A Chemical Failure Mechanism for Aluminum(III) 8-Hydroxyquinoline Light-Emitting Devices

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Introduction
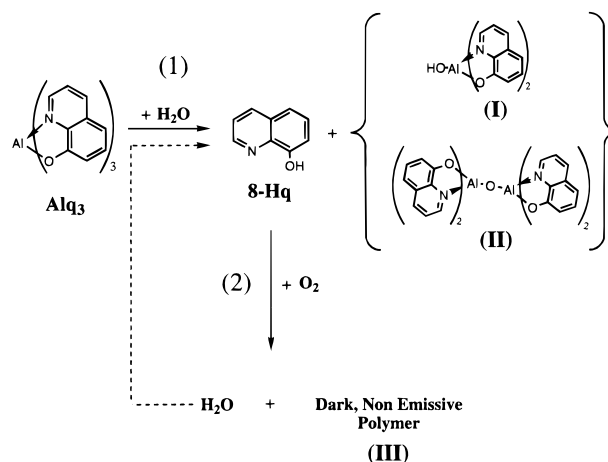
Aluminum(III) 8-hydroxyquinoline (Alq_3)-based light-emitting diodes (LEDs) have exhibited a great potential toward the development of large-area LED illuminators and electroluminescent (EL) displays.[1,2] Recent advances, such as enhancement of EL efficiency and color tuning through molecular doping,[1,3,4] white light emission,[2,5] and microcavity-assisted color tuning and collimation[6] have increased the range of applications. At present, one of the issues impeding this technology is the accelerated failure of these devices at elevated temperatures. This may be due to undesired side reactions with trace amounts of impurities, or degradation at the electrode/organic interface.[7,8]

Limited understanding of the environmental and photochemical stability of Alq_3 is currently available,[8−10] but no satisfactory explanations of the failure mode of the devices have been presented to date. The present communication proposes a chemical mechanism involving replacement of the oxyquinoline moieties in the Alq_3 complex with water. The freed 8-hydroxyquinoline (8-Hq) then undergoes an oxidative condensation to yield a nonemissive polymeric byproduct and water (which in turn stimulates further generation of 8-Hq). Electrochemical and spectroscopic methods were used to determine relative energy levels of key compounds in order to elucidate the nature of luminescence quenching.

Results and Discussion

The initial observation which triggered this investigation was made during the synthesis of Alq_3. When oxygen was not thoroughly excluded from the reaction mixture of $AlCl_3$ and 8-hydroxyquinoline (8-Hq) in base,[11] a brown color formation could easily be discerned. This color originates from oxidation of 8-Hq and is accelerated under basic conditions. In fact, a darken-

Scheme 1. (1) Trans-Complexation of 8-Hq with Water in the Alq_3 Complex and (2) Oxidative Polymerization of 8-Hq

ing of the 8-Hq crystals was witnessed in the unpurified reagent. Further investigation indicated that the color formation is due to an oxidative condensation of 8-Hq, discussed below.

The condensation of 8-Hq in the presence of oxygen was observed in a variety of solvents, as well as in the solid phase. This reaction was greatly accelerated at elevated temperatures (above 150 °C) and pressures and in basic media. The deep brown product formed under these conditions was partially soluble in chloroform and readily soluble in DMF. The chloroform-soluble portion was purified by silica-gel flash-chromatography (with hexane as the eluant) to remove residual 8-Hq monomer and short oligomers. The remaining product was then washed out of the silica gel with chloroform, concentrated, and vacuum dried overnight at 150 °C. Preliminary evidence from Karl Fischer titration showed that water was liberated during this condensation reaction of 8-Hq. When this experiment was repeated in the complete absence of oxygen (carefully removed by performing several freeze−pump−thaw cycles), no darkening (indicative of polymer formation) was observed after 1 week of heating at 200 °C.

A deep brown polymer was also produced by subjecting twice-sublimed Alq_3 to a similar treatment as 8-Hq, where trace amounts of water and/or acid were present in the solvent. Heating the solutions of Alq_3 in dried dichlorobenzene showed dark color formation after a noticeable induction period. When the same experiment was conducted using chloroform as the solvent (known to generate traces of HCl during decomposition at high temperatures or with light), the induction period for the color formation was significantly reduced. This is initiated by the liberation of 8-Hq ligands according to the well-documented instability of Alq_3 in acidic media.[12]

The above experiments have led us to suggest Scheme 1 as a probable mechanism for the failure of Alq_3-based LEDs. The two crucial features of this scheme are (1) the formation of 8-Hq in the presence of water and (2) its oxygen-facilitated condensation to yield a deep brown, nonemissive polymer **III**. Two possible byproducts are illustrated in Scheme 1(1). The analogous compounds from 2-methyl-8-hydroxyquinoline are known

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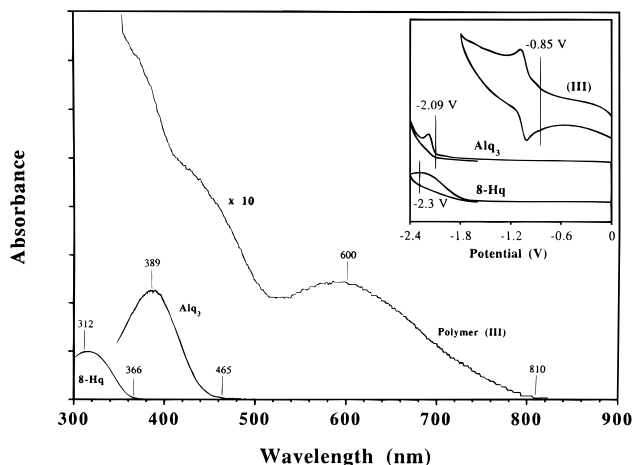(7) Abe, Y.; Onisawa, K.; Aratani, S.; Hanazono, M. *J. Electrochem. Soc.* **1992,** *193,* 641.
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Figure 1. Absorption spectra for 8-Hq, Alq$_3$, and **III** in 10^{-6} M CHCl$_3$ solutions. Inset illustrates the voltammograms and reduction potentials of these compounds in DMF solution.

to be stable.[13,14] Throughout this process, water acts as a catalyst which at first hydrolyzes Alq$_3$, decomplexing 8-Hq, and is then regenerated by the oxidative condensation of 8-Hq. This cycle is sustained so long as oxygen is available.

Figure 1 illustrates the absorption spectra (for 10^{-6} M solutions) of 8-Hq, Alq$_3$, and **III**. The considerable red shifted absorption of **III** relative to Alq$_3$ and 8-Hq is reminiscent of polyaromatic systems. On the other hand, the weak onset of absorption at 810 nm (note the $\times$10 magnification for **III**), along with the 600 nm peak not being the strongest absorption, disfavor an extensively conjugated system. This absorption could be associated with an n $\rightarrow$ π^* transition (typical of quinones and N-oxides) or the presence of a dopant/impurity with a midgap absorption.[15]

The inset of Figure 1 illustrates the reduction potentials of 8-Hq, Alq$_3$, and **III** as determined by cyclic voltammetry relative to the Ag/Ag$^+$ reference electrode. These reduction potentials and absorption edges are listed along with the oxidation potentials in Table 1 and are shown schematically in Figure 2. The HOMO/LUMO separation as calculated by both electrochemistry and absorption onset are in good agreement considering the irreversibility of most redox steps for Alq$_3$ and 8-Hq.

Figure 3 shows the photoluminescence (PL) quenching characteristics of solid mixtures of Alq$_3$ and **III**. Considerable PL quenching occurs at concentrations as low as 0.125%. This can be explained by a direct energy transfer or reabsorption from the excited Alq$_3$ to the nonemissive **III**, as shown in Figure 2. The comparable ionization potential (HOMO) of Alq$_3$ and **III** disfavors, but does not exclude, a charge-transfer quenching mechanism as has been shown in the case of PPV.[16]

The effect of **III** in the recombination interface of LEDs was also investigated. The insoluble nature of PPV allowed us to easily spin coat a thin (ca. 50 Å) layer of **III** on top of it, to give the (+) ITO/PPV/**III**/Alq$_3$/Al (−) device configuration, shown in Figure 4b inset. Forrest et al.[17] have demonstrated that PPV/Alq$_3$ LEDs exhibit an emission from the Alq$_3$ layer, provided it is

thicker than 300 Å. The introduction of the thin film of **III** in the interface of PPV/Alq$_3$ produced a negligible change in the overall device absorbance, while the PL intensity of the combined layers was diminished by about 50%. The EL, however, showed markedly different behavior, resulting in complete extinction of electroluminescence, with little change in the current–voltage characteristics (Figure 4). This could be explained by either of the two following scenarios, with the reabsorption of photons by **III** playing a minor role: (i) holes and electrons recombine in the nonemissive **III** layer; or (ii) excitons form in the Alq$_3$ or PPV regions adjacent to **III**, and get quenched by the nearby **III** polymer. At the present time, we are unable to differentiate between these two mechanisms.

Characterization of **III** is currently underway. Condensation products of 8-Hq have been reported in the literature, although thorough characterization of these polymers and their low molecular weight model compounds has not been conducted.[18,19] Ragimov et al.[19] claimed that the oxidative polycondensation of 8-Hq by oxygen in a basic environment gave a polymer coupled at the 5,7 positions (IR O—H at 3320–3600 cm^{-1}). Upon further oxidation of this polymer with basic H$_2$O$_2$, formation of polymeric N-oxides took place (IR, N$\rightarrow$O at 1350 cm^{-1}).[20] On the other hand, the electrochemical oxidative coupling of 8-Hq to poly(8-quinolinol ethers) was claimed by Pham et al. (IR Ar—O—Ar at 1235 cm^{-1}).[18]

Polymer **III** exhibits a number of functionalities based on IR spectroscopy. The disappearance of OH stretching along with a strong peak at 1320 cm^{-1} could be explained by the presence of N-oxides, where intramolecular hydrogen bonding results in the absence of significant absorption above 3100 cm^{-1}.[20] However, the presence of a weak but clearly discernible carbonyl stretching at 1665 cm^{-1} may indicate the presence of quinoid moieties as well. In addition, two medium-weak peaks at 1236 and 1224 cm^{-1} could also indicate the presence of 8-quinolinol ethers.

8-Hq is prone to oxidation to the 5,8-quinolinequinone.[21] The epoxidation, N-oxidation, and N-methylation of quinolines have also been reported for mutagenic studies on DNA.[22] Clearly, the chemistry of the formation of **III** and its reactive intermediates is complex enough to warrant further study. From initial IR evidence, it is not clear whether **III** is an individual compound or mixture of several oxidation and coupling products. On the basis of the above, the reaction conditions have a large effect on the underlying chemistry. It is crucial to develop an understanding of the local device environment and its effect on the degradation products and reaction kinetics. Further investigations are presently underway to elucidate the competing processes of this system.

Experimental Section

All chemicals were obtained from Aldrich. Care was taken to dry the chemicals, and to minimize the exposure of materials

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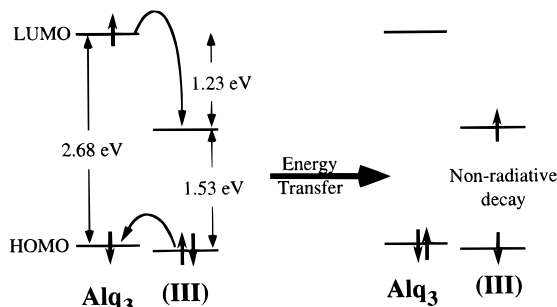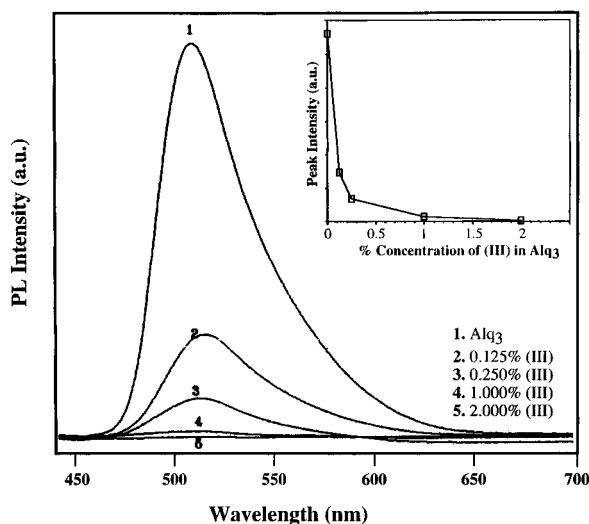
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Table 1. Electrochemically Determined Redox Potentials and Absorption-Edge HOMO−LUMO Energy Separations for 8-Hq, Alq₃, and III
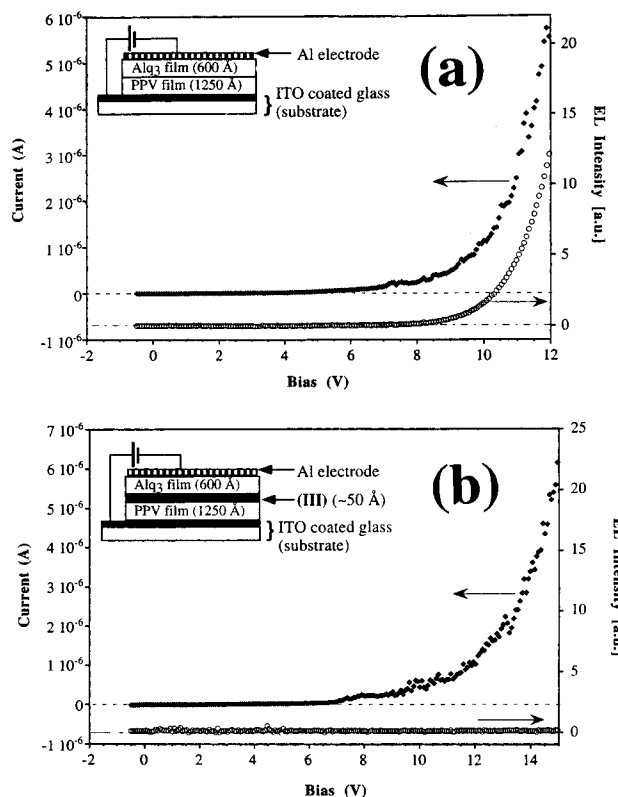
	oxidation potential (V)	reduction potential (V)	redox-derived bandgap (eV)	absorption edge wavelength (nm)	absorption-edge-derived bandgap (eV)
Alq₃	0.6[a]	−2.09	2.6₉	465	2.67
8-hydroxyquinoline	0.8[a]	−2.3[b]	3.1	366	3.39
III	0.68₅	−0.85₀	1.53₅	810	1.53

[a] Irreversible (determined by the anodic wave only). [b] Irreversible (determined by the cathodic wave only).

Figure 2. Relative energy levels for Alq₃ and **III** and schematic illustration for the energy transfer to the nonemissive **III**.

Figure 3. Photoluminescence intensity for different percent concentrations of solid Alq₃/**III** mixtures. Inset plots peak PL intensity as a function of **III**.

Figure 4. Electroluminescent output of devices: (a) PPV/Alq₃; (b) PPV/**III**/Alq₃. Insets illustrate the structure of the devices.

and devices to moisture and blue or ultraviolet (UV) light. Solvents for reactions and spin coating were dried over activated molecular sieves and bubbled with dry, oxygen-free N₂ (the prepurified N₂ was passed over CaCl₂ desiccant and BTS oxygen scavenger). Syntheses of Alq₃[11] and poly(*p*-phenylenevinylene) (PPV)[23] have been reported. Alq₃ was purified twice by zone sublimation and stored away from moisture and blue/UV light until use. The tetrahydrothiophenium precursor of PPV was solubilized in chilled methanol (1% w/v solution), filtered from 5 mm filter, and spun onto ITO-coated glass. Conversion of the precursor was performed at 200 °C in forming gas (85% N₂/15% H₂) for 6 h to yield 1250 Å PPV films.[24]

PL behavior was recorded with a Perkin-Elmer LS50B luminescence spectrometer. Solid samples for measurement of PL quenching were prepared by spray-drying solutions of Alq₃ and polymer onto a clean glass substrate. The spray rate and droplet size were adjusted so that the solvent evaporated before deposition. The resulting deposit (10 mg) was ground with 200 mg of dry KBr powder and compressed into pellets to be used in the spectrometer. The PL spectra of the EL devices were obtained by placing them in the spectrometer directly, using the ITO-coated glass substrates for background.

Absorption spectra of dilute solutions (10⁻⁶ M) and of the devices themselves were obtained from a Perkin-Elmer Lambda Array 3840 UV/vis spectrophotometer. Electrochemical measurements were made with a BAS CV 50 W cyclic voltammeter in nitrogen-flushed, spectrophotometric grade DMF (Burdick and Jackson), containing 0.1 M tetrabutylammonium perchlorate (recrystallized from ethanol) as an electrolyte. The concentration of electroactive species was approximately 1 mg/mL. The working electrode was a 1 mm diameter Pt disk; the counter electrode was a Pt wire; and the reference electrode was a Ag/AgNO₃ in acetonitrile separated from the cell by a Vycor frit.

Thin films were fabricated either by spin coating or by thermal evaporation, the latter with an Edwards Auto 306 vacuum coater equipped with a turbomolecular pump. Thicknesses were measured with a Tencor Instruments Alpha Step 200 stylus profilometer. The *I−V* characteristics and EL output of these devices were measured with a Hewlett-Packard 4155A semiconductor parameter analyzer equipped with a zero-biased photodiode (Newport 818-UV) under an inert atmosphere.

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