Magnetoresistance in organic light-emitting diode structures under illumination

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We have investigated the effect of illumination on the organic magnetoresistance (OMR) in organic light-emitting diode (OLED) structures. The results show that it is possible to obtain OMR at voltages below "turn-on," where no OMR was visible for devices operated in the dark. The photoinduced OMR has a field dependence that is identical to that obtained for OLEDs containing very thin layers, where triplet dissociation at the cathode was a major component of the OMR. At voltages around the open circuit voltage, where the current through the device is very small, very large OMRs of ~300% can be observed. The results support our proposed model for organic magnetoresistance as being caused in part by the interaction of free carriers with triplet excitons within the device. The results suggest that the introduction of a low field magnet could provide a simple means of improving the efficiency of organic photovoltaic cells.

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INTRODUCTION

Giant magnetoresistance is the very large change in the resistance of a device caused by the action of an external magnetic field. The discovery of giant magnetoresistance in metallic spin valves[1] has brought about large improvements in magnetic recording and has introduced the concept of spintronics. The electrical resistance of these spin valves depends on the spin state of the electron passing through a nonmagnetic spacer layer, which can be modified by the application of an external magnetic field. Researchers have been working to include these spin effects into conventional semiconductor systems,[2] and attempts have also been made to fabricate spin valves using organic materials as spacer layers.[3] Recently, organic magnetoresistance (OMR) of up to ~15% has been observed in a number of organic materials commonly used for organic light-emitting diodes (OLEDs), and here the mechanism is still unclear.[4–8] These observations have been made in device structures with no magnetic components, and the effect is found to correlate with the onset of light emission from the device, which suggests that the effect is excitonic in nature.[9] The term organic magnetoresistance is something of a misnomer as the effect is seen in devices that exhibit highly nonlinear current-voltage characteristics and hence cannot be considered as a resistance in the classical sense. However, the term is now widely used to describe a change in the current through the device at constant voltage (i.e., a change in the dynamic resistance), and we will keep that nomenclature.

Although the mechanism for the OMR is not well understood, the effect of a magnetic field on the concentration of singlet and triplet states, as well as the interaction of these excitons with free carriers, has long been an area of scientific research. The main effects that operate to alter the singlet-triplet ratio are magnetic hyperfine interactions, which act to allow interconversion between the singlet and triplet, T_0, states[9,10] and the magnetic field effect on the quenching of triplets through triplet-triplet interactions.[11–13] The role of magnetic fields on the interaction between triplets and paramagnetic centers, such as free carriers, was studied in anthracene crystals by Ern and Merrifield.[14] They showed that the quenching of a triplet exciton by a paramagnetic center (such as free charge carriers) would be suppressed by the presence of a magnetic field and that this can be seen as an increase in the triplet lifetime.

We have suggested[15] that the OMR effect that has been observed in a number of organic systems may be due to carrier trapping at triplet states through the mechanism proposed by Ern and Merrifield.[14] In order to further investigate this, we have introduced excitons into an OLED structure by illuminating it with a 395 nm LED to see if OMR could be observed at voltages below turn-on, i.e., where no electrically generated triplets exist and where OMR is not observed without illumination.

In this paper, we report the magnetoresistance of a standard aluminium tris(8-hydroxyquinolate) (Alq_3) organic light-emitting diode structure under illumination. We have observed that unlike measurements in the dark, OMR can be observed at all drive voltages and that there are three distinct regions of OMR (Fig. 1). At drive voltages below the open circuit photovoltage, the OMR is positive; at drive voltages above the open circuit photovoltage but below the turn-on voltage, the OMR is negative; and above the device turn-on voltage, the OMR becomes positive again and indistinguishable in character from the OMR observed in the dark.[15] At drive voltages around the open circuit photovoltage, where the current through the device is very small, very large magnetoresistances ($\sim \pm 300\%$) can be observed at low fields (~10 mT) in devices operating at room temperature.

EXPERIMENTAL METHOD

Devices were grown on indium tin oxide (ITO) coated substrates with a sheet resistivity of ~13 $\Omega/\square$ and consisted of 500 Å of N,N'-diphenyl-N,N' bis(3-methylphenyl)-(1,1′-biphenyl)-4,4′ diamine (TPD) as the hole transport layer and 900 Å Alq_3 as an emissive/electron transport layer with a cathode of LiF(10 Å)+Al. The TPD and Alq_3 were purchased from Aldrich and purified using train sublimation prior to use. The ITO substrate was patterned using photolithography and cleaned by ultrasonicating in detergent/water, acetone, and chloroform. Following this, the ITO was treated

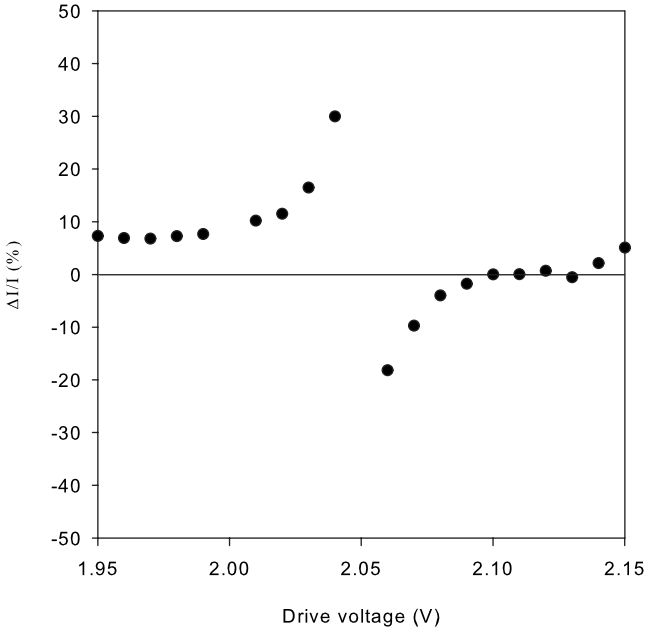

FIG. 1. The magnetoresistance (percentage change in current through the device) of the illuminated device as a function of applied voltage with an applied field of 30 mT. Without illumination, no magnetoresistance is observed.

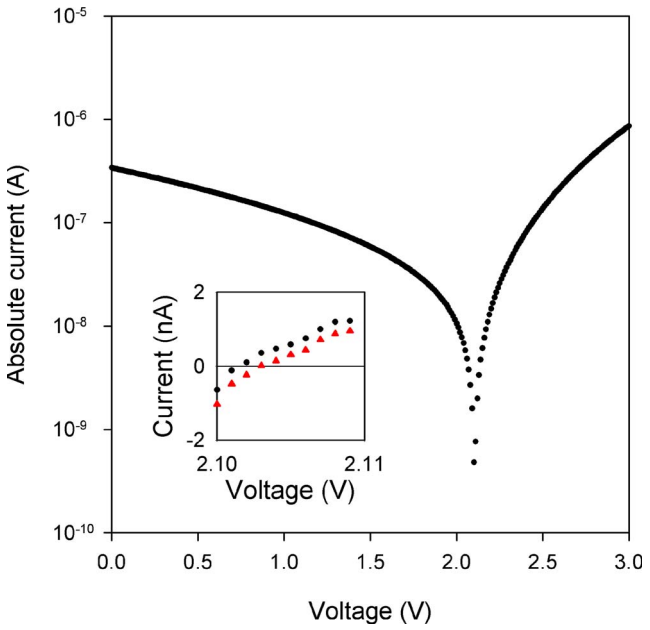

FIG. 2. (Color online) The current-voltage characteristic of the device under 395 nm illumination. The ordinate axis is the absolute current and the minima corresponds to the open circuit voltage.

in an oxygen plasma for 5 min at 30 W and 2.5 mbar pressure using a Diener Electronic femto plasma system. The plasma treated substrate was immediately transferred to the deposition chamber for device fabrication. The deposition of the organic layers and metal electrodes was performed using a Kurt J. Lesker Spectros evaporation system with a base pressure during evaporation of $\sim 10^{-7}$ mbar. The rate of deposition of organic materials was about 2 Å/s, while that of the metal was varied from ~1 to 10 Å/s. A calibrated oscillating quartz crystal monitor was used to determine the rate and thickness of the deposited layer. The whole device fabrication was performed without breaking the vacuum. Final device areas were ~4 mm^2.

RESULTS AND DISCUSSION

Figure 1 shows the magnetoresistance (percentage change in current through the device) as a function of applied voltage at an applied field of 30 mT for the device under 395 nm illumination with an excitation intensity of ~23 mW. The current observed under these conditions is due to the dissociation of excitons at interfaces within the device and, as such, is strictly a photocurrent. However, for the sake of simplicity we will continue to refer to the effect of a magnetic field on this current as magnetoresistance. It can be seen that unlike measurements performed in the dark, OMR can be observed at all drive voltages and that there are three distinct regions. At low voltages, the OMR is positive. An OMR of ~10% at 30 mT is observed up to ~1.95 V; above this, it starts to rise dramatically to ~40% before changing sign to ~−200% (not shown in the figure) before reducing toward zero. The magnetoresistance then becomes positive again once the device turn-on voltage is reached. The point at which the OMR changes from positive to negative is the open circuit voltage for the OLED under the illumination level used. Figure 2 shows the current-voltage characteristic of a nominally identical device under the same illumination. The ordinate axis shows absolute current density, and the minima is the point where the device current changes from negative to positive and corresponds to the open circuit voltage for the device under this illumination level (2.102 V). Figure 3 shows the magnetoresistance (percentage change in the current through the device) as a function of applied field for voltages around the open circuit voltage. At an applied voltage of 2.101 V, 1 mV before the open circuit voltage, we see an increase in the current through the device of ~350% for fields greater than ~25 mT. At 2.103 V, 1 mV after the open circuit voltage, the applied magnetic field causes an ~−100% change in the current through the device. As the applied voltage is increased, the magnitude of the magnetoresistance decreases until, at ~2.15 V, the magnetoresistance becomes positive (Fig. 4). If one looks at the current under a null field and compares it to the current with an applied field as a function of the drive voltage (inset in Fig. 2), it can be seen that the difference in current is approximately constant for voltages around the open circuit voltage. Indeed, the increase in current through the device due to the action of the magnetic field is indistinguishable from an increase in the illumination level. These very large magnetoresistances are therefore due solely to the fact that around the open circuit voltage, the current through the device is very close to zero, and the effect of the magnetic field is to change the current by a fixed amount.

The voltage at which the magnetoresistance becomes positive again is the same as that at which magnetoresistance in the absence of illumination starts to appear and is the point

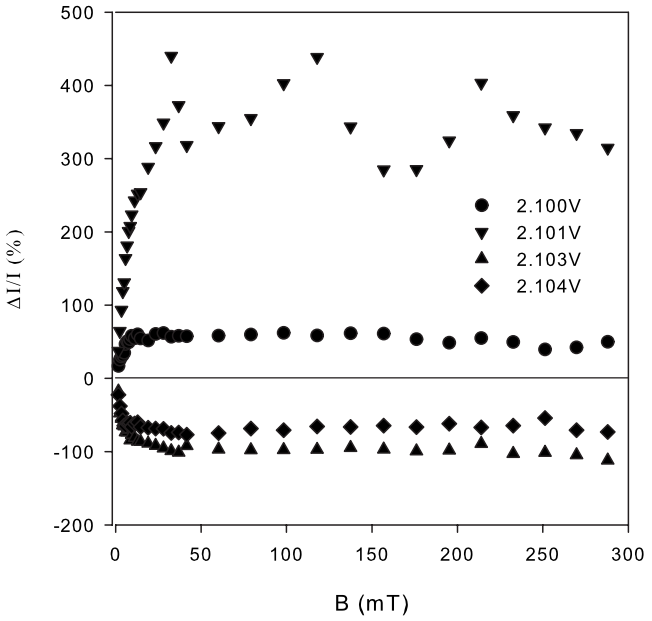

FIG. 3. The percentage change in the current through the device as a function of the magnetic field in the region around the open circuit voltage.

at which electron injection from the cathode occurs and luminescence can be detected. In Fig. 5, we show a simple schematic diagram of the processes controlling the population of singlets and triplets within an organic molecule. There is an excitation pump that can generate either singlets or triplets, recombination of either of these states, and intersystem crossing between the two states. Also shown is a

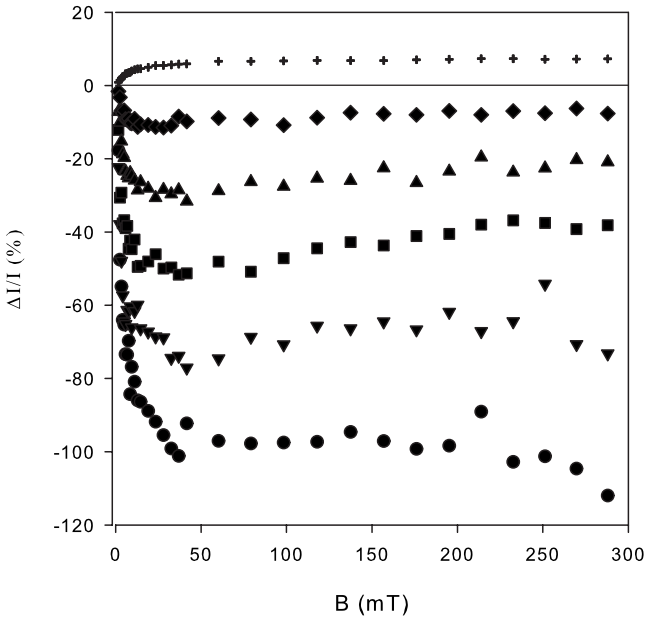

FIG. 4. The percentage change in the current through the device as a function of the magnetic field for applied voltages between the open circuit voltage and the turn-on voltage for the device. The drive voltages are ●, −2.103 V; ▼, −2.104 V; ■, −2.105 V; ▲, −2.107 V; ◆, 2.120 V; and +, 2.200 V.

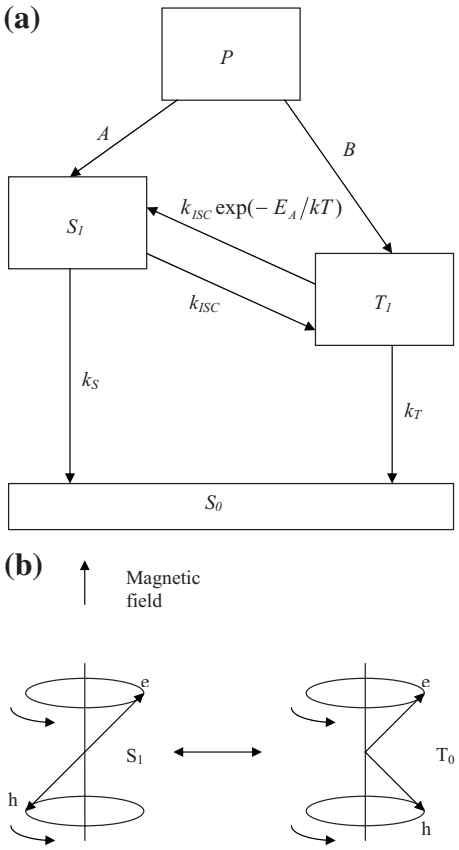

FIG. 5. (a) A schematic diagram of the excitation and recombination pathways in an organic molecule. The excitation pump P produces no triplets under illumination (i.e., $B=0$), but in electrical pumping, $A=0.25$ and $B=0.75$. (b) A vector diagram illustrating the increased singlet $m=0$ triplet intersystem crossing due to a magnetic field.

simple vector diagram showing how the presence of a magnetic field can act to alter the intersystem crossing between the two states. The effect of this magnetic field induced mixing would be to increase the magnitude of k_{ISC} in Fig. 5. The consequence of an increase in k_{ISC} would depend on the relative concentration of singlets and triplets as well as the temperature of the system. If the temperature was sufficiently high to overcome the potential barrier and if there were an excess of triplets in the system, increasing k_{ISC} would lead to a reduction in the triplet concentration. However, if there were an excess of singlets, then increasing k_{ISC} would lead to an increase in the triplet concentration.

In our earlier work,[15] we suggested that without illumination the magnetoresistance was due to the interaction of charge carriers with triplet states affecting the mobility of the Alq layer. Under 395 nm illumination, the effect of the incoming photons is to excite solely singlet excitons ($A=1$ and $B=0$ in Fig. 5). An increase in the intersystem crossing will therefore increase the triplet concentration. The magnitude of this increase will depend on temperature as there can be a thermally enhanced transfer from the triplet back to the singlet state. Under electrical injection, the majority of the excitons formed are triplets ($A=0.25$ and $B=0.75$ from spin statistics), which are long lived compared to singlets (k_S

$\gg k_T$). Therefore, in the steady state, the system would have an excess of triplets, and any increase in mixing the singlet and triplet states induced by the magnetic field will decrease the triplet concentration. This is the situation that occurs above the turn-on voltage of the device where both electrons and holes are being injected into the Alq_3 layer dominating the effect of the 395 nm illumination.

In addition to the recombination of excitons, the possibility also exists for them to dissociate. Given their very large binding energy ($\sim$0.75–1 eV), this is unlikely to occur through simple thermal dissociation. However, strong electric fields or, more importantly, energetically favorable interfaces or impurities can readily cause their dissociation. Again, given the fast recombination time for singlets, their possibilities for dissociation are limited, which accounts for the poor performance of an OLED structure as a photovoltaic cell. However, intersystem crossing into the triplet state results in excitons with much greater lifetimes and hence an increased chance of undergoing dissociation. Using this understanding, we can qualitatively explain the results we have obtained.

Below the open circuit voltage, the current in the device is negative and due primarily to the photocurrent caused by the dissociation of excitons. The only excitons generated within the device in this voltage regime are singlets induced by the incident 395 nm photons. The role of the magnetic field is to increase the intersystem crossing rate between the singlet and the $m=0$ triplet state, resulting in an increase in the triplet concentration and, hence, an increase in the measured dissociation current (a negative current becoming more negative).

Above the open circuit voltage but below the turn-on voltage of the OLED, the observed OMR is negative. In this regime, the current is still primarily due to the photocurrent caused by the dissociation of excitons, but because the applied voltages is greater than the band offset between the injecting electrodes, the device is now in forward bias and the direction of the current flow has changed. From the inset in Fig. 2, it can be seen that this now results in a smaller positive current or a positive current going negative with applied field, and this results in a negative magnetoresistance.

For the measurements immediately around the open circuit voltage, the shape of the magnetoresistance looks like the simple hyperfine scale process that we observed at low voltages in our earlier work. The OMR increases rapidly at low magnetic flux densities before saturating at magnetic flux densities greater than $\sim$50 mT. This behavior is identical to that observed for the efficiency of OLED devices and mirrors the interconversion between the singlet and triplet states. The fact that the OMR follows this curve supports the view that it is due to changes in the photocurrent brought about by the field induced changes in the intersystem crossing. In Fig. 6, we show the data for the device operated at 2.105, 2.107, and 2.12 V plotted on an expanded scale. Here, it can be seen that, in addition to the hyperfine scale component, there is another process that is approximately linear with the applied field and that gives a positive OMR on top of the negative OMR caused by the photocurrent. This positive OMR can be seen at all voltages above 2.105 V. In a recent paper on the effect of the thickness of an Alq_3 layer on

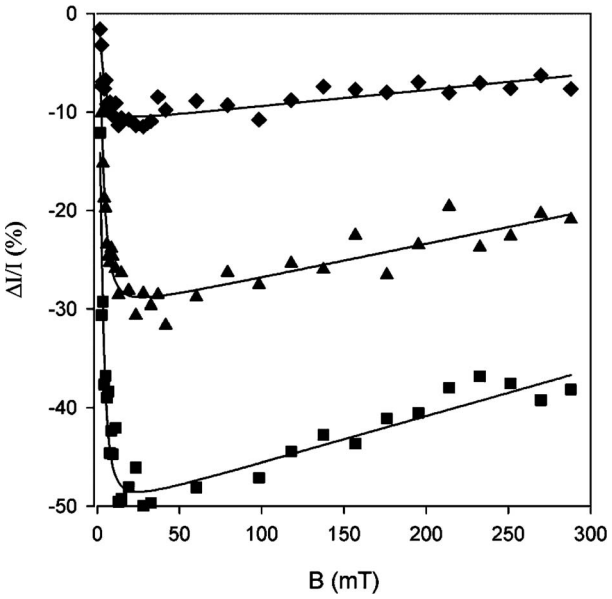

FIG. 6. The percentage change in the current through the device as a function of the magnetic field for applied voltages of ■, −2.105 V; ▲, −2.107 V; and ♦, −2.120 V.

the OMR,[16] we found that a similar behavior could be observed for devices with very thin Alq_3 layers. In these devices just above the turn-on, where the exciton population is small, the magnetoresistance had the same shape as the efficiency, but was negative. This was due to some of the excitons being able to diffuse to the cathode where they could dissociate in a manner analogous to the photocurrent measured here. As the applied voltage was increased, a positive OMR, which was approximately linear with the applied field, was superimposed upon this negative dissociation current. This linear component, which is also seen in thicker Alq_3 based OLEDs, was attributed to the magnetic field dependence of the interaction between a free carrier and the triplet state. The fact that these two processes, light induced OMR below the turn-on and OMR of thin layers above the turn-on, look identical is compelling evidence that they have the same origin and that the linear component of the OMR we have observed here is due to the magnetic field dependence of the interaction between the free carriers and the photoinduced triplets.

Above 2.15 V, the device switches on, and electrically injected electrons and holes begin to dominate the conduction in the device. These recombine within the Alq_3 layer and produce triplet excitons in much larger numbers than those that are photoinduced. In this regime ($A=0.25$ and $B=0.75$), the effect of the magnetic field is now to reduce the triplet concentration. This therefore reduces the amount of electron scattering and hence increases the mobility, resulting in a positive magnetoresistance.[15]

In conclusion, we have investigated the effect of illumination on the OMR of an Alq_3 based OLED. We have shown that illumination induces an OMR where none was present for an unilluminated device and that the results are consistent with OMR being due to the interaction of free carriers with triplet excitons. At drive voltages close to the open circuit

voltage, where the currents are small, we have observed very large magnetoresistances of $\sim\pm 300\%$ in an Alq_3 based OLED structure at room temperature and with applied fields of <10 mT. Magnetoresistances of $>100\%$ can easily be obtained with applied fields of ~ 3 mT. The results show that this process, which affects the mobility of carriers with organics, could play a significant role in the charge transport in organic devices and which to our knowledge has not been incorporated into models for charge transport in OLEDs. The results also suggest that the introduction of a simple and cheap magnet could provide a means of improving the efficiency of organic photovoltaic cells by increasing the intersystem crossing so that more of the photogenerated excitons can be harvested.

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