the magnetic field has been investigated in organic semiconductor devices where the active layer consists of the poly(p-phenylene vinylene) derivative “Super Yellow.” Previous work on Alq3 suggested that the anisotropy was caused either by anisotropic spin-spin interactions or by anisotropic hyperfine fields, but no discrimination could be made. In the present work, the anisotropy at the hyperfine field scale is best explained by dipolar coupling between the spin of polarons. In addition, a high field anisotropy is found with an opposite sign, different angle, and voltage dependence. Spin density matrix calculations were performed of polaron pair interactions for the low field effect, and a Δg-mechanism, triplet-polaron, or triplet-triplet interaction for the high field effect. The simulations confirm that the low field anisotropy can indeed be explained by dipolar coupling. However, the proposed models cannot entirely account for the high field anisotropy. These results show that, although contemporary models can account for (anisotropic) magnetic field effects in organic semiconductors at low field scales, more experimental and theoretical research of high field effects is highly desirable.

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I. INTRODUCTION

Large changes in the current and luminescence with magnetic field have been observed in organic semiconducting devices during the last decade [1–11]. Such effects have been investigated in organic light emitting devices (OLEDs) [1–4], donor acceptor blends [5,6], field effect transistors [7,8], polymer light-emitting electrochemical cells [9,10], and molecular wires [11]. These magnetic field effects (MFEs) manifest themselves at room temperature and small magnetic fields of only a few millitesla, which has led to the suggestion of cheap plastic sensor applications [12]. It was recently shown that the effects are angle dependent [13] and can be exploited as a compass to detect the local earth magnetic field [14]. The spin dependent processes at the origin of these magnetic field effects have undergone an extensive experimental and theoretical investigation [13,15–27]. Nowadays, this knowledge is used to analyze spin dependent processes in greater detail, such as exciton fission in organic solar cells [28], thereby turning the MFEs into a spectroscopic tool themselves. In order to optimally take advantage of these magnetic field effects, a solid fundamental understanding of the underlying physics is required.

Contemporary models regarding a magnetic field sensitive current, or magnetoconductance (MC), generally deal with pairs of spin carrying particles. For example, such models can incorporate spin-blocking mechanisms between polarons with the same charge [18,25] or spin dependent recombination of electrons and holes [15–17,27]. In the past, it was claimed that the MC was isotropic with respect to the magnetic field orientation [1,19]. For this reason, the models did not investigate any mechanisms that incorporated anisotropy in the particle interactions. Wagemans et al. showed that the MC does exhibit a finite angle dependence. In their work, the authors point out that spin-spin interactions between polarons need to be included in the models. With simulations they showed that in order to obtain an angle dependent MC there must be anisotropy in either the spin-spin interactions—through dipolar coupling—or in the hyperfine fields that are responsible for the mixing. However, they were unable to discriminate between these two possibilities. Recently, the calculations on anisotropic spin-spin interactions were reconfirmed with a slightly different method by Harmon and Flatté [25], who also pointed out the need for additional experimental verification.

In this paper, we report on angle dependent measurements of the MC in OLEDs where the active layer consists of the copolymer poly(p-phenylene vinylene) derivative “Super Yellow” (SY-PPV). We find a different angle dependence compared to Wagemans et al. who investigated devices consisting of Tris(8-hydroxyquinolinato)aluminum (Alq3) [13]. Additionally, both low and high field components are found. The low field component arises at magnetic fields on the order of the hyperfine field scale and shows a distinctive feature that can be explained by anisotropic dipole-dipole coupling in polaron pairs. At higher field scales the angle dependence itself changes sign and shape, which points at a different origin of anisotropy. Using spin density matrix simulations we investigate the possible anisotropy in the Δg mechanism, triplet-polaron quenching, and triplet-triplet annihilation, which have been proposed in the literature as possible high field effects for organic magnetoresistance. We find that none of these mechanisms can unambiguously explain the observed high field anisotropy.

II. EXPERIMENTAL DETAILS

The experiments were performed on typical OLED devices with SY-PPV as the active layer (90 nm). The magnetic field effects in this material have been studied thoroughly in the literature [4,27]. The bottom of the devices consisted of patterned indium tin oxide glass substrates on which poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) was spin coated (50 nm). A top electrode consisting of LiF (1 nm)/Al (100 nm) was thermally evaporated in a high vacuum system inside a nitrogen filled glovebox. All devices were then
transported under nitrogen atmosphere to another nitrogen glovebox, where they were placed between the poles of an electromagnet. The current $I$ was measured using a Keithley 2400 series. The magnetic field dependence of the current $I(B)$ is calculated with $MC(B) = [I(B) - I(0)]/I(0)$. A small motor rotated the sample at a constant speed with respect to the magnetic field, where the angle $\theta$ was defined with respect to the sample normal. This can be used to measure the change in current and $MC$ as a function of the angle at a fixed magnetic field. Additionally, this motor can also be used to perform two magnetic field sweeps in quick succession, while rotating the sample 90 degrees in between the sweeps. Thereby, one can look at the difference between the $MC$ as a function of magnetic field in parallel and perpendicular alignment with as little time delay as possible. We note that for all results corrections for the drift in the current were performed.

III. LOW FIELD ANISOTROPY

A typical MC measurement and the angle dependence at a constant magnetic field can be seen in Fig. 1. The angle dependence is periodic over half a rotation and shows a distinctive W shape with two minima around $\theta = 60^\circ$ and $\theta = 120^\circ$. These findings are in clear contrast to the previously reported $\cos^2 \theta$ dependency in the angle dependence of devices created with the small molecule Alq3. However, the theory for such a W shape has already been described in the literature [13,25,29].

Most theoretical work on the MC has focused on the question of how a magnetic field can influence spin dependent interactions and reactions [13,15,16,18,22,23,25,29], such as the recombinination of electrons and holes. Prior to the actual reaction the particles will form precursor pairs in which the total spin of the pair can be mixed due to dephasing reaction the particles will form precursor pairs in which the recombination of electrons and holes. Prior to the actual question of how a magnetic field can influence spin dependent corrections for the drift in the current were performed.

\[ \Delta(\alpha) = \frac{1}{2} D(1 - 3\cos^2 \alpha) - 4 J |, \]

where $\alpha$ is the angle between the polaron separation vector and the applied magnetic field, $D$ is the dipolar coupling strength, and $J$ is the exchange interaction strength. In the case that $|J| > 1/2 |D|$ one finds a $\cos^2 \alpha$ dependency, such as was found in previous experimental studies. In the other case, additional extrema are found, similar to our experimental findings in Fig. 1(b). This strongly suggests the anisotropic dipole-dipole coupling of the polaron spins is at the origin of the angle dependence. However, the energy difference of Eq. (1) cannot perfectly describe the experimental results, mainly because the minima around $60^\circ$ and $120^\circ$ are too sharply defined.

We found that a function derived by Groff et al. [29] does describe the rounded features in our experimental data well. The authors showed with lowest order perturbation theory that...
(at magnetic fields much larger than the hyperfine fields) the fraction of triplet pair states scales with:
\[ f(\alpha) \propto (\Delta(\alpha)^2 + c^2)^{-1}, \]  
(2)
in which \( \Delta \) is the energy difference defined by Eq. (1). The constant \( c \) is independent of the electron-hole interactions, such as the dipolar coupling. Thereby, \( c \) arises from anything else that influences the triplet fraction: the Zeeman interaction, the hyperfine fields, and/or the hopping dynamics. In their work, Groff et al. investigated the angle dependence of the delayed fluorescence in dye sensitized anthracene crystals under the influence of a magnetic field. The authors used Eq. (2) for a qualitative study of the spin-spin interactions of charge transfer states in these crystals.

Here we find that this function seems applicable for polaron pairs in disordered organic semiconductors as well. From our fit in Fig. 1(b) we find only a relatively small exchange interaction strength (\( J = 0.06D \)), as was suggested before. The fact that a weak exchange interaction compared to the dipolar coupling strength is observed in SY-PPV suggests that there is little polaron wave-function overlap in the precursor pair. This could be due to a relatively large polaron pair separation distance in SY-PPV compared to other materials, as the exchange interaction strength is considered to fall off more rapidly with distance than the dipolar coupling strength [30].

In order to more quantitatively study the angle dependence, we have performed numerical density matrix simulations of spin pairs using the stochastic Liouville equation. Such an approach has also been used to describe a large variety of magnetic field dependent effects, such as magnetoelectroluminescence in organic semiconductors [22], magnetic resonance spectroscopy [31], and even magnetoreception in birds [32]. For a complete overview of this calculation method for the MC, we refer to Schellekens et al. [23]. It can be used to describe both bipolaron [18,23] as well as e-h pair models [22,23]. Here we choose an e-h pair approach with spin dependent exciton formation, although we note that the conclusions drawn from this approach can also be generalized to other models with a similar spin mixing mechanism at its basis.

For the calculations we assume a higher triplet polaron pair recombination rate \( k_T \) into excitons than the singlet recombination rate \( k_S \). This will result in an increase in the formation of singlet excitons with magnetic field [22], leading to a positive magnetoelectroluminescence as has been observed in the literature [4,5,20]. A ratio of \( k_T/k_S = 2 \) can be considered realistic based on measurements of the singlet exciton fraction [22]. However, we emphasize that the exact choice merely scales the total MC and does not really influence the shape and relative size of the angle dependence. The increase in current is then attributed to the reduction in triplet excitons with magnetic field, which are generally assumed to hamper the polaron transport [16,21]. Such triplet-polaron interactions are considered to be the dominant cause of the MC in OLEDs by many [6,16,17,21,26,27].

For the hyperfine fields we use a Gaussian distribution with the hyperfine field strength \( \sigma_{hf} \) as standard deviation. The dipolar coupling is incorporated similar to Wagemans et al. with a coupling strength of \( D = 0.5\sigma_{hf} \). We emphasize that its exact value is not critical, and a good match with experimental data can also be found with somewhat different values. Furthermore, we assume that the hyperfine field strength in our SY-PPV is similar to the value of 1.2 mT found for PPV based polymers [20]. In general, the dipolar coupling strength is given by \( D = \mu_B g^2/\langle 4\pi\hbar R^3 \rangle \). Our specific parameter choice would then correspond to a typical displacement of 1.5 nm, which is in the order of the distance between hopping sites found for PPV based polymers [33]. Magnetic resonance measurements of organic semiconductors have so far been unable to detect dipolar coupling in polaron pairs [34], so the actual separation distance is not known. Unfortunately, our magnetoresistive measurements cannot provide information on the exact dipolar coupling strength either. However, in view of the fact that the precise coupling strength is not critical to match our simulations with the experiments, we conclude that our choice of parameters is not unrealistic.

In our model, we then look at the triplet exciton fraction \( \chi_T \) and its relative change with magnetic field \( \Delta \chi_T(B) = (\chi_T(B) - \chi_T(0))/\chi_T(0) \). In most recent work, calculations were performed in the so-called slow hopping limit, where all the rates are much slower than the hyperfine precession frequency \( \omega_{hf} = g\mu_B\sigma_{hf}/\hbar \), in which \( g \) is the polaron \( g \) factor, \( \mu_B \) is the Bohr magneton, and \( \sigma_{hf} \) is the hyperfine field strength.

In order to investigate whether the slow hopping assumption is affecting the anisotropic MC, we first look at the influence of the hopping rate on the total angle dependence. This is done by increasing the rates \( k_T, k_S \), and the e-h pair formation rate \( q \)—all of which incorporate a hop—by the same amount. In Fig. 2(a) the amplitude of the MC as a function of the hopping rate is shown both for a parallel and perpendicular orientation of the magnetic field and polaron separation vector. A clear trend can be observed in both the amplitude of the MC and its angle dependence. In the slow hopping limit \( (k_T \ll \omega_{hf}) \) a surprisingly large angle dependence is found for a realistic dipolar coupling strength. As the hopping rate is increased both the angle dependence and the total magnetic field effect are quenched, however the angle dependence already starts to reduce at lower hopping rates. The quenching of the MFE occurs in the intermediate hopping range (at magnetic fields much larger than the hyperfine fields) the fraction of triplet pair states scales with:
\[ f(\alpha) \propto (\Delta(\alpha)^2 + c^2)^{-1}, \]
(2)
FIG. 2. (Color online) (a) Simulated change in triplet exciton fraction at large magnetic field ($B \gg \sigma_{hf}$) when all rates that incorporate a hop are increased ($q,k_T,k_S$). In both the parallel (0°) and perpendicular (90°) configuration the magnetic field effect is quenched, but the relative difference (red circles) is already quenched at smaller hopping rates. (b) Simulated change in triplet exciton fraction as a function of the angle between the magnetic field and the displacement vector of the polaron pair for a hopping ratio $k_T/\omega_{hf} = 4$. For all simulations we used $q = k_T = 2k_S$ and $D = 0.5\sigma_{hf}$.

IV. HIGH FIELD ANISOTROPY

So far we have only discussed the angle dependence at low magnetic fields. We will now discuss our study of the angle dependence as a function of magnetic field up to 500 mT. An overview of these results can be seen in Fig. 3. What is most remarkable is that the angle dependence is observed to change sign at high magnetic fields, as can be seen in Fig. 3(a). However, the effect at high fields does not have exactly the same shape as at low fields. This is most noticeable at intermediate fields around 200 mT where the angle dependence does not cancel out to zero.

In Fig. 3(b) the MC is shown for the parallel and perpendicular orientation of magnetic field with respect to the sample normal. From their difference one can estimate the amplitude of the angle dependence as a function of magnetic field. This shows that at low fields the angle dependence first has an increasing negative component, while at larger magnetic fields an increasing positive component is observed, eventually leading to a sign change. For the total MC it has already been...
established that a discrimination between a low field effect (LFE) and a high field effect (HFE) can be made [6,35]. Here we find that a LFE and HFE discrimination can be made in the angle dependence as well. The main difference is that in the present device (and typical for pristine polymer devices [6,27]) the HFE in the MC has the same sign as the LFE, whereas the HFE in the angle dependence of the MC has an opposite sign. Clearly, the trend of the angle dependence with magnetic field does not match the trend of the MC, which is again in strong contrast to the work of Wagemans et al. on Alq3.

In addition, we observed that the MC and its angle dependence reduce with applied bias voltage for voltages above the built-in voltage. The reduction in MC with increasing voltage is well known in the literature [1,3,4,13,16,27]. However, when normalizing the angle dependence to the MC, we observe an almost constant LFE anisotropy while the amplitude of the HFE anisotropy actually seems to increase with voltage. The normalized angle dependence is shown in Fig. 3(c) for different applied bias voltages.

Fig. 3(c) also shows a fit of the angle dependence at 5 V. Here an empirical double “non-Lorentzian” function is used,

\[
MC(B) = a_{\text{LFE}} B^2 / (|B| + B_{\text{LFE}})^2 + a_{\text{HFE}} B^2 / (|B| + B_{\text{HFE}})^2,
\]

(3)
to separate the low and high field effect with an amplitude \(a_{\text{LFE}}\) and \(a_{\text{HFE}}\), respectively, and with a width \(B_{\text{LFE}}\) and \(B_{\text{HFE}}\), respectively. In the past, these non-Lorentzian functions have been found to accurately describe the LFE in various materials [2] and numerical spin density matrix calculations can also account for such functions [18,23]. Using two non-Lorentzians to discriminate between the LFE and HFE is an approach that has already been used in the literature [6,35]. With this approach it is possible to extrapolate the size of the LFE at large magnetic fields. Thereby, one can subtract the low field angle dependence from the high field results to find the pure HFE component. In Fig. 3(a) we have shown the pure HFE MC as a function of the angle.

At high fields the Zeeman interaction is much larger than the hyperfine interaction. Therefore, changes in spin mixing have to be attributed to another mechanism. Several suggestions have been proposed for the HFE in the literature; an overview of these is given by Schellekens et al. [23]. One distinct HFE is called the \(\Delta g\) mechanism, where a (slight) difference in \(g\) factor of the polarons is considered to lead to a different spin precession at high fields and thus more spin mixing. Additionally, the reaction of triplet excitons either with polarons or other triplet excitons is spin dependent and considered to cause a high field effect. The linewidth of the high field component is then attributed to the zero field splitting (ZFS) of the triplet exciton, which is generally about two orders of magnitude larger than the hyperfine interaction [36]. In the remainder of this section, we will investigate these possible mechanisms for the high field effect and its anisotropy. Similar to the LFE, we performed numerical density matrix calculations of spin pairs. However, we will find that these mechanisms cannot unambiguously explain the observed HFE anisotropy.

The most unlikely candidate for the HFE and its angle dependence in the present system is the \(\Delta g\) mechanism. First of all, an unrealistically large \(g\)-factor difference is required to obtain a HFE in the correct field range. Secondly, the HFE in the MC will always have a sign opposite to the LFE. Both of these arguments have already been made in the literature [23]. Additionally, there will be no change in the shape of the angle dependence as we observe in our experiments, because the anisotropy in the HFE has the same origin as the LFE, i.e., the dipolar coupling. All of these arguments are also confirmed by our density matrix calculations, shown in Figs. 4(a) and 4(b). The MC as a function of magnetic field shown in Fig. 4(a) clearly shows the opposite sign of the HFE. The angle dependence of this HFE will reduce to zero at large magnetic fields, which can also be seen in Fig. 4(b). We note that the \(g\) factor itself could also be slightly anisotropic. However, Wagemans et al. already excluded this as a possible origin for the angle dependence, because it is generally negligible in disordered organic semiconductors [13].

This leaves us with a triplet based mechanism. Such a mechanism can have a completely different kind of anisotropy compared to a polaron pair spin mixing mechanism, since it can have anisotropy in the zero field splitting of the triplet exciton. This might explain why the HFE has a different angle dependence than the LFE. In addition, the number of triplet excitons in a device will increase with voltage, which could explain why the relative HFE angle dependence increases with voltage. We note that around 1970 triplet-polaron and triplet-triplet quenching mechanisms have already been suggested to be responsible for magnetic field anisotropy in the fluorescence and photoinduced currents in anthracene and tetracene crystals [37,38].

Triplet excitons can react with polarons in the following manner:

\[
T + e \leftrightarrow [T + e] \Rightarrow S_0 + e^* .
\]

(4)

where \(S_0\) is the ground state, and \(e\) and \(e^*\) are the electron and an excited electron, respectively. We note that the reaction with a hole proceeds in an identical way. The reaction in Eq. (4) has been suggested in the literature to significantly influence the current [16,27], either by releasing trapped polarons or by trapping of free polarons. The reaction to the ground state [last step in Eq. (4)] is only possible if the total spin state of the triplet-polaron pair is 1/2, which means it needs to have a doublet character. Therefore, we have, similar to Schellekens et al., calculated the probability \(P_q\) that the triplet-polaron pair is quenched. This density matrix implementation also incorporates a triplet-polaron pair formation rate \(k_1\) and dissociation rate \(k_3\) into free triplets. Additionally, it has a quenching rate \(k_2\) towards the ground state when the pair has a doublet character.

For the triplet-triplet reaction we take a similar approach. Two triplet excitons can annihilate and create a ground state and a singlet exciton:

\[
T + T \leftrightarrow [T + T] \Rightarrow S_0 + S_1.
\]

(5)

Spin conservation rules require the triplet-triplet pair to have zero total spin in order to annihilate, i.e., it needs a singlet character. For that reason, we calculated the effect of a magnetic field on the annihilation chance \(P_q\) via a singlet state. This density matrix implementation also incorporates a triplet-triplet pair formation rate \(k_1\), dissociation rate \(k_3\), and annihilation rate \(k_4\) towards the ground state when the pair has a
FIG. 4. (Color online) Simulations of the MC high field contributions. The effect of a difference in g factor on the magnetic field dependent triplet exciton fraction is shown in (a) and (b). In (a) the magnetic field dependence is shown for a parallel (0°) and perpendicular (90°) orientation of the magnetic field and polaron separation vector. In (b) the actual angle dependence is shown for various magnetic field strengths. These calculations were performed with a dipole coupling strength $D = 0.5 \sigma_{hf}$ and a g-factor difference $\Delta g/g = 0.03$. In (c) and (d) the same is shown for the triplet-polaron quenching probability. The angle $\beta$ is defined as the difference in orientation between the zero field splitting axis and the magnetic field. The magnetic field and angle dependence of triplet-triplet annihilation chance is shown in (e) and (f) respectively. The angle $\gamma$ is defined as the difference in orientation between both zero field splitting axes—which are perfectly aligned—and the magnetic field. The latter two processes are calculated with $D_{zfs} = 30 \mu_B \sigma_{hf}$.

singlet character [23]. A zero field splitting parameter $D_{zfs} = 30 \sigma_{hf}$ is taken for both the triplet-polaron and triplet-triplet reaction. The results of our calculations for triplet-polaron and triplet-triplet interactions are shown in Figs. 4(c)–4(f).

The downside of taking a single zero field splitting axis, i.e., a single molecular orientation, is that our calculations show features that are clearly not observed in the experiments. When the magnetic field is aligned parallel to the ZFS axis, there will be strong level crossing resonances at the magnetic field strength equal to $D_{zfs}$. At these level crossings, states that were initially nondegenerate at zero magnetic field due to the zero field splitting become degenerate, resulting in additional spin mixing. In the literature it is known that these features average out when averaging over all molecular orientations [23]. Additionally, so-called “anticrossings” could affect or cause an absence of these peaks [39].

The angle dependence at large magnetic fields does look different than the angle dependence caused by the $\Delta g$ mechanism. At first glance, this suggests that anisotropic triplet quenching mechanisms could be at the origin of the high field component. However, what is clear from our calculations is that the amplitude of the angle dependence of such triplet quenching mechanisms will reduce with increasing magnetic fields. This is in contrast to the experimental results shown in Fig. 3, where the high field anisotropy is observed to increase with magnetic field. Therefore, we conclude that triplet quenching mechanisms can also not unambiguously explain the high field anisotropy.

V. CONCLUSION

In conclusion, using experiments and spin density matrix calculations we investigated the source of anisotropy in the magnetic field sensitive current of the organic semiconducting polymer “Super Yellow” PPV. Both a low and high field component were identified. The shape of the angle dependence of the low field component of the MC can be explained by anisotropic dipolar coupling. The amplitude of this low field component can most readily be explained if the device is assumed to operate in the intermediate hopping regime. In addition, the experimental results show an anisotropic high field contribution with opposite sign, slightly different shape as a function of the angle, and alternative voltage dependence compared to the low field contribution. A difference in g factor is an unlikely candidate for this high field component. Reactions of triplet excitons with other spin carrying particles are more likely candidates, though they can not fully explain the observed magnetic field dependence of the anisotropy either. These results suggest a more solid theoretical model is required for the high field effects.

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