

Spin and magnetic field effects in organic semiconductor devices

M. Wohlgenannt, Z.V. Vardeny, J. Shi, T.L. Francis, X.M. Jiang, Ö. Mermer, G. Veeraraghavan, D. Wu and Z.H. Xiong

Abstract: The authors describe three spin and magnetic field effects in organic semiconductor devices: First, injection, transport and detection of spin-polarised carriers using an organic semiconductor as the spacer layer in a spin-valve structure, yielding low-temperature giant magnetoresistance effects as large as 40%. Secondly, spin-dependent exciton formation: pairs of electrons and holes show different reaction rates (the reaction products being spin singlet or triplet excitons, respectively) dependent on whether they recombine in spin-parallel or spin-antiparallel orientation. It is believed that this effect ultimately determines the maximum possible electroluminescent efficiency of organic light-emitting diodes (OLEDs). And, finally, a large magnetoresistance (MR) effect in OLEDs in weak magnetic fields that reaches up to 10% at fields of 10 mT at room temperature. Negative MR is usually observed, but positive MR can also be achieved under certain operation conditions. The authors present an extensive experimental characterisation of this effect in both polymer and small molecular OLEDs. The last two effects do not, to the authors' best knowledge, occur in inorganic semiconductor devices and are therefore related to the peculiarities of organic semiconductor physics. The authors discuss their findings, contrasting organic and inorganic semiconductor physics, respectively.

1 Introduction

Organic π -conjugated semiconductors (OSEC), which are usually divided into the classes of small molecular weight compounds (examples shown in Fig. 1) and macromolecular polymers (Fig. 2), have been used to manufacture promising devices such as organic light-emitting diodes (OLEDs) [1], photovoltaic cells [2] and field-effect transistors [3]. A conjugated polymer is a carbon-based macromolecule through which the valence π -electrons are delocalised. Research into the electronic and optical properties of conjugated polymers began in the 1970s after a number of seminal experimental achievements. First, the synthesis of polyacetylene thin films [4] and the subsequent success in doping these polymers to create conducting polymers [5] established the field of synthetic metals. Secondly the synthesis of phenyl-based polymers (e.g. poly(para-phenylene vinylene) (or PPV), Fig. 2) and discovery of electroluminescence (EL) under low voltages in these systems [6] established the field of polymer optoelectronics. The electronic and optical properties of conjugated polymers, coupled to their mechanical properties and intrinsic processing advantages, means that they are particularly attractive materials for the electronics

industry. The discovery and development of conductive polymers was recognised by the award of the Nobel prize for chemistry in 2000 to Heeger, MacDiarmid and Shirakawa.

The π -conjugated polymers exhibit electronic properties that are quite different from those observed in the corresponding inorganic metals or semiconductors. These unusual electronic properties may be attributed essentially to the fact that conjugated polymers are quasi-one-dimensional systems, owing to their strong intramolecular but relatively weak intermolecular interactions. The quantum mechanical wave function is, therefore, usually confined to a single chain. This quasi-one-dimensionality results in weakly screened electron-electron interactions. Thus, electronic correlations are important in determining the character of the electronic states, and the neutral excited states are dominated by excitons. Another important factor in determining the character of the electronic states is that the electrons and lattice are strongly coupled. As for electron-electron interactions, the effects of electron-lattice coupling are enhanced in low dimensions. Hence, charge carriers in these materials are positive and negative polarons, rather than holes and electrons.

In addition to π -conjugated polymers, small-molecular-weight organic compounds have also been extensively investigated. EL from OLEDs made from small molecules was first observed and extensively studied in the 1960s [7]. In 1987, a team at Kodak introduced a double-layer OLED, which combined modern thin-film-deposition techniques with suitable materials and structure to give moderately low bias voltages and attractive luminance efficiency [8]. Intense research in both academia and industry has yielded OLEDs with remarkable colour fidelity, device efficiency and operational stability.

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M. Wohlgenannt and Ö. Mermer are with the Department of Physics and Astronomy, University of Iowa, Iowa City, IA, 52242-1479, USA

Z.V. Vardeny, J. Shi, X.M. Jiang, D. Wu and Z.H. Xiong are with the Physics Department, University of Utah, Salt Lake City, UT, 84112, USA

T.L. Francis and G. Veeraraghavan are with the Department of Electrical and Computer Engineering, University of Iowa, Iowa City, IA, 52242-1595, USA

E-mail: markus-wohlgenannt@uiowa.edu

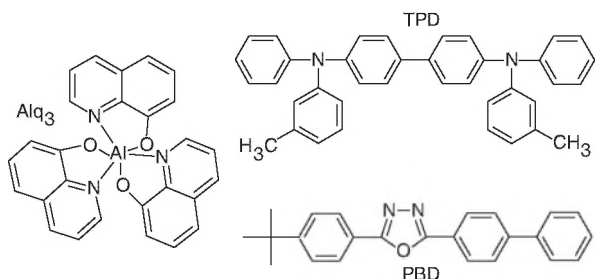


Fig. 1 Structures of some molecular semiconductors that have been used in thin-film electroluminescent devices

Alq₃ is used as an electron transport and emissive layer, TPD is used as a hole transport layer and PBD is used as an electron transport layer

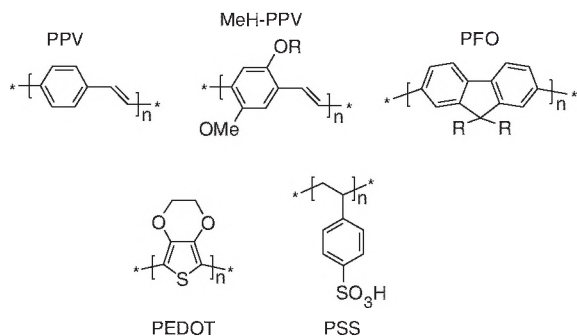


Fig. 2 Polymers used in electroluminescent diodes

The prototypical (green) fluorescent polymer is poly(p-phenylene vinylene) (PPV). One of the best known (orange-red) solution processable conjugated polymers is MEH-PPV. Poly(dialkylfluorene)s (PFO) are blue-emitting, high-purity polymers, which show high luminescence efficiencies. 'Doped' polymers such as poly(3,4-ethylene dioxithiophene) (PEDOT) doped with polystyrenesulphonic acid (PSS) are widely used as hole-injection layers

1.1 Maximum possible electroluminescent efficiency in OLEDs

The maximum possible internal quantum efficiency, η_{max} , of fluorescent-based OLEDs occurs when the probability that the injected carriers form excitons and the quantum yields for singlet emission are both unity. η_{max} is then determined by (and identical to) the fraction, f_s , of injected positive and negative polarons that pair to form emissive spin-singlet excitons, rather than nonemissive triplet excitons. If the process by which these excitons form were spin independent, then η_{max} would be limited to 25%, based on spin degeneracy. However, reports over recent years indicate that η_{max} in OLEDs ranges between 22% to 83% [9–16]. The exact value of η_{max} and the reason for this variation, however, have remained controversial. Indeed, even the notion that η_{max} can be larger than 25% is currently not universally accepted [16]. As $\eta_{max} > 25\%$ implies that exciton formation is spin-dependent, it is therefore interesting to study the spin physics of this process.

Charge injection and transport are other limiting factors determining operating voltage and EL efficiency. The electron current, for example, is strongly influenced by the presence of traps. OSEC used in OLEDs are undoped (or, at least, not intentionally doped). For this reason, OLEDs may belong to the class of injection limited devices, in which the charge carriers are injected into the device channel (e.g. by tunnelling) through the barriers at the metal/organic interface. More recently, there has been growing interest in spin [12, 17, 18] and magnetic field effects [19–22] in organic semiconducting materials.

1.2 Organic semiconductor spintronics

The discoveries of giant magnetoresistance (GMR), colossal magnetoresistance and tunnelling magnetoresistance have not only generated a great deal of excitement in condensed-matter physics and materials sciences, but have also found their applications in magnetic recording and memory technologies [23–25]. Spin-valve read heads and magnetic-tunnel-junction-based random-access-memory devices are two examples of such applications. For both high-density recording and high-density nonvolatile memory, incorporating semiconductor materials into the existing spintronic devices is highly desirable, because among other reasons this would transform the passive devices into active ones. Semiconductor spintronics can offer many other potential applications in information processing, transmission and storage [24], but to realise these potentials, efficient means of injecting spin-polarised charges from metallic or semimetallic electrodes into semiconductors must first be demonstrated. Spin injection from ferromagnetic (FM) metals into nonmagnetic metals has been well studied and documented [26, 27], however spin injection by electrical means from FM into semiconductors remains a challenge.

Schmidt *et al.* [28] have shown that the basic obstacle for spin injection from an FM into a semiconductor originates from the conductance mismatch between the two materials. Rashba [29], Smith and Silver [30], and Albrecht and Smith [31], have shown that the conductance mismatch problem could be circumvented if the injection occurs via tunnelling. As charge injection from metallic electrodes into OSEC occurs mainly through tunnelling [32], OSEC seem to be promising alternatives for semiconductor spintronics [33]. In addition to efficient spin-polarised injection, a long spin relaxation time is also needed for spin-transport applications in the transport layer. The building block atoms of OSEC are light (i.e. having low atomic number Z) with very small spin-orbit coupling. Moreover, the π -electron wave function has zero amplitude on the nucleus sites, thereby minimising the effect of hyperfine interaction. These unique properties show that OSEC may be rather effective for molecular spintronics applications. In addition, OSEC have the potential to bring novel functionalities that do not exist in inorganic spintronic devices. One such functionality is the very efficient light emitting capability of OSEC. Here, we review our recent work [18] where we demonstrated the first organic semiconductor spin-valve based on the small molecule tris-(8-hydroxyquinoline) aluminum (Alq₃, see Fig. 1).

1.3 Magnetic field effects in OLEDs

Davis and Bussmann [21] have shown that the EL intensity can be modulated in OLEDs based on Alq₃ by application of a magnetic field. Frankevich and coworkers reported a similar effect in polymer OLEDs based on a poly(phenylene-vinylene) derivative [34]. While studying semiconducting polymer OLEDs, the authors have recently discovered [20, 22] a large and intriguing magnetoresistance (MR) effect, which we have dubbed organic magnetoresistance (OMAR). OMAR reaches up to 10% (defined as $\Delta R/R = (R(B) - R(0))/R(0)$; R is the device resistance) at room temperature for magnetic fields, $B = 10$ mT. OMAR is therefore amongst the largest of any bulk material. The polymer devices we describe can be manufactured cheaply on flexible substrates, and may be also transparent. Our devices therefore hold promise for applications where large numbers of MR devices are needed, such as magnetic random-access memory (MRAM), and applications related to OLED display screens such as touch screens where the position of a magnetic stylus is detected (patent pending, see demonstra-

tion video at <http://www.iop.org/EJ/mmedia/1367-2630/6/1/185/>). Our devices do not require ferromagnetic electrode materials resulting in a flexibility in material choice not achievable for other MR devices.

2 Experimental

2.1 Fabrication of organic semiconductor spin valves

A vertical spin-valve device consists of three layers, two ferromagnetic electrodes (FM1 and FM2) and a nonmagnetic spacer. By engineering the FM electrodes to have different coercive fields, the magnetisations in FM1 and FM2 can have either parallel or antiparallel alignment in different magnetic field ranges. We have chosen Alq₃ as our OSEC spacer material in the spin valves, because it can be easily evaporated and integrated with other electrode materials. The bottom ferromagnetic electrode (FM1) was a 100 nm-thick La_{1/3}Sr_{2/3}O₃ (LSMO) film, grown epitaxially on a LaAlO₃ substrate. LSMO is believed to be a half-metallic ferromagnet that possesses nearly 100% spin polarisation [35]. (For a recent review of colossal magnetoresistance see [36].) Unlike metallic films, the LSMO films are already stable against oxidation. In fact, our LSMO films were cleaned and reused multiple times without any degradation. The OSEC film (Alq₃) was then thermally evaporated onto the LSMO film, followed by Co film (FM2) evaporation in the same vacuum chamber, using a shadow mask. The active device size was about 2 × 3 nm². The OSEC film thickness ranged from 130 nm to 260 nm. The MR of the obtained spin-valve device was measured in a close-cycled refrigerator from 11 to 300 K, by sending a constant current through it via the two interfaces, while varying an external in-plane magnetic field *H*. The hysteresis loops of the magnetisation against *H* for the FM electrodes were measured by the magneto-optic Kerr effect (MOKE) over the same temperature range.

2.2 Experimental technique for studying spin-dependent exciton formation

Two entirely different experimental approaches have been employed to study spin-dependent exciton formation:

- (i) *Experiments that determine the singlet generation fraction f_S directly in live OLEDs [9–11, 13, 15, 16]*: For fluorescent devices typically only the singlet emission can be measured, information on triplet density is missing and rather involved models have to be employed to obtain f_S [11]. Wilson *et al.*, however, have shown [13] that, in OLEDs made from organic semiconductors that exhibit spin-orbit coupling, the strong intersystem crossing implies that both singlet and triplet emission (fluorescence and phosphorescence) can be simultaneously observed. This could be used to reliably determine f_S . They found $f_S = 57\%$ for devices made from a platinum-containing polymer, but $f_S = 22\%$ for the corresponding monomer OLEDs. This suggests that exciton formation is spin-independent for the monomer, but that a spin-dependent formation process is effective in the polymer.
- (ii) *Experiments that measure the ratio, $r = k_S/k_T$, of the spin-dependent exciton formation rates for singlet and triplet excitons, respectively [12, 14, 37]*: Such experiments manipulate the spin state (using electron spin resonance techniques) of the pairing polarons, and measure the effect on exciton formation rates. These experiments consider photogenerated polarons in the film and use the fact that antiparallel spin polaron pairs can either form singlet or triplet excitons, whereas parallel spin pairs can only form triplets. These optically detected magnetic resonance

(ODMR) techniques are modulation experiments where the resonant μ -wave field is periodically turned on and off. As the experiment is performed at low temperature, spin-alignment is conserved during the halfwave with μ -wave field off, and polaron recombination/exciton formation obeys spin statistics. However, during the halfwave with μ -wave field on, spin-1/2 resonance leads to rapid spin-flips of the recombining polarons. Spin alignment is therefore not conserved, and each pair may choose whether to form a singlet or triplet exciton. It can easily be shown [12, 14] that this leads to enhanced formation of the exciton with larger formation rate (leading to positive ODMR signal), at the expense of the more slowly forming exciton (that gives negative ODMR). In addition, the overall polaron recombination rate is enhanced, because the fast channel becomes allowed for all polaron pairs. Hence, changes occur in the photoinduced absorption (PA) from the triplet state, as well as the fluorescence from the singlet state upon magnetic resonance (see Fig. 3 for experimental observation of these resonant effects). In particular, from the μ -wave induced change in PA of the polaron pairs, $r = k_S/k_T$ could be determined [12].

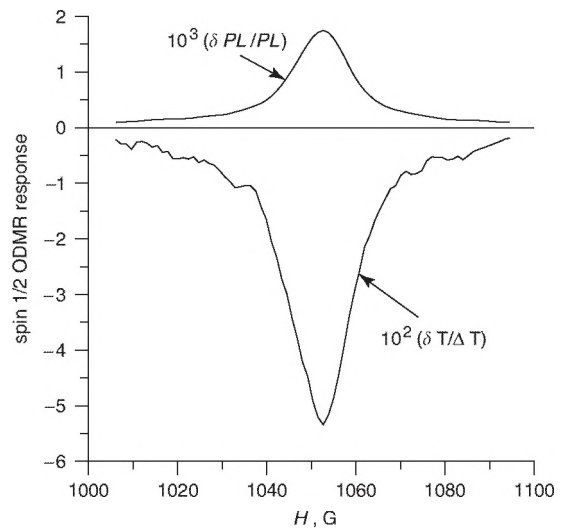


Fig. 3 The spin-1/2 optically detected magnetic resonance response in a PPV film

Upon spin-1/2 resonance, an increase δPL is observed in the singlet exciton emission PL, whereas a decrease δT in polaron and triplet exciton photoexcitation density ΔT is observed. The contributions of polarons and triplet excitons to $\delta T/\Delta T$ can be separated using spectrally resolved PADMR spectroscopy

We used the ODMR technique for measuring r in a large number of π -conjugated compounds with the goal of elucidating the processes that determine r . In the following, the experimental apparatus is briefly described (see Fig. 4), for further details consult recent review papers [38, 39].

For measuring r , we employed the photoinduced absorption (PA) and PA-detected magnetic resonance (PADMR) spectroscopies. The PA technique has been widely used in π -conjugated materials for studying long-lived photoexcitations such as polarons and triplet excitons [40]. Two light beams are used in PA: one to excite the film sample and the other to probe the modulated changes, ΔT in the optical transmission T . The PA spectrum was obtained from the measured T and ΔT spectra by dividing $(-\Delta T/T)$. ΔT is measured using lock-in detection, where the reference signal is tuned to the laser modulation frequency. The PA signal, $-\Delta T/T$, is proportional to the photoexcitation density and optical cross-section, respectively.

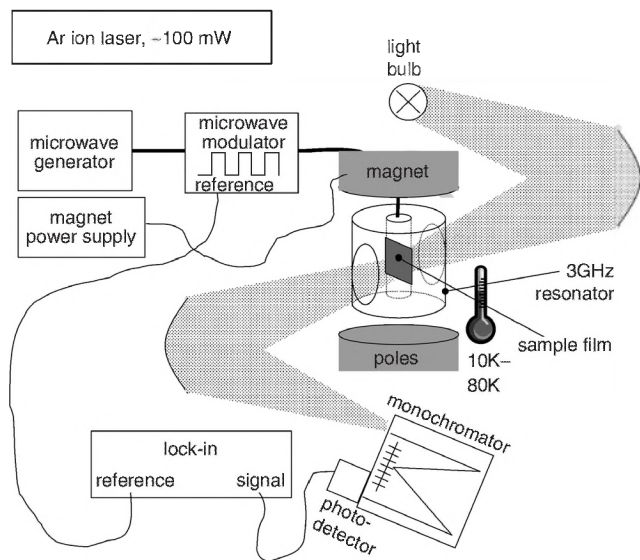


Fig. 4 Schematic drawing of the PADMR experimental set-up used to study spin-dependent polaron recombination and exciton formation

The effect of spin-dependent polaron recombination on the PA bands in the PA spectrum was studied by the PADMR technique [40]. In this technique, we measure the changes, δT , that are induced in ΔT by resonant μ -wave absorption in a magnetic field, H . δT is proportional to δN which is induced in the polaron density, N due to changes in the polaron pair recombination rates. We note that PADMR experiments are performed at low temperature, because (a) the polaron lifetime is sufficiently long for studies using continuous-wave spectroscopies only at low temperatures, (b) the spin-lattice relaxation time becomes very long at low temperatures, such that the spin alignment is conserved during exciton formation. Resonant absorption of microwave photons, on the other hand, leads to spin-randomisation.

2.3 Fabrication of OMAR magnetosensors

Our OMAR devices consist of a thin film of either the polymer PFO (see Fig. 2) or the small molecule Alq₃ (see Fig. 1) sandwiched between a top and bottom electrode. The polymeric film was fabricated by spin-coating, whereas the Alq₃ film was prepared by thermal evaporation at a base pressure of 10^{-6} mbar. The bottom electrode consisted of PEDOT:PSS (see Fig. 2) spin-coated on top of indium-tin-oxide (ITO) covered glass or bare ITO covered glass. The top contact, Ca (covered by a capping layer of Al), was evaporated through a shadow mask (active area: 1 mm^2) at a base pressure of 10^{-6} mbar. All manufacturing steps were performed inside a nitrogen glove box. The MR two-terminal measurements were performed with the sample mounted on the cold finger of a closed-cycle He cryostat located between the poles of an electromagnet. The MR was determined by measuring the current at a constant applied voltage, V .

3 Results and discussion

3.1 Organic semiconductor spin valves

Figure 5 shows the GMR effect that we obtained in an LSMO/Alq₃/Co spin-valve device. A 12% change in resistance is observed at 4K. MOKE measurements made on the LSMO bottom electrode of this device indicate that the coercive field of the LSMO film is about 30 Oe (Fig. 6). While the top Co electrode was not accessible to MOKE

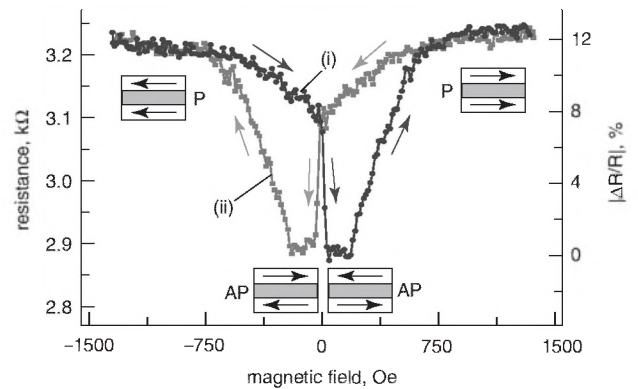


Fig. 5 Magneto-transport response of OSEC spin-valve devices GMR loop of an LSMO (100 nm)/Alq₃ (130 nm)/Co (3.5 nm) spin-valve device measured at 4K. Curves (i) and (ii) denote GMR measurements made while increasing (or decreasing) H , respectively. The antiparallel (AP) and parallel (P) configurations of the FM magnetisation orientations are shown in the insets at low and high H , respectively

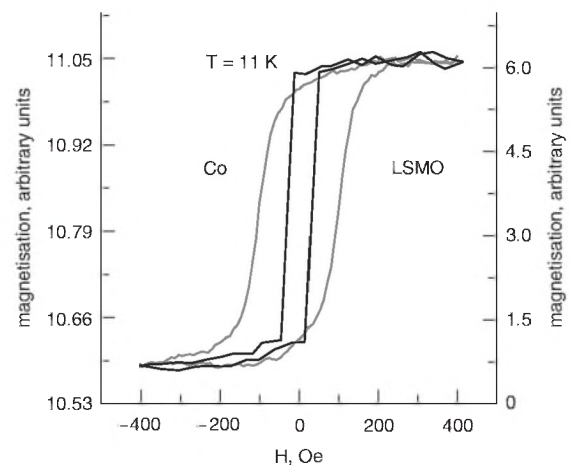


Fig. 6 Magnetic hysteresis loops measured using MOKE for LSMO electrode and Co film The narrow loop is for LSMO, whereas the wider loop is for Co

because it was buried under a thick Al top electrode, the coercive field of a similar Co film of the same thickness deposited under similar condition was about 150 Oe (Fig. 6). The observed GMR is undoubtedly the spin-valve effect, as the GMR traces correlate well with the coercive fields of the electrodes. We note that the obtained resistance in the antiparallel alignment is lower than that in the parallel alignment, which is opposite to the effect in spin valves with two identical magnetic electrodes. For further discussion of this peculiarity consult the original publication [18]. The GMR ratio varies somewhat in devices prepared under similar conditions, which indicates that the state of the LSMO surface may be slightly different each time. However, the highest GMR ratio observed is 40% in a device with 130 nm thick Alq₃ at 11 K [18].

We have also measured the organic spin-valve device temperature, biasing voltage and thickness dependencies [18]. We found that the spin-valve effect typically disappeared at ≈ 200 K, the reason for which is not clear, at present we believe that the diminishing GMR is caused by an increase in spin scattering rate; thus fabricating spin-valves with other OSEC may solve this problem. We also found that the GMR decreases at relatively low bias voltages of ≈ 1 V. Using a different OSEC layer may help in increasing the biasing voltage range. Finally, we obtained a

spin diffusion length, λ_S of ≈ 45 nm [18], from the OSEC thickness dependence of the GMR value in different spin-valve devices involving Alq₃.

3.2 Results of magnetic resonance experiments

Using the ODMR technique described, we found that r is a monotonously increasing function of the conjugation length (CL , see [Note 1] for the definition of CL , which is a quantity of primary importance in the physics of semi-conducting polymers) [14]. This conclusion was based on the experimental data shown in Fig. 7. Figure 7 shows the ratio $r^{-1} = k_T/k_S$ of spin-dependent exciton formation rates in various polymers and oligomers obtained by ODMR spectroscopy [14] as a function of the peak photon energy of the so-called P_1 transition (lower x -axis). The P_1 transition is a transition between the localised polaron level and levels in the valence or conduction band, in the case of positive or negative polarons, respectively. We have previously shown that P_1 is a measure of the polaron wave-function extent and, in addition, a sensitive measure of the polymer's CL [41]. We may, therefore, reinterpret the dependence $r(P_1)$ in terms of the dependence of r on the CL of the polymer films studied. The dependence $r(CL)$ is also shown in Fig. 7, where $1/CL$, which was determined from the measured P_1 , is plotted on the upper axis. The interpretation of negative $1/CL$ values is discussed in [41]. Our data therefore uncover that there exists a (approximately) universal relationship between r and the material's CL . In particular, we found that exciton formation in polymers with long CL is spin-dependent and that the rate

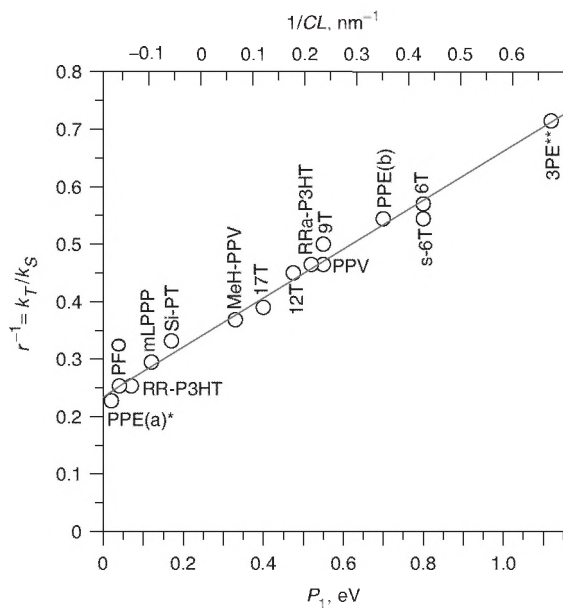


Fig. 7 Magnetic-resonance experimental data for ratio $r^{-1} = k_T/k_S$ of spin-dependent exciton formation rates in various polymers and oligomers as function of peak photon energy of P_1 transition (lower x -axis) and r^{-1} is also shown as function of inverse conjugation length $1/CL$ (upper x -axis) which was determined from P_1 (see text for discussion)

The line through the data points is a linear fit. For further details consult original publications [14, 42]

Note 1: Although the molecular weight of polymers is typically very large, nevertheless it is established that the polymer should be viewed as a string of effectively independent segments, separated by chemical or physical defects. The length of these segments is called the 'conjugation length'.

of singlet formation exceeds that for triplets approximately four-fold. On the other hand, we found, by extrapolation, that $r \approx 1$ in small molecules and monomers, i.e. exciton formation becomes spin-independent in the limit of very small CL . We note that EL measurements [13] performed independently by the Cambridge laboratory arrived at the same qualitative conclusion, namely that exciton formation is spin-independent for the monomer, but that a spin-dependent process is effective in the polymer. As a matter of fact, Yang *et al.* have shown that the two methods even lead to very similar quantitative values [42].

The peculiar dependence of r against CL is examined in several recent theoretical papers [43–47]. Based on our work on spin-dependent exciton formation, we may draw the following conclusions:

- We have shown [12, 14] that pairs of electrons and holes have different reaction rates, dependent on whether they recombine in spin-parallel or spin-antiparallel orientation. This effect is peculiar to π -conjugated polymers and there is no analogous effect (as far as we know) in crystalline inorganic semiconductors. The described effect is caused by strong Coulomb interaction, in particular exchange interaction. This effect demonstrates that spin physics may be very different in organics compared to inorganics.
- The electroluminescence efficiency in polymer OLEDs may exceed 25%. As a matter of fact some groups [15] measured spin statistics of as much as 80% emissive singlets formed against 20% non-emissive triplets. Our measurements indicate, however, that such large singlet fractions should not be possible in small molecular OLEDs.

3.3 Magnetoresistance in OLEDs

3.3.1 Polymer OMAR devices: We first present the results of MR measurements in polymer OMAR devices. Figure 8 shows measured MR traces in a PFO

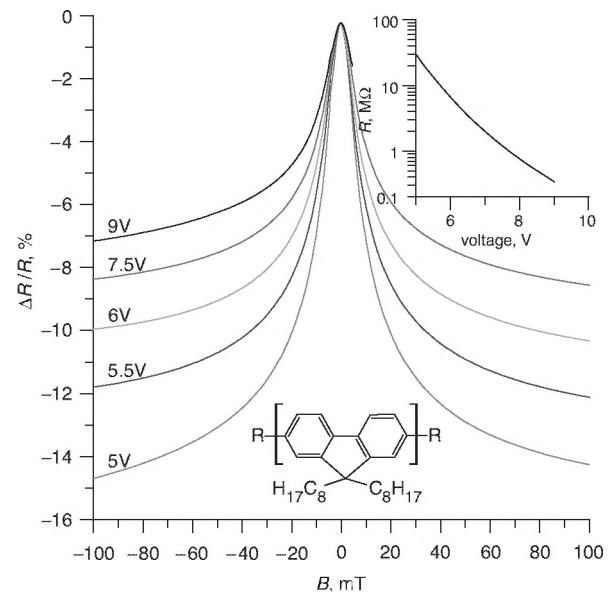


Fig. 8 Magnetoresistance $\Delta R/R$ curves measured at room temperature in an ITO (30 nm)/PEDOT (≈ 100 nm)/PFO (≈ 100 nm)/Ca (≈ 50 nm including capping layer) device (device area = 1 mm²) at different voltages

The inset shows the device resistance as a function of the applied voltage

sandwich device (details are given in the caption) at room temperature at different biasing voltages, V . We found that the obtained OMAR traces are independent of the angle between film plane and applied magnetic field. All measurements shown were performed in an in-plane magnetic field. In [22] we show that the OMAR effect is largely independent of the electron-injection material and, therefore, is related to the hole-transport through the polymer film. In addition, we found that OMAR increases with lowering the barrier for injection of holes. This shows that OMAR is not related to an interface resistance effect. We achieve the best results using PEDOT and Ca electrodes. These materials are commonly used in OLEDs because they result in relatively small barriers for hole and electron injection, respectively. The resistance-voltage characteristics of the measured device are shown as the inset to Fig. 8. It follows that the I - V characteristics of our devices are strongly nonlinear, as is usually the case for polymer sandwich devices. Plotting the I - V characteristics on a linear-linear plot, we found that the onset V is proportional to the polymer film thickness, but otherwise the OMAR device performance is largely independent of film thickness. In Fig. 8 it is seen that $\Delta R/R$ typically increases in magnitude with increasing R . However, we found that R decreases much faster with increasing V than does the magnitude of the OMAR effect. This suggests that the 'intrinsic' MR may be entirely independent of R . The actually observed weak dependence of $\Delta R/R$ on R may be related to series resistances outside of the PFO film, such as hole-injection (Schottky-like) interface resistance.

In Fig. 9 we show OMAR traces in an ITO/PFO (≈ 60 nm)/Ca device. We found that the ITO/PFO interface is less suitable for hole injection than the PEDOT/PFO interface. This results in a drastic increase in turn-on voltage. The data in Fig. 9 were taken at 200 K to improve device stability compared to room-temperature operation. Another striking result shown in Fig. 9 is that, in addition to negative MR, positive MR can be also observed [20] in ITO anode devices at high V .

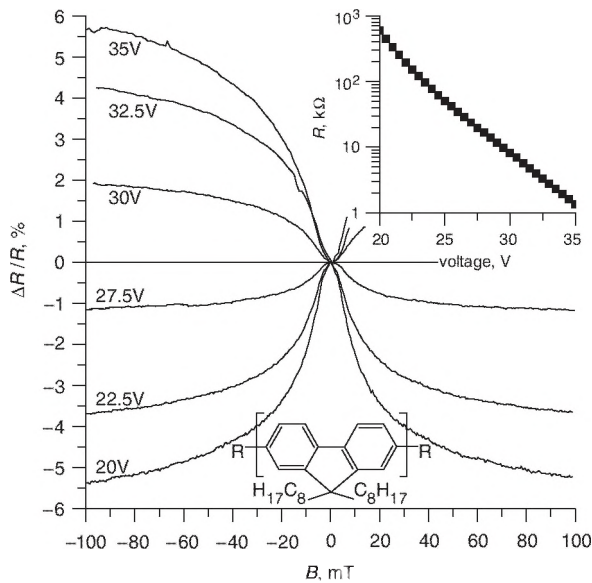


Fig. 9 Magneto-resistance $\Delta R/R$ curves measured at 200 K in an ITO/PFO (≈ 60 nm)/Ca device (device area = 10 mm²) at different voltages

The inset shows the device resistance as a function of the applied voltage

We also found that the magnitude and width of the MR cones are relatively insensitive to temperature [22]. This is somewhat unusual because many other MR effects occur only at low temperature (e.g. classical MR, colossal MR or weak localisation). The observed temperature insensitivity implies that the OMAR effect is likely to be unrelated to thermal equilibrium spin polarisation, which should follow a Boltzmann's distribution.

3.3.2 Small molecular OMAR devices: We now extend our OMAR study to small molecules. Figure 10 shows measured OMAR traces in an Alq₃ sandwich device (details are given in the caption) at room-temperature at different voltages. It is seen that a large OMAR effect can also be achieved in small molecular devices. This extension of our previous results in polymers to small molecules is highly significant from an application and scientific point of view [48]. A comparison shows that even the magnitude of the OMAR effect is very similar in both PFO and Alq₃ devices.

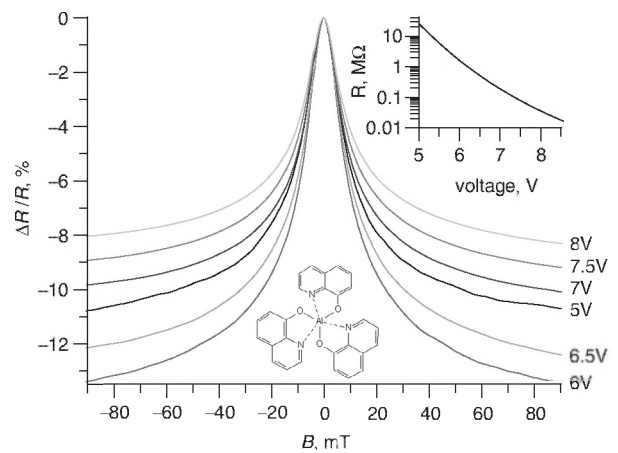


Fig. 10 Magneto-resistance $\Delta R/R$ curves measured at 300 K in an ITO/PEDOT/Alq₃ (≈ 50 nm)/Ca device (device area = 1 mm²) at different voltages

The inset shows the device resistance as a function of the applied voltage

This turns out to be (presumably) coincidental because we found large variations in OMAR magnitude when studying other conjugated compounds. This point will be addressed in a paper by O. Mermer, G. Veeraraghavan, T.L. Francis, Y. Sheng, D.T. Nguyen, M. Wohlgenannt., to be submitted for publication later this year. However, we found that the width of the OMAR cone is largely insensitive to the material used.

3.3.3 Discussion of possible mechanisms to explain OMAR:

Finally, we want to discuss possible mechanisms to explain the observed OMAR effect. We are familiar with the following mechanisms that cause MR in non-magnetic devices: (i) Lorentz force, (ii) hopping magnetoresistance [49], (iii) electron-electron interaction [50] and (iv) weak localisation [51]. It appears that mechanisms (i)–(iii) cannot explain OMAR, because effects (i)–(iii) exclusively lead to positive MR, whereas OMAR is typically negative. We note that the OMAR traces closely resemble MR traces, due to weak localisation (negative MR) and weak antilocalisation (positive MR) well known from the study of diffusive transport in metals and semiconductors [51–53]. This may suggest analysing the

OMAR data using the theory of weak localisation. Such analysis, however, leads to several surprising results that cast some doubt on this interpretation [20]. It therefore appears that a novel explanation for OMAR needs to be found. A theoretical understanding of OMAR will likely lead to advances in the understanding of the transport processes in organic semiconductors, which is still relatively poorly understood. Follow-up experiments performed on current-in-plane devices, and in devices using crystalline or oriented organic semiconductors will likely provide further clues to the origin of OMAR. It appears tempting to draw a connection between the spin-dependent interaction cross-sections between positive and negative polarons, which we have reported here, and OMAR. This connection is however speculative at this point.

4 Conclusions

In summary, we have described three spin and magnetic field effects in organic semiconductor devices: First, we showed that spin-polarised carrier injection, transport and detection, which are the main ingredients of spintronics, can be successfully achieved using OSEC. This may initiate a variety of exciting new applications in organic spintronics. Secondly, we have measured the formation rate ratio r of singlet and triplet excitons that are generated in π -conjugated materials from polaron pairs, using ODMR spectroscopies. We discovered that r^{-1} is linearly proportional to the inverse CL in both polymers and oligomers. Our results show that internal quantum efficiencies exceeding the spin-statistical limit of 25% should be possible in polymer OLEDs. And, finally, we observed a large organic magnetoresistance (OMAR) effect in both polymer and small molecular OLEDs in weak magnetic fields that reaches up to 10% at fields of 10mT at room temperature. Negative MR is usually observed, but positive MR can be achieved also under certain operation conditions. To the best of our knowledge, this effect is not adequately described by any of the MR mechanisms known to date.

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