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Review

# Experimental and theoretical investigation of tris-(8-hydroxy-quinolinate) aluminum ($Alq_3$) photo degradation

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ABSTRACT

We investigate the stability of tris-(8-hydroxyquinolinato) aluminum ($Alq_3$) under UV photo degradation using a combination of experimental and theoretical techniques. $Alq_3$ thin films were irradiated with He–Xe lamp discharges, as a function of the exposition time, at a wavelength $\lambda = 307$ nm. The irradiated and non-irradiated films were analyzed by Fourier transform infrared (FTIR) spectroscopy. The experimental FTIR spectrum of the exposed sample exhibits a band at 1697 $cm^{-1}$, attributed to a carbonyl group. Theoretical calculations of Gibbs free energy and molecular vibrational properties for a variety of possible degradation products allow us to determine the most likely products and produce insight into the degradation mechanisms.

## 1. Introduction

In the last decades, organic light emission diodes (OLEDs) have attracted the interest of researchers and industry due to potential use as integrated light sources with applications in different areas, from display technologies and solid state illumination to medical applications, not to mention manufacturing simplicity, low costs of fabrication, wide range of emission colors, and ability to work with low voltage and low power [1]. Nevertheless, some OLEDs still suffer with poor structural stability resulting from several degradation processes, which limit the device lifetime [2] below the standard value of 10,000 h at initial display brightness (luminance) of 100 $cd/m^2$ [3,4].

Numerous degradation processes of OLEDs have been reported in the literature, primarily associated with degradation of the electrode materials, and transporting molecular layers exposed to ambient factors (like moisture and oxygen). These kinds of degradation involve crystallization of the organic layers [5–7], photo instability of organic materials [8], degradation at the device electrodes such as delamination of electrodes and cathode oxidation, both leading to formation of dark spots (or nonemissive regions) [9,10]; and electrochemical reactions at the electrode/organic interfaces [11]. Such degradation mechanisms are referred to as extrinsic degradation, i.e. the degradation associated with the environment surrounding the device [12].

Additional degradation mechanisms of $Alq_3$ are related to long-term "intrinsic" device degradation due to chemical and physical instabilities under device operation conditions. Such instabilities can be induced by several factors, such as (i) current flow and heating, (ii) chemical reactions driven by singlet or triplet excitons, (iii) self-conversion of the charge transporting molecules to cation, anion, and/or radical species [2,4].

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Although encapsulation of the device can protect it from water and oxygen of the environment and many of the processes cited above have been identified and controlled, few studies have explored degradation of $Alq_3$ films by exposure to light and the related photo degradation products, responsible for quenching of luminescence. Priestley and collaborators [13] studied photo degradation of thermally evaporated $Alq_3$. Photo oxidation was carried out under illumination with full spectrum by a 150 Watt xenon lamp while blowing air or oxygen through the cell. Transient photoluminescence and photoconductive response were measured and the sample which was photo oxidated in oxygen showed more pronounced degradation effects in comparison with that in air, which allowed them to concluded that water vapor, always present in air, does not contribute substantially to the photo oxidation. The same work reported that photo oxidation could introduce chemical modifications in $Alq_3$ through incorporation of $O_2$ molecules in its chemical structure, whose products resulted in quenching of photoluminescence. Thangaraju et al. [14] studied the decrease of photoluminescence of $Alq_3$ films upon the effects of air and white light for various time periods. They concluded that photoluminescence intensity decreases with increasing light exposure time. Infrared (IR) absorption measurements were performed in order to determine the structural changes on $Alq_3$. The spectrum shows a band at 1697 $cm^{-1}$ that corresponds to vibrational band of carbonyl group, which would act as a luminescence quencher. Similar results were also reported by Kumar and collaborators [15]. Nevertheless, neither of these studies concentrated efforts in attempt to elucidate the chemical structures of the degradation products.

In this work we investigate the stability of $Alq_3$ thin films under light and air exposure, with consequent photoluminescence decrease. With this aim, thermally deposited $Alq_3$ thin films were exposed to UV radiation and analyzed through Fourier transform infrared spectroscopy (FTIR) and optical absorption in UV–Vis region. Several possible degradation products are proposed and density functional theory (DFT) calculations of vibrational frequencies and reaction Gibbs free energies are performed. Based on comparisons between experimental and theoretical data, we identify the most likely degradation products of $Alq_3$.

## 2. Experimental details

$Alq_3$ thin films (100 nm thick) were thermally deposited in high vacuum environment onto glass, quartz and silicon substrates. The substrates were initially cleaned by ultrasonication using a detergent solution, followed by toluene degreasing, and then cleaned again by ultrasonication with pure isopropyl alcohol. The base pressure for deposition was $6.67 \times 10^{-4}$ Pa and during the evaporation the pressure was roughly $9.33 \times 10^{-4}$ Pa. The deposition rate was about 0.1 nm/s. The layer thickness was controlled in situ through a quartz crystal monitor and confirmed by perfilometer measurements. The films were exposed for 11 h to UV radiation, using a He–Xe lamp ($\lambda = 307$ nm). The incident power density was roughly 0.42 $mW/cm^2$ for all irradiated samples. The irradiated and non-irradiated films were analyzed through Fourier transform infrared spectroscopy (FTIR) and optical absorption in UV–Vis region. All the measurements were carried out in ambient atmosphere.

## 3. Computational details

The modified mer-$Alq_3$ structures were first submitted to a conformational search using semiempirical methods available on the HyperChem Software [16]. The most stable structures were selected and submitted to *ab initio* density functional theory (DFT) optimization calculations and vibrational frequency calculations, carried out using Gaussian 03 package [17]. Frequency calculations were done to confirm the stability of the structure and to generate the IR spectra. The calculations were performed with TPSS (Tao, Perdew, Staroverov, and Scuseria) meta-GGA functional [18] of Kohn–Sham DFT, in combination with 6–31G(d,p) basis set [17]. TPSS is a nonempirical meta-GGA, which was submitted to several tests on molecules, solids, and solid surfaces, all showing its good performance for a diverse range of properties and systems [19].

Due to the neglect of mechanical anharmonicity, approximations in the treatment of electron correlation and basis set effects, theoretical vibrational frequencies typically overestimate experimental ones. It is a common practice to rescale the theoretical frequencies in order to match experiments, so we use a scaling factor of 0.992, chosen to match experimental and our theoretical spectra for $Alq_3$.

## 4. Results and discussion

### 4.1. Selection of degradation products and reactions

Earlier experimental and theoretical works have shown that meridional (mer) isomer of $Alq_3$ is the predominant form, over facial (fac) form, both in solution and in sublimed films [20–24]. Therefore, structural modifications suggested here are all derived from mer-$Alq_3$, shown in Fig. 1.

$Alq_3$ is a trischelate organic complex with a distorted octahedral symmetry. Consequently, the three quinolate ligands are not equivalent, and receive labels a, b, and c (Fig. 1), according to their different Al–O and Al-N bond lengths, as obtained from X-ray structure analysis [20]. According to Thangaraju et al. [14], only one of the three 8-hydroxyquinoline (HQ) units in the $Alq_3$ molecule suffers chemical structural modifications during light exposure, resulting, as evidenced by infrared absorption spectra, in the introduction of a carbonyl group in the chelate. The same work gives a possible explanation for the chemical modification based on redox behavior associated with Al–O bond. Then, in the present work, our first proposal for degradation products of $Alq_3$ consists in the rupture of one of the Al–O bonds and consequently rupture of the benzene ring of one HQ unit (Fig. 2a). More precisely, the c-quinolate ligand is chosen to be modified since our theoretical calculations (and also previous work [25]) shows that it has the largest Al–O bond length.