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Magnetic field effects on the conductivity of organic bipolar and unipolar devices at room temperature

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ABSTRACT

Magnetic field effects on the conductivity of different types of organic devices: undoped and dye doped aluminium (III) 8-hydroxyquinoline (Alq_3)-based organic light emitting diodes (OLEDs), electron-only Alq_3-based diodes, and a hole-only N,N′-diphenyl-N,N′-bis(1-naphthyl)-1,1′-biphenyl-4,4′-diamine (α-NPD)-based diode were studied at room temperature. Only negative magnetoresistance (MR) was observed for the Alq_3-based devices. The addition of a rubrene dye in Alq_3-based OLEDs quenches the MR by a factor of 5. The α-NPD hole-only device showed only positive MR. Our results are discussed with respect to the actual models for MR in organic semiconductors. Our results are in good agreement with the bipolaron model.

1. Introduction

The discovery of magnetic field effects (MFEs) in organic semiconductors can be attributed to Frankevich and co-workers with their pioneering works in the 60's [1–4]. However, only recently MFEs in organic semiconductors have attracted the interest of different research groups. MFEs in aluminium (III) 8-hydroxyquinoline (Alq_3)-based devices were studied by different groups [5–9]. Nevertheless previous works were focused in bipolar devices. Various models to explain these effects have been proposed [10–12], which are still under debate. The present discussion on MFEs in organic semiconductors is focused between excitonic like models [10,11] and bipolaron model [12]. The excitonic models propose that MFEs are produced by changes in the intersystem conversion rates [10] or by trapping of charge carriers at triplets [11]. The bipolaron model [12] proposes hopping of polarons and bipolaron formation under the existence of magnetic fields. Thus one fundamental difference between these models is that one should not expect any MFE in a purely unipolar device.

In this work, MFEs on the conductivity of different bipolar and unipolar Alq_3-based devices are presented. A doping molecule, rubrene, is used inside the Alq_3 layer to change the nature of the excitons formed during bipolar injection.

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2. Experimental

Fig. 1 shows the structure of the different devices used. Fig. 1(a) shows the conventional Alq_3-based OLED: ITO (O2)/CuPc (12 nm)/α-NPD (40 nm)/Alq_3 (60 nm)/LiF (0.8 nm)/Al, where ITO denotes indium tin oxide, CuPc copper phthalocyanine and α-NPD N,N′-diphenyl-N,N′-bis(1-naphthyl)-1,1′-biphenyl-4,4′-diamine. Fig. 1(b) shows the rubrene dye doped Alq_3-based OLED: ITO (O2)/CuPc (12 nm)/α-NPD (40 nm)/Alq_3: rubrene (20 nm)/Alq_3 (40 nm)/LiF (0.8 nm)/Al. Fig. 1(c) shows the electron-only device, designed to optimize electron injection: Al/Alq_3 (150 nm)/Al; and Fig. 1(d) shows the hole-only device, designed to optimize hole injection: ITO (O2)/α-NPD (150 nm)/Ag. In this study we investigated a total of three conventional Alq_3-based OLED, two rubrene dye doped Alq_3-based OLED, one electron-only and one hole-only device. Details of device preparation are described elsewhere [13]. Despite the small number of devices studied, the observed MFEs were reproducible in each device.

MFEs were detected at room temperature using an especially designed computer controlled setup. The devices were mounted between the poles of a Varian electromagnet, and the changes in the current were detected by a Keithley 2410-C Source-Meter. The measurements were made using magnetic fields in the range of 1 mT to 1 T, and applied voltages up to 8 V. All conductivity changes were detected as a function of time under the application of different pulsed magnetic fields. The rise and fall time of the magnetic field changes took typically 8 s. During these transient times no

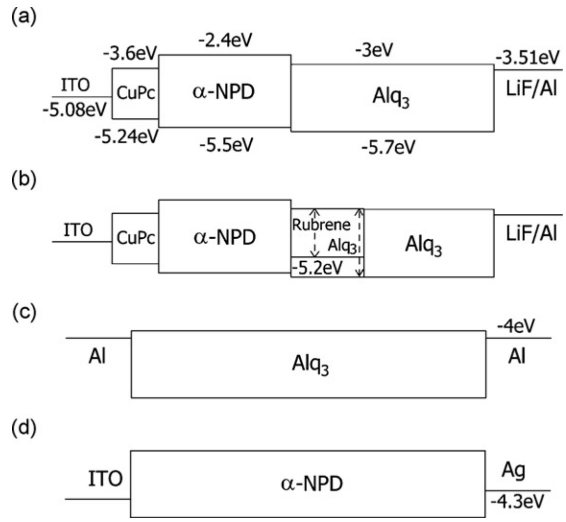

Fig. 1. Schematic representation of the different types of devices studied: (a) conventional Alq_3-based OLED, (b) rubrene doped Alq_3-based OLED, (c) an Alq_3 electron-only device, and (d) an α-NPD hole-only device.

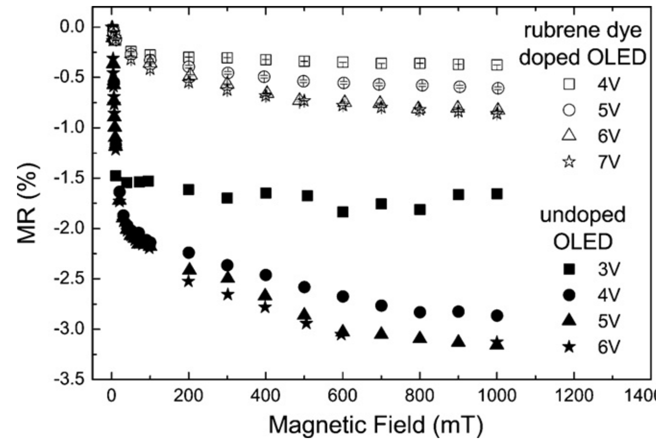

Fig. 3. Magnetoresistance curves of the undoped and rubrene dye doped Alq_3-based OLED.

measurements were taken. The magnetic field after stabilization was kept on or off for 30 s. It was found that the MFEs did not depend on the angle between the device and the magnetic field. All measures were carried out with the magnetic field perpendicular to the device substrate.

3. Results and discussion

Fig. 2 shows the MFEs on the resistance of a conventional OLED. It can be seen that the resistance decreases as the magnetic field is applied. Similar results were observed when magnetic fields up to 1 T were applied. MFEs were detected for magnetic field higher than 3 mT and voltages over 3 V. Only negative MR was observed in these devices, where MR stands for $\Delta R/R = (R(H) - R(0))/R(0)$; where R is the device resistance. Fig. 3 shows the MR curves for undoped and rubrene dye doped OLED. Here it can be seen that the MR tends to saturate for applied voltage over 4 V for the undoped OLED, and over 5 V for the doped OLED. For the undoped OLEDs, the MR reaches up to 2.2% at fields of 100 mT, and 3.1% maximum. In the case of the doped OLEDs the MR reaches up to 0.4% at fields of 100 mT, and 0.8% maximum. For both undoped and doped OLEDs, the MFEs are observable only when EL started, around an applied bias between 2.5 and 3 V.

Fig. 4 shows the MR curves for electron-only and hole-only devices. Differently from the OLEDs, hole-only device has positive MR. The MR are small in these devices, MR ~ 0.03% for the hole-only device and 0.08% for electron-only at fields over 100 mT. A fit made using the empirical law $\mathrm{MR} = \Delta R/R \propto H^2/(H^2 + H_0^2)$, where H denotes the applied magnetic field and H_0 denotes the quarter-saturation field without full success. For low magnetic fields in unipolar devices, MR is not proportional to H^2, while for the OLEDs this trend is observed. We fit also (curves not shown) the empirical "non-Lorentzian" equation $\mathrm{MR} = \Delta R/R \propto H^2/(\left|H\right| + H_0)^2$ in Ref. [9] which do not fits well. Though that these empirical laws could fit the results in bipolar devices, with $H_0 \approx 5$ mT [9], the carrier mobility found using μ is $\mu \approx 1/H_0$ were meaningless.

The observed MFEs in the conductivity of unipolar devices reported in this work shows that this phenomenon is not in principle related to the exciton formation since only a single carrier is present in these devices, and thus excitonic likes models [10,11] cannot be applied to explain the MFEs of our unipolar devices. The bipolaron model [12] is based on unipolar charge transport and relies on the bipolaron formation in the presence of an external magnetic field during the hopping transport through the organic semiconductors. The bipolaron mechanism shows that positive and negative MFEs on the conductivity can occur, since the MF induced change in polaron population as a function of V. Thus, the model identifies two competing effects contributing to the MR: (i) at low

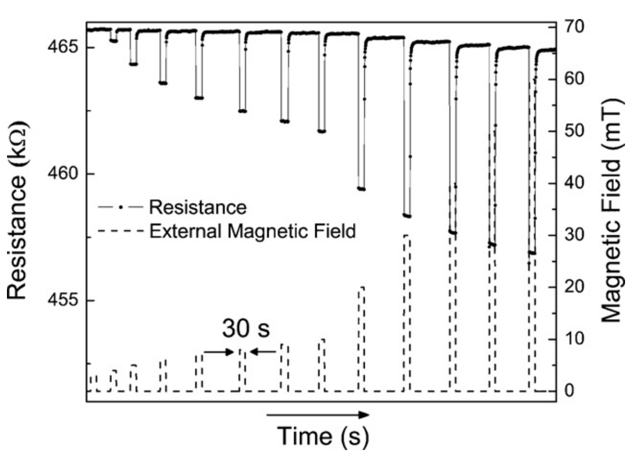

Fig. 2. Resistance of the conventional Alq_3-based OLED as a function of time under the application of different magnetic fields. The intensity of the magnetic fields is on the right axis.

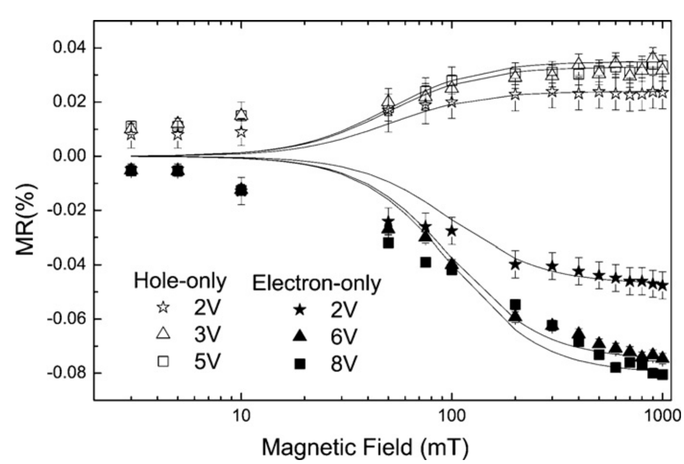

Fig. 4. Magnetoresistance curves of the unipolar devices. The solid curves fits using $\mathrm{MR} = \Delta R/R \propto H^2/(H^2 + H_0^2)$.

V, MF can block the transport (positive MR), since that the number of polarons is small for high offset energies (U–V) between the intrasite Coulomb repulsion energy U and V, and thus a low increase in the bipolaron formation is promoted; and (ii) for high V, MF can increase the transport (negative MR), since that the offset energy (U–V) is reduced, leading to an increase in polaron population at the expense of enhances of bipolaron formation with increase of the magnetic field [12]. This is not in a first analysis what we observe. For hole-only devices the MR is always positive and for electron-only devices the opposite is observed. According to this model, this could indicate that the intrasite Coulomb repulsion energy U is different for positively charged bipolarons with respect to negatively charged bipolarons. Thus, in the hole-only device U should be higher than in electron-only devices, meaning that probably we have not reached V high enough to see the transition from positive to negative MR in the hole-only device. Our findings in the electron-only device are in good agreement with the results by Nguyen et al. [14]. In the case of hole-only devices Wang et al. [15] performed similar measurements in MEH-PPV based devices. They observed both positive and negative MR. A positive MR was observed to change from positive to negative when the magnetic field is increased. The transition occurred at approximately 60 mT. This may indicate that the U for positively charged bipolarons is different in MEH-PPV with respect to α-NPD.

In the case of OLEDs our findings are in good agreement with the previous results found in the literature [6,7,9]. Notice however, that positive MR is also observed in similar devices [16]. The addition of rubrene decreases MR by a factor 5, but does not induce any signal change in the MR. In the bipolaron model one possible explanation is that rubrene is changing the balance of bipolarons/polaron population. Rubrene acts as a hole trap in Alq_3-based OLEDs [17,18]. In this way, one can suppose that it would affect mainly the positively charged bipolarons. A decrease in the MR may indicate that rubrene has a higher U than Alq_3, and thus decrease the population of positively charged bipolarons quenching the MFE. In Alq_3-based OLEDs, positively charged polarons, should dominate the MFEs in the conductivity [14].

4. Conclusion

We have presented MFEs results of undoped and dye doped OLEDs and unipolar organic-based devices at room temperature. Only negative MR was observed for the Alq_3-based devices. Rubrene dye addition in Alq_3-based OLEDs quenches the MR of Alq_3-based OLEDs. Unipolar devices showed a very small MR and the sign of the MR of Alq_3 electron-only and α-NPD hole-only devices are opposite. Our results are in good agreement with the bipolaron model. According to this model, we find that U in the HOMO states of α-NPD is higher than in the LUMO of Alq_3, and that the U in rubrene HOMO states is higher than in Alq_3. Our results indicate that in our OLEDs the HOMO states bipolarons should dominate the MFEs in the conductivity.

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