



Controlling hole-transport in aluminum tris (8-hydroxyquinoline), Alq 3 -based organic light emitting diodes to improve the device lifetime by an oxidized transport layer

Mathew K. Mathai, Fotios Papadimitrakopoulos, and Bing R. Hsieh

Citation: Journal of Applied Physics **95**, 8240 (2004); doi: 10.1063/1.1728289 View online: http://dx.doi.org/10.1063/1.1728289 View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/95/12?ver=pdfcov Published by the AIP Publishing

Articles you may be interested in p -type Zn 1 x Mg x O films with Sb doping by radio-frequency magnetron sputtering Appl. Phys. Lett. **89**, 202102 (2006); 10.1063/1.2388254

p -type conduction in wide-gap Zn 1 x Mg x O films grown by ultrasonic spray pyrolysis Appl. Phys. Lett. **87**, 092101 (2005); 10.1063/1.2035326

Enhancement of p -type conductivity in nanocrystalline Ba Ti O 3 ceramics Appl. Phys. Lett. **86**, 082110 (2005); 10.1063/1.1864232

Properties of nitrogen-implanted p-type ZnO films grown on Si 3 N 4 / Si by radio-frequency magnetron sputtering Appl. Phys. Lett. **84**, 5040 (2004); 10.1063/1.1763640

p-type semiconducting Cu 2 O–CoO thin films prepared by magnetron sputtering J. Vac. Sci. Technol. A **21**, 1336 (2003); 10.1116/1.1580491



This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to] IP: 140.113.38.11 On: Thu, 01 May 2014 04:19:54

Controlling hole-transport in aluminum *tris* (8-hydroxyquinoline), Alq_3 -based organic light emitting diodes to improve the device lifetime by an oxidized transport layer

Mathew K. Mathai and Fotios Papadimitrakopoulos^{a)}

Nanomaterials Optoelectronics Laboratory, Department of Chemistry, Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06269-3136

Bing R. Hsieh

Department of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan

(Received 12 December 2003; accepted 8 March 2004)

A salt containing polymer, called an oxidized transport layer (OTL), was investigated for hole injection and transport into Alq3-based multilayered organic light emitting diode (OLED) devices. The OTL comprises an aryldiamine containing hole transport polymer binder with a corresponding low molecular weight radical cation salt. We demonstrate herein that the OTL behaves like a tunable resistor for holes, and its hole-transport properties can be controlled by the salt concentration and thickness of the OTL. Based on a careful analysis of the current density-voltage (J-V) device characteristics as a function of the above parameters, electron/hole currents were balanced to minimize oxidative degradation of Alq₃. It was found that an OLED device (ITO/OTL/NPB/Alq₃/CsF/Al) with a 5000 Å thick OTL at 5% salt concentration operated with a half-life exceeding 1000 h at a constant current of 10 mA/cm². Similar devices with 2.5% and 10% salt doping showed an order of magnitude lower half-life attributed to unbalanced carrier concentrations. Moreover, by demonstrating that the majority of the field drops across the Alq₃ layer, the doping level as opposed to OTL thickness was established as the primary contributor controlling hole transport in these OLEDs. This beneficial behavior is, however, observed only above a certain OTL thickness in the vicinity of 5000 Å. © 2004 American Institute of Physics. [DOI: 10.1063/1.1728289]

I. INTRODUCTION

Controlling molecular design and device architecture has paved the way to realize organic based optoelectronics. Among different potential applications which have emerged in the past decade, the field of organic light emitting diodes (OLEDs) based on aluminum *tris* (8-hydroxyquinoline) (Alq₃) as an active luminescent material has shown tremendous growth since its inception.^{1,2} However, there are still various obstacles that need to be overcome before reaching extensive commercialization and one of the major challenges is the improvement of device operating lifetime.

Contributing factors to the decay of device performance over time include reaction of Alq₃ with the cathode and its delamination,³ indium diffusion into the organic layers,⁴ interdiffusion,⁵ chemical degradation,⁶ and crystallization of the same.⁷ Careful engineering of device fabrication by manipulating different parameters such as the purity and choice of materials,^{8,9} the rate of film growth during organic layer deposition,¹⁰ the vacuum under which devices are fabricated,¹¹ and encapsulation¹² have improved device performance. At the same time, however, the results of Aziz *et al.*¹³ and our own,¹⁴ clearly underline the importance of curbing the intrinsic degradation associated with the formation of cationic Alq₃ species in OLEDs that utilize this molecule as either a light-emitter, host material for emissive dyes, or electron transporting layer (ETL). More recently, the results of Kondakov *et al.* have demonstrated the effect of trapped immobile positive charge within the OLED which act as nonradiative recombination centers.¹⁵ Accordingly, it can be concluded that in order to reduce the intrinsic degradation in Alq₃ OLEDs a better understanding and control of the *bipolar* nature of charge transport through these devices is required.

In this regard, the development of hole transport layers (HTL) for OLEDs has proceeded in two related but apparently contradictory directions. On one hand, attempts have been made to reduce the injection barriers at device interfaces in order to facilitate hole injection into the Alq₃ devices.¹⁶ This has been indicated to result in improved device efficiency¹⁶ and apparent stability after 10 h.¹⁷ On the other hand, the results of Aziz et al.13 signify the importance impeding the transport of holes into the Alq₃ layer in order to improve device lifetimes. To this extent, venues such as blending HTL and ETL layers,18 using dyes as trap sites within the HTL,¹⁹ hole blocking layers,²⁰ and inducing the formation of emissive sites by dye doping within the HTL itself²¹ have been explored to achieve the same. These research initiatives-one to improve hole injection from the anode and the other to impede the hole transport into the Alq₃ layer—address different aspects of bipolar transport in these devices. Reduction of hole interfacial barriers ensures

8240

[This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to] IP: 140.113.38.11 On: Thu. 01 May 2014 04:19:54

^{a)}Author to whom correspondence should be addressed; electronic address: papadim@mail.ims.uconn.edu

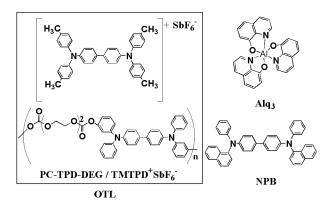


FIG. 1. Chemical structures of the compounds used in this study. The oxidized transport layer (OTL) consists of a hole transporting polycarbonate PC-TPB-DEG containing varying amounts of the SbF_6^- salt of TMTPD⁺. The structures of N,N'-bis(naphthalen-1-yl)-N,N'-bis(phenyl)benzidine (NPB) and Alq₃ are also shown.

ease of hole injection and reduces heating effects which are known to contribute to device degradation. However, among such optimized devices, one has to be concerned with reducing the uncontrolled injection of holes, especially at higher device operating voltages.

Based on the above discussion it is apparent that an approach combining both reduced barriers to hole injection, and modulated hole transport are needed to further improve device lifetime. The balance of charge carrier injection should persist over all applied fields, which is important for display applications, where gray scale is controlled by varying the applied drive voltage. This imposes additional requirements on the choice of materials and device architecture in order to extend the regime of balanced charge transport to larger operating voltages.

In this paper we demonstrate the above device performance enhancing strategy by introducing a salt containing polymer layer between the ITO anode and a conventional hole transporting layer similar to the work of Yamamori et al.²² This layer is henceforth referred to as the oxidized transporting layer (OTL) and consists of a polycarbonate of N, N'-bis(3-hydroxymethyl)-N, N'-bis(phenyl) benzidine and diethylene glycol (PC-TPB-DEG) loaded with the $SbF_6^$ salt of N, N, N', N'-tetrakis(4-methylphenyl) benzidine $(TMTPD'^+ SbF_6^-)$.²³ These components of the OTL along with the other molecules used in this study are shown in Fig. 1. The conductivity of the OTL can be varied over two orders of magnitude by adjusting the concentration of the oxidizing organic moieties in the film.^{24,25} The tunable conductivity ensures that the number of holes being injected into the Alq₃ layer in OTL modified devices are optimized. In addition, the presence of the salt in the OTL ensures minimized interfacial barriers to the injection of holes by means of altering the ionization potential of ITO and thinning of the tunneling barrier at the ITO/OTL interface.²⁶ Based on this, we currently show that the OLEDs thus fabricated exhibit optimized quantum efficiencies and lifetimes. As the conductivity of the OTL is changed to be less or more than an optimum value, device performance degrades. Thus, as indicated in the schematic of Fig. 2, OTL acts both to facilitate hole injection through ITO (which reduces interfacial heating

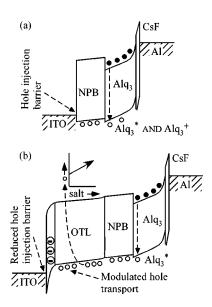


FIG. 2. Schematic illustrating the charge transport of holes and electrons in (a) conventional Alq₃ devices with NPB as hole transport layer without any OTL and (b) OTL modified Alq₃ OLEDs (Ref. 26). In (b) both electron and hole injection barriers are reduced. The variable resistance of the OTL determines the number of holes being injected into the Alq₃ light-emitting layer to reduce formation of Alq₃⁺ cationic species.

effects), along with providing a variable resistor to minimize excess hole injection into Alq_3 (that optimizes device life-time).

II. EXPERIMENT

All the devices made in this study were fabricated on indium tin oxide (ITO) coated glass substrates (Thin Film Devices). The ITO-coated substrates were cleaned by scrubbing gently with detergent solution, washing in distilled water and organic solvents, followed by oxygen plasma treatment for 10 min. The OTL was fabricated by spin casting a 25 mg/ml solution of polymer and salt in methylene chloride onto the ITO-coated glass substrate at 1000 rpm. Under these conditions, the thickness of the OTL obtained is 5000 Å. A series of PC-TPD-DEG solutions were prepared and into these solutions, different salt concentrations were added by weight percent with respect to the polymer weight in the solutions. The films obtained from these solutions were seen to have a thickness variation of less than 150 Å as measured by profilometry. In experiments where the thickness of the OTL is deliberately varied, the desired thickness was achieved by using a diluted solution of the OTL and by increasing the speeds at which spin casting was carried out.

Two sets of experiments were performed to study the effect of the OTL on OLEDs based on Alq₃. In the first set of experiments, three types of devices were fabricated as follows: single layer OTL devices (ITO/OTL/Al), OTL modified Alq₃ devices (ITO/OTL/NPB/Alq₃/CsF/Al), bilayer devices (ITO/NPB/Alq₃/CsF/Al), where ITO and CsF/Al are the anode and cathode, respectively. The CsF layer was deposited in order to improve injection of electrons from the Al cathode.²⁷ The deposition of the organic materials, CsF, and metal electrode was carried out in an Edwards Auto 306 high vacuum coater at 1.5×10^{-6} Torr. The thick-

nesses of the various layers deposited are as follows: NPB and Alq₃ 500 Å each, CsF ca. 10 Å, and Al 1500 Å. Deposition was carried out at a rate of 3 Å/sec for the organic layers.

In the second set of experiments, (ITO/OTL/NPB/ $Alq_3/CsF/Al$) devices were fabricated in which all the fabrication parameters were kept the same except for variation in the thickness of NPB, Alq_3 , and OTL; thus giving three sets of devices. These experiments were carried out in order to verify the nature of electric field distribution and the role of the OTL in device operation.

After fabrication, all the devices were transferred to a nitrogen glove box without exposure to oxygen or moisture for characterization and testing. Current density-voltage (J-V) characteristics were obtained on a Hewlett Packard 4155 semiconductor parameter analyzer and light output was measured by a calibrated Newport UV-818 photodetector. While measuring OLED external quantum efficiency, the absorption of light emitted in the Alq₃ layer by the OTL, before it exits the device has to be taken into consideration as increasing salt loading increases its absorption in the visible range. In order to achieve this, transmittance values were obtained for OTL films with the same thickness and salt loading as utilized in the devices. The actual light output of the device was obtained by using the transmittance as a correction factor for the light measured by the photodiode as each device was tested.

III. RESULTS AND DISCUSSION

A. Single layer OTL devices

The PC-TPB-DEG polymer consists of HTL type monomer units separated by saturated ether linkages. The addition of the TMTPD⁺ SbF₆⁻ salt to this polymer results in the formation of a charge transfer state with an absorption centered at around 1466 nm (spectrum not shown). Thus excess intrinsic charge carriers proportional to the salt loading are generated in the OTL. The result of this is a higher conductivity of the OTL with increasing salt concentration in the polymer.

The relationship between the conductivity of the OTL and the extent of salt loading has been studied by fabricating single layer devices of the OTL containing different salt concentrations sandwiched between ITO and Al contacts (ITO/ OTL/Al). Based on the large band offset between Al and OTL interface with respect to electron injection, along with the fact that these materials are primarily hole transporters,²² we can safely assume that the current being measured is hole dominated. For 5% and 10% salt loading, the current density-voltage (J-V) characteristics of these devices show the typical behavior of unipolar charge transport in an amorphous material with an initial Ohmic region followed by current turn on at around 1 V (Fig. 3). This turn on is followed by an initial higher slope J-V characteristic, which quickly saturates to a $J-V^2$ type behavior above an applied voltage of 2 V. For 2 V and above, the measured current at any applied field increases with increasing salt concentration. This result is in agreement with conductivity measurements carried out on the OTL (Ref. 28) indicating that the current

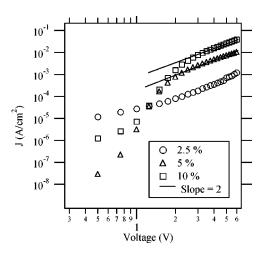


FIG. 3. J-V data plotted for single layer OTL devices with varying (TMTPD⁺SbF₆⁻) salt concentration in the OTL.

values can be tuned over two orders of magnitude while still maintaining the $J-V^2$ behavior. The reproducible, higher magnitude current observed for the 2.5% doped device below 2 V could be due to lesser trapping of holes in the presence of lower salt concentration or preferential confinement of salt to the ITO/OTL interface. However, since in the typical OLEDs the operating voltages extend beyond this Ohmic regime, to the first approximation it can be seen that salt loading in the OTL should control the hole-current passing through the device. This property of the OTL will now be considered within the device architecture of conventional Alq₃ OLEDs.

B. The effect of the OTL on Alq₃-based OLEDs

The comparison of the J-V characteristics of conventional bilayer Alq₃ devices and OTL modified Alq₃ devices in which the salt concentration in the OTL is varied is shown in Fig. 4. The schematic indicates the sequence of deposited layers on the ITO anode. All OTL modified devices show an initial Ohmic $J - V^{I}$ regime below 2 V followed by a power law behavior of $J - V^m$ with m varying between 7 and 10. At higher applied fields, the steep increase in current density is reduced with the value of m plateauing at m=2 above 6 V. behavior is contrast to the This in typical ITO/NPB/Alq₃/CsF/Al device made without the OTL as shown in Fig. 4, where the steeper power law behavior of $J-V^m$ ($m \ge 5$) persists for voltages above 6 V.²⁹ The light emission onset (data not shown) is at the same applied voltage at which the device turn on occurs, indicating that above ca. 2.5 V both holes and electrons are present at the recombination interface.

In addition to the appearance of the $J-V^2$ behavior at low voltage (~6 V), increasing the salt concentration in the OTL results in higher current levels for any given applied field after the turn on voltage. These observations can be explained on the basis of additional hole current in these devices due to the increased conductivity of the OTL as already shown in Fig. 3. However, consideration has to be given to the field distribution over the cross section of the device and barriers to charge injection at the device anode as

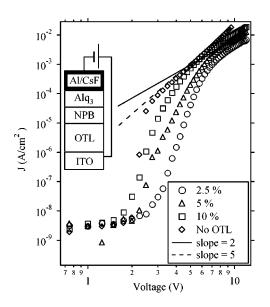


FIG. 4. J-V data plotted for multilayer OLED devices with varying (TMTPD⁺SbF₆⁻) salt concentration in the OTL. For comparison, the J-V characteristics for a typical bilayer device are also shown, along with lines drawn to guide the eye with respect to m=2 and 5 for $J-V^m$.

the salt concentration in the OTL is varied. In order to understand the contribution of these factors, we have varied the thickness and hence the applied field for the active layers (NPB, Alq₃, and OTL) and studied the trends observed in J-V characteristics. In all these devices, the salt concentration in the OTL was maintained at 5% by weight with respect to the polymer.

C. Variation of thickness of OLED layers

The results of the thickness variation of NPB and Alq₃ are shown in Figs. 5(a) and 5(b), respectively. These results agree with those reported for bilayer devices without any ITO modifying layers.²⁹ Increasing the thickness of NPB gives rise to a less pronounced decrease in current densities for any applied voltage as opposed to the case of Alq₃ thickness variation. Furthermore, the varying thickness of the NPB layer does not affect the current level at which the transition to the $J-V^2$ is observed. On the other hand, variation in Alq₃ thickness affects not only the voltage at which the $J - V^{7-10}$ to $J - V^2$ transition occurs but also the value of *m* in the power law regime $(J-V^{7-10})$. The thinner the Alq₃ layer, the steeper the J-V characteristics appeared in this regime. Direct³⁰ and indirect³¹ measurements of electric field distribution for bilayer Alq3 OLEDs indicate that the majority of the applied electric field drops across the Alq₃ layer. The results shown in Fig. 5 indicate that in spite of the presence of the thick OTL, still a considerable fraction of the applied field drops across the Alq₃ layer for these OLEDs.

With this realization, the OTL thickness was varied in order to deliberately alter the electric field applied across it. Any similarity between the trends observed in this experiment and those observed in Fig. 4 for varying salt concentration will indicate field variation and not conductivity as being the possible reason for the current modulation. As shown in Fig. 6, as the OTL thickness decreases, the J-V

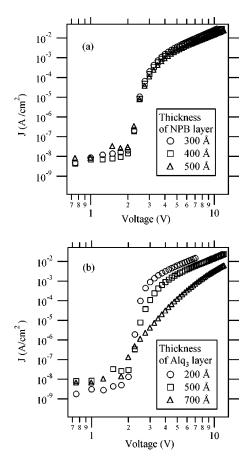


FIG. 5. J-V data plotted for devices (ITO/OTL (5000 Å)/NPB/Alq₃/CsF/Al) with varying thickness of (a) NPB and (b) Alq₃, while keeping the respective (Alq₃ and NPB) layer thickness constant at 500 Å. The OTL in all cases was loaded with 5% salt.

characteristics in the trap charge limited regime (TCL, $J-V^{7-10}$) approach that of the bilayer device (no OTL). This behavior also persists above the TCL regime where the $J-V^m$ characteristics approach the slope of m=5, shown for the bilayer device. As the OTL thickness increases, the slope decreases to a value of 2 shown for the 5000 Å thick OTL devices of Fig. 4. This indicates that the contribution of the OTL to the formation of the $J-V^2$ regime in the device is reduced and there is discernable field variation across the OTL as the thickness is varied from 5000 to 900 Å. However, the trend observed in this case is in contrast to the device characteristics shown in Fig. 4, where the $J-V^2$ behavior persists in spite of varying salt concentration.

In addition, on comparing the device modified with a 900 or 2000 Å thick film of OTL and the conventional bilayer device, it is observed that above the turn on voltage the former has an even higher magnitude of current within the range of applied field investigated in spite of the presence of the additional layer of OTL. This indicates that in OTL modified devices the barrier to hole injection at ITO is reduced as compared to the bilayer device. As was explained earlier in the schematic representation shown in Fig. 2, this is one of the requirements for improved OLED performance. The investigations of the injection of electrons into Alq₃ with LiF and CsF modified cathodes^{27,32} have proved that such modified cathodes have minimized electron injection barriers

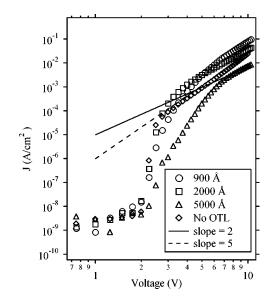


FIG. 6. J-V characteristics plotted for varying thickness of the OTL. Salt concentration in the OTL was kept constant at 5% by weight. For comparison, the J-V characteristics for a typical bilayer device are also shown, along with lines drawn to guide the eye with respect to m=2 and 5 for $J-V^m$.

with respect to the Alq₃ layer. Hence we can conclude that for the Alq₃ OLEDs whose anode and cathode have been modified with OTL and CsF, respectively, the interfacial barriers at the electrodes for hole and electron injection into the Alq₃ layer are minimized. Given this result, the modulation of the salt concentration in the OTL and hence its conductivity should be the governing factor in the variation of the J-V characteristics of the OTL modified Alq₃ devices.³³ Since the OTL primarily transports holes, it can be concluded that in Fig. 4, the variation in the J-V characteristics is due to variation in the number of holes being injected into the Alq₃ layer. Based on a certain capture cross section of holes for Alq3 (Ref. 29) at the NPB/Alq3 carrier recombination interface³⁴ such modulation of holes should control the extent of formation of excitons and cationic species of Alq₃ which is demonstrated by measuring the quantum efficiencies and lifetimes of these devices.

D. The effect of OTL on quantum efficiencies and lifetimes of OLEDs

The variation of external quantum efficiency (QE) plotted versus device current density is shown in Fig. 7 for different salt concentrations. The QE is seen to start from a comparatively lower value for the OLED with the lowest concentration of salt loading in the OTL (2.5%), rise to a maximum for the OLED with intermediate salt loading (5%), and fall again for the one with 10% loading of salt in the OTL. Based on the above discussion on the role played by the OTL, the initial increase in QE as the salt loading is increased can be explained on the basis of a higher concentration of hole injection into the Alq₃ layer as the conductivity of the OTL is raised, thus resulting in the formation of more excitons within Alq₃. Further increase in the salt loading, while improving hole injection into the Alq₃ layer,

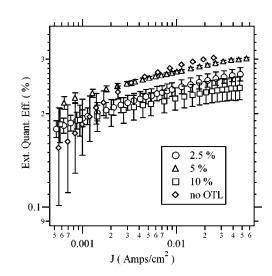


FIG. 7. Variation of OLED external quantum efficiencies (corrected for the OTL absorption) as a function of current density, for different salt concentrations in 5000 Å thick OTL. For comparison purpose, the external quantum efficiency for a typical bilayer device is also shown.

quickly surpasses the available electrons. Since the only barrier to keep excess holes within the recombination interface is the low hole mobility of Alq_3 ,³⁵ above a certain point these holes contribute to leakage current in the device, thus decreasing QE. Moreover, it has been argued by Young *et al.* that cationic species could also be responsible for fluorescence quenching in dye doped Alq_3 devices which are hole current dominated.³⁶

An added benefit of the OTL is reflected in the low variation of the slope in the QE versus J characteristics, attributed to the hole and electron balance within the Alq₃ layer over a wider range of current density. On the other hand, the bilayer device (without OTL) exhibits a much greater variation in quantum efficiency over the range of current density values displayed in Fig. 7. This large variation even results in a slightly higher QE compared to the optimized 5% salt-loaded OTL modified device at higher current densities. In this regime, unlike the OTL device, which controls the hole current, the bilayer device provides an excessive amount of holes. This, together with the field enhanced mobility of electrons, will result in greater radiative recombination and hence, higher QE. However, at these elevated fields a complete capture of holes is not guaranteed as further supported by the lifetime measurements described below. Thus, from the perspective of QE, the OTL devices display enhanced performance as opposed to the bilayer device only for moderate fields (ca. 6 V). At higher fields, QE is partially sacrificed in order to ensure efficient hole capture within the Alq₃ layer thus ensuring increased lifetime.

Based on the above argument, one might wonder why the 10% loaded OTL device has such a lower QE. In order to address this point, one has to account that by insertion of the OTL, all barriers to hole injection are substantially reduced [as contrasted in Figs. 2(a) and 2(b) as well as demonstrated in Fig. 6]. However, the bilayer device, lacking OTL, still has the ITO/NPB interfacial barrier to overcome. Thus, when voltage is increased in the bilayer device, this barrier provides some form of impediment to hole injection unlike that

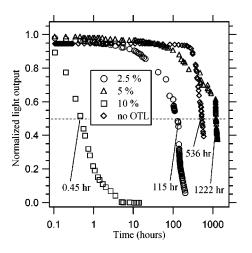


FIG. 8. Lifetimes of OTL modified OLEDs with varying salt concentration in the OTL. For comparison purpose, the lifetime for a typical bilayer device is also shown.

of the 10% OTL device, which has no hole interfacial impediments.

The devices fabricated with varying salt concentration in the OTL were tested for operational lifetimes at a fixed current density of 10 mA/cm². Figure 8 illustrates the normalized fall in light output for these devices. As mentioned before, the *relative* field variation across the OTL is minimal for varying salt concentration in these devices; however, the voltages applied to the devices vary due to the additional field required to pass the same current through the devices. It is important to note that in reporting the lifetimes of these devices, there are different degradation processes taking place. The abrupt and catastrophic failure of devices is due to cathode delamination and degradation and is superimposed over the more gradual oxidative degradation occurring in these devices. Migration of ions under forward bias within the OTL has been ruled out as there is no observable salt migration for single layer OTL devices when 10 mA/cm² was applied over extended periods. The 2.5% OTL device shows a half-life of 180 h and abrupt failure over the next 20-30 h. The 5% OTL device shows a higher lifetime by as much as an order of magnitude with a half-life exceeding 1000 h. The 10% OTL device on the other hand shows drastically reduced lifetime decay with a half-life of less than 1 h. The decay in this case occurs even before the degradation associated with cathode delamination.

The lifetime measurements clearly indicate the detrimental effect the presence of the cationic species has on the device performance when comparing the performance of the 5% and 10% doped OTL devices. The higher rate of hole injection into the Alq₃ layer for the 10% doped OTL device results in a rapid decay of the light output from the device. Based on the analysis of the quantum efficiency measurements, it seems that the 2.5% device should also show lifetimes similar to that of the 5% device. However, the voltage drop required to pass 10 mA/cm² in the 2.5% device is higher than the 5% or 10% doped OTL devices thus leading to considerable heating effects. The high efficiency of the 5% device and its longer lifetime imply a better balance in the multiplicity of parameters including minimal formation of cationic Alq_3^+ light quenching species^{13,36} and trap sites due to oxidative degradation of Alq_3 .¹⁴ Thus the OTL enables the optimization of device performance by tuning the relative transport of holes with respect to electrons in these devices.

E. Controlled hole injection by means of OTL

In any bipolar device the current measured is the sum of electron and hole currents. In both conventional bilayer device schemes and OTL modified devices based on Alq₃, the field is seen to drop mostly across the Alq₃ layer thus indicating that the bipolar charge transport through this layer plays a major role in determining the evolution of the J-Vcharacteristics with respect to the relative contribution of electrons and holes to the measured current. Compounding this fact is the variation of the hole and electron mobilities of Alq₃ with applied field and interfacial charge accumulation at the Alq₃/NPB interface. The electron mobility (1.4 $\times 10^{-6} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$) of Alq₃ is much higher than the hole mobility $(2.0 \times 10^{-8} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1})$ at low applied fields.³⁵ This relatively high electron mobility along with the CsFassisted reduced electron injection barrier into this layer ensures that the charge present in Alq₃ is dominated by the formation of an electron cloud, confined by the high lowest unoccupied molecular orbital of NPB. However, as the applied field increases, the field assisted mobility of Alq₃ causes the difference in electron and hole mobilities to reduce.³⁷ This, along with accumulated holes at the NPB/Alq₃ interface, results in enhanced hole current in the device.³⁸ Given the occurrence of oxidative degradation, fluorescence quenching, and a high value of m in the $J - V^m$ characteristics of conventional bipolar devices, such an enhanced hole current can prove detrimental to device performance. On the other hand, the introduction of a resistor in the form of the OTL at the hole injecting anode ensures the modulation of such charge buildup, thus preventing excessive hole injection due to field-enhanced hole mobility of Alq₃ which is bound to occur at higher applied voltages. The modulation of hole current by the OTL thus allows for improved device quantum efficiency and lifetimes by directly addressing the issue of hole modulation in Alq₃ based OLEDs at the expense of a slightly higher device operating voltage.

IV. CONCLUSION

The results presented above have demonstrated the importance of controlling the bipolar characteristics of devices utilizing Alq₃ as the emitting layer. Excess hole injection in Alq₃-based OLEDs leads to oxidative degradation within the Alq₃ layer and the formation of cationic species that quench electroluminescence of the devices. Both the improvement in hole injection and the modulation of hole concentration in the Alq₃ layer can be achieved by means of an OTL. The latter is achieved by finetuning the conductivity of the OTL by varying the concentration of salt in the same. These OTL modified Alq₃ OLEDs are devices whose properties are governed more by the conductivity of the active layers, rather than interfacial barriers. This leads to the occurrence of a $J-V^2$ type behavior in individual layers, resulting in bal-

anced bipolar charge transport in these devices over a range of operating voltages. This operational stability with respect to long-term chemical degradation is important in display applications where the requirement of gray scale implies that different pixels will undergo different operational conditions over their lifetimes.

ACKNOWLEDGMENTS

This work was supported by the Critical Technologies Program of Connecticut Innovations, Inc., Trans-Lux Corporation, and NSF CAREER Grant No. DMR-970220. The authors also gratefully acknowledge Kodak Corporation for kindly providing NPB as well as Dr. Nguyen Thuc-Quyen for helpful discussions.

- ¹C. W. Tang and S. A. VanSlyke, Appl. Phys. Lett. 51, 913 (1987).
- ²A. Tullo, *Chemical and Engineering News* (American Chemical Society, Washington, D.C., 2001), Vol. 79, pp. 49–54.
- ³J. McElvian, H. Antoniadis, M. R. Hueschen, J. N. Miller, D. M. Roitman, J. R. Sheats, and R. L. Moon, J. Appl. Phys. **80**, 6002 (1996).
- ⁴S. T. Lee, Z. Q. Gao, and L. S. Hung, Appl. Phys. Lett. **75**, 1404 (1999).
 ⁵M. Fujihira, L.-M. Do, A. Koike, and E.-M. Han, Appl. Phys. Lett. **68**, 1787 (1996).
- ⁶L. S. Liao, J. He, X. Zhou, M. Lu, Z. H. Xiong, Z. B. Deng, X. Y. Hou, and S. T. Lee, J. Appl. Phys. 88, 2386 (2000).
- ⁷H. Aziz, Z. Popovic, S. Xie, A.-M. Hor, N.-X. Hu, C. Tripp, and G. Xu, Appl. Phys. Lett. **72**, 756 (1998).
- ⁸ Y. Shirota, K. Okumoto, and H. Inada, Synth. Met. **111–112**, 387 (2000).
 ⁹ S. A. Van Slyke, C. H. Chen, and C. W. Tang, Appl. Phys. Lett. **69**, 2160
- (1996). ¹⁰L. F. Cheng, L. S. Liao, W. Y. Lai, X. H. Sun, N. B. Wong, C. S. Lee, and
- S. T. Lee, Chem. Phys. Lett. **319**, 418 (2000).
- ¹¹A. Bohler, S. Dirr, H. H. Johannes, D. Ammermann, and W. Kowalsky, Synth. Met. **91**, 95 (1997).
- ¹² P. E. Burrows, V. Bulovic, S. R. Forrest, L. S. Sapochak, D. M. McCarty, and M. E. Thompson, Appl. Phys. Lett. **65**, 2922 (1994).
- ¹³H. Aziz, Z. D. Popovic, N.-X. Hu, A.-M. Hor, and G. Xu, Science 283, 1900 (1999).
- ¹⁴F. Papadimitrakopoulos, X. M. Zhang, D. L. Thomsen III, and K. A. Higginson, Chem. Mater. 8, 1363 (1996).

- ¹⁵D. Y. Kondakov, J. R. Sandifer, C. W. Tang, and R. H. Young, J. Appl. Phys. **93**, 1108 (2003).
- ¹⁶C. Giebeler, H. Antoniadis, D. D. C. Bradley, and Y. Shirota, J. Appl. Phys. 85, 608 (1999).
- ¹⁷C. Adachi, K. Nagai, and N. Tamoto, Appl. Phys. Lett. 66, 2679 (1995).
- ¹⁸Z. D. Popovic, H. Aziz, C. P. Tripp, N.-X. Hu, A.-M. Hor, and G. Xu, Proc. SPIE **3476**, 68 (1998).
- ¹⁹H. Aziz and Z. D. Popovic, Appl. Phys. Lett. 80, 2180 (2002).
- ²⁰Z. Y. Xie, L. S. Hung, and S. T. Lee, Appl. Phys. Lett. 79, 1048 (2001).
- ²¹ Y. Hamada, T. Sano, K. Shibata, and K. Kuroki, Jpn. J. Appl. Phys., Part 2 34, L824 (1995).
- ²² A. Yamamori, C. Adachi, T. Koyama, and Y. Taniguchi, Appl. Phys. Lett. 72, 2147 (1998).
- ²³B. R. Hsieh, Xerox Corporation, 1998, US Patent 5,853,906.
- ²⁴ B. R. Hsieh, Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.) 43, 452 (2002).
- ²⁵ Y. Shen, K. Diest, M. H. Wong, B. R. Hsieh, D. H. Dunlap, and G. G. Malliaras, Phys. Rev. B 68, 081204(1) (2003).
- ²⁶C. Ganzorig and M. Fujihira, Appl. Phys. Lett. 77, 4211 (2000).
- ²⁷P. Piromreun, H. Oh, Y. Shen, G. G. Malliaras, J. Campbell, and P. J. Brock, Appl. Phys. Lett. **77**, 2403 (2000).
- ²⁸B. R. Hsieh, Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.) 43, 452 (2002).
- ²⁹ P. E. Burrows, Z. Shen, V. Bulovic, D. M. McCarty, S. R. Forrest, J. A. Cronin, and M. E. Thompson, J. Appl. Phys. **79**, 7991 (1996).
- ³⁰ M. Hiramoto, K. Koyama, K. Nakayama, and M. Yokoyama, Appl. Phys. Lett. **76**, 1336 (2000).
- ³¹F. Rohlfing and T. Yamada, J. Appl. Phys. 86, 4978 (1999).
- ³² M. Stößel, J. Staudigel, F. Steuber, J. Blässing, J. Simmerer, and A. Winnacker, Appl. Phys. Lett. **76**, 115 (2000).
- ³³G. G. Malliaras and J. C. Scott, J. Appl. Phys. 83, 5399 (1998).
- ³⁴C. W. Tang, S. A. VanSlyke, and C. H. Chen, J. Appl. Phys. 65, 3610 (1989).
- ³⁵R. G. Kepler, P. M. Beeson, S. J. Jacobs, R. A. Anderson, M. B. Sinclair, V. S. Valencia, and P. A. Cahill, Appl. Phys. Lett. 66, 3618 (1995).
- ³⁶R. H. Young, C. W. Tang, and A. P. Marchetti, Appl. Phys. Lett. 80, 874 (2002).
- ³⁷A. G. Muckl, S. Berleb, W. Brutting, and M. Schwoerer, Synth. Met. 111–112, 91 (2000).
- ³⁸S. Barth, P. Muller, H. Riel, P. F. Seidler, W. Riess, H. Vestweber, and H. Bassler, J. Appl. Phys. 89, 3711 (2001).