

## Magneto-resistance and efficiency measurements of Alq<sub>3</sub>-based OLEDs

Pratik Desai, P. Shakya, T. Kreouzis, and W. P. Gillin

*Department of Physics, Queen Mary, University of London, Mile End Road, London, E1 4NS, United Kingdom*

N. A. Morley and M. R. J. Gibbs

*Department of Engineering Materials, University of Sheffield, Sheffield, S1 3JD, United Kingdom*

(Received 13 October 2006; revised manuscript received 30 November 2006; published 23 March 2007)

Magneto-resistance and efficiency measurements of indium tin oxide/*N,N'*-diphenyl-*N,N'* bis(3-methylphenyl)-(1,1'-biphenyl)-4,4' diamine/aluminum tris(8-hydroxyquinoline)/cathode organic light-emitting diode structures have been made as a function of magnetic field and cathode type. It has been found that magneto-resistance occurs only when there is light emission from the devices, which suggests that the magneto-resistance is related to exciton formation. Comparison of the effects of applied field on device efficiency and magneto-resistance shows that the magneto-resistance cannot be due to the recombination current. We suggest that the effect may be due to trapping of charge carriers at triplet excitons within the device.

DOI: [10.1103/PhysRevB.75.094423](https://doi.org/10.1103/PhysRevB.75.094423)

PACS number(s): 73.50.Jt, 73.61.Ph, 75.70.-i

### INTRODUCTION

The effect of magnetic fields on the luminescence properties of organic materials has long been an area of scientific research, and it is well known that magnetic fields can affect both the singlet and triplet concentrations as well as their interactions with free or trapped carriers. 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,<sup>1,2</sup> and the magnetic field effect (MFE) on the quenching of triplets through triplet-triplet interactions.<sup>3-5</sup> 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.<sup>6</sup> They showed that the quenching of a triplet exciton by a paramagnetic center (such as a free charge carrier) would be suppressed by the presence of a magnetic field and that this can be seen as an increase in the triplet lifetime.

In 2003 Kalinowski *et al.*<sup>7</sup> studied the MFE on the performance of aluminum tris(8-hydroxyquinoline)-( $\text{Alq}_3$ )-based organic light-emitting diodes (OLEDs) and found that in fields of up to 0.5 T the electroluminescence quantum efficiency increased by  $\sim 3\%$  while at the same time the current through the device changed by  $\sim 2.5\%$ . The MFE on the device efficiency was attributed to the hyperfine scale magnetic-field-dependent mixing of the singlet and triplet states resulting in an increase in the singlet concentration. The MFE on the device current was attributed to an increase in electron injection due to singlet excitons reaching the cathode. The MFE on the current through organic devices was further studied in 2005 by Mermer *et al.*<sup>8-10</sup> who used the term organic magneto-resistance (OMR) to describe the effect. Mermer *et al.* observed that OMR occurred in a number of different organic materials but concluded that the mechanism was unknown. In their work they showed that in some materials both positive and negative OMR could be seen depending on both the drive voltage and the temperature of the measurement. Gärditz *et al.*<sup>11</sup> investigated the effect of magnetic fields on the singlet and triplet emission from an  $\text{Alq}_3$  device and also observed an effect on the drive

voltage and current through the device but similarly provided no explanation. Sheng *et al.*<sup>12</sup> published a further study of OMR in 2006, and because of a weak correlation between the OMR and the apparent efficiency of their devices, concluded that the OMR effect was not excitonic in nature.

In this work we investigate the effect of a magnetic field on the efficiency and current through a series of  $\text{Alq}_3$ -based devices as a function of both drive voltage and magnetic field. We demonstrate that the OMR effect is intimately linked to the presence of excitons within the device and suggest that it may be caused by the trapping of free carriers by triplets through the mechanism proposed by Ern and Merrifield.<sup>6</sup>

### 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, and 500 Å  $\text{Alq}_3$  as an emissive or electron transport layer. On this basic device three different cathode materials were deposited: Al, Mg(90%):Ag(10%), and LiF(10 Å)+Al. The TPD and  $\text{Alq}_3$  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 and water, acetone, and 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 metal was varied from  $\sim 1$  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

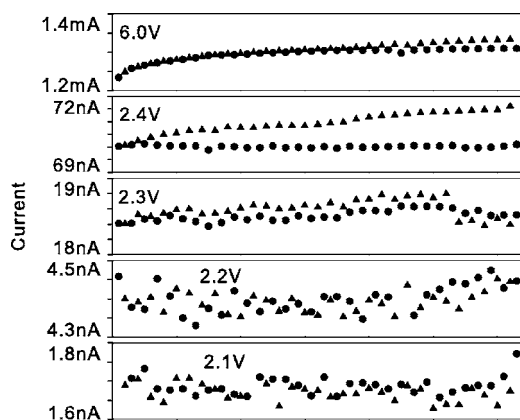


FIG. 1. Raw data for the current through the device with a LiF/Al cathode at different voltages. The null-field measurements are circles and the applied field measurements are triangles. The x axis is the order in which the measurements were performed.

breaking vacuum. Final device areas were  $\sim 4 \text{ mm}^2$ .

All magnetoresistance measurements were performed at room temperature. 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 current through the sample. 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. Magnetic field measurements were made from 0 to 300 mT for positive fields only (earlier tests had shown that the direction of the field did not affect the results). Both before and after each field measurement, a measurement at null field was taken. These two null-field measurements were then averaged and used to calculate the change in current and intensity with applied field. This procedure was adopted to remove any effects due to drifting in the device characteristics, which can be noticeable at high drive voltages. Voltage sourcing and current measurements were performed using a Keithley 236 source-measure unit with current measurements being averaged over 32 readings. The drive voltage was applied to the device only when it was in a stable field. As soon as an individual measurement was made the drive voltage was set to zero while the field was changed. Again this was done in order to minimize drifting in the device characteristic as it was operated in air without encapsulation. The optical power output was measured using a Newport 1830 optical power meter.

## RESULTS AND DISCUSSION

Figure 1 shows the raw data for the current through the device with the LiF/Al cathode at drive voltages of 2.1, 2.2, 2.3, 2.4, and 6.0 V. Each plot shows successive measurements taken first with a null field and then with the field applied, with the applied field increasing as one goes from left to right in the figure. From these raw data it can clearly be seen that at 2.1 and 2.2 V there is no effect of the mag-

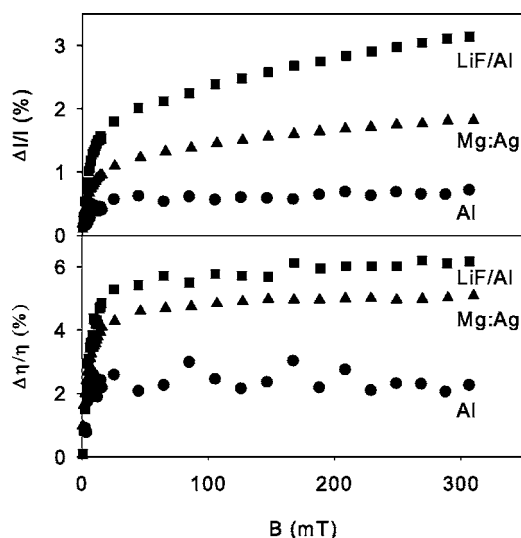


FIG. 2. Differential current  $\Delta I/I$  and differential efficiency,  $\Delta \eta/\eta$  plots for the three devices as a function of applied field. Circles (Al cathode), triangles (Mg:Ag cathode), and squares (LiF/Al cathode). The drive voltages were 2.7 V for the LiF/Al cathode, 3.2 V for the Mg:Ag cathode, and 4.0 V for the Al cathode.

netic field upon the current through the device. Using our experimental setup we were also unable to see any light output at these drive voltages. The same effect was also seen for each of the cathodes we used in this work. This result suggests that the OMR of these devices is intimately linked to the presence of excitons within the device. The 6.0 V data also show the importance of recording null measurements both before and after a field measurement as the drift in the device can be clearly seen. By taking these two null measurements and using the average as the baseline for the differential measurement the effect of this drift can be minimized.

Figure 2 shows the differential current  $\Delta I/I$  and differential efficiency  $\Delta \eta/\eta$  plots for the three devices as a function of applied field. Each plot was taken when the  $\Delta I/I$  [Fig. 4(b)] was at a maximum and corresponds to drive voltages of 2.7 V for the LiF/Al cathode, 3.2 V for the Mg:Ag cathode, and 4.0 V for the Al cathode. In each case this corresponds to a current density through the device of  $\sim 0.5 \text{ A/m}^2$ . It can be seen that for the  $\Delta I/I$  data there is a dramatic difference in the OMR of the devices with  $\Delta I/I$  at 300 mT varying from 0.7% for the Al cathode to 1.8% for the Mg:Ag cathode and 3.1% for the LiF/Al cathode. The onset of OMR in each of these devices correlated perfectly with the onset of light emission. As light emission can only occur once bipolar carrier conduction is present (i.e., once both electrons and holes are being injected) this is strong circumstantial evidence that excitons are essential for the OMR process. This is in agreement with the observation of Gärditz *et al.*<sup>11</sup> who saw no OMR in electron-only Al/Alq/Ca/Al devices.

From Fig. 2 it can also be seen that, although the OMR continues to markedly increase with increasing field, the efficiency of all the devices appears to almost saturate at applied fields above 50 mT. Above this field  $\Delta \eta/\eta$  rises linearly with field at a rate of  $\sim (1.5 \times 10^{-3}) \text{ \% / mT}$ . This linear

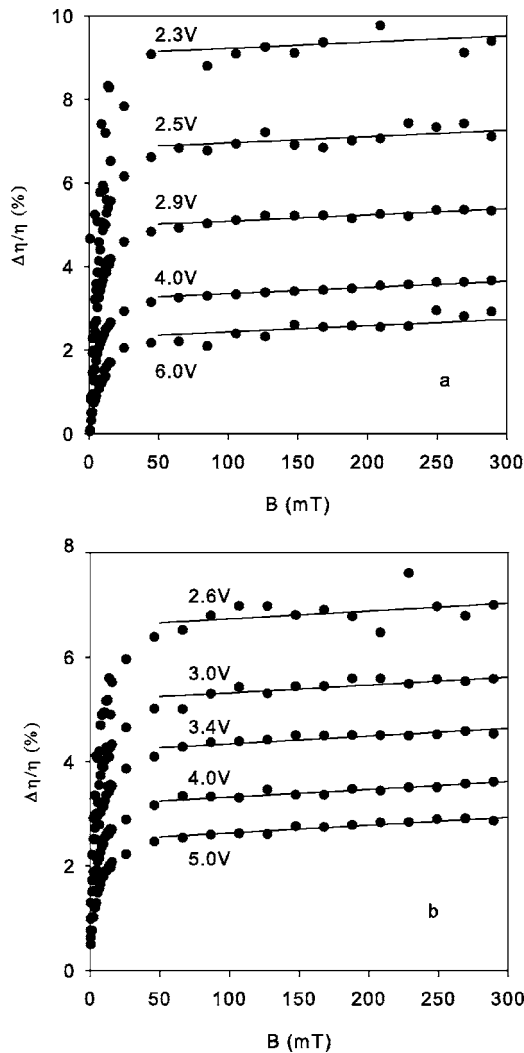


FIG. 3. Differential efficiency  $\Delta\eta/\eta$  of LiF/Al cathode (a) and Mg:Ag cathode (b) devices as a function of applied field for various voltages. Above  $\sim 50$  mT all the curves turn over and the straight lines are a guide to the eye with a slope of  $(1.5 \times 10^{-3})\%/mT$ .

rise is independent of both the drive voltage on the device and the cathode (Fig. 3) and suggests that the effect is not dependent on the concentration of excitons within the device. This further suggests that triplet-triplet annihilation (TTA) is unlikely to play a significant role in the MFE on efficiency. This does not mean that TTA is not occurring, particularly at higher current densities where it may play a significant role in the OMR, only that it is not significantly contributing to the light output of these devices.

Figure 4 shows the  $\Delta I/I$  at 200 mT for each device as a function of both the applied voltage [Fig. 4(a)] and the current density [Fig. 4(b)] through the device. Figure 4(a) clearly shows the abrupt turn-on in the OMR for each device. For the LiF/Al cathode device, for example, there is no OMR at 2.2 V, a 0.92% OMR at 2.3 V, and 1.9% OMR at 2.4 V. For all the devices the OMR increases with increasing drive voltage up to a maximum and then decays. When this same data is plotted against the current density in the device [Fig. 4(b)] it can be seen that the different devices all look very similar in shape with the OMR rising to a maximum at

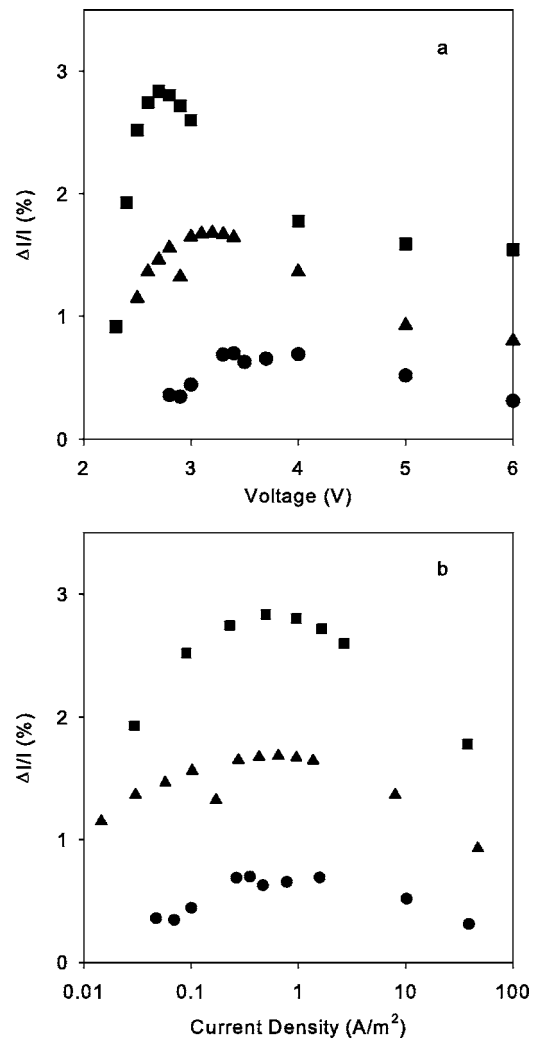


FIG. 4. The differential current  $\Delta I/I$  through each device at 200 mT as a function of both applied voltage (a) and current density (b) through the device. Circles (Al cathode), triangles (Mg:Ag cathode), and squares (LiF/Al cathode).

$\sim 0.5$  A/m<sup>2</sup> before decaying with increasing current density.

Prigodin *et al.*<sup>13</sup> have proposed a model for OMR which is excitonic in nature. They suggest that OMR is due to changes in the recombination rate for electron-hole pairs due to the change in the singlet-triplet mixing introduced by the magnetic field. However, as noted by Prigodin *et al.*, simply changing the degree of singlet-triplet mixing would affect only the recombination current if the triplets were dissociating back into free carriers. This is because once an electron and hole have recombined to form any exciton, they have formed a neutral state that no longer plays any role in the conduction process. Prigodin *et al.* derive an expression for a maximum magnetoresistance of theoretically up to  $-50\%$ . However, this relationship contains only the dissociation and recombination rates for triplets and implicitly assumes that the dissociation rate is considerably greater than the recombination rate. This dissociation may occur at interfaces, if energetically favorable, but is less likely in the bulk given the very large binding energy of the triplet state ( $>1$  eV). However, if such a dissociation were occurring at a signifi-

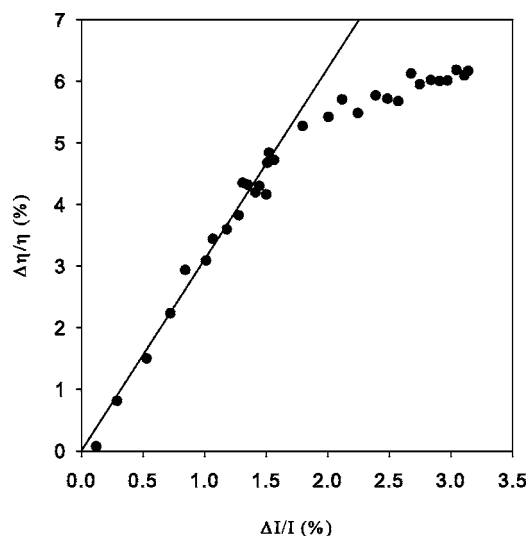
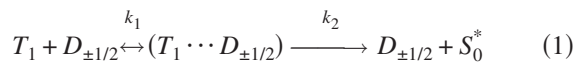


FIG. 5. Differential current  $\Delta I/I$  through the LiF/Al cathode device at an operating voltage of 2.7 V plotted against the differential efficiency  $\Delta\eta/\eta$ .

cant rate, this model would demonstrate the intimate relationship between OMR and device turn-on that we observe, but it would also be expected to result in a linear correlation between the  $\Delta\eta/\eta$  of device and the  $\Delta I/I$ . In Fig. 5 we show  $\Delta I/I$  for the LiF/Al cathode device plotted against  $\Delta\eta/\eta$ . What can be seen is that below  $\Delta I/I \approx 1.5\%$ , which corresponds to a field of  $\sim 25$  mT, we see a linear increase in  $\Delta\eta/\eta$  with  $\Delta I/I$  but above this the value of  $\Delta\eta/\eta$  effectively saturates while  $\Delta I/I$  continues to increase. Therefore although Prigodin *et al.*'s model could provide a mechanism for the low-field magnetoresistance it does not satisfactorily explain the high-field results.

One subject that has received relatively little attention in OLED research is the role played by triplets on the electrical performance of devices. Once turn-on has been reached in an OLED, triplets are generated and due to their long lifetime, estimated to be  $\sim 25$   $\mu$ s in Alq<sub>3</sub>,<sup>14</sup> they will diffuse throughout the active layer until they spontaneously recombine or are quenched, most probably at interfaces. This diffusion will be relatively slow and will result in a large concentration of triplets being present in devices. Hence their equilibrium concentration would be expected to increase with increasing current density. As has been shown by Ern and Merrifield<sup>6</sup> triplets can interact with paramagnetic centers such as free carriers. The reaction can be written as



where  $T_1$  is the triplet state,  $D_{\pm 1/2}$  is the spin  $\pm 1/2$  paramagnetic center,  $(T_1 \cdots D_{\pm 1/2})$  is a pair state, and  $k_1$  is the rate of formation or backscattering from the pair state. The right-hand side of the equation shows that the pair state can also dissociate into a free carrier and an excited vibrational level of the ground state with a rate constant  $k_2$ . The left-hand side of this equation describes a scattering event between a free carrier and a triplet which will result in a decrease in the carrier mobility. One can see therefore that, as the concen-

tration of triplets increases, so should the probability of scattering events, and hence the mobility should decrease. Therefore, as one of the effects of the magnetic field on an OLED is to increase the efficiency of the device, this means that triplets are being converted into singlets. The result is a decrease in the triplet concentration and consequently a decrease in the scattering and hence an increase in mobility. Ern and Merrifield<sup>6</sup> also demonstrated that the quenching of triplets by paramagnetic centers, the right-hand side of the equation, is also magnetic field dependent and that this route is suppressed with increasing field. This will have the effect of quenching another route for triplet annihilation and hence altering the observed magnetoresistance. The ratio of the two rate constants  $k_1$  and  $k_2$  will be a function of the organic material in which the interaction is occurring.

Prigodin *et al.*<sup>13</sup> also looked at the effect of doping Alq<sub>3</sub> devices with the phosphorescent guest molecules tris(2-phenylpyridine) iridium [Ir(ppy)<sub>3</sub>] and 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphine platinum (PtOEP). These molecules are known to greatly improve the efficiency of OLEDs as they allow for the rapid luminescent recombination of triplets. Prigodin *et al.* found that the introduction of the molecules into an Alq<sub>3</sub> device reduced the OMR by a factor of 10 for Ir(ppy)<sub>3</sub> and completely quenched it for PtOEP. This is in agreement with our model as the rapid removal of triplets from the devices removes their trapping of free carriers as a major contributor to the carrier mobility.

All of the interactions referred to so far will also have a temperature dependence. For example, in the simple hyperfine interaction between the singlet and triplet states,



where  $S$  is the singlet state and  $T_0$  is the  $m=0$  triplet state, there is an energy difference between the  $S$  and  $T_0$  states. The relative transfer between the two states therefore depends not only on the magnetic field but also on the relative lifetimes of the two states and on the temperature. It is therefore possible that, while in some systems a reaction may lead toward a decrease in triplet concentration at one temperature, the opposite may occur as the temperature is changed. As we have shown that there is probably more than one process occurring to modify triplet concentrations, which may depend on the current regime in which a device is operated, a range of magnetoresistance effects, both positive and negative, may be seen. Much careful work will be needed to fully elucidate all the processes occurring in any given device structure.

Given the proposed model for OMR how can we explain the differences in  $\Delta\eta/\eta$  and  $\Delta I/I$  in our devices with different cathode materials? These three cathodes were chosen because they have substantially different electron injection efficiencies into Alq<sub>3</sub>. Absolute efficiency measurements at zero field give an efficiency at 100 A/m<sup>2</sup> for the Mg:Ag cathode which is  $\sim 3.6$  times greater than for the Al cathode while for the LiF/Al cathode the improvement over the Al cathode is  $\sim 4$  times. This improvement in efficiency is, in part, due to the increase in the number of electrons that are injected into the devices, which increases exciton generation

within the Alq<sub>3</sub> at any given current density. This will therefore result in an increase in the triplet concentration and hence in the scattering of carriers through carrier-triplet interactions.

These results also have implications for the understanding of current transport in OLEDs. It is believed that in OLEDs the device current is ultimately limited by a trap-charge-limited conduction mechanism where the injected charge is trapped in a distribution of traps of characteristic energy which can be determined from the slope of the log-log *JV* plot. For Alq<sub>3</sub>-based devices these measurements consistently give trap energies of ~150–200 meV, although the nature of these traps has received relatively little attention. From our results presented here it appears that trapping of free carriers by triplet states may be a dominant contribution to the carrier mobility in OLEDs once turn-on has been reached, and as the triplet concentration will depend upon

the drive voltage on the device their role in current transport should be further investigated.

## CONCLUSIONS

Magnetoresistance and efficiency measurements of ITO/TPD/Alq<sub>3</sub>/cathode OLED structures have been made as a function of magnetic field and cathode type. It has been found that magnetoresistance is intimately linked to light emission from the devices which suggests that the magnetoresistance is due to exciton formation within the device. The observation that the efficiency of the devices tends to saturate whilst the magnetoresistance continues to increase suggests that it is not simply the recombination current which is responsible for the observed magnetoresistance. We suggest that the effect may be due to trapping of charge carriers at triplets.

<sup>1</sup>R. P. Groff, R. E. Merrifield, A. Suna, and P. Avakian, *Phys. Rev. Lett.* **29**, 429 (1972).

<sup>2</sup>R. P. Groff, A. Suna, P. Avakian, and R. E. Merrifield, *Phys. Rev. B* **9**, 2655 (1974).

<sup>3</sup>R. E. Merrifield, *J. Chem. Phys.* **48**, 4318 (1968).

<sup>4</sup>R. C. Johnson and R. E. Merrifield, *Phys. Rev. B* **1**, 896 (1970).

<sup>5</sup>A. Suna, *Phys. Rev. B* **1**, 1716 (1970).

<sup>6</sup>V. Ern and R. E. Merrifield, *Phys. Rev. Lett.* **21**, 609 (1968).

<sup>7</sup>J. Kalinowski, M. Cocchi, D. Virgili, P. Di Marco, and V. Fattori, *Chem. Phys. Lett.* **380**, 710 (2003).

<sup>8</sup>Ö. Mermer, G. Veeraraghavan, T. L. Francis, and M. Wohlgenannt, *Solid State Commun.* **134**, 631 (2005).

<sup>9</sup>Ö. Mermer, M. Wohlgenannt, T. L. Francis, and G. Veeraraghavan, *IEEE Trans. Magn.* **41**, 3682 (2005).

<sup>10</sup>Ö. Mermer, G. Veeraraghavan, T. L. Francis, Y. Sheng, D. T. Nguyen, M. Wohlgenannt, A. Köhler, M. K. Al-Suti, and M. S. Khan, *Phys. Rev. B* **72**, 205202 (2005).

<sup>11</sup>C. Gärditz, A. G. Mückl, and M. Cölle, *J. Appl. Phys.* **98**, 104507 (2005).

<sup>12</sup>Y. Sheng, D. T. Nguyen, G. Veeraraghavan, Ö. Mermer, M. Wohlgenannt, S. Qiu, and U. Scherf, *Phys. Rev. B* **74**, 045213 (2006).

<sup>13</sup>V. N. Prigodin, J. D. Bergeson, D. M. Lincoln, and A. J. Epstein, *Synth. Met.* **156**, 757 (2006).

<sup>14</sup>M. A. Baldo and S. R. Forrest, *Phys. Rev. B* **62**, 10958 (2000).