Chem. Mater. **2007,** *19,* 2079−2083

Similar Roles of Electrons and Holes in Luminescence Degradation of Organic Light-Emitting Devices

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Received November 2, 2006. Revised Manuscript Received December 22, 2006

Intrinsic degradation in organic light-emitting devices (OLEDs), the dominating cause of the short device lifetime, continues to be a critical issue for wider commercial application. For many years, intrinsic degradation in tris(8-hydroxyquinoline) aluminum (AlQ_3)-based OLEDs has been known to be caused by excessive hole injection into the AlQ_3 emissive layer, due largely to earlier observations that electrons and holes act differently in the devices. However, a further investigation here leads to the discovery that excessive electrons can also induce significant degradation of the AlQ_3 layer, similar to what has been established for holes. The new understanding of the degradation mechanism of OLEDs is instrumental in directing the efforts of developing stable devices.

Introduction

Although the operational stability of organic light-emitting devices (OLEDs) has realized significant improvements over the past decade, it continues to be insufficient for many commercial applications. Operational stability is generally governed by intrinsic degradation (or electrical aging) phenomena, which lead to a decrease in device luminescence efficiency during prolonged device operation.[1,2] A number of degradation models have been developed, aiming at a comprehensive description of intrinsic degradation mechanism. In these models,[2] the intrinsic degradation is generally attributed to the role of positive charges (holes) in decreasing the luminescence efficiency during device operation and explained in terms of the widely accepted unstable cationic AlQ_3 model,[3,4] or the immobile positive charge accumulation model.[5]

OLEDs as dual charge injection devices, however, require the simultaneous supply of both holes and electrons into the emitting layer. While the role of holes in device degradation has been investigated and identified, only little is known about the effect of electrons. Here we report further investigation that leads to the discovery that excessive electrons can also induce significant degradation of the AlQ_3 layer. It is found that electron-only current can induce photoluminescence (PL) degradation of AlQ_3, similar to what has been established for holes before.[2] The rate of degradation is found to be primarily determined by the density of charges (regardless of whether they are holes or electrons) in the vicinity of the HTL/AlQ_3 interface, where the higher the charge density, the faster the device degradation.

Methods

In this study, two groups of devices, with structures as shown in Figures 1a and b, were used for investigating AlQ_3 degradation. Devices with the structure in Figure 1a are electron-only devices (i.e., the flow of current proceeds predominantly by the transport of electrons), whereas devices with the structure in Figure 1b are hole-only devices (i.e., the flow of current proceeds predominantly by the transport of holes). In these devices, indium-tin-oxide (ITO) and Mg:Ag are used as an anode and a cathode, respectively. *N*,*N*′-Bis(naphthalen-1-yl)-*N*,*N*′-bis(phenyl)benzidine (NPB) and 4,4′-bis-[2-(4,6-diphenyl-1,3,5-triazinyl)]1-1,1-biphenyl (BTB)[4] are used as HTL and an electron transport layer (ETL), respectively. In devices with the structure in Figure 1a, the AlQ_3 layer and a buffer layer are sandwiched between two ETL layers, and the devices include a thin hole blocking layer (HBL), at the ITO anode contact, made out of Mg. Because of its lower work (work function of Mg and ITO is ∼3.6 and ∼4.8 eV, respectively), the Mg suppresses hole injection from the ITO anode, thus allowing the carrying out of the PL measurements under essentially electron-only currents. (Although no EL is observed in the presence of an HBL, weak EL from AlQ_3 is observed when the layer is missing, suggesting that a limited injection of holes from the anode can occur in the absence of the HBL.) The buffer layer is made of a mixture of NPB (hole transport material) and BTB (electron transport material) and is used to change the electron density at the buffer-layer/AlQ_3 layer interface by means of changing the NPB/BTB concentration ratio in the buffer layer. For instance, reducing the NPB/BTB concentration ratio in the buffer layer leads to a more facile electron transport across the layer (due to the higher concentration of the electron transport BTB in this case[4]), resulting in an easier transport of electrons from the AlQ_3 layer into the buffer layer and hence lowers electron density at the interface, and vice versa. In devices with the structure in Figure 1b, the AlQ_3 layer and a buffer layer are sandwiched between two HTLs, and the devices include an electron blocking layer (EBL) made of tetrafluorotetracyanoquinodimethane (F_4TCNQ)-doped NPB. Because F_4TCNQ acts as a p-type dopant in NPB,[6] including the EBL suppresses electron injection from the Mg:Ag cathode, thus allowing the carrying out of the PL measure-

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10.1021/cm062621i CCC: $37.00

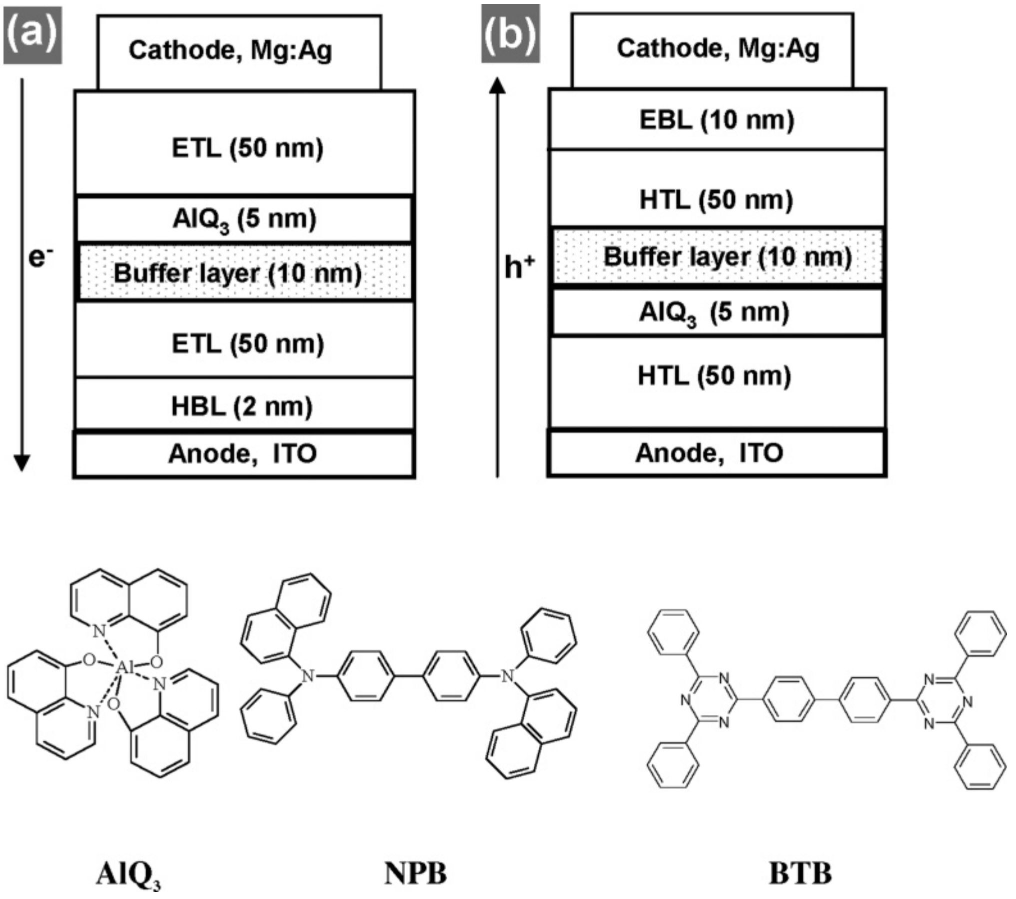

Figure 1. Schematic diagram of two device structures: (a) structure for electron-only devices and (b) structure for hole-only devices. Molecular structures of AlQ_3, NPB, and BTB used in this study.

ments under essentially hole-only currents. (Although no EL is observed in the presence of an EBL, weak EL from AlQ_3 is observed when the layer is missing, suggesting that a limited injection of electrons from the cathode can occur in the absence of the EBL.) The buffer layer is made of a mixture of NPB and BTB and is used to change the hole density at the buffer-layer/AlQ_3 layer interface by means of changing the NPB/BTB ratio in the buffer layer as explained above.

The devices were produced through the deposition of the organic materials and metals at a rate of 0.3−3 Å s^{-1} using thermal evaporation at vacuum base pressure of about 5×10^{-6} Torr on ITO-coated glass substrates (sheet resistance $\sim 15\ \Omega\ \square^{-1}$) precleaned using UV ozone cleaning. Other details of device fabrication are reported elsewhere.[4] Device aging of electron-only devices and hole-only devices is carried out under (dc) driving at a constant current density of 50 mA cm^{-2}, with the devices being continuously purged with pure N_2. PL is obtained using 430 nm excitation (where optical absorption by all other materials, aside from the AlQ_3, is negligible).[4] Integrated PL is collected every 6 min using a photomultiplier tube equipped with 500 nm long wavelength pass filter to eliminate the signal of the excitation beam. To avoid electric field induced exciton dissociation effects, the bias is automatically switched off during PL collection (50 s).

Results and Discussion

Electron-Induced PL Degradation. Figure 2a shows normalized PL (PL/initial PL) from the AlQ_3 layer versus aging time at a constant current density of 50 mA cm^{-2} for a group of electron-only devices (Figure 1a), with various NPB concentrations in the buffer layer. As shown, the device with 0% NPB in the buffer layer shows only very little PL degradation after 100 h of aging. This result is consistent with our earlier observation,[4] which led to the conclusion that electrons do not play a dominant role in inducing degradation in OLEDs.[3,4] However, on a closer look, one realizes that any formation of an electron space charge in the AlQ_3 layer of this particular device must be very low since AlQ_3 itself is a good electron transport material,[7] and the buffer layer with 0% NPB (i.e., 100% BTB) should not substantially block the transport of electrons.[4] As such, the entire device is formed of electron transport materials that streamline the transport of electrons and hence limit any buildup of an electron space charge across the AlQ_3 layer. In standard (i.e., bipolar) OLEDs, on the other hand, a significant electron space charge can be formed in the AlQ_3 layer near the HTL interface, which sometimes can even surpass the magnitude of the hole space charge.[8,9] As such, the device with 0% NPB in the buffer layer may not closely resemble a standard OLED.

Therefore, to investigate possible electron-induced PL degradation under conditions that more closely resemble

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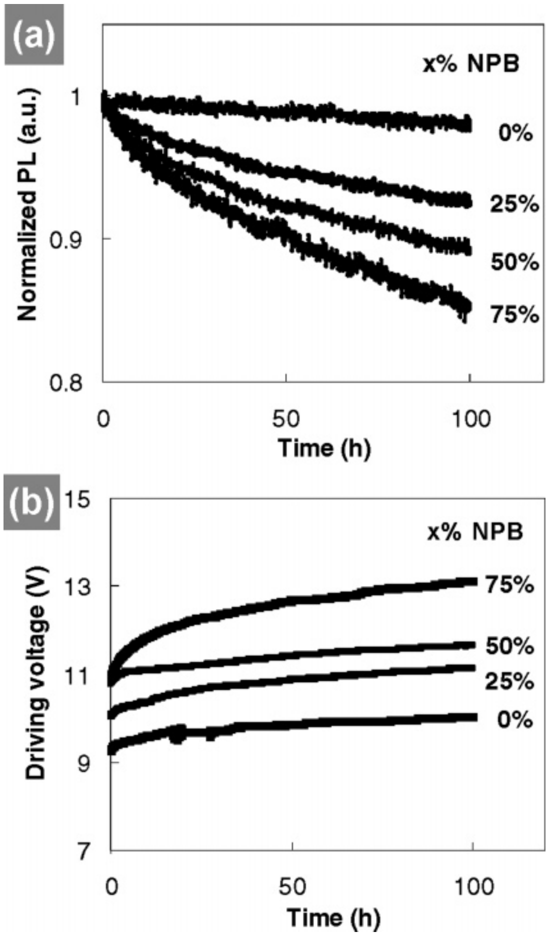

Figure 2. PL degradation of a group of electron-only devices (Figure 1a): (a) normalized PL of the AlQ_3 layer versus aging time and (b) driving voltage versus aging time of the same devices. The devices contain 0%, 25%, 50%, or 75% NPB in the buffer layer and were aged at the electron current density of 50 mA cm^{-2}.

those in a standard OLED, it is essential to increase the electron density in the AlQ_3 layer. This process is implemented by introducing various amounts of NPB in the buffer layer (25%, 50%, and 75%), thereby replacing the electron transport material, BTB, in the buffer layer with a lower electron mobility material.[10,11] As the results show (Figure 2a), the PL intensity decreases much more significantly after 100 h of aging in this case, and the magnitude of degradation increases with NPB/BTB concentration ratio. The increase in PL degradation upon increasing NPB/BTB concentration ratio can be plausibly attributed to an increase in the formation of an electron space charge in the AlQ_3 layer, perhaps in the vicinity of the AlQ_3 layer/buffer layer interface, as a result of the more difficult electron transport across the buffer layer. Such space charge formation is also evident from the increase in driving voltage observed upon increasing the NPB/BTB concentration ratio (Figure 2b).

In general, it is also possible that the PL degradation observed upon increasing NPB/BTB concentration ratio in the buffer layer is the result of chemical rather than electrical phenomena, such as chemical/electrochemical interactions between NPB and BTB, or between NPB in the buffer layer and the AlQ_3 layer, or interlayer diffusion processes. To investigate this possibility, another set of electron-only devices, similar in structure to those discussed above but with the exception that the locations of the AlQ_3 layer and the buffer layer are swapped, has also been studied. In this case, the devices still have the same "chemical" nature of the buffer-layer/AlQ_3 layer interface like in the first set of devices. However, increasing NPB/BTB concentration ratio in the buffer layer should not, in this case, lead to an increase in electron space charge in the AlQ_3 layer, as electrons reach the AlQ_3 layer after (and not before) crossing the buffer layer. The PL measurements results indeed show that increasing the NPB/BTB concentration ratio (from 0% to 75%) does not accelerate PL degradation in this case, where the decrease in PL of these devices after 100 h of aging remains below 3% (Figure 3). This observation convincingly proves that the faster PL degradation observed upon increasing the NPB/BTB concentration ratio in the buffer layer in the first set of devices is predominantly due to space charge effects rather than chemical phenomena.

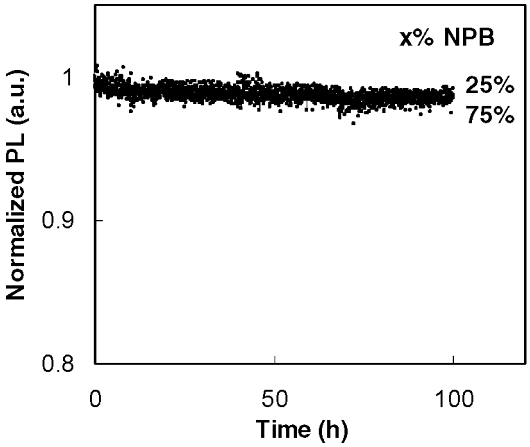

Figure 3. PL degradation of two electron-only devices (similar to structure in Figure 1a, but with the exception that the locations of the AlQ_3 layer and the buffer layer are swapped). The devices contain 0% or 75% NPB in the buffer layer and were aged at the electron current density of 50 mA cm^{-2}.

To check if the observed AlQ_3 PL degradation is reversible upon removing electrical bias, we remeasured PL intensity of the devices after 10 h of resting (i.e., no bias). Measurements show that the PL recovery is less than 2% of the initial intensity, indicating that the electron-induced PL degradation in AlQ_3 is primarily irreversible. Although the nature of PL degradation phenomena by electrons is still unknown, the irreversibility under resting conditions may suggest that some chemical change is involved. It is also possible that the residence of a high density of electrons on AlQ_3 induces the formation of deep electron traps, which in-turn lead to luminescence quenching.[12]

Hole-Induced PL Degradation. Figure 4a shows normalized PL (PL/initial PL) from the AlQ_3 layer versus aging time at a constant current density of 50 mA cm^{-2} for a group of hole-only devices (Figure 1b), with various NPB concentrations in the buffer layer. In general, PL intensity in all devices decreases with time by the flow of hole currents, in

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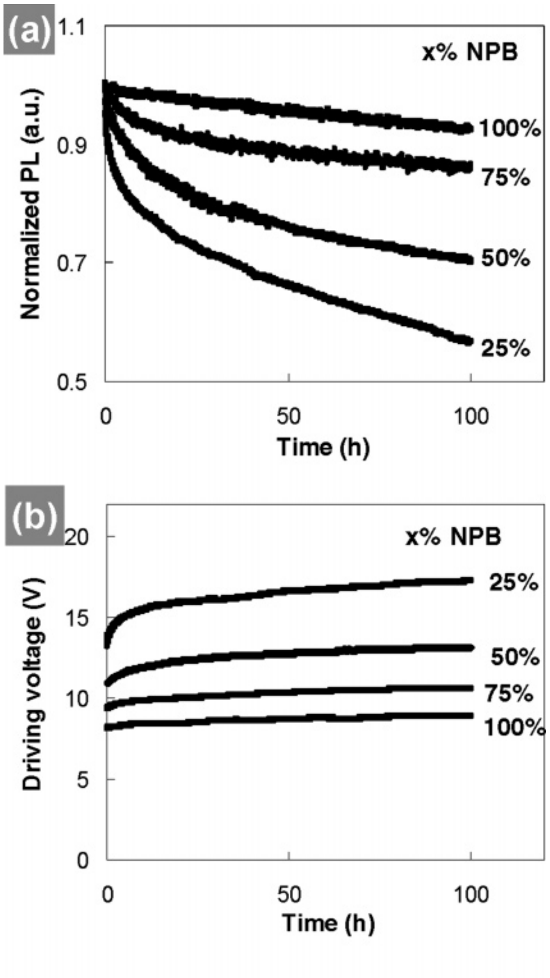

Figure 4. PL degradation of a group of hole-only devices (Figure 1b): (a) normalized PL of the AlQ_3 layer versus aging time and (b) driving voltage versus aging time of the same devices. The devices contain 25%, 50%, 75%, and 100% NPB in the buffer layer and were aged at the hole current density of 50 mA cm^{-2}.

agreement with earlier observations.[3] In this case, decreasing NPB/BTB concentration ratio in the buffer layer (thereby impeding hole transport across the layer) leads to faster PL degradation, where impeding hole transport across the layer in this case leads to the formation of a hole space charge in the AlQ_3 layer. Again, the increase in driving voltage (Figure 4b) observed upon decreasing NPB/BTB concentration ratio supports this conclusion. The PL degradation caused by the buildup of a hole space charge in the AlQ_3 layer can be attributed to the notion that cationic AlQ_3 species is unstable and that the degradation byproducts lead to luminescence quenching.[3,4] It can also be attributed to the possible creation of deep hole traps in AlQ_3 layer induced by the space charge buildup, which in-turn leads to luminescence quenching.[13] In general, the more significant PL degradation observed in Figure 4a (i.e., in the case of hole currents) in comparison to that in Figure 2a (i.e., in the case of electron currents) is perhaps due to the fact that AlQ_3 itself is an electron transport material with only very limited hole mobility (hole mobility in AlQ_3 is about 2×10^{-8} cm^2 V^{-1} s^{-1}, 2 orders of magnitude lower than its electron mobility[7,14]). As such, the AlQ_3 layer itself induces the formation of a positive space charge in the case of hole currents, apart from any additional contributions from the buffer layer.

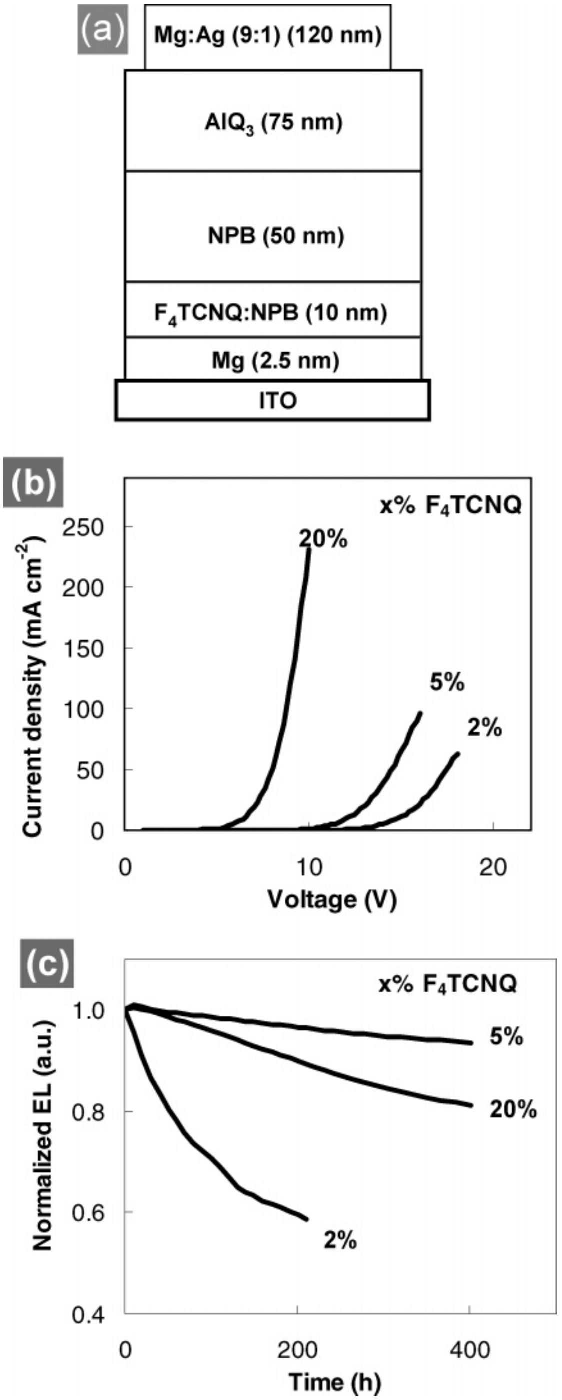

Figure 5. EL degradation of standard OLEDs. (a) schematic diagram illustrating the structure of a standard (i.e., bipolar) OLED containing a thin Mg anode buffer layer and an F_4TCNQ-doped hole injection layer (HIL) at the ITO contact, (b) J−V characteristics of the devices with F_4TCNQ concentration of 2%, 5%, or 20%; (c) normalized EL from the AlQ_3 layer versus aging time of the devices.

EL Degradation in Standard OLEDs. It has been known that the more facile injection and transport of holes (versus electrons) in AlQ_3-based OLEDs leads to the buildup of a hole space charge at the HTL/AlQ_3 interface and leads to EL degradation.[15,16] Finding that the accumulation of electrons leads, over time, to an irreversible decrease in the PL yield of AlQ_3 in electron-only devices (as discussed above),

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one naturally wonders if a similar phenomenon also plays a role in EL degradation in OLEDs. To address this question, we studied standard (i.e., bipolar) OLEDs containing a thin Mg anode buffer layer and an F_4TCNQ-doped hole injection layer (HIL) at the ITO contact (device structure shown in Figure 5a).[17] In these devices, the presence of Mg at the hole injection contact reduces hole injection,[18] whereas the presence of F_4TCNQ in the HIL enhances it.[6] As such, varying the concentration of F_4TCNQ in the HIL leads to a change in its counterbalancing effect and allows changing the hole injection efficiency of the contact, as explained elsewhere in more detail.[17] Figure 5b shows current−voltage, J−V, characteristics of such devices with 2%, 5%, and 20% F_4TCNQ in the HIL. As shown from the figure, increasing the F_4TCNQ concentration shifts the J−V characteristics to lower voltages, pointing to the increase in the hole injection efficiency. Figure 5c shows normalized EL (EL/initial EL) from the AlQ_3 layer versus aging time under ac driving at a current density of 62.5 mA cm^{-2} and 50% duty cycle of the same devices At these driving conditions, the initial luminance, L_o, is 228, 844, and 716 cd m^{-2} for devices with 2%, 5%, and 20% F_4TCNQ, respectively. The device containing 5% F_4TCNQ in the HIL demonstrates the highest operational stability, reflected in the smallest decrease in EL with time. On the other hand, higher and lower F_4TCNQ concentrations give lower stability. Since increasing F_4TCNQ concentration from 2% to 20% facilitates hole injection (from Figure 5b), the peak in stability observed with 5% F_4TCNQ suggests reaching some optimum hole injection conditions that result in more favorable electron/hole balance and lead to improved EL stability. The improved electron/hole balance with 5% F_4TCNQ is also evident from the higher EL efficiency observed at this concentration [gives highest L_o ($\sim$844 cd m^{-2}) at 62.5 mA cm^{-2} and 50% duty cycle]. Deviation from these optimum conditions results in the formation of a space charge near the recombination zone, and consequently increased EL degradation. It follows that the type of space charge (i.e., electron or hole) must change depending on whether the deviation from these optimum conditions leads to a decrease or increase in the hole injection efficiency. As such, the space charge must be negative at lower F_4TCNQ concentrations (i.e., $<5\%$) due to the more difficult hole injection, and positive at higher F_4TCNQ concentrations (i.e., $>5\%$) as a result of the more facile injection. The rapid EL degradation observed at lower F_4TCNQ concentrations, associated with the formation of an electron space charge, suggests that excessive electron accumulation can indeed be behind the EL degradation, similar to what has been established for holes before.[3] From these results it can be concluded that the rate of AlQ_3 EL degradation is primarily determined by the density of charges (regardless of whether they are holes or electrons) in the vicinity of the HTL/AlQ_3 interface, and that the higher the charge density, the faster the device degradation. This conclusion perhaps also explains the known higher AlQ_3 EL stability observed on using an emitting layer containing a mixture of AlQ_3 and a hole transport material.[19−21] Unlike in bilayer heterojunction devices, the relatively wider recombination zone in these mixed emitting layers prevents the confinement of the space charge to a narrow area, and therefore leads to a lower charge density.[21]

Conclusion

Intrinsic degradation in AlQ_3-based OLED has been known, for many years, to be caused by excessive hole injection into the AlQ_3 emissive layer. However, further investigation here leads to the discovery that excessive electrons can also induce significant degradation of the AlQ_3 layer, similar to what has been established for holes. The rate of degradation is found to be primarily determined by the density of charges (regardless of whether they are holes or electrons) in the vicinity of the HTL/AlQ_3 interface, where the higher the charge density, the faster the device degradation. It is noteworthy to mention that preliminary studies on 4-[dicyanomethylene]-2-*tert*-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4*H*-pyran, DCJTB red emitter[5] also give similar observations, suggesting that the phenomena may have a wider occurrence that extends to other organic electroluminescent materials.

Acknowledgment. One of the authors, Y.L., appreciates the financial support of the Natural Sciences and Engineering Research Council of Canada (NSERC).

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