Spin in organics: a new route to spintronics

BY BERT KOOPMANS1,*, WIEBE WAGEMANS1, FRANCISCO L. BLOOM1, PETER A. BOBBERT1, MARTIJN KEMERINK1 AND MARKUS WOHLGENANNT2

1Department of Applied Physics, and Center for NanoMaterials, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands
2Department of Physics and Astronomy, and Optical Science and Technology Center, University of Iowa, Iowa City, IA 52242-1479, USA

New developments in the nascent field of organic spintronics are discussed. Two classes of phenomena can be discerned. In hybrid organic spin valves (OSVs), an organic semiconducting film is sandwiched between two ferromagnetic (FM) thin films, aiming at magneto resistive effects as a function of the relative alignment of the respective magnetization directions. Alternatively, organic magnetoresistance (OMAR) is achieved without any FM components, and is an intrinsic property of the organic semiconductor material. Some of the exciting characteristics of OMAR, in both electrical conductance and photoconductance, are presented. A systematic, combined experimental–theoretical study of sign changes between positive and negative magnetoresistance is shown to provide important insight about the underlying mechanisms of OMAR. A simple explanation of experimental observations is obtained by combining a ‘spin-blocking’ mechanism, an essential ingredient in the recently proposed bipolaron model, with specific features of the device physics of space charge limited current devices in the bipolar regime. Finally, we discuss possible links between the physics relevant for OMAR and that for OSVs. More specifically, weak hyperfine fields from the hydrogen atoms in organic materials are thought to be crucial for a proper understanding of both types of phenomena.

Keywords: spintronics; organic electronics; magnetoresistance; organic magnetoresistance

1. Introduction

Two areas that have been among the highlights in physics in the past decade are the rapid development in organic (semi)con ducting materials—leading to organic (opto)electronics—and the explicit use of electron spin in electronic devices—so-called spintronics. By combining the two, in organic spintronics, the aim is to add a spin or magnetic functionality to organic devices or, vice versa, to profit from specific properties of molecular materials (such as their long spin coherence time) in order to improve the operation of spintronic devices [1,2]. While different prototype devices have been successfully developed, their

*Author for correspondence (b.koopmans@tue.nl).

One contribution of 10 to a Discussion Meeting Issue ‘The spin on electronics’.

This journal is © 2011 The Royal Society
unexpected behaviour is presently posing intriguing scientific puzzles—mixing key concepts of spin-polarized transport and charge transport through organic materials.

From the conceptual point of view, the most straightforward use of organic materials in spintronics is to use them as a spacer layer in organic spin valves (OSVs), aimed at either an organic magnetic tunnel junction (OMTJ) or a ‘spin-injection’ type of device. In the first case, spin-conserving quantum mechanical tunnelling between two ferromagnetic (FM) layers separated by an ultrathin organic layer provides the main mechanism for sizable magnetoresistance (MR), or equivalently magnetoconductance (MC), values. Throughout our article, MC is defined as $MC = (I(H) - I(0))/I(0)$, where $I(H)$ is the current at applied field $H$. OMTJs with an MC of around 10 per cent up to room temperature have been reported recently, e.g. with rubrene barriers [3]. In the ‘spin-injection’ type of devices, spin-polarized carriers are injected from an FM electrode into an organic semiconductor (OSC), and extracted by a second FM electrode. Such a scenario provides the option to manipulate the electron (or hole) spin while it is residing in the OSC. After the first claims of its experimental development [4,5], several groups reported similar results. Implementations with LaSrMnO as the bottom electrode and Alq3 (tris-(8-hydroxyquinoline)aluminium) as the OSC have become popular, but a wide variety of other materials have been used as well [6,7]. More recently, multipurpose magnetic organic hybrid devices that combine an MR with a non-volatile electrical memory function have been reported [8]. Despite this promising progress, devices often suffer from strong inter-diffusion of the top FM layer into the OSC, forming ill-defined layers, and the results are often difficult to reproduce. Specific emphasis has been given to better monitor and control these effects, e.g. by inserting thin Al2O3 or LiF layers between the organic film and the top electrode [9].

Complementary to the spin-valve route towards organic spintronics an entirely new MR effect in OSC devices—even without any FM components—has been discovered. The latter effect, dubbed ‘organic magnetoresistance’ (OMAR), was first reported by Francis et al. [10]. It provides a surprisingly high MR of up to 20–30%, at room temperature, and at relatively small magnetic fields (approx. 50mT) [11]. In comparison with OSVs, preparation of OMAR devices is significantly more reliable. In fact, devices are very similar or even identical to organic light-emitting diodes (OLEDs), and can be produced by common spin coating and/or thermal evaporation techniques. Moreover, interface effects, which are of crucial relevance for the operation of OSVs, are thought to play just a minor role in OMAR. This simple preparation technique and robustness of the effect have triggered ideas for applying the OMAR effect in devices such as low-cost field-sensing and magnetic pen-input display applications. However, the underlying physics has remained a mystery for a couple of years. Very recently, interesting progress with respect to its fundamental understanding has been made.

The research community now agrees on the notion that OMAR is caused by spin correlations between different carriers. These correlations are affected by the randomly oriented hyperfine fields produced by the hydrogen nuclei and sensed by the $\pi$-conjugated molecular orbitals contributing to the charge transport. At applied magnetic fields larger than the typical hyperfine fields (a few millitesla) the random fields are overruled, leading to the OMAR contrast.
In spite of this consensus, there is ongoing intense debate as to which carriers are of relevance, and which detailed mechanisms give rise to the large MR. Hyperfine field-induced spin mixing can induce singlet–triplet transitions of two-carrier states or their precursor pairs, affecting the current. One class of models describes interactions involving electron–hole (e–h) pairs (or excitons) [12–15], while another class describes interactions between carriers of like sign, including the formation of electron–electron or hole–hole bipolarons [16]. Also, it has been suggested that neither of the two classes is capable of reconciling the complete picture, and different mechanisms are acting in parallel [17].

In this article, we will first review some of the basic characteristics of OMAR, and discuss some of our recent observations (§2). Efforts to explain OMAR as a combination of a microscopic bipolaron mechanism in combination with new insights about device physics will be elaborated in §3. In the final discussion (§4), we compare other recent work, and address some of the similarities in the underlying physics of OSVs and OMAR, particularly focusing on the role of hyperfine fields.

2. An experimental exploration of organic magnetoresistance

A typical device structure for measuring OMAR is shown in figure 1a. Usually, deposition using a simple cross-strip geometry with active areas of a few square millimetres is used. Engineering of proper contacts is essential to control injection of the right carriers into the device. Aiming for bipolar operation, it is common to use transparent indium tin oxide (ITO) substrates with spin-coated PEDOT:PSS (poly[3,4-ethylenedioxythiophene] poly[styrenesulfonate], a hole-conducting polymer blend) as a hole injector, while LiF/Al or Ca/Al top electrodes can be used for injecting electrons from the opposite side. OMAR has been observed for a large number of small molecules and polymers, which are thermally evaporated or spin coated, respectively. Molecules used in the present work, Alq3 and MDMO-PPV (poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-p-phenylenevinylene]), are represented in figure 1b. Although our devices include a PEDOT:PSS layer, we verified that OMAR is entirely dominated by the OSC. All sample handling was performed in a glove-box.

After preparation, samples were transported under inert atmosphere to a separate glove-box for I(V) (current–voltage) transport studies, and MR studies at variable temperatures down to 10 K. All experiments included in the present paper were performed at room temperature unless otherwise specified. A special magnetic-field modulation approach was developed [18], which allowed for rapid and low-noise measurements of (magneto)transport. Some of the measurements displayed in this article were performed before this set-up was completed. Furthermore, we carried out photoconductance studies of OMAR, for which a dedicated modulation scheme was also implemented. The scheme allowed us to carefully separate the photo-induced part of the current from the electrically injected current, as discussed in more detail by Wagemans et al. [18].

It had already been noticed in early studies on OMAR that, for the wide range of materials that display OMAR, the line shape comes in only two forms [19]. In some cases, MC as a function of field is described by a Lorentzian, MC(H) = H^2/(H^2 + H_0^2), where H_0 is a (Lorentzian) broadening parameter. However, in
Figure 1. (a) Device structure, cross strip and stack. (b) Typical molecules used: Alq3 and MDMO-PPV. (c) MC(H) measurements of devices with Alq3 (triangles) and PPV (squares), fitted with a non-Lorentzian (solid lines) and also a Lorentzian for the Alq3 (dashed line). PPV under illumination (circles) is also shown fitted with an additional $\sqrt{H}$ contribution. (d) 1100% MC close to short-circuit with Alq3. (e) MC versus $V$ for Alq3, both with and without illumination. (f) MC versus $V$ for PPV (as deposited; lower curve) increases after conditioning with a current of $10^3$ A m$^{-2}$ for 30 min (upper curve). (Online version in colour.)

In the majority of cases, MC is described by $MC(H) = H^2/(|H| + H_0)^2$, which was found empirically. The latter line shape is generally referred to as the ‘non-Lorentzian’. Figure 1c shows line shapes for a number of devices, demonstrating that the non-Lorentzian indeed fits experimental data over a surprisingly large field width.

Another intriguing feature of OMAR is the occurrence of both positive and negative MC for a single device depending on operating conditions. An example is shown in figure 1c, where positive and negative MC for MDMO-PPV is displayed. Recently, detailed studies have resolved the clear systematics of the occurrence of the different signs as a function of temperature and applied bias voltage [20–22]. Understanding the sign changes may provide an essential key towards resolving the microscopic origin of OMAR. Such experimental efforts will be presented later on in this section.

In addition to being found in the transport of injected charges, OMAR has been found in the photo-current when illuminating devices by light with a sufficiently large photon energy. Again, this provides a complementary view of OMAR, which may be useful in working towards identifying the relevant microscopic mechanisms. In our set-up, the specific modulation method allows us to separate photocurrent and injected current contributions. Figure 1c shows an example of the photocurrent contribution to OMAR for an MDMO-PPV-based device. Interestingly, an additional component to the line shape is observed. Apart from the non-Lorentzian, a contribution that scales with $\sqrt{H}$ is resolved. The latter is a fingerprint of a so-called $\Delta g$ mechanism [17]. This results from different
$g$-factors of electrons and holes, giving rise to a phase difference of electron and hole spins which increases with increasing magnetic field, which in turn results in inter-conversion of singlet and triplet character.

A particularly interesting dependence of the total MC (photocurrent plus injected current) develops when changing the applied bias, as shown in figure 1e. An anomaly around 1.4 V is witnessed, which corresponds to the open circuit voltage of the specific device. At that specific voltage, the injected current and photocurrent cancel, leading to a vanishing total current. Since the net change in current remains finite, it leads to a divergence in the relative effect. As an example, a record-high OMAR of 1100 per cent is plotted in figure 1d. For a more detailed investigation, we refer to Wagemans et al. [18].

A final general feature of OMAR that we would like to present is the possibility of ‘conditioning’ the device. It seems that applying a large current through the device can lead to a transition to a significantly larger OMAR, while successive annealing brings the device back to more or less its original state [23,24]. A typical example is shown in figure 1e, where the peak value of OMAR of around 2.2 V is increased from 2.1 to 4.4 per cent by conditioning at a current of $10^3 \text{A m}^{-2}$ for 30 min. An interpretation in terms of energetic disorder in the OSC will be given in §3.

Having introduced some of the general peculiarities of OMAR, we will now discuss a more systematic study on the sign change. In figure 2, MC($H$) is plotted for both an Alq$_3$-based (figure 2a) and an MDMO-PPV-based (figure 2b) device. In both cases, a transition from negative MC at low bias to a positive MC at high bias is seen. Similar sign changes have been observed [14,17,19], from which it could be concluded that this is a general property of OMAR devices. In passing, we note that at very high bias a reversed sign change (from negative to positive MR) has been observed, e.g. for polyfluorene-based devices [19].

In search for the mechanism behind the sign change, figure 3a displays a result of $I(V)$ in a log–log plot. We first focus on the dataset for $T = 240 \text{K}$. At low bias a clear power-law behaviour is observed, representative of space charge

---

Figure 2. MC($B$) at different voltages for comparing (a) an ITO/PEDOT:PSS/Alq$_3$/LiF/Al device and (b) an ITO/PEDOT:PSS/MDMO-PPV/Ca/Al device. The open squares represent the measured data, while the lines represent fits which are described in Bloom et al. [20,21] for (a,b), respectively. (Online version in colour.)
limited current (SCLC), in the regime of single-carrier conduction. The exponent found, $n \approx 6$, is significantly larger than 2 owing to charge trapping [25]. Above $V = 8.0\,\text{V}$ an upturn in the current is observed. This is interpreted as a signature of minority charge carrier injection, driving the device into bipolar operation. Such a behaviour is in agreement with the notion that in this device electrons are majority carriers with a significantly higher mobility than the holes, while the holes face a large injection barrier at the Alq$_3$–PEDOT:PSS interface. Interestingly, the voltage at the onset of minority charge carrier injection corresponds to the voltage $V_{tr}$ at which the sign change from $-\text{MC}$ to $+\text{MC}$ occurs, as shown in figure 3b. Reducing the temperature, both the onset of minority carrier injection and the OMAR sign change are postponed to $V = 9.4\,\text{V}$, keeping the correlation intact.

Finally, we turn our attention to a similar dataset for an MDMO-PPV-based device. Again we see a deviation from power-law behaviour in $I(V)$, but at a voltage near the built-in voltage of the device (figure 3c). For MDMO-PPV, the role of minority and majority carriers is reversed when compared with Alq$_3$, PPV being a hole-transporting material. The lower transition voltage is a consequence of the lower injection barriers, which makes the device a better OLED. We have identified the upturn in current to a transition from a unipolar (hole) diffusive transport regime into a bipolar regime exhibiting drift transport. In this specific case, we explicitly measured the electroluminescent efficiency (figure 3c). A sharp increase was found at the same voltage where the upturn occurred,
confirming the onset of bipolar injection in this regime. As in the Alq3 device, the transition voltage corresponds remarkably well with the sign change in OMAR (figure 3d).

Altogether, we have outlined a general trend that devices in the single-carrier regime display a negative MC, which becomes positive right at the onset of minority carrier injection, when the device becomes bipolar. In the next section, we will discuss a simple explanation of this behaviour.

3. Modelling organic magnetoresistance

As mentioned in §1, over recent years several models for OMAR have been proposed. Quite soon after its discovery, it was concluded that conventional mechanisms such as classical MR, hopping MR, MR caused by electron–electron interactions and MR caused by weak localization do not apply to the large, room temperature and small-field effects in OSCs [19]. More recently, the importance of spin mixing owing to random hyperfine fields was generally agreed on to be at the basis of OMAR. Very recently, experiments using deuterated (PPV-based) devices unambiguously demonstrated the relevance of such hyperfine interactions [26]. What remains is a discussion of whether e–h pair interactions, or interactions between polaron pairs of like sign, are of relevance, and how they affect the charge transport. Here, we provide an explanation for OMAR based on a bipolaron model, in combination with consequences of the peculiar device physics for devices operating in the regime of SCLC at the transition from single-carrier to bipolar transport [27]. Thus, we provide a coherent description of all the sign changes discussed in §2. However, we do emphasize that, despite this agreement with recent experimental findings, we are not able to provide unambiguous proof that e–h mechanisms are not of relevance.

Charge transport in disordered OSCs is via variable-range hopping. Charge carriers are formed by quasi-particles consisting of electrons in the lowest unoccupied molecular orbital or holes in the highest occupied molecular orbital accompanied by a lattice distortion, called polarons. The energetic disorder in the density of states can be described well by a Gaussian disorder characterized by a 1/e half-width (σ) of typically 0.1–0.2 eV (figure 4a). Interestingly, the energy penalty \( U \) to form a doubly occupied site (bipolaron) is relatively modest owing to charge screening and the charges sharing a common lattice distortion. Therefore, one finds \( U \) to be approximately equal to \( \sigma \).

The current flow through such a disordered energy landscape is characterized by a filamentary network of interconnecting paths. Along these paths electrons that are quasi-trapped at low-energy sites tend to block further current. Additional electrons could potentially pass the blocking site by forming an intermediate doubly occupied site, since \( U \sim \sigma \). However, they can only do so when the two polarons are in a singlet spin configuration. Electrons entering in a triplet configuration cannot pass, unless their spin orientation can mix to a singlet configuration—a situation called ‘spin blocking’ (figure 4a). Spin relaxation can happen because of the presence of the randomly oriented hyperfine fields (typically a few millitesla) owing to the surrounding hydrogen nuclei. Thus, random hyperfine fields tend to release spin blocking, and increase the current in the device. In contrast, when applying an overall external magnetic
Review. An organic route to spintronics

Figure 4. (a) Energy diagram showing two sites, both occupied by one spin. The typical width of the energy distribution is $\sigma$. The energy of the second site shifts by $U$ when a spin is added. (b) Two typical line shapes from the model, fitted with either a Lorentzian or a non-Lorentzian function. (c) MC as a function of $U/\sigma$ in the bipolaron model. (d) MC versus $\sigma/kT$. (Online version in colour.)

Field much larger than the typical hyperfine fields, spin precession at different sites will proceed in a coherent way. Thus, spin correlations (including blocking configurations) will be preserved for a longer time. The foregoing analysis provides a simple explanation for the negative MC (decrease of $I$ at large fields) in the bipolaron model.

In previous work, the bipolaron model has been implemented along two approaches. Bobbert et al. [16] used a Monte Carlo code to describe transport of carriers on a large grid of lattice sites. Alternatively, Wagemans et al. [28] mapped the problem onto two characteristic sites embedded in an environment. The latter approach allows for a more transparent analytical description, while the Monte Carlo approach obviously provides a more realistic description. Both approaches reproduce the two characteristic line shapes (figure 4b). In figure 4c a characteristic result from the Monte Carlo studies is presented, showing MC as a function of $U/\sigma$. Significant negative MC values of several tens of per cent are observed, with a clear optimum around $U \approx \sigma$. The latter corresponds to a situation where formation of bipolarons is optimally facilitated by the energetic disorder. The importance of energetic disorder may provide insight as to why the highest OMAR values so far reported were for Alq3—this material being known to have a particularly large $\sigma \approx 0.3\text{eV}$ for electrons (while slightly less for holes). Moreover, it may provide an elegant explanation for the increases of OMAR upon device conditioning, as shown in figure 1f.
Next, we address some of the predictions of the Monte Carlo implementation of the bipolaron model in more detail. First of all, it should be emphasized that a finite MC is observed at all in a model that exploits only one type of carrier. Thereby, unlike e–h pair mechanisms, it explains the observation of OMAR in single-carrier devices, or in bipolar devices below the onset of minority carrier injection (cf. figure 3). Second, it may come as a surprise that significant OMAR of several tens of per cent is calculated for relatively small carrier densities. This is a result of the filamentary current caused by the disordered energy landscape, making spin blocking a more prominent effect. Third, it has been shown that depending on model parameters the two line shapes that have been observed experimentally are exactly reproduced by the bipolaron model (figure 4b). Fourth, OMAR has been calculated as a function of temperature, as displayed in figure 4d. Taking into account that at room temperature $\sigma/kT \sim 5–10$, the results show that OMAR is not specifically a low-$T$ effect. Rather, the magnitude of OMAR is typically constant up to room temperature. Finally, we stress that within the bipolaron model it is possible to obtain the reversed sign (positive MC) as well. The latter occurs when parameters are chosen such that bipolaron formation becomes an efficient process. Upon conservation of carriers, the density of immobile bipolarons then grows at the expense of the density of mobile polarons, thus increasing the current at large applied magnetic field. However, the latter would provide no specific reason why the sign change would occur right at the onset of minority carrier injection. Below we will propose a more simple explanation.

In the preceding paragraphs, we basically described OMAR as an intrinsic materials effect; as such, it can be expressed by a magnetomobility, $\Delta\mu_i/\mu_i$, i.e. the relative magnetic field induced a change in the mobility $\mu_i$ of a specific carrier ($i = e$ or $h$). Spin blocking then corresponds to $\Delta\mu_i/\mu_i < 0$. Therefore, in the following, we assume that $\Delta\mu_i/\mu_i < 0$ for both majority and minority polarons. Furthermore, experiments on complementary single-carrier devices show only a $-\text{MC}$, and it was found that devices based on the less mobile carrier usually display a significantly stronger OMAR effect [17]. This could possibly be a consequence of the more prominent role of disorder in the minority channel. Thus, we assume that $|\Delta\mu_{\text{min}}/\mu_{\text{min}}| > |\Delta\mu_{\text{maj}}/\mu_{\text{maj}}|$. In the following, we will show how these assumptions affect the total current when driving a device from the single-carrier to the bipolar regime. We do so for devices that have no intrinsic doping, and where charge density is induced by applying a voltage, i.e. describing an SCLC.

First, we discuss an analytical approach. We solve the current density in the drift regime, subject to Poisson’s law and fulfilling the continuity equation. We closely follow the original derivation by Parmenter & Ruppel [29], but extend it by investigating the role of magnetic field effects on the mobility, and solve explicitly the current in the transition regime from single carrier to bipolar [27]. We use ohmic conditions for the majority carrier injection, while assuming an injection-limited minority contact, in line with the experiments displayed in figure 3. Without loss of generality, we present results assuming electrons to be the majority carriers. An essential step beyond [29] is that we explicitly specify the minority carrier current at the anode $J_{ah}$ as a function of the local electrical field $E_a$. Here, we use as a model function $J_{ah} = J_0[(E_a - E_0)/SE_0]^2$, where $J_0$ is a prefactor, $E_0$ defines the onset of minority carrier injection and $S$ defines the sharpness of the onset. This specific choice allows for a fully analytical treatment.
Review. An organic route to spintronics

Some typical results are shown in figure 5. Figure 5a displays \( J(V) \) on a log–log scale, emphasizing the power-law dependence (power \( n = 2 \)) at low voltage, and a transition to similar power-law dependence but with a larger prefactor upon transition to the bipolar regime. This \( V^2 \) dependence is a well-known behaviour for SCLC devices, for which the current density can be written as

\[
J = \frac{9}{8} \varepsilon \varepsilon_0 \mu_{\text{eff}} \frac{V^2}{d^3},
\]

where \( d \) is the device thickness and \( \varepsilon \varepsilon_0 \) is the the permittivity. The ‘effective mobility’ \( \mu_{\text{eff}} \) is simply given by \( \mu_e \) in the single-carrier regime, while it is

\[
\mu_{\text{eff}} = \frac{2}{3} \sqrt{\frac{2\pi \mu_e \mu_h}{\mu_t} \left( \mu_e + \mu_h \right)}
\]

in the completely bipolar regime, as already derived by Parmenter & Ruppel [29]. In this equation, \( \mu_t \) is the ‘recombination mobility’. In the case of Langevin recombination, one writes \( \mu_t = L(\mu_e + \mu_h) \) with \( L \) as a prefactor. In the case of most interest to us here, one has \( L \ll 1 \), whereby electrons and holes form a very broad recombination zone, spanning the whole thickness of the device. In that case equation (3.2) accounts for a large enhancement of the current in

\[
\text{Phil. Trans. R. Soc. A} (2011)
\]
the bipolar regime. Although the less mobile minority carriers do not directly contribute significantly to the current, their presence reduces the space charge limitation on the majority carriers, allowing more majority carriers to the device, resulting in an increased net current.

Next, we calculated the MC with the model introduced. Surprisingly, we are able to reproduce a transition from negative to positive MC, even though we assumed $\Delta \mu_i/\mu_i < 0$ for both carrier types. A glimpse of the answer to this unexpected result is obtained by inspection of normalized magnetoconductivity (NMC), which we define as $\text{NMC}_i = (\Delta J/J)/(\Delta \mu_i/\mu_i)$ for the respective carrier type $i$. From figure 5b, we learn that majority carriers (electrons) behave in an expected fashion, since a positive NMC means a reduction of the current upon a reduction of the electron mobility. However, minority carriers (holes) behave anomalously—their negative NMC means that reducing the carrier mobility increases the total current.

An intuitive explanation of this surprising observation emerges once one realizes that the minority contact in this specific device acts at a constant current source at the onset of minority carrier injection. Then, reducing the minority carrier mobility enhances the minority carrier density in order to keep the current constant, this in turn attracts more majority carriers. Thereby, we end up with the counterintuitive situation that reducing the minority carrier mobility enhances the total device current.

Although the foregoing analysis unambiguously demonstrates the occurrence of a negative NMC for an ideal, drift-limited SCLC device without traps, one may wonder whether this behaviour also exists in realistic devices with a finite density of traps, and when carrier diffusion is no longer neglected. In the study of Bloom et al. [27], explicit device modelling for a more realistic device such as this is presented. Some results are reproduced in figure 5c, d. Overall, we obtain the same systematics, i.e. an increase in current at the onset of minority carrier injection, accompanied by a reversal of the MC (figure 5d, triangles). Interestingly, however, the positive MC appears to be more pronounced. In the analytical, simplified treatment, it is only possible to obtain a sizable positive MC when choosing extremely small values of $L$, while in our numerical device modelling including traps a sizable positive MC is possible for much more moderate values of the recombination prefactor. We conclude that the sign reversal in OMAR is explained well by a combination of a microscopic spin-blocking (bipolaron) mechanism with specific behaviour of SCLC devices.

4. Discussion and outlook

In the foregoing sections, we presented a combined experimental and theoretical study of sign changes in OMAR. Although the outcome may seem convincing, research is certainly still in an exploratory phase. From the device modelling perspective, it would be expected that a second sign reversal could occur, back from positive to negative MC, at higher bias. Although in a few cases such a sign change has been reported [10,19], it has not been possible yet to observe a double sign reversal in a single experiment. It might be difficult to cover enough orders of magnitude in the current in a single device to account for all regimes. We also found that for specific parameters and implementation of $J_{th}[E_a]$ in our model
the device cannot be pushed into the completely bipolar regime. This leads to
a convergence to a positive value of MC at $V \to \infty$. Clearly, more research is
needed to further validate the model in all its aspects.

As to some of the possible future routes, work has begun on modifying OMAR
by doping the organic films with organic molecular dye molecules. Appropriately
chosen dye molecules can act as recombination centres, which can be described by
an enhanced recombination mobility $\mu_0$ in our device theory. Preliminary results
indicate that observations are indeed in agreement with such a description.

The notion that the bipolaron model in combination with proper device physics
does not provide a solution for all observations is shown, for example, by the
photoconductivity measurements displayed in figure 1c. There, the occurrence
of a contribution owing to a $\Delta g$ mechanism can only be explained by an e–h
mechanism. It is not surprising that in photoconductivity an e–h mechanism is
of relevance. In that case, conduction starts by dissociation of photo-generated
e–h pairs into free carriers, a process that may well be sensitive to hyperfine
field-induced spin mixing

A closer look at the recent work of Wang et al. [17] illustrates how
complicated the situation can be. They performed magnetotransport experiments
on blends of 2-methoxy-5-(2′-ethylhexyloxy)-PPV (MEH-PPV) and 1-(3-
methoxycarbonyl) propyl-1-phenyl-[6,6]-methanofullerene (PCBM). For MEH-
PPV, they demonstrated that single-carrier devices with the less mobile carriers
(electrons) displayed a much higher MC than those devices using the more mobile
carriers (holes). Next, they showed that the MC($V$) behaviour was similar to
what we found for MDMO-PPV (figure 3b), i.e. a transition occurred from a
negative MC at small $V$ to a positive MC at large $V$. It was observed that
the positive component disappeared upon blending PPV with PCBM. Since it is
known that the two materials phase separate, and holes flow through the MEH-
PPV while electrons move through the PCBM, it was concluded that the positive
MC is a consequence of an e–h polaron pair model. Although the arguments
seem reasonable, the same results can be explained entirely by the bipolaron
picture. In the blend, electrons (minority carriers in the PPV) are transported as
majority carriers along the fullerene units. In combination with small hyperfine
fields on the fullerene units, the magnetomobility of the electrons will drastically
reduce with respect to the pure MEH-PPV device, and thereby the strong sign
reversal may disappear. Altogether, even this nicely engineered set of experiments
is not able (yet) to give an unambiguous answer as to which are the relevant
mechanism(s). We do stress that a weak $\Delta g$ contribution was observed in the
OMAR of devices with small MC. The latter should unambiguously be assigned
to an e–h mechanism, but is—at least in this case—a relatively small effect.

After having extensively discussed OMAR and having addressed the essential
role played by the hyperfine fields, we return to the physics of OSVs. As mentioned
before, experiments are presently intensively debated, and experimental probes to
unambiguously demonstrate spin-polarized carriers inside the OSC are anxiously
awaited. It should be noted that magneto-optical techniques used extensively in
the field of inorganic spintronics cannot be applied owing to the low spin–orbit
coupling and different selection rules in OSCs. Recently, Cinchetti et al. [30]
reported the observation of spin transport in OSCs by probing spin diffusion
by time-resolved two-photon photoemission, while Drew et al. [31] reported on
probing of electrically spin-polarized carriers by muon spin resonance. However,
those experiments are not straightforward to interpret, and require extensive data analysis. Therefore, it would be tempting to perform MR studies using a Hanle configuration. In such an experiment, spin-polarized carriers are injected from an FM electrode in the presence of an orthogonal magnetic field. While being transported through the spacer layer, the electrons precess around the field lines, giving rise to an oscillatory signal as a function of the magnetic field. However, the low mobility of disordered OSC devices causes transit times of many microseconds. This means that magnetic fields of no more than a few microtesla should be applied to see the lowest order Hanle oscillations. Such fields are much smaller than the random hyperfine fields. As a consequence, even in the absence of any other spin-relaxation mechanism, a decoherence by hyperfine fields will hide any Hanle signal, and in fact will result in a vanishingly small MR.

The previous description can be made more quantitative by treating spin relaxation in the presence of random hyperfine fields in a quantitative way. Bobbert et al. [32] did so in 2009, using both Monte Carlo calculations and analytical one-dimensional modelling. They specifically addressed the dependence of the spin diffusion length on magnetic- and electric-field strength. It was shown that a symmetric contribution to the MC($H$), with a tendency to lower the MC at small magnetic fields, may be used as a fingerprint of hyperfine field interaction in OSVs.

In conclusion, we extensively discussed OMAR and its various properties. We focused specifically on sign changes, for which we presented a coherent explanation based on the microscopic bipolaron mechanism in combination with specific features of the device physics in the SCLC regime. We compared these results with other recent studies, and briefly discussed the importance of hyperfine interactions for both OMAR and OSVs. Altogether, we can conclude that research in organic spintronics is gaining momentum, and the first evidence for new physical mechanisms ruling this nascent field is being gathered. However, more dedicated experiments will certainly be needed to unambiguously map the presently proposed mechanisms on experimental findings. A further future challenge would be to search for predictive and materials-specific models that can guide further optimization and tailoring of effects—finally, aiming at a real assessment of potential applications.

This work was supported by the Dutch Technology Foundation (STW) via the NWO VICI grant ‘Spin Engineering in Molecular Devices’. The authors would like to thank Wouter Engelen, Frank van Oost and Tho Nguyen for their experimental and theoretical work and Martijn Wienk for his help in sample fabrication.

References

Review. An organic route to spintronics


