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T L Francis[1], **Ö Mermer**[2], **G Veeraraghavan**[1] **and M Wohlgenannt**[2,3]

[1] Department of Electrical and Computer Engineering, The University of Iowa, Iowa City, IA 52242-1595, USA
[2] Department of Physics and Astronomy, The University of Iowa, Iowa City, IA 52242-1479, USA
E-mail: markus-wohlgenannt@uiowa.edu

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Abstract. We report on the discovery of a large, room temperature magnetoresistance (MR) effect in polyfluorene sandwich devices in weak magnetic fields. We characterize this effect and discuss its dependence on field direction, voltage, temperature, film thickness, electrode materials, and (unintentional) impurity concentration. Negative MR is usually observed, but positive MR can also be achieved under high applied electric fields. The MR effect reaches up to 10% at fields of 10 mT at room temperature. The effect shows only a weak temperature dependence and is independent of the sign and direction of the magnetic field. We find that the effect is related to the hole current in the devices. To the best of our knowledge, the discovered effect is not adequately described by any of the MR mechanisms known to date.

[3] Author to whom any correspondence should be addressed.

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Contents

1. Introduction

Organic conjugated materials have been used to manufacture promising devices such as organic light-emitting diodes (OLEDs) [1], photovoltaic cells [2] and field-effect transistors [3]. In particular, polyfluorene has emerged as a high brightness, high-efficiency π-conjugated polymer for use in OLEDs [4]. Recently, there has been growing interest in spin [5]–[7] and magnetic field effects [8]–[10] in organic semiconducting materials. Xiong *et al* [7] recently demonstrated the first organic semiconductor spin-valve based on the small molecule Tris-(8-hydroxyquinoline) aluminum (Alq_3); Davis and Bussmann [10] showed that the electroluminescence intensity can be modulated in OLEDs based on the same small molecule by application of a magnetic field. Very recently, we obtained a preprint from E L Frankevich where a similar effect is reported in polymer OLEDs based on a poly(phenylene-vinylene) derivative [11].

While studying semiconducting polymer OLEDs we surprisingly discovered [9] a large and intriguing magnetoresistance (MR) effect. In our best devices this MR effect reaches up to 10% (defined as $\Delta R/R \equiv (R(B) - R(0))/R(0)$; R is the device resistance) at room temperature for magnetic fields, $B = 10\,\mathrm{mT}$. This MR effect is therefore, amongst the largest of any bulk material.[4] The polymer devices we describe can be manufactured cheaply on flexible substrates, and can be 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 the accompanying video). Our devices do not require ferromagnetic electrode materials resulting in a flexibility in material choice not achievable for other MR devices.

In the following we will describe the device fabrication, the MR measurements, and perform an extensive characterization of the MR effect. At the end of the paper, we will discuss possible mechanisms that cause the MR effect. We anticipate that a theoretical understanding of this MR effect will lead to advances in the understanding of transport processes in organic semiconductors.

[4] Conjugated polymers are quasi-one dimensional systems owing to their strong intra-molecular interactions and rather weak inter-molecular interactions. The wavefunctions are therefore primarily localized on a single chain. A thin film with thickness larger than the polymer's conjugation-length may therefore be considered as bulk.

2. Experimental procedure

Our thin-film-sandwich devices consist of the polymer poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO, see figure 1 inset) sandwiched between a top and bottom electrode. The polymer was purchased from American Dye Source (ADS), as well as from H. W. Sands Corp. (HWS) and was used as received. The ADS PFO had an average molecular weight of 78 000 Da and a polydispersity of 2.8, whereas the HWS PFO had a molecular weight between 80 000 to 120 000 Da according to the manufacturer's specifications. Very similar results were obtained for both ADS and HWS polymer, the data shown are for ADS polymer. The polymeric film was fabricated by spin-coating from chloroform solution at 2000 rpm. Very similar results were also obtained from toluene solutions. For varying the film thickness, different concentrations were used, namely 7–30 mg ml^{-1}. The bottom electrode consisted of either indium-tin-oxide (ITO) covered glass, poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT) spin-coated on top of ITO, or Au evaporated onto a glass slide. The top contact, either Al, Ca (covered by a capping layer of Al), or Au, 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. We performed atomic force microscopy on our device films and x-ray diffraction on thick (several microns), free-standing PFO films. Neither measurement showed any sign of crystallinity or directional order. 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

Figure 1 shows measured MR traces in a PFO sandwich device (details are given in the caption) at room-temperature for different voltages. We found that the measured MR traces are independent of the angle between the film plane and applied magnetic field. All measurements shown were performed with an in-plane magnetic field.

3.1. MR devices using different electrode materials

Figure 2 shows the dependence of the magnitude of the MR effect at 100 mT and 200 K (to reduce thermal drift during measurements) on V in a variety of devices using different electrode materials (details are given in the caption). PEDOT and Ca are commonly used in OLEDs since they result in relatively small barriers for hole and electron injection, respectively. ITO and Au are other common contacts for hole injection because of their large work function. We used Ca, Al (data not shown), or Au as the top electrode material, resulting in efficient (Ca) or moderately efficient (Al) electron injection or hole-only devices (Au). The current–voltage (I–V) characteristics of the measured devices are shown as an inset to figure 2. It is seen that the I–V curves are strongly nonlinear as is usually the case in polymer sandwich devices. We found that both I–V and MR curves do not critically depend on whether Au or ITO is used as the anode. However, using PEDOT as the anode results in a significant reduction in the onset voltage and an increase in the observed MR effect. The reduced onset voltage and increased MR can be rationalized considering the decrease in the hole-injection barrier and the resulting reduction of the interface series resistance, respectively when using PEDOT anodes [1]. For this reason

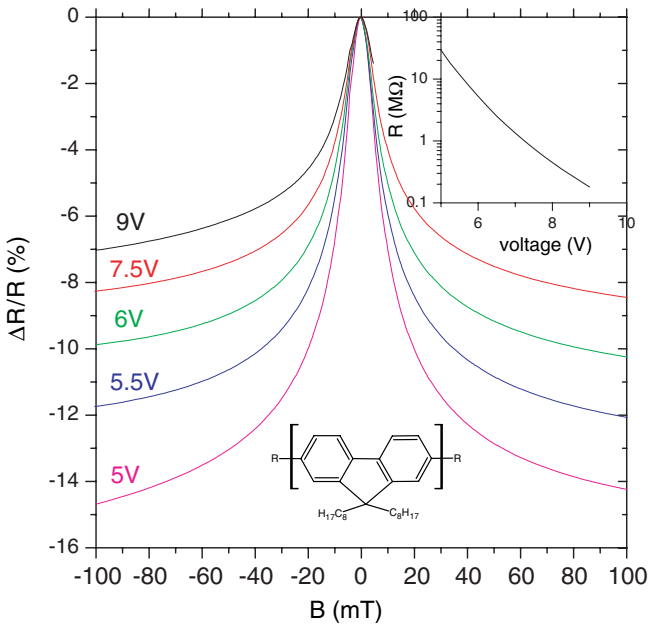

Figure 1. Magnetoresistance, $\Delta R/R$ curves, measured at room temperature in an ITO (30 nm)/PEDOT (≈100 nm)/PFO (≈100 nm)/Ca (≈50 nm including capping layer) device at different voltages. The inset shows the device resistance as a function of the applied voltage.

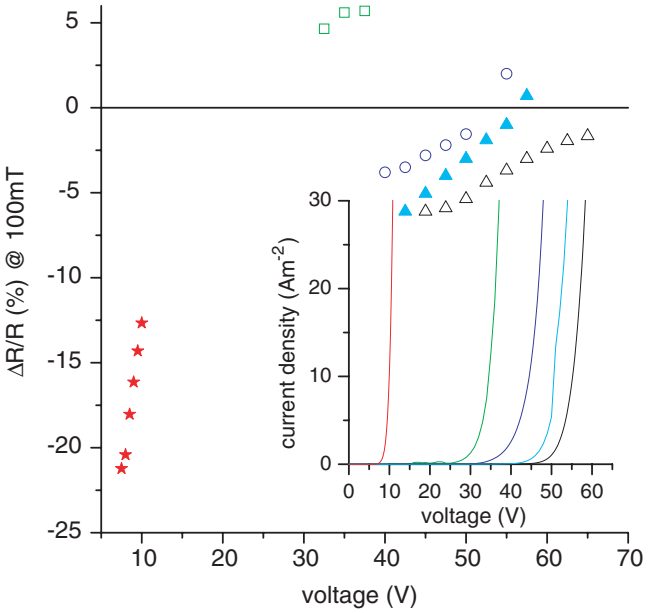

Figure 2. Dependence of $\Delta R/R$ at 100 mT and 200 K on the device voltage in a variety of PFO devices with different electrode materials. The inset shows the current–voltage characteristics of these devices using the same colour code as for $\Delta R/R$. ★, PEDOT/PFO (≈100 nm)/Ca; ○, ITO/PFO (≈140 nm)/Ca; ▲, ITO/PFO (≈150 nm)/Au; △, Au/PFO (≈150 nm)/Ca; □, ITO/PFO (≈100 nm)/Ca at high applied voltages.

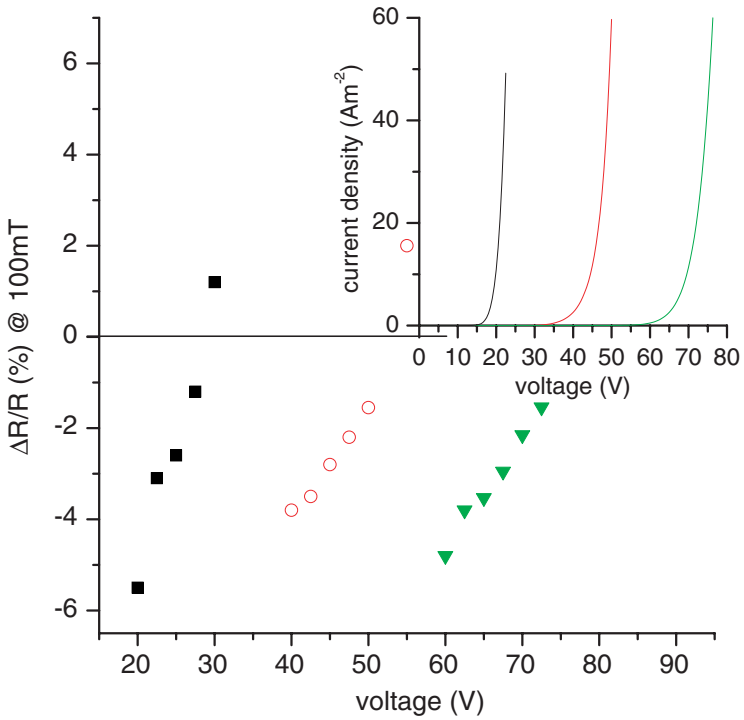

Figure 3. Dependence of $\Delta R/R$ at 100 mT and 200 K on the device voltage in a variety of devices with different polymer film thickness. The inset shows the I–V characteristics of these devices using the same colour code as for $\Delta R/R$. ■, ITO/PFO (≈60 nm)/Ca device; ○, ITO/PFO (≈140 nm)/Ca; and ▼, ITO/PFO (≈300 nm)/Ca.

PEDOT is the preferred anode material in OLEDs. *Importantly, the observed MR effect is largely independent of the top electrode (electron injector) material and occurs also in hole-only devices*, namely those with Au cathodes where only very weak electroluminescence is observed. Devices with a Ca cathode, however, showed strong electroluminescence with a spectrum typical of PFO OLEDs. This clearly indicates that the MR effect is due to hole transport, and not connected to electron transport or electron–hole recombination processes that also occur in OLED devices. Most of the data shown is measured in PEDOT/PFO/Ca devices since this is the preferred OLED configuration.

3.2. MR devices using different polymer film thickness

Figure 3 shows the dependence of the magnitude of the MR effect in ITO/PFO/Ca devices with different polymer film thickness (details are given in the caption) on V. We found that the onset voltage in the linear–linear I–V plot in these devices is determined mostly by the PFO film thickness. Since similar results (not considering the shift in operating voltage) are achieved, independent of PFO film thickness, this clearly suggests that the observed MR effect is a bulk, rather than an (electrode) interface effect. This conclusion is further supported by the fact that the MR effect is observed for PEDOT, ITO and Au anodes. We note that the observation that the MR effect in PEDOT devices is considerably larger than for Au and ITO devices is not in contradiction

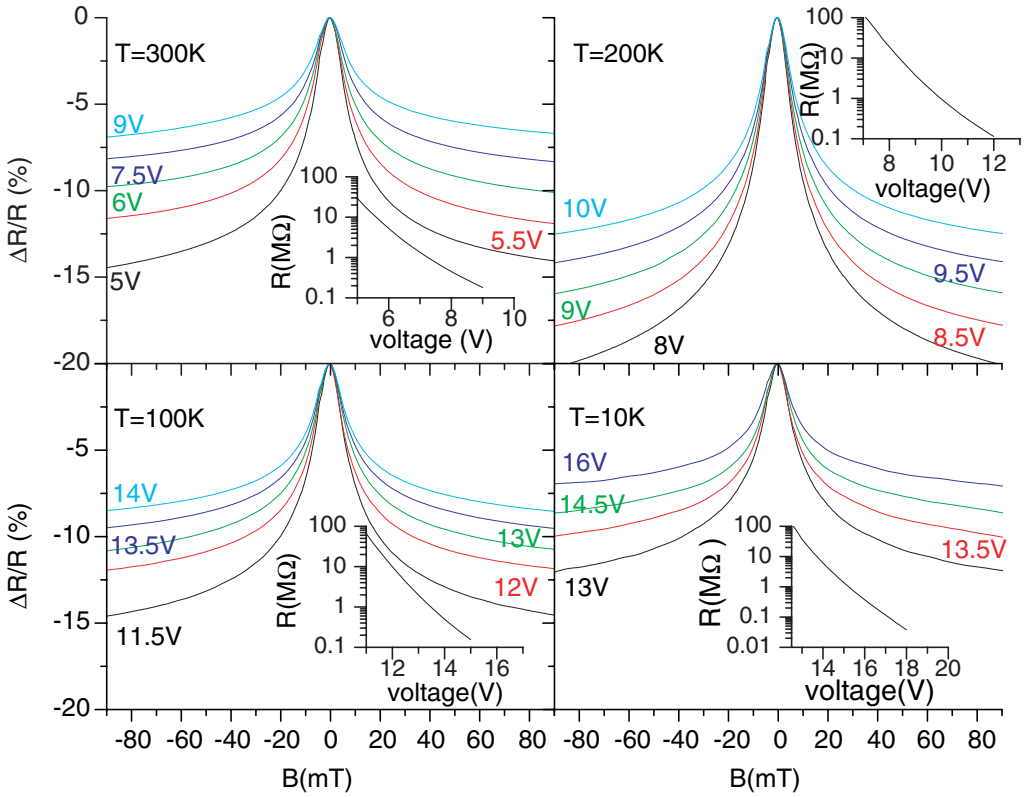

Figure 4. Magnetoresistance, $\Delta R/R$ curves in the device of figure 1 measured at different temperatures, namely 10, 100, 200 and 300 K. The applied voltages are assigned. The insets show the device resistance as a function of the applied voltage.

with our conclusion, but can be attributed to a reduction in interface series resistance in the device when using PEDOT.

Returning to the data in figure 1 it is seen that $\Delta R/R$ typically increases in magnitude with increasing R. However, we find that R of our devices decreases much faster with increasing V than does the magnitude of the MR 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. Another striking result shown in figures 2 and 3 is that, in addition to negative MR, positive MR can be observed [9] in ITO and Au anode devices at high V. We note that we have never observed positive MR in PEDOT devices and speculate that this may be related to the significantly reduced onset voltage in these devices. We note that the applied electric fields are very large in polymer sandwich devices (typically 10^5–10^6 V cm^{-1}).

3.3. Temperature dependence

Figure 4 shows MR traces in a PEDOT/PFO/Ca device for four different temperatures between 300 and 10 K. We find that the magnitude and width of the MR cones are relatively insensitive to temperature. Figure 4, inset shows R as a function of V at the different temperatures.

Similar experiments were also performed on devices made from other π-conjugated polymers and small molecules and will be reported elsewhere [12].

3.4. MR devices with different impurity concentrations

It is important to address the question of whether the MR effect may be related to (unintentional) impurities, such as left over catalysts from the polymerization reaction. Elemental analysis (performed by ADS) of our ADS PFO batches showed signals for only one impurity, namely Ni related to the catalyst bis(1,5-cyclooctadiene)nickel ($NiCOD_2$) at levels less than 20 ppm. In addition, we commissioned five new batches of PFO that have been purified to a different degree after synthesis, resulting in Ni content of 21, 177, 683, 3460 and 8840 ppm, respectively. Our MR measurements on these batches showed no significant dependence on Ni impurity concentration, the noise level however increased with increasing impurity concentration. In addition, very similar results were obtained in devices made from HWS and ADS batches, respectively. We consider this as strong evidence to conclude that the MR effect is not related to (unintentional) impurities.

3.5. Discussion of possible MR mechanisms

Finally, we want to discuss possible mechanisms to explain the observed MR effect. We are familiar with the following mechanisms that cause MR: (1) Lorentz force, (2) hopping magnetoresistance [13], (3) electron–electron interaction [14] and (4) weak localization [15]. It appears that mechanisms (1)–(3) cannot explain our MR effect, because effects (1)–(3) exclusively lead to positive MR, whereas our effect is typically negative. We note that the observed MR traces closely resemble MR traces due to weak localization (negative MR) and weak antilocalization (positive MR) well known from the study of diffusive transport in metals and semiconductors [15]–[17]. This suggests an analysis of the MR data using the theory of weak localization. Such analysis however leads to several surprising results that cast some doubt on this interpretation [9]. It therefore appears that a novel explanation for the observed MR effect needs to be found. A theoretical understanding of this MR effect will likely lead to advances in the understanding of transport processes in organic semiconductors. 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 the MR effect.

Frankevich and co-workers [18, 19] have shown that lifetimes of pairs of paramagnetic species (such as holes and electrons), which may be in singlet and triplet states, are very sensitive to external magnetic fields within the range of hyperfine interaction. In addition, Wohlgenannt, Vardeny and co-workers showed [5, 20] that pairs of electrons and holes show different reaction rates depending on whether they recombine in spin-parallel or spin-antiparallel orientation. Spin-dependent scattering between holes therefore is a candidate mechanism, but more future work is necessary to study this possibility.

4. Summary

In summary, we discovered a large MR effect in PFO sandwich devices. The magnitude of the effect is several per cent for fields of the order of 10 mT and can be either positive or negative,

depending on V. The effect is independent of the sign and direction of the magnetic field, and is only weakly temperature dependent. The MR effect appears to be a bulk effect related to the hole current.

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