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Magnetic field-effects in bipolar, almost hole-only and almost electron-only tris-(8-hydroxyquinoline) aluminum devices

T. D. Nguyen, Y. Sheng, J. Rybicki, and M. Wohlgenannt*
Department of Physics and Astronomy and Optical Science and Technology Center, University of Iowa, Iowa City, Iowa 52242-1479, USA

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We present magnetoconductivity and magnetoluminescence measurements in sandwich devices made from the π-conjugated molecule tris-(8-hydroxyquinoline) aluminum (Alq_3) and demonstrate effects of more than 25% and 50% magnitude, respectively. These effects are known to be caused by hyperfine coupling in pairs of paramagnetic species, and it is often assumed that these are electron-hole pairs. However, we show that the very large magnitude of the effect contradicts present knowledge of the electron-hole pair recombination processes in electroluminescent π-conjugated molecules and that the effect persists even in almost hole-only devices.

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I. INTRODUCTION

Organic magnetoresistance (OMAR) is a recently observed[1–9] large, low-field magnetoresistive effect (up to 10% at 10 mT and 300 K) in organic light-emitting diode (OLED) structures. Similar effects have also been observed in various measurements ranging from electroluminescence to photoconductivity.[10–15] OMAR poses a significant scientific puzzle since it is the only known example of large room-temperature magnetoresistance in nonmagnetic materials with the exception of very-high-mobility materials.[16,17] The exact mechanism causing OMAR is currently not known with certainty. Three kinds of models based on spin-dynamics induced by hyperfine interaction have recently been suggested as possible explanations of OMAR: (i) Electron-hole pair (EHP) mechanism models[4–6,8,18] based on concepts borrowed from the so-called magnetic field-effects in radical pairs.[10,19] In this model the spin-dependent reaction between oppositely charged polarons to form an exciton ("recombination") is of central importance. (ii) The triplet-exciton polaron quenching (TPQ) model[7] that is based on the spin-dependent reaction between a triplet exciton and a polaron to give an excited singlet ground state (i.e., the "quenching" of the triplet exciton by the polaron). (iii) The bipolaron mechanism[20] that treats the spin-dependent formation of doubly occupied sites (bipolarons) during the hopping transport through the organic film. Whereas mechanisms (i) and (ii) are excitonic in nature, the bipolaron mechanism can exist also in unipolar devices. We anticipate that the quantitative modeling of OMAR will yield sensitive tests of our understanding of organic semiconductor devices. At present, however, any analysis of OMAR experiments is plagued by ambiguity: experiments must be devised that will allow one to distinguish between the three mechanism mentioned above. Specifically, if model (i) is correct, then measurements of OMAR allow determination of the singlet:triplet ratio in OLEDs, whereas if (ii) is correct it will yield insights into the physics of triplet excitons, and finally if (iii) is correct OMAR can be used to test our understanding of charge and spin transport as well as bipolaron formation. In the present paper we will study OMAR in tris-(8-hydroxyquinoline) aluminum (Alq_3) devices with different electrode materials to put the three models of OMAR to a test.

II. EXPERIMENT

Our devices used an undoped organic semiconductor layer, and consequently the carriers that result in electrical current must be injected from the electrodes. If both the anode and cathode are chosen suitably, both form Ohmic contacts and the device is bipolar and shows efficient electroluminescence. If one of the electrodes is chosen to enforce a large barrier to the injection of this carrier type, then the device is (almost) unipolar and therefore shows ideally no electroluminescence. With this in mind we have fabricated devices with a large number of electrode material combinations. The fabrication started with glass substrates coated with either 30 nm of Al, 40 nm of Ag, 25 nm of Cr, 40 nm of Au (prepared by electron-beam evaporation at 10^{-6} mbar), 40 nm of indium-tin-oxide (ITO, purchased from Delta Technologies), or the conducting polymer poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT, purchased from H C Starck) spin-coated onto ITO as the anode. Since we need to measure the electroluminescence output to assess the carrier balance in the device, the thickness of the anode electrode had to be carefully chosen; It has to be thick enough to show high conductivity but has to be thin enough to be optically semitransparent. The transmission spectrum of the electrodes was measured and was used to correct the externally measured electroluminescence intensity. The Alq_3 (sublimed, HW Sands Corp.) layer was thermally evaporated in high vacuum (10^{-6} mbar) onto the bottom electrode, yielding an organic semiconductor layer thickness of ≈ 100 nm, without breaking the vacuum. The cathode, either Ca (with an Al capping layer), Al, or Au was then deposited by thermal (Ca) or electron-beam evaporation (Al, Au) on top of the organic thin film. The device area was 1 mm^2 for all devices.

The samples were operated in dynamic vacuum inside a cryostat located between the poles of an electromagnet, although the measurements were all taken at room temperature. The magnetoconductance (MC) ratio was determined

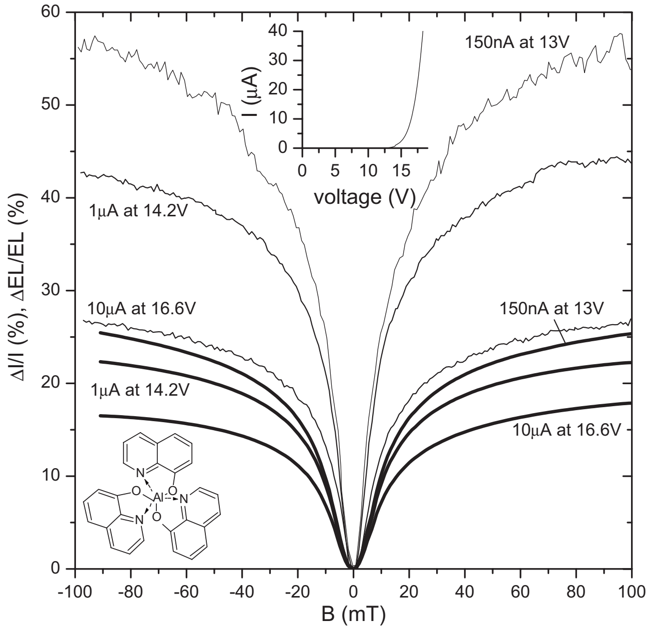

FIG. 1. Magnetic-field effect (MFE) on current (bold lines) and EL (thin lines) in a PEDOT/Alq$_3$($\approx$150 nm)/Ca device measured at several different constant voltages at room temperature. The current-voltage characteristics of the device and the chemical structure of Alq$_3$ are shown as insets.

by measuring the change in current $\Delta I/I$ with magnetic field under constant bias voltage. For measuring the magnetoluminescence traces, ΔEL/EL, a lock-in modulation technique was used. The electroluminescence (EL) intensity was detected as a function of the magnetic field, B, through the anode electrode by a photomultiplier tube that was shielded from the magnetic field using a high saturation mu-shield foil. The EL was not spectrally resolved. The transmission spectra of the anode electrodes were collected in uncompleted devices using an Ocean Optics USB-2000UV spectrometer, and were used to estimate the intensity that can be compared to devices with a highly transmitting electrode (ITO and PEDOT). It is this corrected intensity that will be reported throughout this paper.

As a control experiment, we also measured the quenching (dissociation) of singlet excitons by an applied electric field. For this photoluminescence (PL) quenching experiment, an ITO/Alq$_3$($\approx$100 nm)/Al (40 nm) device with an area of 10 mm^2 was fabricated. A light beam of 400 nm wavelength selected from a tungsten halogen lamp (250 W) was used to excite the device from the ITO side. A photomultiplier tube was used to measure the PL intensity reflected from the device at 508 nm wavelength, and its strength was recorded as a function of the applied reverse bias.

III. EXPERIMENT RESULTS

Figure 1 shows $\Delta I/I$ (bold lines) and ΔEL/EL (thin lines) in a PEDOT/Alq$_3$/Ca device measured at different constant voltages. Very large effects can be achieved, especially at very low current densities. It is shown that ΔEL/EL is somewhat larger in magnitude than $\Delta I/I$. In particular, we observed the following trend: At currents larger than $\approx$10 μA there exists a fixed ratio between the two effects, whereas ΔEL/EL increases more strongly than $\Delta I/I$ with decreasing current at currents below $\approx$10 μA. We believe that a careful study of the relative behavior of the two effects may lead to important insights into the mechanism behind OMAR, but such a study is beyond the scope of the present work. We note that effects as large as 300% have recently been reported in photocurrent measurements.[21] Next we study the magnitude of the observed MC in devices that use different anode and cathode materials. We performed two series of experiments: one, in which we keep a near-Ohmic cathode for all devices and chose different anode materials that are more or less suitable for hole-injection, spanning the range between bipolar and almost electron-only devices, and vice versa for the second series of experiments. We chose Ca as the near-Ohmic cathode and PEDOT as the near-Ohmic hole injector. Using Al as the anode and Au as the cathode results in effectively electron-only and hole-only devices, respectively, as we will show below. In selecting electrode materials of intermediate injection ability, we were guided by the materials' work function. In summary, our experiments allow us to compare OMAR measured in well-balanced bipolar devices, which therefore have a large electroluminescence efficiency, η, to OMAR measured in effectively electron-only or hole-only devices that show only a very poor η.

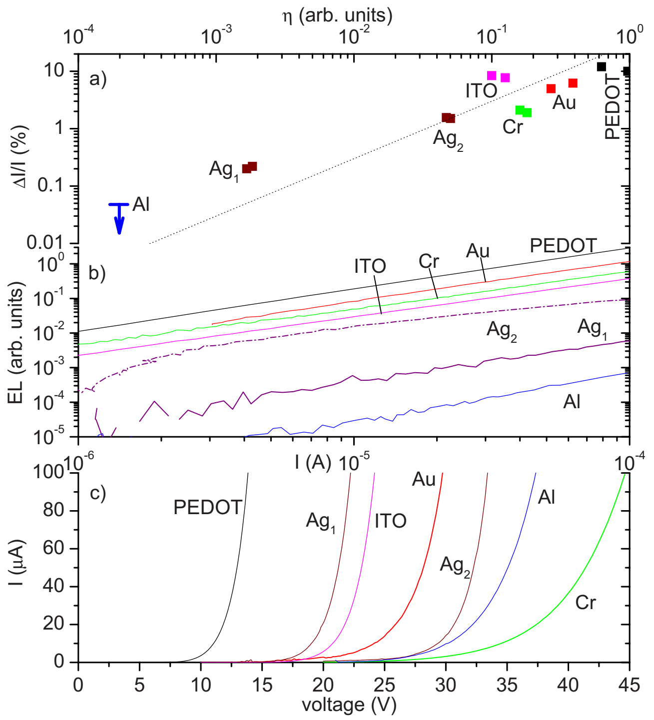

FIG. 2. (Color online) (a) Magnetoconductance ratio, $\Delta I/I$ at B=100 mT in several anode/Alq$_3$($\approx$100 nm)/Ca devices with PEDOT, Au, Cr, Ag, or Al as the anode as a function of the exciton/carrier ratio η. The dotted line shows a linear dependence of MC on η. The value for the Al anode is $\Delta I/I = 0 \pm 0.05\%$. (b) EL as a function of current. (c) Current-voltage (I-V) characteristics.

Figure 2(a) shows the measured MC ratio, $\Delta I/I$ at B =100 mT and the two constant applied voltages resulting in a current flow of approximately 10 μA and 100 μA as a

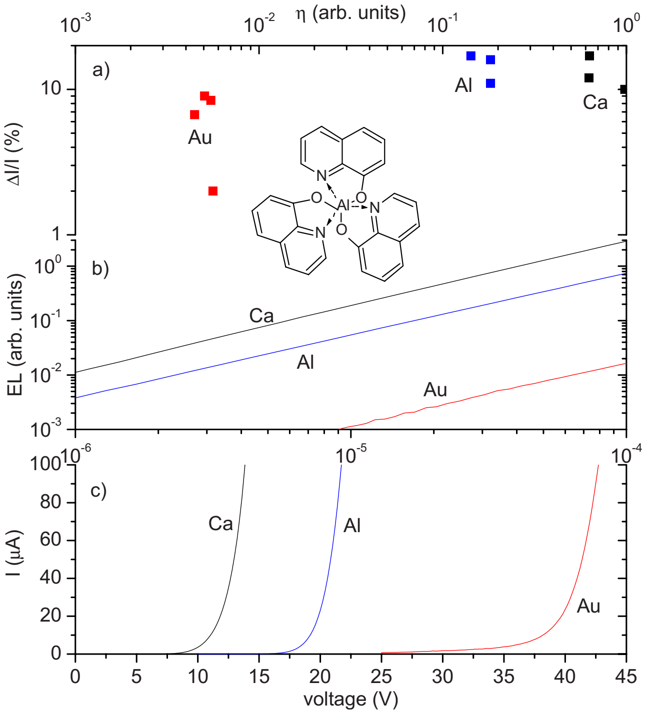

FIG. 3. (Color online) (a) Magnetoconductance ratio, $\Delta I/I$ at B=100 mT in several PEDOT/Alq_3($\approx$100 nm)/cathode devices with Ca, Al, or Au as the cathode as a function of the exciton/carrier ratio η. (b) EL as a function of current. (c) Current-voltage (I-V) characteristics.

function of η in devices ranging from bipolar to almost electron-only. η was determined from the ratio between emitted EL intensity (corrected for the anode transmission) to the driving current. We note that we fabricated several devices of each type, and the reproducibility was good with the exception of Ag-anode devices. In this case we found considerable variation between different devices, and two extremes are shown in the figure as Ag_1 and Ag_2. We spent considerable effort in trying to increase the consistency of the Ag-anode devices but without success. The reason for the large variation is at present not clear to us. Nevertheless, even in the Ag devices the trend regarding $\Delta I/I$ vs η consistently fits in with the other materials shown in the figure. A linear function $\Delta I/I \propto \eta$ is also shown as a dotted line as a guide to the eye. The figure reveals that the measured OMAR effect in devices with poor EL is much smaller than that measured in highly electroluminescent devices. In particular, when using an Al anode, no OMAR effect could be detected. Figure 3(a) shows the measured MC ratio, $\Delta I/I$ at B=100 mT and several constant applied voltages resulting in a current flow between 1 to 100 μA as a function of η in devices ranging from bipolar to almost hole-only. In contrast to the situation shown in Fig. 2, the maximum $\Delta I/I$ in Fig. 3 remains constant within a factor of two, whereas η changes by more than two orders of magnitude. For completeness, the EL-current characteristics and current-voltage characteristics of the devices are shown in Figs. 2(b), 2(c), 3(b), and 3(c). We also note that there exists a clear relation between onset voltage and η for the data of Fig. 3(c). The increase in driving voltage when going from bipolar to unipolar devices is usually attributed to a reduced cancellation of the space-charge fields of the electrons and holes.[22] However, this correlation is much weaker in the data of Fig. 2(c) indicating that space-charge cancellation is less efficient in devices that do not use a PEDOT anode.

IV. DISCUSSION

First we note that the largest observed magnitude of $\Delta EL/EL \approx 56\%$ exceeds the maximum possible value predicted by the electron-hole pair model. A simple calculation shows (Refs. 4 and 23, and references therein) that the maximum positive effect predicted by the electron-hole pair mechanism equals $\Delta EL/EL = 50\%$. The predicted $\Delta EL/EL$ depends mainly on the ratio $r = k_S/k_T$ between the formation rate of singlet excitons and triplet excitons, k_S and k_T, respectively. If $k_S < k_T$, $\Delta EL/EL$ is positive and vice versa. Furthermore, $\Delta EL/EL = +50\%$ corresponds to the limit $k_S = 0$. Even when allowing for uncertainties in measurement and model calculation, we can conclude that values of $\Delta EL/EL \approx +50\%$ require $k_S \ll k_T$. This, however, would imply essentially nonluminescent devices, since the ratio between luminescent singlet excitons and nonluminescent triplet excitons formed is given by $r/(r+3)$ (Ref. 24). Therefore, $k_S \ll k_T$ clearly contradicts the well-known fact that Alq_3 is one of the most efficient OLED materials. As a matter of fact, Baldo *et al.*[25] had measured the excitonic singlet to triplet ratio in Alq_3 to be equal to $22 \pm 3\%$, which is close to the value predicted for spin-independent exciton formation ($k_S \approx k_T$), i.e., 25%. Therefore the claim that the singlet formation rate is much smaller than that for triplets is clearly in contradiction with published measurements.

Figure 2 shows that there exists a correlation between $\Delta I/I$ and the density of injected holes. Since electrons are abundant because of the Ohmic cathode, this suggests an excitonic origin of OMAR. These results are in agreement with published results of other groups: Gärditz *et al.*[15] studied OMAR both in bipolar and electron-only Alq_3 devices, and observed only a very small effect in the latter. Based on this result, they concluded that the observed effects must be excitonic in origin. Desai *et al.*[7] studied OMAR in Alq_3 devices and showed that OMAR occurs only above the onset of electroluminescence. Again, they concluded that OMAR must therefore be of an excitonic origin. However, our measurements in hole-only devices show that the measurements cited above do not present the complete picture and lead, in our opinion, to an incorrect conclusion. Figure 3(a) shows that a large OMAR effect is also observed in effectively hole-only devices using a Au cathode. Whereas the number of exciton detected in devices using a Au cathode is more than 100 times smaller than in well-balanced devices using a Ca cathode, they have similar OMAR magnitude. In our opinion, this is a very strong evidence against an excitonic effect as the origin of OMAR. However, the Au-cathode devices also show a much larger onset voltage in addition to being less electroluminescent. Therefore it is possible that the large electric field rather than the poor electron injection causes the low η. In particular, the electric field could lead to the dissociation of excitons and prevent them from being

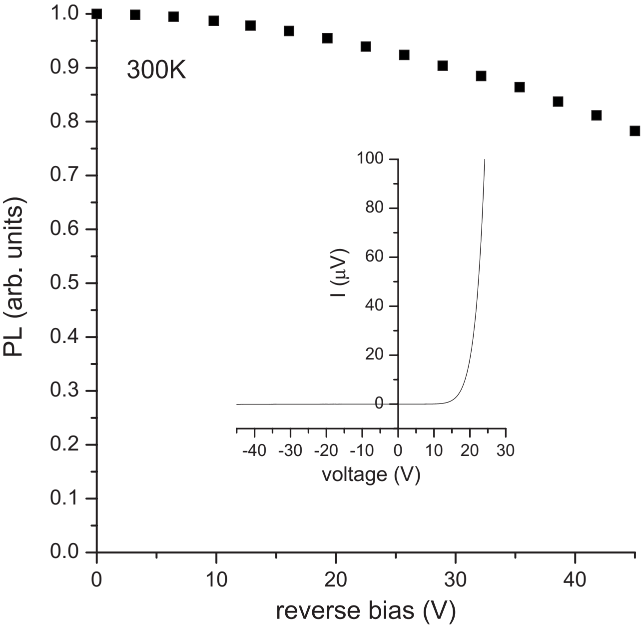

FIG. 4. Photoluminescence (PL) measured at 508 nm and excited at 400 nm as a function of reverse bias in an ITO/Alq_3 (≈100 nm)/Al device. The inset shows the current-voltage (*I*-*V*) characteristics of this device.

detected using the EL measurement. Therefore we completed a control experiment: Figure 4 shows the measured PL as a function of the applied reverse bias in an ITO/Alq_3 (≈100 nm)/Al device. Using reverse bias prevents carriers from being injected into the device (see inset). Indeed, some excitons get quenched at large reverse bias but the effect is rather small because of the large exciton binding energy in Alq_3. Therefore the reduced η must be assigned to poor electron injection when using Au cathodes.

OMAR should therefore be explained using a single carrier mechanism, such as the bipolaron model[20] we had suggested. However, the reason why OMAR should exist only in hole-only Alq_3 devices but not in electron-only devices must still be uncovered. If the bipolaron model were to be able to explain this observation, it would be required that hole bipolarons, but not electron bipolarons, exist in this material. At present there is no evidence for this scenario. In fact, very little seems to be known about bipolarons in Alq_3. Nevertheless, we now present a brief review of the literature relevant to the present discussion. Theoretical calculations of isolated molecules[26,27] showed that Alq_3 can exist as two geometrical isomers, one called facial fac-Alq_3 and the other called meridianal mer-Alq_3. The two isomers have different electronic structures. In the fac isomer, the three ligands are transformed into each other under the operation of a threefold axis, whereas the three ligands are inequivalent in the mer isomer. Therefore, the molecular orbitals of mer-Alq_3 are localized on a single ligand. Moreover, a doubly charged molecule will have its two charges localized on different ligands, and bipolarons, which are defined as two charges with significant exchange coupling, are not formed. In contrast, for fac-Alq_3, the molecular orbitals are symmetric orbitals delocalized over all three ligands. Therefore, bipolarons can exist in this from, either as electron or hole bipolarons. Furthermore, these calculations predict the mer isomer to be energetically more favorable and x-ray diffraction studies in crystalline Alq_3 confirm this.[28,29] The green emission from our devices coincides well with the calculated transition energy for mer-Alq_3 and indicates that the Alq_3 in our devices exists as mer-Alq_3, which does not form bipolarons. However, a comparison between the experimental data in films and the results of the calculations must be viewed with care because it is known that there exist significant differences between gas-phase molecular orbital energies and molecules in films, to a significant part due to dielectric screening. It is also not clear whether the isomer properties in crystals are equivalent to those in amorphous films. However, even if bipolarons exist in Alq_3, they are expected to be very high in energy because of the strong Coulomb interaction within this small molecule. For example, the singlet exciton binding energy in Alq_3 is believed to exceed 1 eV (Ref. 30). However, the bipolaron energy is reduced by electron-phonon interaction, which also increases with decreasing molecule size (Ref. 31, and references therein). For example, the very large Stokes shift of 0.4 eV in the Alq_3 emission was assigned[32] to lattice relaxation upon exciton formation and the relaxation energy of the polaron and bipolaron may be expected to be larger than that. In addition, it is possible that there exists significant exchange interaction between neighboring molecules, resulting in interchain bipolarons. Another possibility is that bipolarons form in deep traps. Indeed, it was recently shown that a large trap density leads to larger OMAR.[34] Since the hole mobility in Alq_3 is smaller than that for electrons,[33] more deep traps may exist for holes and this may explain why OMAR is only observed for holes in Alq_3. But these points are entirely speculative at the moment and further study is clearly required.

V. CONCLUSION

We studied magnetoconductivity and magnetoluminescence in sandwich devices made from Alq_3 using different electrode materials resulting in either bipolar or almost electron-only or hole-only devices and intermediate cases. The magnetoconductivity and magnetoluminescence reach more than 25% and 50% magnitude in fields of 100 mT. We showed that the very large magnitude of the effect contradicts present knowledge of the electron-hole pair recombination processes in electroluminescent π-conjugated molecules, which rules out one particular model of OMAR that was previously proposed. Moreover, we find large OMAR effects in bipolar as well as effectively hole-only devices, which shows that OMAR is most likely not excitonic in origin. However, no OMAR effect appears to exist in electron-only devices.

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*markus-wohlgenannt@uiowa.edu

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