Long-term Degradation Mechanism In Small Molecule Based OLEDs

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Abstract

Intrinsic degradation, which leads to the long-term decrease in the electroluminescence (EL) efficiency of the devices, has been a major limitation facing the new technology of organic light emitting devices (OLED). Recently we investigated degradation in OLEDs based on tris(8-hydroxyquinoline) aluminum (AlQ_3), a widely used electroluminescent small molecule. These studies showed that injection of holes in AlQ_3 is the main factor responsible for device degradation. Devices in which predominantly holes were transported through a 5 nm thick AlQ_3 layer showed a significant decrease in the photoluminescence (PL) efficiency upon prolonged current flow. In the present work we will also show that similar devices constructed in such a way to allow only electron flow through AlQ_3 did not show any decrease in PL efficiency under similar current driving conditions. This demonstrates that AlQ_3 cations are unstable and their degradation products lead to device degradation, while AlQ_3 anions are stable. Further studies of time resolved fluorescence show that the AlQ_3 degradation products are fluorescence quenchers, which cause decrease in device efficiency during prolonged operation. Comparison between fluorescence and electroluminescence decay of AlQ_3 shows that PL decay is consistently smaller than EL decay indicating that decrease of PL efficiency is not the only mechanism leading to EL degradation of AlQ_3.

Introduction

Poor device stability has been one of the major issues facing OLED technology[1-4]. In general, degradation in OLEDs occurs through the formation of non-emissive regions as well as through a long-term “intrinsic” decrease in the electroluminescence efficiency of the device[5]. The mechanisms giving rise to the non-emissive regions have been identified[5-8] and effectively controlled by encapsulation.[9] We recently found that intrinsic degradation in OLEDs based on tris(8-hydroxyquinoline) aluminum (AlQ_3), the most widely used organic small-molecule electroluminescent material, is primarily caused by the injection of holes and the subsequent formation of the unstable cationic AlQ_3 species.[10] Photoluminescence measurements have shown that the luminescence quantum efficiency of AlQ_3 decreased when predominantly hole currents were transported through it.

In the present paper we will address some additional questions regarding the proposed degradation mechanism based on instability of AlQ_3 cations. We will first present data, which show that electron injection into AlQ_3 leaves photoluminescence unchanged. Using time resolved fluorescence measurements we will then show that the degradation of AlQ_3 leads to formation of fluorescence quenchers. Finally we will present evidence that the decrease of electroluminescence is not only caused by decreased photoluminescence yield, but that AlQ_3 degradation products may also be acting as carrier traps further decreasing electroluminescence efficiency.

Experimental

In order to study details of device degradation mechanism, OLEDs of various configurations are fabricated and tested. In these experimental devices, *N,N'*–di(naphthalene-1-yl)-*N,N'*-diphenyl-benzidine (NPB) and tetraphenyl-triazine (TPT) are used as a hole transport material (HTM) and an electron transport material (ETM), respectively. The molecular structures of NPB and TPT are shown in Figure 1. In all devices, the organic layers are interposed between an indium-tin-oxide (ITO) anode and a Mg:Ag cathode. All layers are deposited by vacuum evaporation at $6x10^{-6}$ Torr on ultraviolet-ozone cleaned ITO-patterned glass substrates. The organic layers are deposited at a rate of 0.2 to 0.4 nm/s. Following the deposition of the organic layers, the 200 nm thick cathodes are fabricated by co-evaporation of Mg and Ag (deposited at 0.9 nm/s and 0.1 nm/s, respectively) without breaking the vacuum.

Device aging is carried under a constant current density of 50 mA/cm^2. Electroluminescence and photoluminescence spectra are measured using a Products for Research, Inc. 191933-93 cooled photomultiplier, Oriel Hg arc lamp excitation source, and two Instruments SA, Inc. monochromators (DH-10 for illumination and DH-20 for light detection). For photoluminescence degradation studies as a function of OLED stressing time, a pulsed Xenon lamp and an Instruments SA, Inc. H-20 monochromator is used to illuminate the device at 440 nm excitation light. Device photoluminescence, integrated over the pulse duration, is measured using a 550 nm long-pass optical filter to eliminate excitation radiation. Photoluminescence was measured in 30 min intervals while the device is temporarily shorted for about 30 sec to avoid luminescence quenching effects by the electric field.

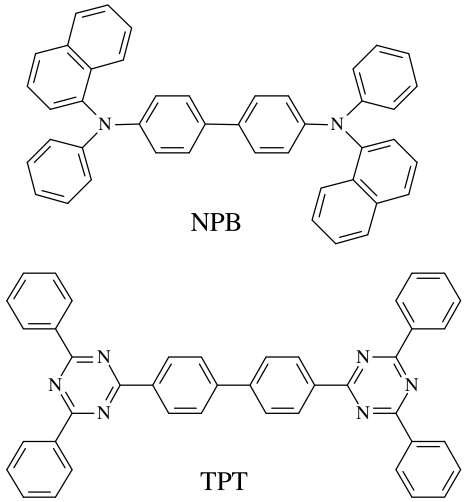

Figure 1. The molecular structures of the hole transport (NPB) and the electron transport (TPT) materials.

For time-resolved fluorescence measurements, light excitation is provided by a synchronously pumped, mode-locked dye laser system equipped with a cavity dumper. Excitation wavelength is 420 nm, using 5-ps pulses and a repetition frequency of 20 kHz. Fluorescence is detected by a SPEX 1681 monochromator equipped with a Hamamatsu 3809U microchannel plate photomultiplier tube. Photon count from the PM tube is processed by an EG&G ORTEC TAC system and accumulated in a PC equipped with a multichannel analyzer board and Edinburgh Instruments software package to control the measurements. Data is taken with a resolution of 6.68 ps per channel. All measurements as well as device aging are performed with the devices being continuously purged with dry N_2.

Results and Discussion

Our previous study indicated that intrinsic degradation of AlQ_3-based OLEDs occurs primarily in the AlQ_3 layer in the vicinity of the HTM/AlQ_3 interface.[10] We will now present data comparing photoluminescence changes when only holes or only electrons are transported though an AlQ_3 thin layer sandwiched between suitable hole transport (NPB) or electron transport (TPT) materials. The structures of the cells used in these studies are shown in Figs. 2a and 2b. Results of integrated photoluminescence measurements as a function of time, as the cells are aged at 50 mA/cm^2, are shown in Figs. 3a and 3b. Consistent with our previous measurements, which were based on recording the whole photoluminescence spectrum,[10] substantial reduction of integrated photoluminescence is observed in cells allowing only hole transport through AlQ_3 (Fig. 3a). In contrast, aging of cells (again at 50 mA/cm^2), which allowed only electron transport through AlQ_3 did not lead to any appreciable photoluminescence decrease (Fig. 3b).

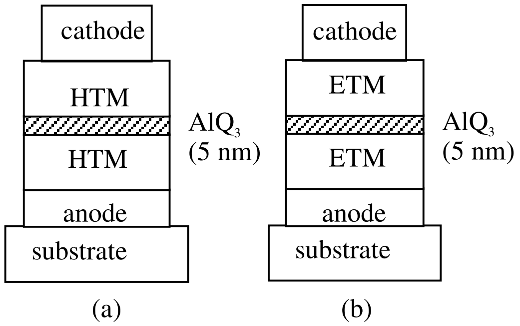

Figure 2. Schematic diagrams of (a) predominantly hole-current OLED structure, and (b) predominantly electron-current OLED structure.

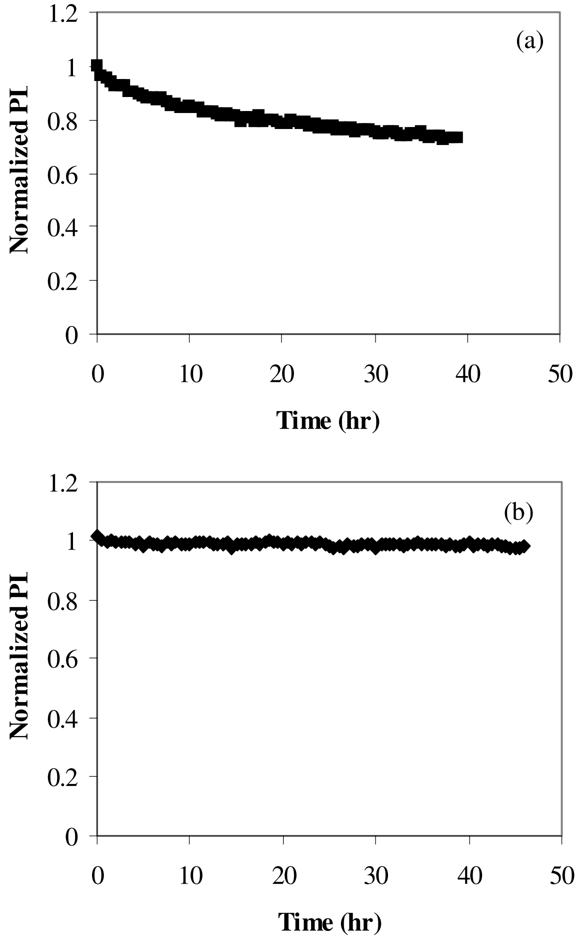

Figure 3. Normalized AlQ_3 photoluminescence (PL) intensity versus time for (a) OLED of structure as shown in figure 3a, and (b) OLED of structure as shown in figure 3b. Both OLEDs are stressed at 50 mA/cm^2.

The decrease in PL quantum efficiency of ALQ_3 resulting from the degradation of the unstable cationic species can, in principle, be attributed to two mechanisms. In the first mechanism, the degradation products act as fluorescence quenchers, in which case, only relatively few degraded AlQ_3 molecules are sufficient to effectively reduce the macroscopic quantum efficiency of the whole AlQ_3 population by quenching the luminescence of the surrounding molecules. In the second mechanism, on the other hand, the AlQ_3 degradation products do not act as fluorescence quenchers, but are, themselves, not luminescent, in which case, much larger numbers of degraded AlQ_3 molecules are required to achieve a similar decrease in PL. In order to explore the nature of the quantum efficiency loss mechanism, time-resolved fluorescence measurements are employed to measure the rate of decay of the AlQ_3 excited states in a device having the structure shown in Fig. 2a, before and after aging. The time-resolved fluorescence from ALQ_3 before device aging and after aging for about 40 hours at a current density of 50 mA/cm^2 are shown in Fig. 4. The fact that the fluorescence decay of AlQ_3 becomes faster upon device aging reveals that the decrease in photoluminescence is caused by the creation of fluorescence quenchers, therefore suggesting that the first mechanism is dominant. In fact, the increased rate of decay of the AlQ_3 excited states after aging for 40 hours is equivalent to a fluorescence quenching factor of 0.243 (calculated by integrating the time-resolved fluorescence decays and assuming that the initial luminescence amplitudes are the same before and after aging). This value almost coincides with a decrease in the photoluminescence intensity of about 25% (i.e. 0.25) in figure 3a, noting that the two measurements have been performed on the same device.

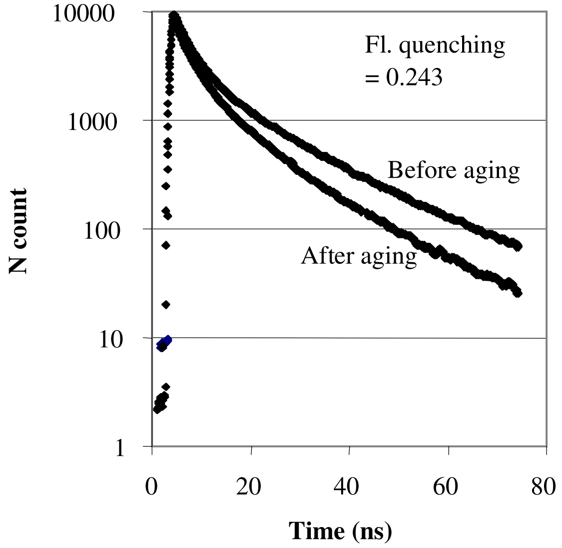

Figure 4. Time-resolved fluorescence of AlQ_3 layers in OLEDs of structure as shown in figure 2a, before aging and after aging for 40 hours at 50 mA/cm^2. Time evolution of integrated photoluminescence for the same sample is given in Fig. 3a.

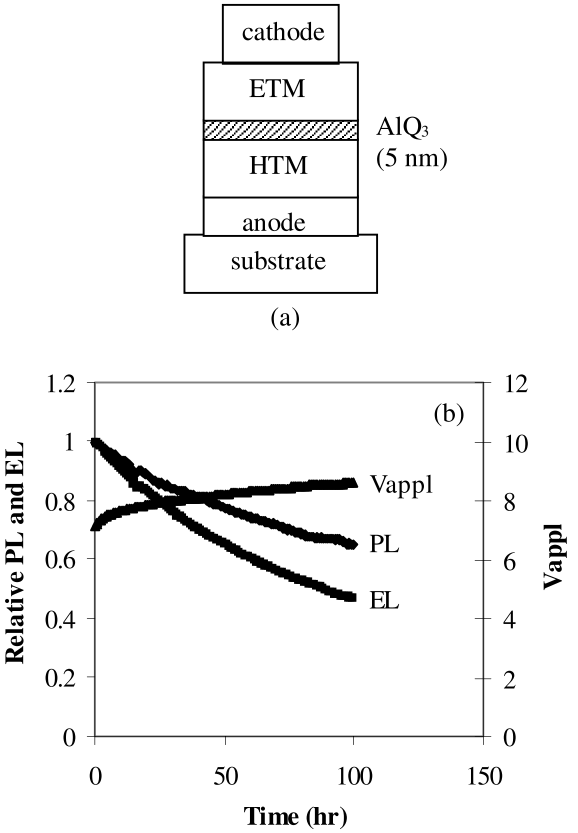

Figure 5. (a) Schematic diagram of the OLED structure used to compare photoluminescence (PL) and electroluminescence (EL) decay. (b) Normalized AlQ_3 photoluminescence (PL) and electroluminescence (EL) intensities versus time for the device operated at 50 mA/cm^2.

So far we demonstrated that luminescence quenchers are produced by degradation of AlQ_3 cations, but we cannot ascertain conclusively if introduction of photoluminescence quenchers is the only phenomenon leading to electroluminescence decrease upon device aging. To further investigate the origins of electroluminescence decrease, OLEDs containing a very thin layer of AlQ_3 (about 5 nm thick) interposed between relatively thick HTM and ETM layers (each about 40 nm thick) with structure as shown in figure 5a are fabricated and operated at a constant current. The electroluminescence emission spectrum of the devices closely resembles that of AlQ_3 thus showing that light emission comes primarily from the thin AlQ_3 layer. To detect changes in the AlQ_3 layers during device aging, the AlQ_3 photoluminescence (PL) intensity under 440 nm. excitation (where the absorption of both NPB and TPT is negligible) is also monitored. The use of only thin AlQ_3 layers is essential for increasing interface to bulk ratios of the produced PL, and hence for enabling the detection of changes in the PL of the AlQ_3 molecules in the vicinity of the interface. Figure 5b shows both EL and PL intensity as well as driving voltage *versus* time for a device operated at a constant current density of 50 mA/cm^2. As is always observed in OLEDs, the EL intensity decreases in time during device operation indicating a decrease in the EL quantum efficiency that reflects the intrinsic degradation behavior. Associated with the decrease in EL during device aging, a decrease in PL intensity of the AlQ_3 layer is observed, as revealed by the PL measurements. The decrease in PL intensity indicates a decrease in the PL quantum efficiency of the AlQ_3, thus revealing degradation in the AlQ_3 layer. It is important to point that no detectable decrease in EL or PL intensities has been observed over the same period of time in identical devices that have not been operated, thus showing that AlQ_3 degradation occurs only during device operation. Clearly, the decrease in device EL during operation is primarily attributed to AlQ_3 degradation and it has two components. The first is associated with decreased photoluminescence yield. The second one is attributed to an additional efficiency loss mechanism. One possibility for the second loss mechanism could be due to creation of charge traps, as a result of AlQ_3 degradation, which act as recombination centers. The creation of additional charge traps is also supported by the fact that during device aging at constant current, the operating voltage increases (Fig. 5) indicating an increase in the amount of trapped charge. Another possibility is that creation of new traps leads to redistribution and increase of the electric field inside the AlQ_3, thus leading to electric field induced fluorescence quenching of the excited states.[11] Of course both mechanisms could be operating simultaneously to varying degrees.

Conclusion

In conclusion, intrinsic degradation in ALQ_3-based OLEDs is found to be primarily caused by the degradation of AlQ_3 molecules in the vicinity of the HTM/AlQ_3 interface as a result of the injection of holes and the formation of the unstable cationic AlQ_3 species. From time-resolved fluorescence measurements, the degradation productions of the unstable cationic species are found to act as fluorescence quenchers which lead to a decrease in the quantum efficiency of AlQ_3 , and therefore to a decrease in OLED efficiency during operation. In simultaneous measurements of electroluminescence and photoluminescence degradation, it is observed that electroluminescence decreases faster than photoluminescence. This suggests that AlQ_3 degradation products act also as charge traps, which further decrease the EL efficiency of the device.

Acknowledgements

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Biography

Zoran Popovic received his Ph.D. degree in Materials Science from McMaster University, Hamilton, Ontario, Canada in 1974. In the same year he joined Xerox Research Centre of Canada where he presently holds a position of Research Fellow. Dr. Popovic's main research interests are in photoelectronic properties of organic materials, particularly as they relate to xerographic technology and organic electroluminescent devices. He is a member of the IS&T and the American Physical Society. e-mail: zoran.popovic@crt.xerox.com