

## Environmental Stability Of Aluminum Tris(8-Hydroxyquinoline) ( $Alq_3$ ) and Its Implications in Light Emitting Devices

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### Abstract

The thermal stability of the aluminum tris(8-hydroxyquinoline) ( $Alq_3$ ) is currently discussed, in light of its vital role in failure mechanisms of molecular-based light emitting diodes (LEDs). This was investigated with the use of gas chromatography/mass spectroscopy (GC/MS), assisted by a specialized accessory that permits heating of powders or thin films of  $Alq_3$  under a controlled environment. We have shown that at elevated temperatures,  $Alq_3$  undergoes a ligand exchange reaction with water, which readily adsorbs on its surface. The increased sensitivity of GC/MS in detecting the liberated 8-hydroxyquinoline (8-Hq) indicates that  $Alq_3$  is extremely sensitive to the moisture above 90 °C. The surface of a freshly sublimed  $Alq_3$  powder or film becomes saturated with water in less than 2 minutes, under normal laboratory conditions. The implications of the underlying chemistry are discussed in relation to failure mechanisms observed in  $Alq_3$  based LEDs.

Keywords: Aluminum tris(8-hydroxyquinoline) ( $Alq_3$ ), light emitting diodes, GC/MS, failure mechanisms.

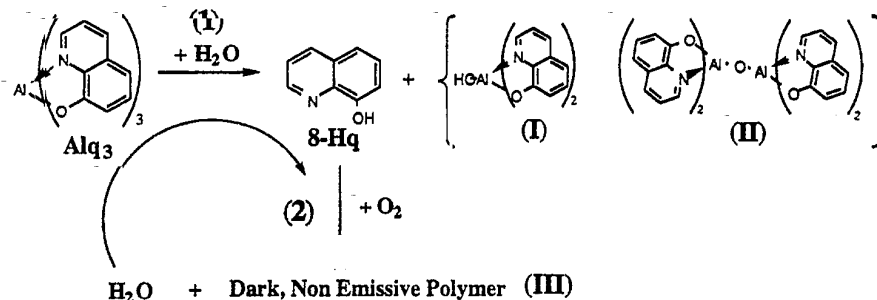
### 1. Introduction

Aluminum tris(8-hydroxyquinoline) ( $Alq_3$ ) has shown to be one of the most promising material for the fabrication of organic light emitting diodes (LEDs). These devices are presently under intense investigation as the next generation of the high brilliance, cost-effective, flexible displays and illuminators[1,2]. Even though substantial progress has been made towards performance enhancement, color tuning and light-outcoupling[3-6], device lifetime issues impede widespread commercialization of this technology[6-10]. Accelerated failure of these devices at elevated temperatures was attributed to degradation of materials and electrode/organic interfaces[10], together with morphological changes (crystallization) of the organic layers[7,9,11].

Our laboratory has recently published a chemical degradation mechanism for  $Alq_3$  (see Scheme A) where the

presence of moisture and oxygen was found detrimental to the production of luminescence quenching byproducts[12,13]. This was attributed to a condensation polymerization of the freed 8-hydroxyquinoline (8-Hq), to form a dark, non-emissive residue, whose structure has not yet been fully determined[13]. This mechanism is in agreement with the recent ultrafast luminescence lifetime results of Sokolik *et al.*[14].

Attempting to detect the degradation reactions and byproducts in the actual device geometry (of thickness in the order of 600-1200 Å), has proven a formidable task[15,16]. In addition, realizing that impurities generated only at the recombination interface (c.a. 10-50 Å) could have a catastrophic effect on the device performance, sensitivity issues and detection limits quickly discriminate most analytical techniques. Based on the above limitations, mass spectroscopy has proven a crucial technique for the analysis of



Scheme A. (1) Transcomplexation of 8-Hq with water and (2) oxidative polymerization of 8-Hq.

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device structure and materials interdiffusion at atomic concentration up to  $10^{-6}$  % [17]. The present paper describes the use of gas chromatography/mass spectroscopy (GC/MS) to investigate the reaction (1) in Scheme A. Quantitative information regarding the extent of this reaction was obtained by observing the release of 8-hydroxyquinoline (8-Hq). The volatile nature of 8-Hq has sparked a number of additional observations into the failure mechanism of  $Alq_3$  based LEDs, as discussed at the following section.

## 2. Results and discussions

Revealing the chemical reactions that could take place within an organic-based LED and ultimately connecting them to a particular failure mode is generally limited by detection limits of analytical instruments. Chemical degradations that involve small molecules such as water and oxygen have long been suspected. For example, poly(phenylenevinylene) based LEDs are prone to oxidation [18], while ZnS based thin-film electroluminescence (EL) devices are extremely susceptible to electrolytic degradation by water [19]. The amorphous portions of the semicrystalline films used in organic EL contributes substantially to the amenability of these small molecules to interdiffuse and have adequate space and mobility to cause side reactions, catalyzed by either local heat, or electronic excitations (excitons, polarons, bipolarons, etc.). Intrinsic decay of dyes and side reaction between dyes that could take place, for example, at the *p-n* junction is another possibility that also needs to be investigated.

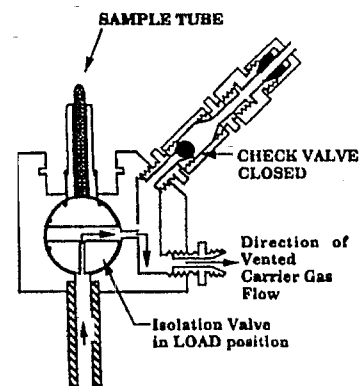
The decomplexation of  $Alq_3$  in the presence of water (Scheme A(1)) and/or weak acids have been observed with the help of chemical (NMR, IR, etc.) and electrochemical methods [13,20]. On the other hand, the reaction environment within the device is markedly different since it involves gaseous water within the semicrystalline layer of  $Alq_3$ . The amount of water present depends on the purity of the sublimed  $Alq_3$  powder as well as the level of atmospheric exposure. Based on the purity of  $Alq_3$ , the water contamination upon deposition is expected to be minimal since the material used in this study was successively zone-sublimed twice and the deposition pressures were below  $10^{-6}$  torr. On the other hand, when exposed to air, the freshly sublimed  $Alq_3$  powders and films were subjected to water contamination. In this paper we will try to elucidate the interaction between water and  $Alq_3$ , in light of subsequent reactions that could lead to device failure. For this purpose, we have used a Direct Dynamic Headspace Injector (DDHI), a specialized accessory for gas chromatography/mass spectroscopy (GC/MS), discussed below.

### a) Direct Dynamic Headspace Injector (DDHI)

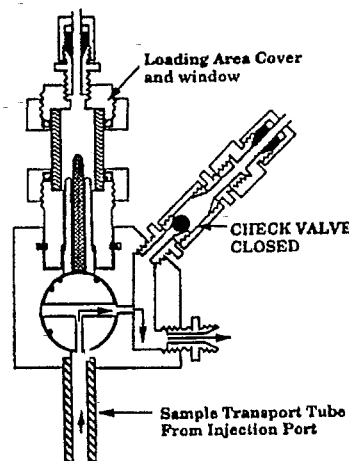
The direct dynamic headspace gas-chromatograph injecting head was originally designed and built by Ezrin and Lavigne at the University of Connecticut, in order to quantitatively analyze the chemical decomposition components derived from solid plastics at elevated temperatures [21]. Coupling the DDHI equipped gas-chromatograph (GC) with a mass-spectrometer (MS), dramatically improved its sensitivity towards the analysis of the volatile materials formed by subjecting non-volatile solid

materials to elevated temperatures. The schematic drawing and operation of the DDHI head is shown in Figure 1.

### Direct Dynamic Headspace Accessory LOAD Position



Step #1 Load Sample Tube into DDHI A



Step #2 Secure Sample Loading Area

Fig. 1. Schematic Diagram of the Direct Dynamic Headspace Injector (DDHI) and its two step operation.

The DDHI unit is placed directly in the heated injection port of the GC. The sample (powder or evaporated films (c.a. 1000 Å on aluminum foil) which was placed in small glass tubes (ca. 1" x 1/8" OD) and was held in place by glass wool) is delivered automatically into a preset temperature heated zone of the injected port of the GC and is removed at the end of the desired heating period. The volatile components of the sample generated in the heated injection port were directly transferred into the gas chromatography column preset between 35 and 40 °C. The sample tube can be subsequently returned back to the injection port for another analysis without exposure to air, since the time for lowering the sample tube into the injection port, heating cycle and its removal are all controlled separately and automatically. During the entire course of the measurement, the sample remains under high purity helium.

### b) Generation of 8-Hq at elevated temperatures

Freshly sublimed  $Alq_3$  powders or thin films were placed into the DDHI accessory of a GC/MS spectrometer and heated at various temperatures. Surprisingly enough, significant amounts of 8-Hq were detected only when the temperature of the injected port was set above 90 °C. Performing the same experiment at temperatures up to 250 °C (where from thermogravimetric analysis (TGA),  $Alq_3$  was found to be extremely stable), we observed only 8-Hq (see Figure 2), whose signal increases with increasing the injection temperature.

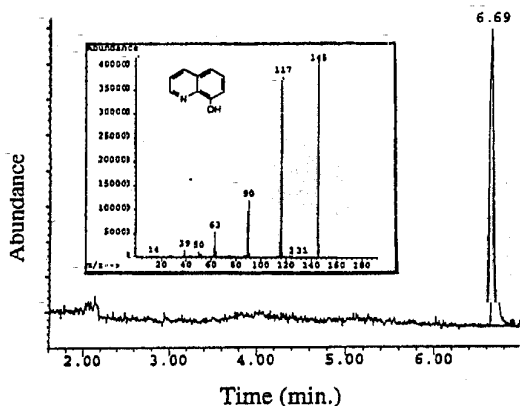


Fig. 2. Gas Chromatograph trace of the detected 8-Hydroxyquinoline (8-Hq) as a result of reaction (1) in Scheme A at 120 °C. Inset the MS spectra of the detected peak at 6.69 min. (8-Hq).

The above suggests that the volatility of  $Alq_3$  and reaction byproducts I and II is minimal up to 250 °C at the elevated pressure that the GC operates. Below 90 °C, the 8-Hq signal diminishes below detection, suggesting an activation based process, that is currently under investigation. Moisture levels were found to play a crucial role in the generation of 8-Hq. The peak area (or amount) of the 8-Hq formed, dramatically decreased as the sample tube was repeatedly injected without exposure to air (of about 40% humidity), as shown in Figure 3. Interestingly enough, the peak area of 8-Hq regained its original value after the  $Alq_3$  sample tube was exposed to air for 5 minutes and reinjected. The similar trend observed in the decay of 8-Hq signal as the sample tube was repeatedly reinjected without opening to the air indicates that the duration of injection (2 minutes) is smaller than that required to entirely consume the reagent in minority ( $H_2O$ ).

Based on the inert and continuously purged atmosphere of the DDHI accessory, we can firmly eliminate the possibility that the atmosphere during injection contained moisture. Therefore, the water that caused this decomplexation (Scheme A(1)) originated from moisture adsorbed on the  $Alq_3$  surface. It will be of interest to determine the time necessary to saturate the surface of the  $Alq_3$  solid with water from air (40% humidity). For that, we increased the injection duration to 4 minutes and the  $Alq_3$ -containing sample tube was reinjected after exposure in air for different time intervals. Figure 4 indicates that the amount of freed 8-Hq saturates in less than 2 minutes for 4 minute injection duration. This rapid adsorption

of moisture on the fresh surface of  $Alq_3$  indicates that considerable care must be exerted to avoid water contamination to the finished devices.

The fact that no significant formation of 8-Hq at temperatures below 90 °C was observed might provide a hint

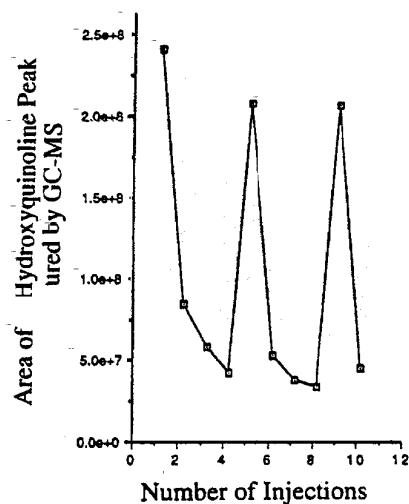


Fig. 3. Variation in evolution of 8-Hq from  $Alq_3$  as a function of adsorbed moisture. At injections 1, 5 and 9 the sample was exposed to air for 5 min. prior been heated to 180 °C and at injections 2-4, 6-8 and 10 the sample was reheated to 180 °C without exposure to air.

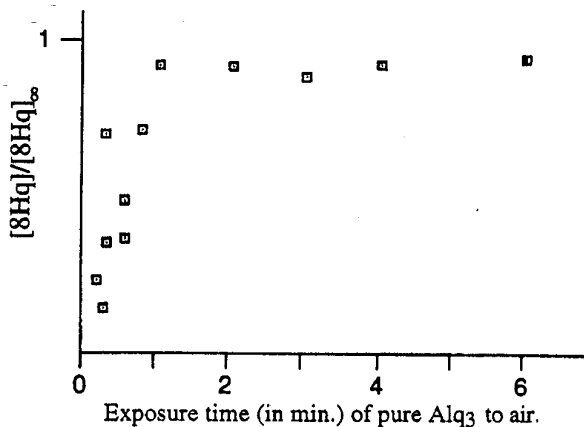


Fig. 4. Variation in evolution of 8-Hq from  $Alq_3$  (180 °C) as a function of the time it was exposed to air.

to the accelerated failure of  $Alq_3$  devices at elevated temperatures (above 80-100 °C). At the end of all GC/MS tests, the samples continue to photoluminescence the bright greenish-yellow light upon exposure to UV excitation. Although the sample form and geometry hinder quantitative comparison in relative photoluminescence (PL) intensity, PL quenching by formation of byproducts such as III (Scheme A(2)) has not been observed[13]. This is attributed to the

efficient removal of the volatile 8-Hq, as well as to the inert atmosphere (lack of O<sub>2</sub>). On the other hand, in a LED configuration the diffusion of 8-Hq would be blocked by the sandwich electrodes. To make matters worse, the apparent diffusivity of 8-Hq would be markedly lower relative to that of H<sub>2</sub>O and O<sub>2</sub>.

Generation of 8-Hq within a LED device could provide valuable insight into the explanation of the observed failure mechanisms. The frequently witnessed formation of black spots in either operational or dormant mode have been attributed to electrode delamination[22]. The volatile 8-Hq could explain the pressure built-up to obtain such action. Usually at the center of the delaminating areas a dark non PL emitting discoloration can be witnessed[22]. This could be explained by the reaction (2) in Scheme A. The slow and more gradual decay of Alq<sub>3</sub> based LEDs could also be originated by oxidative oligomerization of 8-Hq. Clearly, the broad array of chemical reactions that 8-Hq can undergo following its release within the LED structure could yield a variety of byproducts responsible for the decay of this class of devices. Encapsulation techniques (protection from H<sub>2</sub>O and O<sub>2</sub>) and operation at moderate low voltages and currents (low heating) have shown to slow down degradation, especially due to black spot formation[22]. The above observations coincide well with the discussed model, necessitating further investigation in this direction.

### 3. Conclusions

The present paper demonstrates the sensitivity of Alq<sub>3</sub> to hydrolytic decomplexation at elevated temperatures. With the help of the extremely sensitive GC/MS analysis, we were able to determine that significant generation of 8-Hq occurs above 90 °C. On the other hand, the fresh surface of Alq<sub>3</sub> (powder or films) would be saturated with moisture from air in less than 2 minutes. The volatile nature of 8-Hq along with its relative ease in forming oxidation byproducts could be related to device failures.

### 4. Experimental Section

A Hewlett/Packard 5985 GC/MS equipped with the direct dynamic headspace injector was used with capillary column. The column used is OV-1 fused silica capillary column 0.32 mm X 50 m, 1.2 μm in size. Injection port temperature was set as required to evolve volatiles completely using the direct dynamic headspace injector, (typically at 150-250 °C): Samples heating time in the injection port was set 2 minutes. Column oven temperature was raised from 35 to 300 °C. The chromatography was carried out by temperature programming at 15 °C/min. rate, rising up to the top temperature. The mass spectroscopy had a range of 10 to 1000 atomic mass units. Electron impact ionization was used at 70 electron volts and the scanning rate was 400 atomic mass units per second.

Alq<sub>3</sub> was synthesized according to the literature method and purified by double zone-sublimation[13].

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