The role of magnetic fields on the transport and efficiency of aluminum tris(8-hydroxyquinoline) based organic light emitting diodes

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(Received 19 June 2007; accepted 14 August 2007; published online 9 October 2007)

Magnetoresistance and efficiency measurements of aluminum tris(8-hydroxyquinoline) (Alq_3) based organic light emitting diode structures have been made as a function of magnetic field and Alq_3 thickness. Both positive and negative magnetoresistances can be observed depending on the thickness of the Alq_3 layer, the drive voltage, and the applied field. In all devices, large increases in device efficiency are observed. We suggest that the increase in device efficiency is due to conversion of triplet states into singlets through a hyperfine scale interaction. The changes in the magnetoresistance are a result of the reduction in the triplet concentration and operate either through the reduced role of free carrier trapping at triplet states or through the reduction in triplet dissociation at the cathode interface depending on the Alq_3 thickness. © 2007 American Institute of Physics. [DOI: 10.1063/1.2787158]

I. INTRODUCTION

The use of magnetic fields to study the electrical and optical properties of organic materials has a long history. It has been known since the 1970s that the presence of a magnetic field can alter the intersystem crossing between the singlet and the $m=0$ triplet states through the hyperfine scale interaction and that this can affect the luminescence efficiency of organic materials.^{1,2} It was demonstrated in 2003 that the presence of a magnetic field can increase the efficiency of an aluminum tris(8-hydroxyquinoline) (Alq_3) based organic light emitting diode (OLED) while at the same time changing the current through the device at a given driving voltage (magnetoresistance).³ This change in the device efficiency was attributed to a hyperfine scale magnetic field dependent mixing of the singlet and triplet states resulting in an increase in the singlet concentration, hence greater light output. The effect of the magnetic field on the current through the device was attributed to an increase in the electron injection due to singlet excitons reaching the cathode and dissociating. The effect of a magnetic field on the current through organic materials was investigated further by Mermer *et al.*^{4–6} They observed that organic magnetoresistance (OMR) can be observed in a number of different systems and that the effect could be both positive and negative. Desai *et al.*⁷ investigated the role of the cathode material on the OMR of a typical Alq_3 based OLED structure and found that the OMR was intimately correlated with the light emission from the device so that at drive voltages below “turn on,” no OMR was observed. They suggested that the link between OMR and the turn on of the OLEDs was evidence that the OMR was excitonic in nature and that it could be due to the interaction of free carriers with triplet states first proposed by Ern and Merrifield.⁸ The effect of the magnetic field would then be to alter the triplet concentration which would alter the probability of an interaction between a free

carrier and a triplet in the device, hence changing the mobility. In order to investigate this process, we have recently studied the role of illumination on the OMR of an OLED structure. This work has shown that, under illumination with 395 nm light, which was used to inject excitons, giant magnetoresistances of $>300\%$ can be obtained at operating voltages where no OMR is observed without illumination.⁹ The effects were consistent with the expected changes in triplet concentration caused by the increased intersystem crossing induced by the magnetic field.

In this paper, we present results on the effect of the Alq_3 thickness, from 115 to 900 Å, on the OMR of OLED devices. We observe that while for all thicknesses, the effect of the magnetic field is to increase the device efficiency, which implies an increased singlet concentration, the effect of the magnetic field on the current through the device is highly dependent of the device thickness. For Alq_3 thicknesses greater than 200 Å, we observe positive magnetoresistance whereas for low thicknesses, <200 Å, we observe a negative magnetoresistance at low drive currents which becomes positive as the current density in the device increases. These results are discussed in line with models for the role of triplet concentrations within the various devices.

II. EXPERIMENTAL METHOD

The basic device structure consists of an indium tin oxide (ITO) coated glass substrate (purchased from Merck) with a sheet resistivity of $\sim 13 \Omega/\square$, 500 Å of N,N' -diphenyl- N,N' bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TPD) as the hole transport layer (HTL) and between 115 and 900 Å Alq_3 as an emissive/electron transport layer. Onto these devices, a cathode was deposited consisting of a 10 Å LiF layer followed by 1000 Å of aluminum. 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 ultrasonication in detergent solution, water, acetone, and

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chloroform. Following this, the ITO was treated in an oxygen plasma for 3 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 were 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 aluminum 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 vacuum.

Immediately after growth, the devices were placed in a light-tight sample holder with a calibrated silicon photodetector (Newport 818-SL) placed on the top surface of the device. The sample holder was placed between the poles of an electromagnet with the magnetic field perpendicular to the direction of current flow in the device. The photodetector was tested under various illumination levels to make sure there was no field dependence on its output. Measurements were taken with the device operated in constant voltage mode. Before and after each field measurement, a measurement at null field was taken. These two readings were averaged and used to determine the effect of the magnetic field. This procedure was performed in order to remove any effects due to drifting in the device characteristics. Voltage sourcing and current measurements were performed using a Keithley 236 source-measure unit with current measurements being averaged over 32 readings. The optical power output was measured using a Newport 1830 optical power meter.

III. RESULTS AND DISCUSSION

Figure 1 shows the magnetoresistance (percentage change in current) and the percentage change in efficiency for devices with different thicknesses of Alq₃ as a function of magnetic flux density. Each of these curves is taken with a current density through the device of ~ 0.1 A/m². It can be seen that all the devices show a similar change in the efficiency with magnetic flux density. The efficiency curves show a typical hyperfine scale increase, with the efficiency rising rapidly up to a flux density of ~ 50 mT after which it is roughly constant. This hyperfine scale process has been attributed to an increase in the mixing of the singlet and triplet states with applied field.^{1,2} In the theory of Groff *et al.*,^{1,2} this mixing occurs for the correlated electron-hole pair states, before exciton formation, and results in a reduction of the intersystem crossing between the singlet and triplet states. This would therefore result in an increase in the singlet exciton concentration with applied magnetic field and the resulting increase in efficiency seen here. However, this process would not explain the recently observed magnetic field effect on the magnetoresistance of an OLED structure under illumination. In that work, the device was illuminated with 395 nm photons to generate singlet excitons within the device and the effect of the magnetic field was to increase the photocurrent which was consistent with an increase in the intersystem crossing from the singlet to triplet state, where

FIG. 1. (Color online) (a) The percentage change in the current through the devices and (b) the percentage change in device efficiency, at drive currents of ~ 0.1 A/m². The Alq₃ layer thickness and drive voltages are (●) 900 Å (3.6 V), (▲) 700 Å (3.0 V), (+) 500 Å (2.5 V), (■) 300 Å (2.4 V), (◆) 150 Å (2.2 V), (▼) 115 Å (2.25 V), and (×) 150 Å Alq₃+200 Å BCP (2.4 V).

the increased lifetime of the triplet encourages diffusion to interfaces where dissociation can occur. Luminescence studies of Alq₃ have also shown that there is mixing of the singlet and triplet excitons¹⁰ and that it is possible to transfer from the triplet to the singlet exciton state through thermally activated intersystem crossing. The results from Ref. 9 seem to suggest that this intersystem crossing rate, k_{ISC} , is magnetic field dependent and the shape of the observed field dependence is identical to that seen here. The process is schematically illustrated in Fig. 2. From Fig. 2, it can be seen that the effect of a change in the rate constant for intersystem crossing, k_{ISC} , on the steady state population of singlets and

FIG. 2. (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.

triplets is dependent on the rate constant for recombination for each type of exciton, the pump rate into the two states, and the temperature of the system. Given that for electrical generation of excitons, the triplet/singlet generation ratio is 3:1 and the radiative recombination time for singlets in Alq_3 is of the order of 10–20 ns,¹¹ while that for triplets is of the order of 25 μs (Ref. 12) to 1 ms.¹³ It can be seen that the steady state population of triplets will be much greater than for singlets. It has also been shown that by exciting Alq_3 with 488 nm illumination, it is possible to obtain triplet luminescence at 80 K but that as the temperature increases toward 300 K, intersystem crossing from the triplet to singlet state can occur resulting in the luminescence peak shifting from ~ 600 to ~ 520 nm.¹⁰ This shows that the energy barrier E_A in Fig. 2 can be overcome at room temperature. Therefore, as the magnetic flux density increases, one would

expect to see an increase in the conversion of triplets into singlets and a concomitant increase in the device efficiency. This schematic ignores thermal dissociation of singlets and triplets back into free carriers as both states have binding energies of >0.4 eV which makes dissociation in the absence of an energetically favorable interface improbable, which is part of the reason why Alq_3 based OLEDs do not make very efficient solar cells. The schematic also ignores other potential processes such as triplet-triplet annihilation or free carrier quenching of triplets, which will be discussed later.

The effect of device thickness on the magnetoresistance of these devices is more striking. Although each device shows an increase in the efficiency with applied field, the change in the current through the device is strongly dependent on device thickness. For a 195 Å Alq_3 device, not presented, the magnetoresistance is roughly zero at this low current density. For devices with thicker Alq_3 layers, the magnetoresistance is positive, whereas for the devices with thinner Alq_3 layers, the magnetoresistance is negative. Despite the change in sign of the magnetoresistance, the shape of each curve is essentially identical to that of the efficiency and suggests that the process controlling the magnetoresistance is intimately linked to that controlling the efficiency.

In an earlier paper,⁷ we suggested that the magnetoresistance may be due to the interaction of free carriers with triplets within the device through the mechanism proposed by Ern and Merrifield.⁸ They showed that triplets can interact with paramagnetic centers, such as free carriers, and the interaction can result in either the quenching of the triplet state or scattering of the free carrier, both of which result in a decrease of the carrier mobility. The reaction can be written as

where T is the triplet state, $D_{\pm 1/2}$ is the spin $\pm \frac{1}{2}$ paramagnetic center, $(T \cdots D_{\pm 1/2})$ is a pair state, S_0^* is an excited singlet state, and k_1 and k_2 are the rate constants for backscattering and quenching, respectively. According to this mechanism, any process which reduced the concentration of triplets would have the effect of increasing the mobility of free carriers within the device and hence increase the current. This process explains the observed magnetoresistance for the thick devices but does not account for the negative magnetoresistance observed for the thin devices. We believe that in these thin devices, the triplets that are formed are able to diffuse to the cathode interface where they can dissociate. Under forward bias, an exciton dissociating at the cathode will release a hole into the cathode and an electron back into the Alq_3 layer that will then transit the device again, further contributing to the current. Thus, a reduction in the triplet concentration due to the increased intersystem crossing will reduce this dissociation current and result in a negative magnetoresistance. In order to test this hypothesis, we grew each of these structures with an exciton blocking layer consisting of 200 Å of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) on top of the Alq_3 layer and found that all devices showed only a positive magnetoresistance as the triplets

FIG. 3. (Color online) The magnetoresistance of the 900 Å Alq_3 device at different drive voltages. The solid lines are a guide to the eyes.

were stopped from reaching the cathode and dissociating. The data for the 150 Å Alq_3 device with the BCP exciton blocking layer are included in Fig. 1.

Figure 3 shows the magnetoresistance of the 900 Å Alq_3 device as a function of magnetic flux density for different drive voltages. As was shown in Fig. 1 at low drive voltages, the data show a hyperfine scale increase with magnetic field which looks very similar to the corresponding efficiency curve. As the drive voltage, and hence the current density, in the device increases, the efficiency curves for the device keep the same shape although the maximum percentage increase in efficiency changes from $\sim 4.5\%$ at low drive voltages to $\sim 2\%$ at a drive voltage of 9 V. The magnetoresistance, however, changes dramatically. In addition to the rapid rise at low fields, there is a further approximately linear increase in current with increasing field. At a drive voltage of 6 V (corresponding to a current density of $\sim 15 \text{ A/m}^2$) the change in the current density in the device more than doubles from $\sim 0.5\%$ at 16 mT to 1.24% at 300 mT, whereas at 9 V (corresponding to a current density of $\sim 200 \text{ A/m}^2$), the change in current density in the device triples from 0.6% at 16 mT to 1.81% at 300 mT. Very similar results were obtained for the magnetoresistance of the 700, 500, and 300 Å Alq_3 devices.

For the 150 and 115 Å devices (Fig. 4), the same process is visible as the current density is increased, whereas the hyperfine scale reduction in triplet concentration which dominated at low drive current densities produced a negative magnetoresistance. This process produces the same positive effect on the magnetoresistance, as observed in the thicker devices, and acts in addition to the negative magnetoresistance due to the reduced triplet concentration modifying the recombination current. Because the field dependence of the two processes are different, one sees at increasing current densities an initial negative OMR which becomes positive as the magnetic flux density is increased. This does not neces-

FIG. 4. (Color online) The magnetoresistance of the (a) 150 Å Alq_3 device and (b) 115 Å Alq_3 device at different drive voltages.

sarily mean that other processes such as triplet-triplet annihilation are not present, only that they are insignificant compared to the other processes discussed here. The efficiency data for all these devices remain identical in shape with only the hyperfine scale process being visible.

The fact that this high current density process produces a positive magnetoresistance which acts in addition to the negative magnetoresistance produced by the hyperfine scale interaction shows that it cannot be due to a process which is changing the triplet concentration as this would also change the recombination current in these thin devices and hence produce a magnetoresistance in the same direction as the hyperfine scale process. The process is not seen in the efficiency plots for any of the devices. This rules out processes such as triplet-triplet annihilation which would be expected to be magnetic field dependent and would both reduce the

triplet concentration and result in increased efficiency as triplets were converted to singlets. The process must therefore be due to a magnetic field effect on the interaction between free carriers and the triplets. In their original paper, Ern and Merrifield⁸ assumed that the backscattering process would be field independent because there were no spin selection rules and thus only k_2 in Eq. (1) would be modified not k_1 . This assumes that the intermediate state in the backscattering only consists of a carrier being “associated” with the triplet. If the carrier were to directly interact with the triplet state, then there would be spin selection rules to determine the final state and hence some field dependence would be expected. Subsequent work by Wittmer and Zschokke-Gränacher¹⁴ showed that for free carrier interactions with triplet pairs, the effect of a magnetic field was to increase the rate constant for the dissociation of the combined state rather than to enhance the quenching of the triplet pair state into a singlet. Such an increase in the rate constant for dissociation, k_1 , would correspond to a reduction in the trapping time for carriers and, hence an increase in the mobility. The field dependence observed for this process was qualitatively similar to the higher field effects we have observed here.

IV. CONCLUSIONS

We have shown that the magnetoresistance of an Alq₃ based OLED is strongly dependent on the thickness of the Alq₃ layer, the current density in the device, and the applied magnetic field. We have suggested that the magnetoresistance is primarily dominated by the concentration of triplets within the device with the effect of free carrier trapping at these triplets being the dominant mechanism although triplet dissociation at interfaces can play a role and result in negative magnetoresistances.

The triplet concentration appears to be dominated by changes in the intersystem crossing rate between the triplet and singlet states through hyperfine scale interactions and within these devices, at the current densities studied, it appears that triplet-triplet quenching is not a significant effect. The scattering time for free carriers at triplet states appears to be strongly field dependent.

These results demonstrate that organic magnetoresistance can have several contributions and hence the magnitude and sign of the observed effect will be dependent on a number of material parameters for the organic material, such as intersystem crossing rate, triplet lifetime and diffusion coefficient, triplet dissociation constants at interfaces and the carrier trapping, and scattering at these triplet states. In addition, the design of the structure will play a very large role on the magnetoresistance through the effect of triplet trapping and dissociation at interfaces.

These results also demonstrate a new method for understanding charge transport in organic devices. Not only do they demonstrate that the trapping of carriers at triplet states is an important contributor to the mobility of the organic layers but also that the use of magnetoresistance also allows an insight into other contributions to the current in devices such as carrier recycling caused by the dissociation of excitons at interfaces.

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