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Tuning organic magnetoresistance in polymer-fullerene blends by controlling spin reaction pathways

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Harnessing the spin degree of freedom in semiconductors is generally a challenging, yet rewarding task. In recent years, the large effect of a small magnetic field on the current in organic semiconductors has puzzled the young field of organic spintronics. Although the microscopic interaction mechanisms between spin-carrying particles in organic materials are well understood nowadays, there is no consensus as to which pairs of spin-carrying particles are actually influencing the current in such a drastic manner. Here we demonstrate that the spin-based particle reactions can be tuned in a blend of organic materials, and microscopic mechanisms are identified using magnetoresistance lineshapes and voltage dependencies as fingerprints. We find that different mechanisms can dominate, depending on the exact materials choice, morphology and operating conditions. Our improved understanding will contribute to the future control of magnetic field effects in organic semiconductors.
The field of organic spintronics deals with spin physics and magnetic field effects (MFEs) in organic materials.3-5. Besides spin injection into organic semiconductors6-8, a lot of attention was drawn to non-spin-polarized organic semiconductor device. Despite the absence of magnetic elements, they show a large room-temperature magnetoresistance effect at relatively small magnetic fields of only a few milliteslas, an effect sometimes referred to as organic magnetoresistance (OMAR)9-22. Cheap plastic sensor technology has been suggested as an example of its application potential23. However, because this MFE was discovered a decade ago, the desire to unravel the exciting new physics behind the intrinsically magnetic field-dependent charge-transport properties of organic semiconductors has been the major motivation for intensive experimental23-24 and theoretical25-26 research.

Several mechanisms have been suggested to explain OMAR. All these mechanisms rely on spin-selective reactions between pairs of particles, where a magnetic field suppresses the spin mixing of the particle pairs before the reaction, thereby changing the spin fraction and the outcome. Partly based on recent studies—where the MFEs from standard and deuterated polymers were compared—there is a growing consensus about the importance of hyperfine fields (hfs) for spin mixing.12 The principal question in the field is now which particle pairs and subsequent reactions are dominating this MFE. The possible mechanisms are currently divided into three categories: reactions of polarons with the same charge into bipolarons15, reactions of polarons with opposite charge into excitons16 and reactions of triplet excitons with polarons17 or with other triplet excitons24. We will refer to those mechanisms as bipolaron, electron–hole (e–h), triplet–polaron and triplet–triplon mechanism, respectively.

Most experimental studies have focused on trying to isolate a certain mechanism, for example, by creating a device where only one type of polaron is present; however, a magnetoresistive response was always observed and no mechanism could be excluded. So far the largest effects have been observed in organic light-emitting materials and devices, where all particle reactions can potentially occur. To proactively unravel the underlying mechanism, an exquisite control of the spin-carrying particle interactions and subsequent magnetic field-dependent reactions is required.

In this article, we propose a polymer-fullerene blend as most suitable candidate. Introducing fullerene to the polymer system enables a detailed control of the particle and spin interactions and provides a novel method to investigate the different mechanisms. At low concentration, the fullerene effectively quenches excitons into weakly bound, spatially separated charge-transfer (CT) states (CTSs), thereby reducing the exciton densities25,26. At higher concentration, phase separation additionally leads to separate electron and hole current pathways through the device25,26. Following earlier suggestions by Wang et al.8 on MFEs in polymer-fullerene blends, we succeeded in fully correlating pronounced changes in the MFEs to the complementary (spin) physics in the different concentration regimes. Using detailed experimental analysis, explicit microscopic and numerical device simulations, we thus unravel the dominant underlying mechanisms of OMAR. In contrast to earlier work, our analysis allows us to quantitatively explain the observed linewidths and sign changes.

Results

Relevant OMAR mechanisms and their fingerprints. A unified picture of the relevant particles and their (spin dependent) reactions is shown in Fig. 1. The left panel shows possible polaron pairs in an organic semiconductor as a function of energy. Free charges can form precursor pairs in a singlet or triplet configuration. From this pair state, the precursor pair can either

Figure 1 | Unified picture of relevant particles and their spin-dependent reactions. (a) Possible polaron pairs in an organic semiconductor as a function of energy. Free charges can form precursor pairs in a singlet (S) or triplet (T) configuration. From this pair state, the precursor pair can either recombine into a S or T exciton (in the case of an e–h pair), a S bipolaron (in the case of a bipolaron pair) or dissociate back into free carriers again. Because of hyperfine fields (hf) the S and T precursor pairs can mix and an external magnetic field can suppress this mixing. The magnetic field-dependent transitions between the pair states are indicated with curved arrows. The energy levels and possible mixing mechanisms of a CTS are also included in the diagram (shaded area). Electrons and holes are interchangeable in this diagram. (b) The characteristic low (red) and high (blue) field lineshapes of the (i) bipolaron, (ii) e–h and (iii) triplet-polaron mechanism, all according to explicit calculations using a density matrix formalism.
recombine into a singlet or triplet exciton (in the case of an e–h pair), a singlet bipolaron (in the case of a bipolaron pair) or dissociate back into free carriers again. Within the precursor pairs, the separation between the two carriers is such that exchange interactions are still negligible, enabling hf-induced mixing of the singlet and triplet precursor pairs29. An external magnetic field suppresses this mixing and thereby changes the transition to the singlet and triplet exciton or bipolaron state. Such a MFE governed by the hf strength, typically on the order of milliteslas, is referred to as a low field effect (LFE). Recently, it has been shown that the LFE can be accompanied by a distinct MFE at ultra-small field effect (USFE, ≤ mT) scales1,2,20.

The magnetic field-controlled transitions between singlet and triplet precursor pair states can have profound LFEs on the current through the organic semiconductor. First, within the bipolaron mechanism15, an external magnetic field will decrease the current by spin-blocking, an effect well known from low-temperature transport studies on double-quantum dot systems29. The bipolaron model treats the scenario where a charge carrier is quasi-stationary trapped at an energetically relatively low-lying state. A nearby free carrier, which contributes to the current, has to pass this site by—at least as a temporary intermediate state—forming a doubly occupied site, that is, a bipolaron. It should be noted that because of the large exchange within the bipolaron state, its formation is spin dependent. Therefore, it is well possible for a pair of polarons in a singlet configuration but very unlikely for the triplet, as depicted in Fig. 1a. Then, if the two carriers in the precursor pair are in a triplet configuration, the current is effectively blocked. At low magnetic fields, the spin-blocking is lifted due to the hfs efficiently mixing the precursor spin states, as indicated by the curved arrows in Fig. 1a. At high fields, blocking is regained, because random hfs are overruled, and spin character becomes well preserved. Thus, the bipolaron mechanism gives rise to a magnetic field dependence of the charge-carrier mobility μ and leads, in this case, to a negative magnetoconductance (MC).

Next, within the e–h pair model as proposed by Prigodin et al.16, the crucial reaction is between weakly, Coulombically bound, e–h precursor pairs as shown in Fig. 1a. These pairs form statistically with a \( (e + h)_2 \) ratio of 1:3. They can dissociate to form free polarons, but can also react to form an exciton from where they finally can recombine to the ground state. If at least one of the two reactions is spin selective, the magnetic field will control the charge balance in the device, and thereby the current. Prigodin et al.16 derived a magnetic field-dependent recombination rate, which was then linked to a so-called recombination mobility \( \mu_r \). The authors assumed a different recombination rate for singlets and triplets. So, with less mixing due to a magnetic field, there is less recombination. In the space charge-limited (SCL) regime, this reduction leads to more current because of compensation of positive and negative space charge and thus gives rise to a positive MC16. In passing, we note that generally the e–h pair mechanism is unlikely to produce large MFEs, because it requires a competition between recombination and dissociation of precursor e–h pairs—that is, e–h pairs that in a single step can form an exciton. Usually, this is highly unlikely, because once the electron and hole have approached each other that close, they are well within the Coulomb radius, making dissociation a very unlikely event. However, in organic polyanionic carbons, the e–h pairs are in the form of CTs, where dissociation does become relatively large26 and, as we show, the e–h mechanism can result in significant MFEs.

Lastly, we will discuss the triplet–polaron mechanism as first proposed by Desai et al.17. In this model, triplet excitons can react with polarons by scattering events, which effectively reduce the mobility of the free charges and thereby decrease the current through the device. As triplet excitons in general have a much longer lifetime than singlet excitons, their concentration can become large enough so that these reactions become significant. By applying a magnetic field, less triplet excitons are formed, and thereby the current is increased, thus giving rise to a positive MC.

It is emphasized that even though the current is now influenced by the reaction of triplets with polarons, the LFE arises from the magnetic field-dependent formation of these triplet excitons. Therefore, the hyperfine-induced spin mixing of e–h precursor pairs, as indicated in Fig. 1a, is a crucial ingredient of the triplet–polaron mechanism.

In addition to the LFEs, so-called high field effects (HFEs) occur at field scales much larger than the local hfs. Within the triplet–polaron model, spin mixing occurs between doublets (D) and quadruplets (Q) of triplet exciton–polaron pairs. Because of the zero-field splitting (ZFS, typically 80 mT (ref. 31)) of the triplet exciton, the hf-induced spin mixing now manifests itself as a HFE at a broader linewidth. Using the same arguments as for the LFE, this HFE gives rise to a positive MC. The mutual annihilation of triplets also gives rise to a HFE with a linewidth determined by the ZFS21. However, because the triplet–triplet mechanism creates free charges, an increasing magnetic field effectively reduces the amount of available triplets, this leads to a negative MC. A distinctly different HFE displays in the e–h mechanism. The opposite polarons in the e–h pair will generally have a (slightly) different \( g \)-factor, leading to dephasing of the precession electron and hole spins29. As a consequence, additional spin mixing occurs at large fields (typically 1 T), referred to as Ag-mechanism. The associated HFE on the current will necessarily have a sign opposite to the corresponding LFE, which is based on the suppression of spin mixing. All the above-mentioned LFE and HFE mechanisms have been explicitly calculated using a density matrix formalism (also see Schellekens et al.17), and the characteristic resulting MFE lineshapes are depicted in the right panel of Fig. 1b. For more details on these calculations, we refer to the Supplementary Note 1.

In passing, we note that other models—based on spin mixing by hfs—have been proposed in the literature. These models are mostly different implementations of one of the mechanisms as discussed before. For example, Harmon and Flatt12 recently proposed a model that is a percolation implementation of the spin-blocking—or bipolaron—mechanism, whereas Hu and Wu7 combined e–h pair mixing with triplet–polaron interactions and included dissociation processes. Besides hfs, other mixing mechanisms such as spin–orbit coupling have been proposed to explain OMAR22,33. However, for the organic materials that consist of low-molecular-weight organic semiconductors, as used in this work, this process is of minor relevance. Finally, completely different mechanisms have been introduced in the literature such as Lorentz-force deflection, hopping magnetoresistance or effects like weak localization and wave function shrinking34,35. However, most of them seemed not viable candidates to explain the effect or not needed to fully explain experimentally observed trends.

Summarizing, the three mechanisms display clear fingerprints, with distinguishable characteristics such as sign and field scale of the LFE and HFE. These characteristics, which have been calculated and are schematically shown in Fig. 1b, will prove invaluable in identifying the relevant mechanisms.

**MFEs in polymer-fullerene blends.** In this study, we used a variety of blends, but most focus will be on blends of poly(2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylenevinylene) (MDMO-PPV):[6,6]-phenyl-C61-butyric acid methyl ester (PCBM), where PPV acts as hole-conducting polymer and electron donor, whereas PCBM acts as electron acceptor. This blend is a well-known and extensively studied organic photovoltaic system25-28,36-43. We will exploit the thorough understanding of
the charge transport and morphology of this model system as a basis of our identification.

We have systematically investigated the MFE on the current (MC) as a function of the applied magnetic field B and the bias voltage V for a broad range of PCBM concentrations x; for the complete data set, we refer to Supplementary Fig. S2 in the Supplementary Information. We observed an extremely rich behaviour of the MFE with very pronounced changes in both the amplitudes and line widths. Typical results for three different concentrations x are shown in Fig. 2. At low PCBM concentrations (0–10 wt.%, Fig. 2a), we observe a positive LFE, which is accompanied by a positive HFE with a width on the order of 100 mT. The corresponding USFE is shown in Fig. 2b. In sharp contrast, at intermediate concentrations (30–60 wt.%, Fig. 2c), a positive LFE and an opposite (negative) HFE at much larger field scale (~1 T) are observed. When increasing the PCBM content over 70%, all MC curves only show a negative LFE and almost no HFE. Based on these fingerprints, we raise the hypothesis that the triplet–polaron, e–h and bipolaron mechanism, respectively, are the dominant underlying mechanisms. This conjecture will be put on more solid ground using quantitative arguments in the remainder of this article.

**Analyzing the MFE.** We performed a detailed analysis of the experimental results by fitting the MC (B) data at all x and V, with a superposition of a LFE (including USFE) and a HFE (see Methods and Wagemans et al.4). Thus, for each measurement, we get an amplitude of the LFE and HFE, but also the intrinsic hf scale \(B_{hf}\), as well as the half-width at quarter-height of the HFE \(B_{HFE}\). The extracted parameters are shown in Fig. 3. Figure 3a presents the maximum observed magnitude of the LFE and HFE in each specific blend, whereas the line widths are shown in Fig. 3d. In both figures, we observe very pronounced trends, which can be correlated with changes in Fig. 3a,d, such as sign changes and abrupt changes in linewidths, exactly correlate with boundaries between the three morphology regimes.

**Discussion**

We start our discussion with regime (1). In the pristine polymer, triplet exciton densities can be very high because of the long triplet lifetime, making the triplet–polaron mechanism a likely candidate. The positive sign of the LFE and the width of the HFE (~80 mT), a typical value for the ZFS3, is consistent with this interpretation. Very remarkably, we observe that the magnitude of both the LFE and HFE are quenched by adding just a few wt.% PCBM, consistent with PCBM acting as an efficient quencher of excitons. Note that the LFE responds more sensitively to adding PCBM, which can be assigned to the relative alignment of CT and triplet exciton energy as is discussed in detail in the Supplementary Note 2.

Next, we will discuss regime (2). In these blends, PCBM is still homogeneously distributed throughout the PPV but forms percolative current paths for electrons27. Excitons are effectively quenched and transferred into CT pairs, which in our blend are known to be energetically aligned with the triplet excitons on the PPV (Fig. 1a) (refs 40,41). This would provide an ideal scenario...
we observe the LFE changing to a negative value and we observe a quenching of the HFE caused by the $\Delta g$-mechanism.

After this satisfactory identification of the dominant mechanisms in all three regimes, we show that we can also quantitatively describe the voltage dependence and that specific features herein are in full agreement with our assignment. As such, this provides an alternative route towards unravelling underlying mechanisms. To do so, we performed finite element drift-diffusion simulations\textsuperscript{19,31,38,41} for realistic parameters (please refer to the Supplementary Note 3 for more details). Here we will briefly discuss the MC(V) in all three regimes, starting with regime (2).

In Fig. 3b it is displayed whether at a certain $x$, a sign change in MC(V) is observed in LFE and HFE. Apparently, regime (2), dominated by the e–h mechanism, is a special regime, where experiments on both the LFE and HFE show a sign change. The experimental LFE(V) and current density, $J(V)$, are plotted in Fig. 4b,d, respectively. Therefore, it gets clear that the sign change in the LFE occurs around the built-in voltage $V_{bi}$, where the current undergoes a transition from the (exponential) diode-like diffusion regime to the (power law) SCL drift regime\textsuperscript{25}.

We can provide an intuitive explanation for the sign change. In the drift regime, enhancing recombination by applying a magnetic field reduces space charge compensation of the electron and hole currents and hence reduces the current of bipolar SCL devices, whereas in the diffusion regime carriers recombining in the ‘depletion zone’ of the diode enhance the current. To quantify this prediction, we performed simulations for devices consisting of homogeneous blends of the polymer and fullerene. The calculated current density, as shown in Fig. 4d, matches the experimental result using realistic parameters\textsuperscript{39,42}.

Also regime (1) shows a very characteristic MC(V) dependence (Fig. 4a), vanishing below the built-in voltage and peaking somewhat above. A full description of those dependencies goes beyond the scope of our present article, but more information on the calculation is provided in the Supplementary Note 3. Here we will briefly discuss these recent advances, where trap states have will be widely applicable and can be used to explain the full range of device behavior in a single simulation.

Finally, in regime (3) the blends are separated into two phases. The electrons are primarily transported through a PCBM phase, and the holes are transported through a mixed phase of PPV and PCBM\textsuperscript{27,28}. With separate current paths for electrons and holes, locally the device will perform as a single-carrier device. Thus, the bipolaron mechanism, the only mechanism not relying on charge carriers with opposite charges, is expected to become dominant over the e–h pair mechanism in phase-separated blends. Indeed,

Figure 3 | Global trends of the MFEs in the current. (a) The top figure shows the maximum value of the magnitude of the MC for the low (LFE, left axis, red squares) and high MFE (HFE, right axis, blue circles) as a function of PCBM content at voltages higher than the built-in voltage $V_{bi}$. The lines provide a guide to the eye. (b) This panel shows if there is a sign change in the MFE as a function of voltage. (c) An illustration of the morphology of the organic layer with the three distinct regions indicated. (d) The bottom figure shows the width of the two MFEs (B$_{LFE}$ and B$_{HFE}$). The error bars represent the uncertainty in the fitting values.
As an example of the former, we are currently investigating polymer-fullerene blends using different material combinations. A result for two different polymers is shown in Fig. 5, where we have added 5 wt.% PCBM to the regular MDMO-PPV (Fig. 5a,b) and a phenyl-substituted poly(1,4-phenylenevinylene) polymer called SY-PPV (Fig. 5c,d). We observe a distinctly different lineshape at low magnetic fields, revealing an additional negative LFE.

We can explain this contribution by a small shift in the energetic alignment of the CTS with respect to the triplet exciton as illustrated in Fig. 6. In a large applied magnetic field (Fig. 6a), additional triplet excitons are created by process (3). Without an external field, spin mixing of the CTS, indicated by process (2) in Fig. 6b, leads to a reduction of process (3). In other words, applying a magnetic field leads to more triplet excitons and thereby less current due to scattering of triplet excitons with charges, and consequently thus a negative MC. The insights obtained in our present work seem invaluable in understanding these novel MFEs.
Figure 6 | Fastest relevant recombination routes in a different polymer-fullerene blend. Here the CTS is higher in energy than the triplet state in the polymer: (a) in a large external magnetic field and (b) in the absence of an external magnetic field. Processes (1) and (3) lead to an increase in triplet (T) in the absence of an external field, while process (2) decreases T.

Concluding, in this article we presented a proof of concept study, unravelling the role of the relevant particle pairs and their reactions for OMAR. Furthermore, we explained how striking differences in the MFE lineshapes are correlated with the underlying microscopic mechanisms and have shown the important role of device physics. Our findings open up unprecedented means to bring OMAR research from a phase of passively observing MFEs in the current, to really engineering device characteristics by tailoring the molecular system.

Methods

Samples. In this work, we studied the MFEs on the current for devices consisting of a blend of MDMO-PPV and PCBM. The MDMO-PPV was purchased from American Dye Source Inc. and the PCBM (>99% pure) from Solenne B.V. The devices were prepared on glass substrates with patterned indium tin oxide (ITO) anodes. After careful cleaning, followed by a ultraviolet-ozone treatment, a thin layer of poly(3,4-ethylenedioxythiophene)poly(styrenesulfonate) (PEDOT/PSS) was applied by spin coating. The MDMO-PPV and PCBM were both dissolved in orthodichlorobenzene, with a concentration of 10 and 20 mg ml⁻¹, respectively, and stirred on a hot plate at 50 °C for at least 2 h after appropriate blending. The blends were spin coated at 1,200 r.p.m. for 60 s. Subsequently, the samples were transferred to a nitrogen-filled glove box where the cathode, consisting of LiF and Al, was evaporated in a high-vacuum system (~10⁻⁷ bar). From this point on, the samples always remain in a dry nitrogen environment. The total junction stack was composed of ITO/PEDOT:PSS (60 nm)/[PPV - x - x - x - x - x - x - x - x - PCBM] (≈ 80 nm)/LiF (1 nm)/Al (100 nm), with the PCBM concentration x in wt.%. 

Measurements. MFE measurements were performed in a cryostat that is attached to a glove box with a nitrogen environment [([O₂] < 0.3 p.p.m., [H₂O] < 0.3 p.p.m.). The cryostat is placed between the poles of an electromagnet. The measurements described in this article were performed at room temperature. The devices were driven at a constant voltage V using a Keithley 2400 Series Source-Meter. We measured the current I through the device while sweeping the magnetic field B. From this measurement, the MC was calculated with MC (B) = (I (B) – I (0))/I (0).

Empirical lineshapes. We have analysed our experimental results using the following fitting function: MC: (B) = LFE * f(B, B₀, Bₘ, r) + HFE * (|B| + B₂ₘ)². The function f(B, B₀, Bₘ, r) is explained in full detail by Wagemans et al. and is used to correctly describe the LFE including the USFE as shown in Fig. 2b. This empirical function allows us to separately extract the role of the hf (B₀) and the additional broadening (Bₘ) induced by the microscopic mechanisms involved. The USFE is incorporated by the parameter r that describes the limit in which hopping of carriers is no longer slow compared with spin precession in the hfs. The HFE is fitted with a so-called non-Lorentzian lineshape. In the fitting procedure, for each specific blend x, the line widths (B₀, Bₘ, and Bₘ) were shared fit parameters, whereas the magnitudes (LFE and HFE) and the hopping ratio (r) were free fit parameters. In this study, we investigated the amplitudes and line widths. The discussion of the other fitting parameters, although extracted and analysed, is beyond the scope of the present work.

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