Substitution effects of metal quinolate chelate materials for organic electroluminescence applications

Asanga Bimalchandra Padmaperuma

University of Nevada, Las Vegas

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SUBSTITUTION EFFECTS OF METAL QUINOLATE CHELATE MATERIALS FOR ORGANIC ELECTROLUMINESCENCE APPLICATIONS

by

Asanga Bimalchandra Padmaperuma

Bachelor of Science
University of Colombo, Sri Lanka
1996

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Asanga B. Padmaperuma

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Examination Committee Chair

Dean of the Graduate College

Examination Committee Member

Examination Committee Member

Graduate College Faculty Representative
ABSTRACT

Substitution Effects of Metal Quinolate Chelate Materials for Organic Electroluminescence Applications

By

Asanga B. Padmaperuma

Dr. Linda S Sapochak, Examination Committee Chair
Assistant Professor of Chemistry
University of Nevada, Las Vegas.

A technology that shows great promise for application in novel flat panel displays is based on electroluminescence (EL) of organic light-emitting devices (OLEDs). Aluminum tris(8-hydroxy quinoline) (Alq$_3$)-type materials are very important as emitter materials in OLEDs. Systematic experimental and theoretical studies of these materials are crucial in order to elucidate the relationship between structure and function of EL materials and ultimately optimize device performance. It has been demonstrated both theoretically and experimentally that the photoluminescence (PL) emission energies of Alq$_3$ can be tuned by adding substituents to the quinolate ligand. The electronic and structural changes associated with such substitutions can dramatically affect the resulting PL and EL efficiencies. The first systematic study of the PL and EL properties of a series of methyl-substituted quinolate tris-chelates of aluminum, gallium, and indium is reported. Detailed description of synthetic routes, characterization results, photophysical data, device data, and x-ray absorption data are presented. The effect of methyl and metal ion substitution on EL is discussed with respect to changes in required parameters.
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CHAPTER 1

ORGANIC ELECTROLUMINESCENCE

1.1 Introduction

As consumers demand less expensive, high quality electronic equipment containing flat-panel display components (e.g. televisions, cellular phones, computers), the market for new display technology will continue to increase. This market is a $30 billion per year industry and research is currently dominated by cathode ray tube (CRT) and liquid crystalline display (LCD) technologies. A relatively new goal for the scientific community is development of full-color flat-panel display technologies. This research is primarily motivated by the need to replace the bulky and inefficient CRT displays with high efficiency flat panels. Although LCDs have been used as a substitute for CRTs in the marketplace for many years, they are reflective displays and exhibit poor viewing-angle ability and glare problems in bright environments. Furthermore, LCDs require high-energy consuming backlighting. While LCDs are a good substitute for CRTs in some applications, it would be much better to have an emissive display rather than a reflective display, as is the case for LCDs. An emissive technology that shows great promise utilizes the electroluminescence (EL) of organic light emitting devices (OLEDs).\(^{(1)}\)
OLEDs are composed of thin films of organic materials sandwiched between a cathode and an anode, where an applied voltage causes the generation of light emission. The light is emitted in all directions and is very bright, thus eliminating the problems associated with LCD technology. Practical indoor and portable display applications require a brightness of around 100 cd/m\(^2\) at an operational voltage between 5 – 15 V, and a lifetime of 10,000 h of continuous operation.\(^{(2)}\) These requirements have been achieved in OLED-based displays for applications such as the 3-color OLED display for car radios, currently being marketed by the Japanese company Pioneer. In addition to the advantage of high brightness at low drive current, other major advantages of organic EL technology include potentially low cost manufacturing, and the ability to fabricate devices on almost any type of substrate.\(^{(2)}\) For a full-color display, achievement of all necessary colors is possible because the “emitter materials” in OLEDs are composed of chemically distinct organic molecules which can be synthetically tuned to emit different colors. Synthetic tunability is one of the major advantages of organic electroluminescence technology.\(^{(1,2)}\)

Although some displays based on OLED technology are entering the marketplace, the achievement of a full-color, flat-panel display is complicated by the complex fabrication procedures necessary to produce a three-color pixel device and requires increased understanding and control of material properties.\(^{(1,2)}\) The following describes a systematic investigation of the relationship between the molecular and electronic structure of organic metal complexes and their ability to serve as optimal emitter materials in OLEDs. This is accomplished by a detailed examination of the physical properties, photophysical properties, electronic structure, and electro-
luminescence efficiencies of metal (Al, Ga, and In) tris-chelates of 8-hydroxyquinoline and methyl-substituted 8-hydroxyquinoline derivatives.

1.2 Background

It has been known that fluorescent organic molecules could exhibit electroluminescence since the 1960's. Pope and Kallamann \(^{(3)}\) reported EL from a crystal of anthracene when electrodes were attached and a voltage applied across the crystal, as shown in Figure 1.1. The drawback of this device was that it required a very high voltage to produce light. Organic materials are insulators, but electrons and holes can be forced to move through them by an applied voltage. In most cases, organic materials will preferentially transport one type of charge more efficiently than the other and therefore are characterized as "hole-transporting" or "electron-transporting". \(^{(4)}\) In this device, pushing both types of charges through the anthracene crystal necessitated a very large applied voltage. Other major problems associated with the anthracene crystal electroluminescent device included charge carrier imbalance and poor charge-transport because of the thickness of the crystal.

![Figure 1.1. Device by Pope and Kallamann.](https://example.com/figure1.png)

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Nearly three decades after this important discovery, researchers at Kodak reported the first efficient EL device based on organic materials. In 1987, Tang and VanSlyke reported the results of efficient green electroluminescence from aluminum tris(8-hydroxyquinoline) (Alq3), an organic metal-chelate material.\(^5\) The organic light-emitting device consisted of very thin layers of vapor-deposited films of the organic material. Alq3 that served both as the electron-transporting layer (ETL) and the emitter. In order to achieve efficient injection of holes into Alq3 another organic layer N,N'-diphenyl-N,N'-bis(3-methylphenyl)1.1' -biphenyl-4.4' diamine (TPD) was introduced as the hole transport layer (HTL). Figure 1.2 depicts the device architecture developed by Kodak. This device provided improved confinement of charge carriers in the active emitting organic layer resulting in enhancement of electron and hole recombination and higher electroluminescence efficiency. It's now known that efficient EL requires the confinement of the charge carriers in the active emitter material.\(^5-8\)

Although the mechanism of organic electro luminescence is not completely understood, it is proposed that holes and electrons are injected from electrodes into a fluorescent-active (emitter) organic material and these charges combine to give light emission (Figure 1.3).\(^8,9\) Molecules in the HTL are oxidized by the indium tin oxide (ITO) anode creating a positively charged excited molecule (radical cation), or "hole" that migrates to the interface with the ETL/emitter material. These "holes" are chemically injected into the ETL layer by the HTL. The result is a "hole" carried now by molecules in the ETL layer. Electrons are injected into the ETL/emitter layer (reduction) by the cathode (Mg:Ag), thus creating a negatively charged excited molecule (radical anion), or "electron" that migrates to the interface with the HTL. The
negatively charged "electron" and the positively charged "hole" interact in the emitter layer near the EML/HTL interface to form a molecular exciton that relaxes to give light emission. In almost all cases, the energy of light emission from electroluminescence is similar to that produced by photoluminescence, and therefore it is assumed that the same excited state is involved in both phenomena.

Figure 1.2. OLED reported by Tang and Van Slyke.

Based on the proposed mechanism of organic electroluminescence, the design of efficient organic emitter materials requires the optimization of several parameters, to include: 1) high photoluminescence (PL) efficiency in the solid-state; 2) volatility and good film forming ability; 3) environmental and morphological stability; 4) adequate
charge-transport properties: and 5) electronic compatibility with injection layers of the device. These necessary parameters are strongly coupled to the molecular and electronic structure of the emitter material, as well as to the bulk molecular packing character of the material in vapor deposited films.

![Diagram of electroluminescence mechanism]

**Figure 1.3. Proposed mechanism for electroluminescence.**

Since it was assumed that the light emission produced by electroluminescence results from the same excited state as photoluminescence (PL), molecules with high PL efficiencies have been studied as emitter materials in OLEDs.\(^{1,5-10}\) It is very important however, to remember that high PL efficiency is only one requirement for an efficient
emitter material. Alq$_3$ exhibits a relatively high PL quantum efficiency in the solid state ($\phi = 0.32$)$^{11}$). Since the excited state of Alq$_3$ responsible for PL is a localized Frenkel exciton$^{12}$, intermolecular interactions that could lead to self-quenching are reduced. Although there are many other organic materials with much higher PL quantum efficiencies, Alq$_3$ exhibits the best balance of the necessary parameters outlined above, and as a result is the most thoroughly studied molecular emitter material for OLEDs.$^{10}$

Alq$_3$ and other metal tris-chelates of 8-hydroxyquinoline are octahedral complexes where the central metal ion is surrounded by three bidentate 8-hydroxyquinoline ligands. The net charge of the metal chelates is zero and the coordination sphere around the metal ion is filled. As a result, Alq$_3$-type molecules are very stable in the solid state. This is in contrast to many other metal chelates which in solution are stabilized by coordinating solvent molecules, but become unstable in the solid state.$^{10}$ The molecular shape of Alq$_3$ roughly resembles a sphere, as determined by single crystal x-ray crystallography.$^{13}$ It is believed that this shape imparts little or no propensity to form exciplexes with the highly conjugated hole transporting molecules at the ETL-HTL interface which can lead to a decrease in hole injection.$^{10}$

One of the best attributes of Alq$_3$ compared to other organic materials examined as emitter materials in OLEDs is its propensity to form uniform thin-films upon vacuum deposition. It also has a relatively high T$_g$ (glass transition temperature) of about 175$^\circ$C, resulting in high morphological stability. Vapor deposited films of Alq$_3$ have been shown to be amorphous, which means it shows no x-ray diffraction pattern.$^{11}$ It is believed that the thin film consists of a mixture of two geometric isomers of Alq$_3$ (Figure 1.4), meridional (mer) and facial (fac), that may hinder the recrystallization of

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Alq₃ films under device operational conditions and explain the long-term stability of Alq₃-based OLEDs.

Figure 1.4. Geometric isomers of Alq₃.

A comparison of Alq₃ and gallium tris(8-hydroxyquinoline) (Gaq₃) OLEDs demonstrates how the parameters outlined in the preceding paragraphs can affect electroluminescence. It is understood that the substitution of a heavier gallium atom for aluminum in complexes such as the tris-chelate of 8-hydroxyquinoline will result in lower PL efficiencies due to the heavy atom effect. In fact, Gaq₃ exhibits a PL efficiency four times lower than Alq₃ in solution and thin film forms. However, Gaq₃-based OLEDs exhibited EL efficiencies comparable to Alq₃. The relatively high EL efficiency of Gaq₃ may be attributed to a more favorable energy band lineup of Gaq₃ at the charge injection interface(s) and/or enhanced charge-transport properties compared to Alq₃. A clear explanation for these differences has not been put forth.

Alq₃ preferentially transports electrons versus holes, and therefore it is an electron transporting material. The ability to transport electrons, defined as electron mobility, is estimated to be around 10⁻⁵ cm²/Vs. The 8-hydroxyquinoline ligands of Alq₃ consist of two types of ring systems, one which is electron deficient (pyridyl ring) and one which is electron rich (phenoxide ring). Electrons are injected into the lowest
unoccupied molecular orbital (LUMO) located on the pyridyl ring. The electron withdrawing nature of the pyridyl ring system can stabilize the formation of the resulting radical anion excited state of Alq₃. On the other hand, holes are created by removal of an electron from the highest occupied molecular orbital (HOMO) located on the phenoxide ring. The electron rich character of the phenoxide ring can stabilize the resulting cation excited state of Alq₃. However, the measured hole mobility is only 1/100th of the electron mobility and it is not completely understood why electron mobility is favored. ¹⁶

It has been shown both theoretically and experimentally, that the PL emission energies of Alq₃ can be tuned by adding substituents to the 8-hydroxyquinoline ligand thus changing the energies of the filled and vacant orbitals. ¹⁷ For example, aluminum tris(8-hydroxy-4-methylquinoline) (4Meq₃Al) was studied in OLEDs. ¹⁸,¹⁹,²⁰ The absorption and PL emission energies are shifted to higher energy as predicted by theory. This tris-chelate was reported to exhibit an external EL quantum efficiency of 2.5%, which is more efficient than what has been reported for Alq₃ devices (1%). ⁵ The only explanation provided for this increase in EL efficiency upon methyl-substitution was based on the increase in PL efficiency of the 4Meq₃Al, which was double the efficiency of Alq₃ in both solution and in the solid-state. ²¹ Previously, Kodak researchers claimed that alkyl substitution in metal tris(8-hydroxyquinoline) chelates provided no advantages in EL properties. ¹²,¹⁷

It is obvious from the preceding paragraphs that Alq₃ and its derivatives are important materials for EL applications. Electronic and molecular structural changes in metal tris(8-hydroxyquinoline) materials have significant effects on EL efficiencies, via
changes in PL efficiencies, charge transport, injection efficiencies, or some combination of each. A better understanding of these structure/function relationships will provide crucial information for understanding EL phenomena and for designing new emitter materials. There have been many reports of electroluminescent metal chelate materials (1,10) and numerous detailed studies of Alq₃ (10). However, few detailed systematic studies have been reported.

Reference


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2.1 Synthesis of Methyl-Substituted Quinolate Ligands

The ligand 8-hydroxyquinoline consists of two types of ring systems, one is electron deficient (pyridyl ring) and the other is electron rich (phenoxide ring). It is expected that substituent effects at the positions ortho and para to the pyridyl nitrogen and phenoxide oxygen will have the most dramatic electronic effects on the overall system. Of course this is predicted because those are the positions that are most electron deficient in the pyridyl ring and the most electron rich in the phenoxide ring. This is reflected in the chemistry of this molecule. For example, electrophilic substitution occurs only on the phenoxide ring. On the other hand, nucleophilic substitution reactions occur only on the pyridyl ring. Therefore, it is not surprising that methyl-substitution on these different ring systems has dramatic effects on the physical properties and photophysical properties of the ligand and the resulting metal tris-chelates.

The methyl-substituted 8-hydroxyquinoline ligands were prepared by modifications to published procedures and are depicted in Figure 2.1. All the methyl-substituted ligands can be synthesized by the Doebner-Von Miller reaction starting with
the appropriately substituted o-aminophenol and unsaturated aldehyde or ketone \(^{(1)}\) as depicted in Figure 2.2.

![Figure 2.1. Methyl-substituted 8-hydroxyquinoline ligands.](image)

8-hydroxy-3-methylquinoline (3Meq) 8-hydroxy-4-methylquinoline (4Meq) 8-hydroxy-5-methylquinoline (5Meq)

**Figure 2.1. Methyl-substituted 8-hydroxyquinoline ligands.**

The Doebner-Von Miller reaction involves three steps. 1) Michael addition of an aldehyde or ketone and aromatic amine to form a \(\beta\)-arylaminocarboxylic acid or ketone; 2) ring closure to a dihydroquinoline intermediate; and 3) oxidation to give the final product. There are many choices for the oxidizing agent \(^{(1,2,3)}\), but for all compounds synthesized in this work \(\alpha\)-nitrophenol was utilized. This is the most practical method for preparing derivatives of 8-hydroxyquinoline substituted on the pyridyl ring. The ligands 4Meq and 3Meq were prepared by this method, but were difficult to isolate. After extraction of the reaction mixture, the ligands were isolated in low yields by distillation under reduced pressure. The 4Meq ligand was used without further purification to synthesize the chelate complexes, as \(^1\)H NMR and elemental analysis confirmed the purity. Although both ligands were highly soluble in polar solvents such as alcohols and methylene chloride, the 3Meq compound could only be purified by sublimation.
5-Methyl-substitution of the phenoxide ring of 8-hydroxyquinoline is accomplished in high yields by electrophilic substitution with formaldehyde and hydrochloric acid followed by reductive catalytic hydrogenation (Figure 2.3). This approach is advantageous because the Doebner-Von Miller ring-forming reaction is tedious and only produces low yields of product. The 5Meq ligand was easily recrystallized from alcoholic solutions and was further purified by sublimation similar to the unsubstituted analogue, 8-hydroxyquinoline.
2.2 Syntheses of Metal Tris-Quinolate Chelates

All metal tris-chelates were prepared according to published synthetic procedures outlined in Figure 2.4.\(^6\)

![Chemical reaction](image)

**Figure 2.4.** General synthetic scheme for metal tris-chelates.

Like the ligand precursors, metal tris-chelates of the methyl-substituted 8-hydroxyquinoline ligands also exhibit different physical properties. The tris-chelates of 3Meq and 5Meq were easily recrystallized from methanol but the tris-chelates of 4Meq exhibited high solubility in moderately polar solvents and precluded purification by recrystallization. Metal chelates Alq\(_3\) (obtained from Aldrich Chemical Co.). 4Meq\(_3\)Al. 3Meq\(_3\)Al. 5Meq\(_3\)Al. Gaq\(_3\). 4Meq\(_3\)Ga. 5Meq\(_3\)Ga and Inq\(_3\) were purified by high-vacuum, gradient-temperature sublimation.\(^7\) Attempts to purify the 4Meq\(_3\)In material by this technique resulted in very low yields accompanied by decomposition.

2.3 Material Characterization

All materials described in the preceding sections were characterized using conventional techniques described below. Proton nuclear magnetic resonance (\(^1\)H NMR) spectra were obtained in CDCl\(_3\) using a BRUKER 400MHz NMR. Elemental analysis for C. H and N was obtained from NuMega Resonance Labs. Inc. San Diego, Ca. FT-IR spectra of solid samples were obtained as KBr pellets using a NICOLET 210 FT-IR. The
melting transitions of the metal tris-quinolates were obtained using a Netzsch Instrument Simultaneous Thermal Analyzer (STA) that performs differential scanning calorimetry (DSC) simultaneously with thermal gravimetric analysis (TGA). Samples were run in alumina crucibles at a heating rate of 20 °C/minute under a nitrogen atmosphere.

2.3a NMR Spectroscopic Characterization

Variable temperature $^1$H NMR studies of the monohydrates of Alq$_3$, Gaq$_3$, and the corresponding methyl-substituted derivatives were reported by Schmidbaur.$^{(6)}$ According to this author, only the mer isomer was observed for all metal chelates at low temperatures. In addition, the mer isomer of methyl-substituted derivatives will exhibit three distinct methyl resonances, because in that configuration the methyl groups are inequivalent. On the other hand, the methyl groups are all equivalent in the fac configuration. At elevated temperature the methyl resonances were observed to coalesce while the aromatic resonances broadened. This fact was explained as a ligand-equilibrating process that gives rise to a mixture of both isomers.

Room temperature $^1$H NMR spectra were obtained for the aluminum, gallium, and indium tris-quinolate chelates discussed in this thesis. For the methyl-substituted derivatives all NMR spectra obtained at room temperature were similar to that reported by Schmidbauer for the mer isomer.$^{(6)}$ Elemental analysis confirmed that all metal tris-chelates reported here contain no water of hydration after purification by sublimation. Further confirmation of this was provided by thermal gravimetric analysis. A detailed NMR study of the methyl-substituted indium chelates has not been reported. Interestingly, for our indium series only one methyl resonance was observed for all chelates, indicating that the facial isomer is dominant. All NMR spectra of the ligands and metal chelates are found in Appendix I.
2.3b Infrared Spectroscopic Characterization

The infrared spectra of metal tris-quinolates have also been reported in the literature. The geometry and normal modes of vibrations for the facial isomer of Alq3 in the ground state, were recently calculated using ab initio methods and reported with vibrational spectrum. (8)

Experimental FT-IR spectra for the methyl-substituted chelates of aluminum and gallium were recorded (Appendix II) and peak assignments for the major transitions were consistent with those determined for Alq3 by ab initio methods. (Table 2.1)

Table 2.1 Assignments of FT-IR Peaks for Metal tris Quinolates.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Alq3</th>
<th>4Meq3Al</th>
<th>5Meq3Al</th>
<th>Gaq3</th>
<th>4Meq3Ga</th>
<th>5Meq3Ga</th>
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<td>C-O str + C-H bend</td>
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<tr>
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<td>1314</td>
<td>1325</td>
<td>1327</td>
<td>1311</td>
<td>1323</td>
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<td>1600</td>
<td>1597</td>
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<tr>
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</table>

2.3c Thermal Analysis Characterization

Thermal analysis of Alq3 has been reported previously. (9) Differential thermal analysis (DTA) showed one endothermic transition for Alq3 at 416 °C and two endothermic transitions at 394°C and 418°C for a sample of Alq3 sublimed multiple times. These melting transitions were assigned to the fac and mer isomers. Differential scanning
calorimetric analysis (DSC) of Alq₃ purified by high-vacuum gradient-temperature sublimation is reported in this thesis work. The DSC scans for Alq₃ are shown at two different temperature rates in Figure 2.5. Unlike the previous report discussed above, at the same heating rate, Alq₃ exhibits four thermal transitions. The first transition is a broad endotherm occurring at 358°C, most likely due to crystallization. This is followed by a small, but sharper endotherm (399°C) and exotherm (402°C). The fourth transition is a large endothermic melting transition occurring at 424°C. The DSC scan of Alq₃ was also run at a slower heating rate of 5°C/min., which resulted in one sharp thermal transition occurring at 418°C. The differences in temperature of these transitions to what has been reported previously is most likely due to the fact that DSC is a better quantitative and more sensitive thermal method than DTA. The second endothermic peak may be the melting transition of one of the isomers of Alq₃ (assigned as the facial isomer previously). In the “melt” state it is possible that the additional heating provides enough energy to induce the “ligand equilibrating process” suggested by Schmidbauer in solution NMR studies. The exothermic transition observed would be consistent with energy release of the Al-N bond breaking and reforming as the isomers interconvert. The final large endothermic transition is due to melting of the other isomer (assigned as the mer isomer previously). Slowing the heating rate would affect this equilibrium and thus only the major endothermic transition is observed. The derivatives 4Meq₃Al and 5Meq₃Al only exhibit one large endothermic transition. However, 3Meq₃Al exhibits similar endothermic transitions compared to Alq₃ but no exothermic transition. In the gallium series, only Gaq₃ exhibits more than one endo-thermic transition. The indium tris-quinolates exhibited more complicated thermal behavior and warrant more detailed investigations.
Figure 2.5  DSC scans for Alq$_3$ are shown at two different temperature rates (a) 20 °C/min, (b) 5 °C/min.

Table 2.2. Melting Point Data.

<table>
<thead>
<tr>
<th>Material</th>
<th>Melting Transitions (°C)</th>
</tr>
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<tbody>
<tr>
<td>Alq$_3$</td>
<td>356*, 399.402°, 424</td>
</tr>
<tr>
<td>3Meq$_3$Al</td>
<td>239*, 370, 404</td>
</tr>
<tr>
<td>4Meq$_3$Al</td>
<td>358</td>
</tr>
<tr>
<td>5Meq$_3$Al</td>
<td>414</td>
</tr>
<tr>
<td>Gaq$_3$</td>
<td>391, 412</td>
</tr>
<tr>
<td>3Meq$_3$Ga</td>
<td>411</td>
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<td>200</td>
</tr>
<tr>
<td>5Meq$_3$In</td>
<td>349</td>
</tr>
</tbody>
</table>

* - Broad endothermic transition corresponding to heat of crystallization.

* - sharp exothermic peak
2.4 Synthetic Procedures

8-Hydroxy-3-methylquinoline (3Meq): 27.76 g (0.2330 mol) of o-aminophenol, 12.58 g of o-nitrophenol, and 100 mL of concentrated hydrochloric acid were placed in a 1L 3-neck round-bottom flask fitted with an addition funnel and reflux condenser. The reaction mixture was heated with stirring to 60°C for 30 minutes to ensure all solids were dissolved. 21.17 g (0.3020 mol) of methacrolein was added dropwise to the mixture, via the addition funnel, over 2.5 hours. Following the addition the mixture was refluxed for an additional 24 hours. Subsequently the reaction mixture was steam distilled to remove o-nitrophenol. Potassium carbonate (50.00 g) was then added to neutralize the excess acid. The product was extracted with methylene chloride and the resulting brown oil was vacuum distilled to give the product as a crystalline solid. This material was purified by sublimation (twice) to give 10.00 g (27% yield) of a tan solid melting at 109-111°C (Lit., 110°C) \(^{(1)}\) \(^1\)H NMR (CDCl\(_3\), 25°C) \(\delta\)H2 = 8.63(s); \(\delta\)H4 = 7.92(s); \(\delta\)H5 (J5.6) = 7.25(d) (7.90); \(\delta\)H6(J6.7) = 7.42(t) (7.55); \(\delta\)H7 = 7.10(d); \(\delta\)Me = 2.75(s).

8-Hydroxy-4-methylquinoline (4Meq): The synthesis and isolation of this ligand was the same as above for 3Meq, with the following modifications: methyl vinyl ketone was the unsaturated ketone utilized and the reaction mixture was refluxed for an additional 6 hours following the complete addition of the ketone. The product was purified by recrystallization from methanol and water to yield 12.20 g (33%) of a brown hygroscopic solid melting at 143°C (Lit.,141°C) \(^{(12)}\) \(^1\)H NMR (CDCl\(_3\), 25°C) \(\delta\)H2 (J2.3) = 8.58 (d) (4.37); \(\delta\)H3 = 7.21 (d); \(\delta\)H5 = 7.41 (d); \(\delta\)H6 (J6.5/J6.7) = 7.13 (d,d) (5.05/3.72); \(\delta\)H7 = 7.40 (d); \(\delta\)Me = 2.64 (s). C\(_{10}\)H\(_{9}\)N\(_2\)O\(_1\) (159.19). Calculated: C-75.45%; H-5.70%; N-8.80%; Experimental for purified compound: C-75.15%; H-5.55%; N-8.68%.
5-Chloromethyl-8-hydroxyquinoline hydrochloride (5ClMeq.HCl): This compound was prepared as follows according to published procedures. (6) 50.54 g (0.3482 mol) of 8-hydroxyquinoline, 125 mL of 37% formaldehyde, and 125 mL of concentrated HCl were combined in a 500 mL 3-neck round-bottom flask fitted with a condenser and a gas inlet adaptor. While stirring, HCl gas was bubbled through the reaction mixture, over a period of 3 hours whereupon the product precipitated out of the solution. The mixture was cooled overnight and refrigerated to complete the precipitation. Following filtration, the highly crystalline solid was washed with ether, air-dried, and then dried over KOH/CaCl₂ under vacuum for 4 hours. 67.27 g (84%) of the product was obtained as yellow crystals melting at 280°C (Lit., 283°C) (6) ¹H NMR (D₂O, 25°C) δH2 (J2,3) = 8.72 (d) (8.66); δH3 (J3,4) = 7.66 (t) (5.40); δH4 = 8.54 (d); δH6 (J6,7) = 7.16 (d) (7.99); δH7 = 6.75 (d); δMeCl = 4.63 (s).

8-hydroxy-5-methylquinoline (5Meq): 10.00 g (0.4621 mol) of 5-chloromethyl-8-hydroxyquinoline hydrochloride was dissolved in 150 mL of methanol and placed in a 500 mL hydrogenation bottle. 1.00 g of 10% Pd/C was carefully added, and the reaction mixture was subjected to 50 psi of H₂ gas at room temperature for 4 hours. The catalyst was removed by gravity filtration and methanol was removed by rotary evaporation. The resulting 5Meq. hydrochloride was dissolved in a minimum amount of water and the free base was generated by addition of sodium acetate. The product was purified by recrystallization from methanol to yield 3.54 g (57%) of tan. needle-like crystals. Following sublimation, the product was obtained as white fluffy needle-like crystals melting at 121°C (Lit., 122-123°C). (5) ¹H NMR (CDCl₃, 25°C) δH2 (J2,3/J2,4) = 8.77 (d,d) (4.22/1.55); δH3 (J3,4) = 7.44 (d,d) (8.50); δH4 = 8.25 (d,d); δH6 (J6,7) = 7.25 (d)
(7.70): $\delta H7 = 7.06$ (d); $\delta Me = 2.56$ (s). $C_{10}H_9N_3O_1$ (159.19). Calculated: C–75.45%; H–5.70%; N–8.80%; Experimental for purified compound: C–75.33%; H–5.66%; N–8.81%.

**Aluminum tris-(8-hydroxy-3-methylquinoline) (3Meq3Al):** 2.50 g (32.5 mmol) of ammonium acetate and 0.55 g (2.3 mmol) of aluminum chloride hexahydrate were dissolved in 25 mL of deionized water. 1.04 g (6.53 mmol) of 8-hydroxy-3-methylquinoline was dissolved in 50 mL of acetic acid (1M) and was added dropwise to the buffered metal salt solution with almost immediate formation of precipitate. The mixture was stirred an additional 40 minutes. The yellow precipitate was filtered, washed with water, air-dried then recrystallized from methanol to yield 0.75 g (86%) of a yellow microcrystalline solid. $^1$H NMR (CDCl$_3$, 25°C) $\delta H2 = 8.70$(s), 8.65(s), 7.01(s); $\delta H4 = 8.08$(s), 7.99(s), 7.98(s); $\delta H5$ ($J_{5.6}$) = 7.04(d) (7.1); $\delta H6 = 7.45$(d,d); $\delta H7$ ($J_{7.6}$) = 6.98(d) (8.13); $\delta Me = 2.47$(s), 2.40(s), 2.24(s). $C_{30}H_{24}AlN_3O_3$ (501.52). Calculated: C–71.85%; H–4.82%; N–8.38%; Experimental for purified compound: C–71.88%; H–4.86%; N–8.45%

**Aluminum tris-(8-hydroxy-4-methylquinoline) (4Meq3Al):** Synthesized using the same procedure described for 3Meq3Al. utilizing 8-hydroxy-4-methylquinoline. The resulting precipitate was filtered, washed with water, and air-dried to yield 97% of a yellow powder. The high solubility of this metal chelate in common recrystallizing solvents precluded the practicality of purification by recrystallization. The material was purified by high-vacuum temperature gradient sublimation. $^1$H NMR (CDCl$_3$, 25°C) $\delta H2$ ($J_{2.3}$) = 8.82(d) (4.71), 8.78(d) (4.71), 7.02(d) (Br); $\delta H3 = 7.21$(d), 7.14(d), 6.96(d); $\delta H5$($J_{5.6}$) = 7.10(d) (8.24), 7.09(d) (8.24), 7.07(d) (8.24); $\delta H6$($J_{6.7}$) = 7.48(d) (9.62), 7.46(d) (9.62), 7.44(d) (9.62); $\delta H7 = 7.07$(s), 7.04(s) 7.02(s); $\delta Me = 2.66$(s), 2.61(s).
Aluminum tris-(8-hydroxy-5-methylquinoline) (5Meq₃Al): Synthesized using the same procedure described for 3Meq₃Al, utilizing 8-hydroxy-5-methylquinoline. The precipitate was filtered, washed with water, air-dried then recrystallized from methanol with yield of 97% of a greenish-yellow microcrystalline solid. ¹H NMR (CDCl₃, 25°C) δH2 (J2.3/J2.4) = 8.89(d,d) (4.29/1.42), 8.83(d,d) (4.29/1.42), 7.23(d,d) (4.29/1.42); δH3 = 7.45(d,d), 7.37(d,d), 7.19(d,d); δH4(J3.4) = 8.40(d,d) (8.57), 8.33(d,d) (8.57), 8.30(d,d) (8.57); δH6(J6.7) = 7.30(d) (7.18); δH7 = 7.00(d), 6.99(d), 6.98(d); δMe = 2.52(s), 2.52(s), 2.50(s). C₃₀H₂₄AlN₃O₃ (501.52) Calculated: C-71.85%; H-4.82%; N-8.38%; Experimental for purified compound: C-71.70%; H-4.72%; N-8.45%

Gallium tris-(8-hydroxyquinoline) (Ga₃q): 5.00 g (65.0 mmol) of ammonium acetate and 1.28 g (5.00 mmol) of gallium nitrate hexahydrate were dissolved in 50 mL of deionized water. 2.55 g (16.60 mmol) of 8-hydroxyquinoline was dissolved in 100 mL of acetic acid (1M) and added dropwise to the buffered metal salt solution with almost immediate formation of precipitate. The reaction mixture was stirred an additional 40 minutes. The precipitate was filtered, washed with water, air-dried then recrystallized from methanol to yield 2.12 g (78%) of greenish-yellow crystals. FT-IR(KBr) (cm⁻¹) – 1600, 1576, 1496, 1463, 1327, 1227, 1113, 823, 787, 741, 644, 627. ¹H NMR (CDCl₃, 25°C) δH2(J2.3) = 8.87(d) (4.55), 8.83(d) (4.55), 7.38(br); δH3 = 7.43(m), 7.36(m), 7.19(m); δH4(J3.4) = 8.29(d) (8.18), 8.24(d) (8.18), 8.20(d) (8.18); δH5 = 7.14(s), 7.12(s), 7.10(s); δH6 = 7.51(s), 7.49(s), 7.47(s); δH7 = 7.06(s), 7.04(s). C₃₀H₂₄GaN₃O₃ (544.26)
Calculated:  C – 66.21%; H – 4.44%; N – 7.72%  Experimental for purified compound:  
C – 66.41%; H – 4.53%; N – 7.71%

**Gallium tris-(8-hydroxy-3-methylquinoline) (3Meq₃Ga):** Synthesized using the same procedure described for Gaq₃, utilizing 8-hydroxy-3-methylquinoline. The precipitate was filtered, washed with water, and air-dried to give a dark yellow powder which was recrystallized from methanol to give a yield of 82%. \(^1\)H NMR (CDCl₃, 25°C) \(\delta\)H₂ = 8.73(s), 8.68(s), 8.10(s); \(\delta\)H₄ = 8.02(s), 8.01(s); \(\delta\)H₅ = 7.09(s), 7.07(s), 7.06(s); \(\delta\)H₆ = 7.48(s), 7.46(s), 7.44(s); \(\delta\)H₇ = 7.01(s), 7.00(s), 6.98(s); \(\delta\)Me = 2.49(s), 2.42(s), 2.26(s). \(\text{C}_{30}\text{H}_{24}\text{GaN}_3\text{O}_3\) (544.26). Calculated: C–66.21%; H–4.44%; N–7.72%; Experimental for recrystallized compound: C–66.23%; H–4.49%; N–7.80%

**Gallium tris-(8-hydroxy-4-methylquinoline) (4Meq₃Ga):** Synthesized using the same procedure described for Gaq₃, utilizing 8-hydroxy-4-methylquinoline. The precipitate was filtered, washed with water, and air-dried to give a brown-tinted yellow powder in yield of 70%. The high solubility of this metal chelate in common recrystallizing solvents precluded the practicality of purification by recrystallization. The material was purified by high-vacuum temperature gradient sublimation. \(^1\)H NMR (CDCl₃, 25°C) \(\delta\)H₂(J2,3) = 8.73(d) (4.53), 8.69(d) (4.72), 7.28(d) (4.84); \(\delta\)H₃ = 7.25(d), 7.16(d), 7.00(d); \(\delta\)H₅ = 7.49(m), 7.47(m), 7.45(m); \(\delta\)H₆ = 7.10(s), 7.08(s), 7.07(s); \(\delta\)H₇ = 7.12(s), 7.09(s), 7.08(s); \(\delta\)Me = 2.66(s), 2.62(s), 2.60(s). FT-IR(KBr) (cm⁻¹) – 1597, 1571, 1505, 1460, 1311, 1245, 1154, 840, 754, 739, 598. \(\text{C}_{30}\text{H}_{24}\text{GaN}_3\text{O}_3\) (544.26). Calculated: C–66.21%; H–4.44%; N–7.72%; Experimental for purified compound: C–66.41%; H–4.53%; N–7.71%
Gallium tris-(8-hydroxy-5-methylquinoline) (SMeqGa): Synthesized using the same procedure described for Gaq3, utilizing 8-hydroxy-5-methylquinoline. The yellow precipitate was filtered, washed with water, air-dried then recrystallized from methanol to yield 71% of greenish-yellow plate-like crystals. $^1$H NMR (CDCl$_3$, 25°C) δH2(J2.3) = 8.92(d) (3.40), 8.84(d) (3.40), 7.38(d) (3.12): δH3 = 7.45(m), 7.36(m), 7.21(m); δH4(J3.4) = 8.39(d) (8.23), 8.34(d) (8.23), 8.31(d) (8.23): δH6 = 7.31(s), 7.29(s); δH7 = 7.03(s), 7.01(s), 6.99(s); δMe = 2.50, 2.48. FT-IR(KBr) (cm$^{-1}$) – 1600, 1579, 1505, 1462, 1323, 1243, 1098, 831, 759, 786, 641, 628. C$_{30}$H$_{43}$GaN$_3$O$_3$ (544.26) Calculated: C-66.21%; H-4.44%; N-7.72%; Experimental for purified compound: C-66.11%; H-4.24%; N-7.84%

Indium tris-(8-hydroxyquinoline) (Inq3): 10.00 g (130.0 mmol) of ammonium acetate and 2.80 g (7.16 mmol) of indium nitrate hexahydrate were dissolved in 100 mL of deionized water. 3.20 g (22.0 mmol) of 8-hydroxyquinoline was dissolved in 200 mL of acetic acid (1M) and added dropwise to the metal salt solution with almost immediate formation of precipitate. The mixture was stirred an additional 40 minutes. The yellow precipitate was filtered, washed with water, air-dried then recrystallized from methanol to yield 3.66 g (86%) of a yellow microcrystalline solid. $^1$H NMR (CDCl$_3$, 25°C) δH2 = 8.56(s); δH3 (J3.2) = 7.43(t) (4.70); δH4 (J4.3) = 8.32(s) (8.40); δH5 (J5.6) = 7.19(d) (7.53); δH6 (J6.7) = 7.51(t) (7.94); δH7 = 7.05(d). C$_{27}$H$_{18}$InN$_3$O$_3$ (547.28) Calculated: C-59.26%; H-3.32%; N-7.68%; Experimental for purified compound: C-59.28%; H-3.30%; N-7.69%

Indium tris-(8-hydroxy-3-methylquinoline) (3MeqIn): Synthesized using the same procedure described for Inq3, utilizing 8-hydroxy-3-methylquinoline. The yellow
precipitate was filtered, washed with water, air-dried to give a dark yellow powder which was recrystallized from methanol to yield 62%. \(^1\)H NMR (CDCl\(_3\), 25°C) \(\delta H2 = 8.41(s)\); \(\delta H4 = 8.07(s)\); \(\delta H5 (J5.6) = 7.11(d) (7.82)\); \(\delta H6 (J6.7) = 7.46(t) (7.29)\); \(\delta H7 = 6.97(s)\); \(\delta Me = 2.44\). C\(_{30}H_{24}InN_3O_3\) (589.36) Calculated: C–61.14%; H–4.10%; N–7.13%;

Experimental for crude product: C–61.38%; H–4.06%; N–7.20%

**Indium tris-(8-hydroxy-4-methylquinoline) (4Meq\(_3\)In)**: Synthesized using the same procedure described for Inq\(_3\). utilizing 8-hydroxy-4-methylquinoline. The precipitate was filtered, washed with water, air-dried to yield 71% of a fine yellow powder. The high solubility of this metal chelate in common recrystallizing solvents precluded the practicality of purification by recrystallization. High-vacuum temperature gradient sublimation gave low yields and caused degradation of the material. \(^1\)H NMR (CDCl\(_3\), 25°C) \(\delta H2 = 8.41(s)\); \(\delta H3 (J2.3) = 7.23(s) (4.60)\); \(\delta H5 (J5.6) = 7.50(d) (8.20)\); \(7.46(d) (8.11)\); \(\delta H6 = 7.11(d)\); \(\delta H7 (J6.7) = 7.15(d) (7.77)\); \(\delta Me = 2.68\). C\(_{30}H_{24}InN_3O_3\) (589.36)

Calculated: C–61.14%; H–4.10%; N–7.13%;

Experimental for crude product: C–60.18%; H–4.00%; N–7.07%

**Indium tris-(8-hydroxy-5-methylquinoline) (5Meq\(_3\)In)**: Synthesized using the same procedure described for Inq\(_3\). utilizing 8-hydroxy-5-methylquinoline The precipitate was filtered, washed with water, air-dried then recrystallized from methanol to yield 71% of a bright yellow microcrystalline solid. \(^1\)H NMR (CDCl\(_3\), 25°C) \(\delta H2 (J2.4) = 8.58(d) (1.54)\); \(\delta H3 (J2.3) = 7.44(t) (4.41)\); \(\delta H4 (J4.3) = 8.30(d) (8.30)\); \(\delta H6 = 7.32(d)\); \(\delta H7 (J6.7) = 7.08(d) (7.81)\); \(\delta Me = 2.52\). C\(_{30}H_{24}InN_3O_3\) (589.36)

Calculated: C–61.14%; H–4.10%; N–7.13%;

Experimental for purified compound: C–60.72%; H–3.76%; N–6.99%

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References


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3.1 Introduction

Modern x-ray techniques, using x-rays from synchrotron radiation (SR) facilities have unique advantages for probing complex systems. The x-ray wavelength, in contrast to laboratory-based x-ray techniques, can be tuned to study specific elements allowing determination of atomic-scale electronic structure. Synchrotron radiation (SR) is electromagnetic radiation emitted by electrons or positrons moving at relativistic velocities along a curved trajectory with a large radius of curvature. A typical electron accelerator such as the Advanced Light Source (ALS), located at Lawrence Berkeley National Laboratory (LBNL) emits SR in a very broad range of photon energies and provides electromagnetic radiation in spectral regions for which no other usable source exists.

In general x-ray spectroscopy is a powerful probe of individual atomic species in different chemical environments because core-ionization thresholds of different elements are well separated in energy. The most common x-ray spectroscopic technique, x-ray absorption spectroscopy (XAS), in which atomic core electrons are promoted via selective photon absorption into bound valence states, can provide a map of normally unoccupied electronic states (or levels). A complementary technique, x-ray emission
spectroscopy (XES), monitors x-rays emitted as the sample relaxes to fill a core vacancy created by x-ray absorption. If the electrons that fill this core vacancy come from the valence shell or conduction band of the sample, then XES will directly probe the occupied valence states. The combination of these two techniques will provide a map of the electronic structure of a material. In the 1980’s the near edge x-ray absorption fine structure (NEXAFS) technique was developed with the aim of elucidating the structure of molecules containing important atomic building blocks such as hydrogen, carbon, nitrogen, oxygen, and fluorine. Probing with x-rays can provide a powerful method for investigating how the electronic environment around an atom changes as a function of synthetic modification in organic materials of interest for electroluminescent applications, such as the metal tris-quinolates. This information may be important for explaining the dramatic differences in PL and EL efficiencies observed for the series of materials studied in this thesis work.

3.2 Background

Recently, Curioni. et.al. reported the first detailed electronic-structure study of Alq3. These authors reported Density Functional Theory (DFT) based calculations, as well as photoemission (XES), and near-edge x-ray absorption fine structure (NEXAFS) studies performed at the ALS with synchrotron radiation. A picture of the orbital structure of Alq3 was presented and the nature of the distinct features of the observed spectra were explained in terms of contributions from the different atoms in different molecular orbitals. As determined previously by semi-empirical calculations, both the occupied and unoccupied π-states of Alq3 near the HOMO-LUMO gap group into sets that have the same orbital character on each of the three ligands making up the metal tris-
chelate. The HOMO set is mainly localized on the electron rich phenoxide ring and the LUMO set is mainly localized on the electron deficient pyridyl ring. Curioni compared the NEXAFS spectrum of Alq$_3$ with the calculated photoabsorption spectra and assigned the spectral peaks as transitions from the Is orbital to various available unoccupied states corresponding to four different LUMO "sets" generated by the theoretical treatment of the molecule. The probability isodensity surface of these orbital sets and the density of states plot generated by Curioni are depicted in Figure 3.1. The experimental Is NEXAFS spectrum and calculated photoabsorption spectra for C, N and O is reproduced in Figure 3.2. The results reported by Curioni are discussed below in some detail and will be referred to extensively in the discussion of the x-ray absorption data obtained for the series of metal tris-quinolates reported in this thesis.

![Figure 3.1](image)

**Figure 3.1.** (a) Probability Isodensity surface of LUMO(I), LUMO+1(II), LUMO+2(III) and LUMO+3(IV) sets of orbitals. Only one ligand is shown. (b) Projected Density of States calculated for these empty states. (Reproduced with permission from A. Curioni.)
The lowest energy unoccupied orbital set, and the one believed to be most involved in the PL process, LUMO state (I), contains the majority of the electron density distributed around the pyridyl ring nitrogen and carbon atoms and very little on the oxygen of the phenoxide ring. This set of transitions is effectively due to donor-acceptor transitions from the phenoxide ring donor to the pyridyl ring acceptor. The higher energy unoccupied orbital sets include: LUMO+1 state (II) containing a symmetric distribution of electron density mainly on the carbon atoms of both rings; LUMO+2 state (III) containing electron density mainly on the phenoxide ring oxygen and carbons but with some density on the pyridyl nitrogen; and LUMO+3 state (IV) containing an almost symmetric distribution of electron density over both rings and all atoms.

![Figure 3.2. 1s NEXAFS spectrum (solid) compared to calculated (dashed) photoabsorption for C, N and O for Alq as reported by Curioni.. The labels are as figure 3.1. (Reproduced with permission from A. Curioni.)](image-url)
An analysis of the nitrogen-edge of Alq₃ experimentally and theoretically indicated that three peaks were dominant. These three peaks were assigned to the following transitions and are listed in order of increasing energy:

N 1s to LUMO (I) (Highest intensity transition)
N 1s to LUMO + 2 (III)
N 1s to LUMO + 3 (IV)

As predicted by theory, no peak was observed for the N 1s to LUMO + 1(II) set because the electron density is distributed primarily on the carbon atoms.

The carbon-edge of Alq₃ is much more complicated because there are so many different carbons in the molecule and therefore was predicted to exhibit broader peaks with overlapping contributions from more than one orbital set. Only the lowest energy peak assigned to the C 1s to LUMO (I) was well defined in the NEXAFS spectrum (see Figure 3.2). This peak is dominated by transitions to the LUMO of the carbon atoms at the 4-position of the pyridyl ring. Two higher energy broad peaks were observed with the lower energy one assigned to mixtures of contributions from the C 1s to LUMO (I), LUMO +1 (II), and LUMO +2 (III) sets. The maximum relative intensity is due to the C 1s to LUMO +2 (III) of the carbon atoms at the 5-position of the phenoxide ring. The third peak is mainly due to the C 1s to LUMO +2 (III) of the carbon atoms at position 8 (directly bonded to the phenolic oxygen).

Excitations from the O atom in Alq₃ gives rise to three peaks similar to what was observed for the N atom and were assigned similarly. The major difference between the two spectra was that the transition O 1s to LUMO + 3 (III) state was the highest intensity transition as expected based on the electron distributions of the LUMO sets.
The NEXAFS spectra of the C and N edges for a series of metal tris-quinolates and methyl-substituted tris-quinolates are presented here. Attempts to study the O-edge of these materials were unsuccessful. The major problem was interference from the sample substrate. In future studies, thicker films of the sample will eliminate this problem. The assignments for the spectral peaks discussed in preceding paragraphs serve as a reference for evaluating changes in NEXAFS spectra due to synthetic modification of metal tris-quinolate molecules.

3.3 Experimental Method

X-ray absorption spectroscopy experiments were performed at the Advanced Light Source (ALS), Lawrence Berkeley National Lab (LBNL). The storage ring at the ALS has a stored electron beam with energy of 1.0 – 1.9 GeV. The photon energy extends from far IR to x-rays (15 KeV). The ring is optimized for extremely high brightness in the vacuum UV and soft x-ray ranges. During the multi-bunch operations the filling pattern is 320 bunches, 2 ns apart. All experiments were performed on beamline 6.3.2 which is a bend magnet beamline dedicated to extreme ultraviolet (EUV) and soft x-ray reflectometry and scattering designed for high spectral purity and wavelength accuracy. The beamline has a photon energy range from 50 to 1300 eV, photon flux of $10^{11}$ photons/sec/0.01%BW at 100 eV. This is a relatively new beamline up and running since February 1995. It previously had not been used for the investigation of organic materials. However, it accesses the appropriate energy range (285 eV to 550 eV) for probing C, N, and O edges. The development of the experimental procedure for conducting x-ray absorption spectroscopy of organic materials at beamline 6.3.2 is discussed below. This beamline had been predominantly used as a calibration beamline.
for inorganic samples and exhibits a much higher resolution than beamline 8.0 utilized by Curioni to study Alq3.

Unoccupied electronic states of metal tris-quinolates were probed using NEXAFS with a reflectometer chamber at the beamline 6.3.2. The order sorter was set at the off position during the experiments and exits slits were placed at -50.1 and 49.9. The sample was placed at 90° angle to the beam. The 600 l/mm gratings were selected for all studies. For carbon and nitrogen edges a thallium filter was used. Data was collected at a rise time of 100 ms and presample decay of 300 ms. 10 samples/point were taken to improve the signal to noise ratio.

X-ray absorption was performed via the total electron yield method. When the x-ray beam impinges on the sample a core level electron (1s) is promoted to a higher unoccupied level. This gives rise to an excited molecule, which does not bear a charge, thus a core hole is created. This excited state can decay in many ways, including; recombination of the hole and the excited electron, production of photoelectrons, and Auger emission, the latter being the major pathway of decay. Depending on the penetration depth, these electrons can escape from the sample and are measured using detectors placed close to the sample. The current necessary to balance the charge referred to as the drain current is measured and is proportional to the total amount of electrons emitted by the molecule. The total electron yield method is preferred over XAS via transmission because there is no need to have a transparent substrate and there may be less charging up of the organic material that can lead to decomposition during the experiment.

NEXAFS spectra were generated as the change in drain current as a function of photon energy of the x-ray beam. There must be an electrical connection between the
sample and the detector. thus the sample must be in contact with a conducting substrate. The most common substrate used in this type of experiment is conducting Carbon tape mounted on a glass substrate. In preliminary experiments powdered samples were crushed and applied to Carbon tape. However, this method gave poor results due to large scattering and increased noise in the spectra. The data presented in this thesis was obtained from samples of vapor-deposited thin films on aluminum substrates. These samples were mounted on carbon tape and applied to a glass substrate. Reference spectra were obtained at each atomic edge investigated, using an etched silicon wafer. All experimental spectra were normalized using these reference spectra.

3.4 The Effect of Methyl-Substitution on the N-Edge

The NEXAFS spectra of the N-edge for the aluminum tris-quinolates series are shown in Figure 3.3. All spectra are dominated by a high intensity peak found at low energy, assigned by Curioni to the transition N 1s to the LUMO (I) state for Alq3. The energy of this transition does not shift significantly in any of the methyl-substituted derivatives. However, there are observable differences in the higher energy transitions caused by methyl-substitution (see Figure 3.3b). For 4Meq3Al and 3Meq3Al, the transition assigned to the LUMO + 3 (IV) state is shifted to lower energy relative to Alq3. The shift of this peak to lower energy may be a result of stabilization of the nitrogen K-hole due to an increase of electron density on the nitrogen. On the other hand, the nature of the electron distribution of this LUMO set may be significantly modified upon substitution. A theoretical treatment of the methyl-substituted tris-quinolates is necessary before reasons for these shifts can be put forth. There is no significant shift of this peak for 5Meq3Al compared to Alq3. According to the probability isodensity surface of this
LUMO set for Alq₃ (see Figure 3.1) the carbon at the 5-position contains very little electron density and therefore is less affected by substitution.

Figure 3.3. a) Full NEXAFS spectra of aluminum tris-quinolate chelates at the N-edge; b) higher energy transitions only.

The same trends are observed for the gallium and indium series of metal tris-quinolates. (The spectra can be found in Appendix III)

3.5 The Effect of Methyl-Substitution on the C-Edge

The NEXAFS spectra of the C-edge of the aluminum tris-quinolate series are shown in Figure 3.4. There are significant changes in the spectra of the methyl-substituted derivatives compared to Alq₃. The NEXAFS spectrum of the C-edge for Alq₃ is consistent with the data presented by Curioni (see Figure 3.2), but with better resolution of the peaks. For the 4Meq₃Al the lowest energy transition, C 1s to LUMO (I) state is shifted to higher energy. Significant changes are seen in the second peak, which splits in to two peaks due to methyl substitution. For 4Meq₃Al and 5Meq₃Al the transition C 1s to the LUMO+2 (III) state of C5 of the phenoxide ring is shifted towards
lower energy and a shoulder appears at higher energy. For 3Meq\textsubscript{3}Al the transition C\textsubscript{1}s to the LUMO+2 (III) state of C5 of the phenoxide ring is shifted further towards lower energy and a new peak, which has highest intensity, appears at higher energy. As discussed in preceding section, a theoretical treatment of the methyl-substituted tris-quinolates is necessary before reasons for the appearance of this new peak can be put forth.

Figure 3.4. **NEXAFS spectra of aluminum tris-quinolate chelates at the C-edge.**

A comparison of NEXAFS spectra of Alq\textsubscript{3} to Gaq\textsubscript{3} is shown in figure 3.5. There is no observable change in the lowest energy transition leading to the conclusion that there is no significant change in the energy of this LUMO state due to metal-ion substitution. However, there is an observable change in the highest energy peak in the Ga series which was not assigned by Curioni. The effect of methyl-substitution on the C and N-edges, discussed above for the aluminum tris-quinolates, is similar for the gallium series (see Appendix III).
Figure 3.5. Comparison of the Alq₃ and Gaq₃ NEXAFS spectra at the C-edge.

Reference

CHAPTER 4

PHOTO-PHYSICAL STUDIES OF METAL-QUINOLATE CHELATES

4.1 Optical Absorption Characterization

The optical transition most responsible for the photoluminescence in metal quinolate chelates is centered on the organic quinolate ligand. This transition is effectively a $\pi-\pi^*$ charge-transfer from the phenoxide ring to the pyridyl ring. The electron rich phenoxide ring is the location of the highest occupied molecular orbital (HOMO) and the electron-deficient pyridyl ring is the location of the lowest unoccupied molecular orbital (LUMO). Depending on the electron donating or electron withdrawing character of a substituent and the location of substitution on the quinolate ligand the HOMO and LUMO energies will change. Semi-empirical calculation methods, such as ZINDO have been shown to accurately predict the excited state energies of Alq$_3$ and several of its substituted derivatives.\(^{(1,2)}\) It is predicted that the LUMO is raised in energy upon substitution of an electron donating group and lowered in energy by the substitution of an electron withdrawing group on the pyridyl ring. Upon substitution of the phenoxide ring the HOMO energy changes similarly. These predictions have been confirmed experimentally.\(^{(1,2,3)}\)

For the metal tris-quinolate chelates discussed in this thesis, methyl-substitution (electron donating group) at C-5, C-6, and C-7, is predicted to increase the energy of the
HOMO resulting in a red shift of absorption energy. On the other hand, methyl-substitution of C-4 and C-3 is predicted to increase the energy of the LUMO. Thus, the energy for absorption should increase and a blue shift should be observed compared to the unsubstituted analogue. The aluminum tris-chelate with substitution of the methyl group at C-2 cannot be prepared because steric hindrance prevents the formation of a stable chelate. These predicted changes in the energies of the HOMO and LUMO for 4Me- and 5Me-substituted Alq are depicted in Figure 4.1.

We previously reported the theoretically calculated 1st excited state energies of Alq and its methyl-substituted derivatives. Geometry optimizations were performed by a number of different methods (HF and B3LYP) and basis set (STO-3G, 3-21G, 6-31G*) combinations using the Gaussian98 program. Prediction of the excitation energies and oscillator strengths were accomplished by the semi-empirical method ZINDO CI = [FULL]. Since our interest was in proper trends of the energetic, we found that HF/STO-3G geometry coupled with ZINDO CI = [FULL] was sufficient. (Table 4.1)

Figure 4.1. Schematic representation of the relative changes in HOMO and LUMO energies upon methyl-substitution of the ligand in metal tris-quinolates.
Absorption spectra were recorded with a VARIAN CARY 3BIO UV-Vis Spectrophotometer. Samples were run as dimethyl formamide (DMF) solutions in 1 cm fused quartz cuvettes. The theoretical calculations of the 1\textsuperscript{st} excited state energies of Alq\textsubscript{3} and its methyl-substituted derivatives exhibit the same trend in energy shifts upon methyl-substitution as observed experimentally. Importantly, larger shifts are exhibited by methyl-substitution on the phenoxide ring compared to substitution on the pyridyl ring. This is also observed experimentally in the corresponding gallium chelates. It is also noted that 4MeAlq\textsubscript{3} exhibits the largest oscillator strength for the 1\textsuperscript{st} excited state. This may be important since we have shown that the 8-hydroxy-4-methylquinoline chelate derivatives of Al, Ga, In and Zn all exhibit significantly higher photoluminescent quantum efficiencies than all other methyl substituted and unsubstituted derivatives.\textsuperscript{(5,6)}

<table>
<thead>
<tr>
<th>Metal-tris-chelate</th>
<th>Experimental Absorbance, (\lambda_{\text{max}}) (nm) (DMF solution)</th>
<th>Calculated Excited State Energies\textsuperscript{(4)} [\text{HF/STO-3G Geometries} \quad \text{ZINDO CI} = [\text{FULL}]]</th>
<th>1\textsuperscript{st} Excited state Energy (nm)</th>
<th>Oscillator strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alq\textsubscript{3}</td>
<td>321, 334, 388*</td>
<td>395</td>
<td>0.1712</td>
<td></td>
</tr>
<tr>
<td>3Meq\textsubscript{3}Al</td>
<td>318, 334, 388*</td>
<td>393</td>
<td>0.1659</td>
<td></td>
</tr>
<tr>
<td>4Meq\textsubscript{3}Al</td>
<td>321, 333, 383*</td>
<td>390</td>
<td>0.1928</td>
<td></td>
</tr>
<tr>
<td>5Meq\textsubscript{3}Al</td>
<td>329, 341, 405*</td>
<td>408</td>
<td>0.1667</td>
<td></td>
</tr>
<tr>
<td>6Meq\textsubscript{2}Al</td>
<td>322, 338, 387\textsuperscript{a}</td>
<td>391</td>
<td>0.1651</td>
<td></td>
</tr>
<tr>
<td>7Meq\textsubscript{3}Al</td>
<td>320, 335, 401\textsuperscript{a}</td>
<td>405</td>
<td>0.1626</td>
<td></td>
</tr>
</tbody>
</table>

\*Band appearing at longest wavelength. This is the highest intensity peak for all compounds.
\*Determined in CHCl\textsubscript{3} by Schmidbaur.\textsuperscript{(7)}

The theoretically determined excited state energies for the Ga and In tris-quinolate series could not be obtained because of the absence of basis sets for these...
metals. However, similar shifts in absorption energies upon methyl-substitution are observed experimentally as indicated in Table 4.2.

Experimentally, the energy shifts are largest for substitution of the phenoxide ring versus the pyridyl ring as predicted by theory. In general, for all metal chelates, 4-methyl substitution causes a blue shift or shift towards high energy relative to the unsubstituted analogues with energy differences of 336 cm$^{-1}$ (Al), 263 cm$^{-1}$ (Ga) and 325 cm$^{-1}$ (In). 5-methyl substitution causes a red shift or shift towards lower energies relative to unsubstituted analogues with much larger energy differences of 1082 cm$^{-1}$ (Al), 1060 cm$^{-1}$ (Ga) and 1103 cm$^{-1}$ (In).

**Table 4.2  Long Wavelength Absorption Energies for Ga and In Tris-Quinolates.**

<table>
<thead>
<tr>
<th>Metal-tris-chelate</th>
<th>Experimental Absorbance $\lambda_{\text{max}}$ (nm)(DMF solution)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gallium</td>
</tr>
<tr>
<td>Mq$_3$</td>
<td>323. 335. 392*</td>
</tr>
<tr>
<td>3Meq$_3$M</td>
<td>321. 335. 392*</td>
</tr>
<tr>
<td>4Meq$_3$M</td>
<td>322. 334. 388*</td>
</tr>
<tr>
<td>5Meq$_3$M</td>
<td>330. 343. 409*</td>
</tr>
<tr>
<td></td>
<td>Indium</td>
</tr>
<tr>
<td></td>
<td>323. 336. 395*</td>
</tr>
<tr>
<td></td>
<td>320. 335. 395*</td>
</tr>
<tr>
<td></td>
<td>322. 335. 390*</td>
</tr>
<tr>
<td></td>
<td>330. 343. 413*</td>
</tr>
</tbody>
</table>

*Band appearing at longest wavelength. This is the highest intensity peak for all compounds.

A comparison of the solution absorption spectra of Alq$_3$ and 5Meq$_3$Al is shown in Figure 4.2(a). The absorption spectrum of Alq$_3$ exhibits a long wavelength broad peak with two high-energy peaks that appear as shoulders. On the other hand, the absorption spectrum of 5Meq$_3$Al shows a large red-shift of the long wavelength peak relative to Alq$_3$, with a smaller shift of the higher energy peaks. As a result, the higher energy peaks in 5Meq$_3$Al are well separated from the major absorption band. Interestingly, although
separated from the long wavelength absorption band the peaks are less resolved than in Alq₃ and exhibit an increase in intensity. This is also observed for the Ga and In chelates of 5-methyl-substituted ligands, but with a larger increase in intensity of the high energy peaks (Figure 4.2(b)). Smaller shifts in the absorption energies are observed for methyl-substitution at the 4-position in all metal tris-quinolates with no dramatic changes in the relative intensities of the absorption bands. On the other hand, the smallest absorption energy shifts are observed for methyl-substitution at the meta-positions to the phenoxide oxygen (C-6) and pyridyl nitrogen (C-3). Absorption spectra can be found in Appendix IV.

Figure 4.2. Solution absorption spectra for; (a) Alq₃ and 5Meq₃Al (b) Gaq₃ and 5Meq₃Ga.

Substitution of the heavier metal ions gallium and indium in all derivatives causes a red shift of absorbance compared to the Al chelates due to the heavy atom effect as discussed previously by Burrows and Sapochak.⁸
4.2 Photoluminescent Characterization

Photoluminescent (PL) studies of metal tris-quinolates have been reported in the literature for samples run in CHCl₃⁹ and DMF.⁷ However, in those reports there was some question about the structure of the materials. In this thesis, the structures of all materials have been verified by ¹H NMR and elemental analysis. Furthermore, when possible, samples were purified by high-vacuum gradient-temperature sublimation before analysis.

PL spectra were obtained with a SLM 48000 Spectrofluorometer. Samples were run as dilute solutions in DMF that were purged with argon before analysis. The concentrations of the sample solutions were adjusted by UV-Vis spectroscopy so that the optical densities at 390 nm (excitation wavelength) were all close to 0.18. The emission maxima, full width at half maxima (FWHM), and the area under the emission spectra were calculated using the graphing software, Origin. Samples were run on the same day and all instrument parameters were kept constant. Each series of samples were run in triplicate.

4.2.1 Calculation of Relative PL Quantum Yields (φₚₐₐ)

The most common method employed for the calculation of PL quantum yields is by using optically dilute solutions¹⁰. The optically dilute measurement rests on Beer's Law.

\[ I_oB = I_o(1-10^{-AL}) \]  

(1)

where \( B \) is the fraction of light absorbed by the sample, \( I_o \) (quanta/sec) is the intensity of the incident light, A is the absorbance/cm for incident light and L(cm) is the path length. If the luminescence intensity for each compound is proportional to \( I_oB \), then the expression for quantum yield (\( Q_x = \text{photons emitted} / \text{photons absorbed} \)) becomes¹¹,¹²: \( \text{Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.} \)
By substitution of a more commonly used relation for $B$, which is a derivation of equation (1), a working equation to calculate quantum yields which is limited to optically diluted solutions is obtained.

$$Q_t = Q_r \left( \frac{B_x}{B_r} \frac{I(\lambda_x)}{I(\lambda_r)} \frac{\eta^2_x}{\eta^2_r} \frac{D_x}{D_r} \right)$$

In these equations $B$ is the fraction of incident light absorbed, $I(\lambda)$ is the relative intensity of the exciting light at wavelength $\lambda$, $\eta$ is the average refractive index of the solution to the luminescence. $D$ is the integrated area under the emission spectra, and $A$ is the absorbance/cm of the solution at the excitation wavelength $\lambda$. Subscripts $x$ and $r$ refer to the unknown sample and the reference sample ($Alq_3$ in this study). This simplified equation (3) was used without any correction factors. It is assumed that for both unknown and reference sample that the integrated luminescence intensity is proportional to the fraction of light absorbed. This has been confirmed for the samples under study in this thesis. There is a linear relationship between concentration and emission intensity at low concentrations ($< 10^{-5}$ M) as shown in Figure 4.3 for Alq3. The linearity is lost at higher concentrations, therefore all PL studies were conducted at $\sim 10^{-5}$ M concentrations. Furthermore, equation (3) is appropriate for calculating quantum yields when the following additional criteria are met: 1) all geometrical factors are identical; 2) the excitation beams are nearly monochromatic; 3) reflection losses are the same; 4) internal reflection effects are equal; 5) reabsorption and reemission are negligible; and 6) all light emanating from the cuvette is isotropic. Since all samples are run exactly the same way without changing any of the instrument parameters, criteria 1), 3), 4), and 6) are met. All
samples exhibit a small overlap of absorbance and emission curves (<2.5%) therefore reabsorption and reemission behavior is neglected, and therefore criterion 5) is satisfied.

All samples have significant absorbance at the excitation wavelength. Since the samples are prepared identically for all runs and the materials are chemically similar to Alq₃, the reference, we can assume that average refractive index is the same. These assumptions further simplify equation (3) to give.

\[
Q_r = Q_r \left( \frac{A_r(390nm)}{A_s(390nm)} \right) \left( \frac{D_r}{D_s} \right)
\]

(4)

The quantum yield \((Q_r)\) of Alq₃ is reported in DMF to be 0.116. \(^{(13)}\) the optical density at 390 nm is used as \(A_r\), area under the emission spectrum is used as \(D_r\). Using the above relationship, if absorbance at 390 nm \((A_x)\) and area under the emission spectrum \((D_x)\) is known for an unknown sample, \(Q_x\) can be calculated.

![Figure 4.3. Plot of emission intensity as a function of concentration of Alq₃ in DMF solution.](image-url)
4.2.2 Results

4.2.2a PL Spectral Data

The PL spectra of the Al tris-quinolates are shown in Figure 4.4. The energy shifts observed in the PL spectra are similar to the absorption spectra with a few interesting differences. 4Meq₃Al (494 nm) emits at a shorter wavelength, as expected, compared to Alq₃ (520 nm) giving rise to an energy difference of 1049 cm⁻¹. This is a much larger energy difference than what is observed for the absorption data. On the other hand, although 5Meq₃Al (546 nm) emits at a longer wavelength, the energy difference of 878 cm⁻¹ is smaller than what is observed for the absorption data. These differences are similar in the Ga-chelate series (energy difference of 1008 cm⁻¹ for 4Meq₃Ga and 722 cm⁻¹ for 5Meq₃Ga compared to Gaq₃, respectively). Interestingly, the PL emission energy shifts for In chelates, 4Meq₃In and 5Meq₃In are similar (805 cm⁻¹ compared to Inq₃). The PL spectra for the Ga and In tris-quinolates are found in Appendix IV.

![Emission spectra of Alq₃'s.](image-url)

Figure 4.4. Emission spectra of Alq₃'s.
The PL data for all metal tris-quinolates is tabulated in Table 4.3. The energy differences between absorption and emission (Δ) and the FWHM of emission are also included. There are notable trends in these two parameters as a result of methyl-substitution. The energy difference between absorption and emission is smallest for 4Meq3Al (5912 cm⁻¹) compared to Alq3 (6623 cm⁻¹). This suggests that there is less vibrational distortion in the excited state of 4Meq3Al compared to the unsubstituted analogue, Alq3 and the other methyl-substituted derivatives. Furthermore, the FWHM of emission for 4Meq3Al is also the narrowest. This same trend is observed for the gallium chelates, but is less dramatic for the indium chelates.

The energy difference between absorption and emission of 5Meq3Al (6376 cm⁻¹) is only slightly smaller than Alq3. This is true for both the gallium and indium chelate series. However, the FWHM is the broadest for the 5-methyl-substituted materials. Interestingly, 3-methyl-substituted derivatives exhibit similar emission energy shifts, Δ, and FWHM compared to the unsubstituted analogues for all metals.

Table 4.3. Photoluminescence and Absorbance Data for Metal Quinolate Chelates.

<table>
<thead>
<tr>
<th>Metal Chelate</th>
<th>Emission (nm)</th>
<th>FWHM (nm)</th>
<th>Δ (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alq3</td>
<td>522</td>
<td>105</td>
<td>6.623</td>
</tr>
<tr>
<td>3Meq3Al</td>
<td>523</td>
<td>106</td>
<td>6.668</td>
</tr>
<tr>
<td>4Meq3Al</td>
<td>494</td>
<td>92</td>
<td>5.912</td>
</tr>
<tr>
<td>5Meq3Al</td>
<td>546</td>
<td>113</td>
<td>6.376</td>
</tr>
<tr>
<td>Gaq3</td>
<td>541</td>
<td>110</td>
<td>7.026</td>
</tr>
<tr>
<td>3Meq3Ga</td>
<td>542</td>
<td>109</td>
<td>7.060</td>
</tr>
<tr>
<td>4Meq3Ga</td>
<td>513</td>
<td>103</td>
<td>6.280</td>
</tr>
<tr>
<td>5Meq3Ga</td>
<td>563</td>
<td>119</td>
<td>6.688</td>
</tr>
<tr>
<td>Inq3</td>
<td>546</td>
<td>109</td>
<td>7.001</td>
</tr>
<tr>
<td>3Meq3In</td>
<td>545</td>
<td>110</td>
<td>6.968</td>
</tr>
<tr>
<td>4Meq3In</td>
<td>523</td>
<td>104</td>
<td>6.520</td>
</tr>
<tr>
<td>5Meq3In</td>
<td>570</td>
<td>114</td>
<td>6.669</td>
</tr>
</tbody>
</table>

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PL quantum yields in DMF solution for Alq$_3$, Gaq$_3$, and Inq$_3$ have been reported previously by Lytel. However, in that study only the structure of the Alq$_3$ molecule matched elemental analysis data. The authors suggested that the structures for the Gaq$_3$ and Inq$_3$ contained Cl, which is not unlikely because the chelates were prepared from the metal chloride salt. In this present study, the structures of all metal chelates were confirmed by $^1$H NMR and elemental analysis. The PL quantum yields were calculated relative to the known quantum yield for Alq$_3$ in DMF and reported normalized to $\phi_{PL}(Alq_3) = 1.00$ for clarity in Table 4.4. The relative values of for Gaq$_3$ and Inq$_3$ are higher than those reported by Lytle, but consistent with those reported by Burrows and Sapochak. This is most likely due to the elimination of Cl contamination (chelates were prepared from metal nitrates) and the higher level of purification of the materials.

<table>
<thead>
<tr>
<th>Metal Chelate</th>
<th>Rel. $\phi_{PL}$ $^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alq$_3$</td>
<td>1.00</td>
</tr>
<tr>
<td>3Meq$_3$Al</td>
<td>1.36</td>
</tr>
<tr>
<td>4Meq$_3$Al</td>
<td>3.07</td>
</tr>
<tr>
<td>5Meq$_3$Al</td>
<td>0.29</td>
</tr>
<tr>
<td>Gaq$_3$</td>
<td>0.28</td>
</tr>
<tr>
<td>3Meq$_3$Ga</td>
<td>0.38</td>
</tr>
<tr>
<td>4Meq$_3$Ga</td>
<td>0.79</td>
</tr>
<tr>
<td>5Meq$_3$Ga</td>
<td>0.08</td>
</tr>
<tr>
<td>Inq$_3$</td>
<td>0.38</td>
</tr>
<tr>
<td>3Meq$_3$In</td>
<td>0.39</td>
</tr>
<tr>
<td>4Meq$_3$In</td>
<td>1.72</td>
</tr>
<tr>
<td>5Meq$_3$In</td>
<td>0.07</td>
</tr>
</tbody>
</table>

$^*$ - The relative $\phi_{PL}$ values reported here are the averages of 3 studies on different days with a maximum relative standard deviation (RSD) of 3%. Uncorrected spectra were utilized and the error in signal detection is approximately 7% at $\lambda < 520$ nm and up to 22% for $\lambda > 520$nm.
The highest relative PL quantum efficiency is exhibited by 4Meq₃Al (3 times Alq₃). This is higher than what has been reported by Murata (¹⁵) in CHCl₃ (2 times Alq₃) and in the solid-state (1.7 times Alq₃). The high polarity of the DMF solvent may enhance the quantum efficiency more for 4Meq₃Al relative to Alq₃. The 3Meq₃Al derivative exhibited a small enhancement in PL quantum efficiency compared to Alq₃. On the other hand, the 5Meq₃Al derivative exhibits a large decrease in PL quantum efficiency (approximately 3 times less than Alq₃). In general, methyl-substitution of the pyridyl ring of the 8-hydroxyquinoline ligand enhances PL quantum efficiency and substitution of the phenoxide ring decreases it. This trend is also observed for the gallium and indium series of metal chelates. The quantum efficiency of the 4Meq₃In is more enhanced than the corresponding 4Meq₃Ga. This may be due to some impurity in the material. Attempts to purify the 4Meq₃In by high-vacuum gradient-temperature sublimation led to decomposition. However, the material was purified by recrystallization and no apparent contaminant was detectable by ¹H NMR or elemental analysis.

The enhanced PL quantum efficiency of the 4-methyl substituted derivatives might be due to less energy lost in vibrational states of the molecule in the excited state as indicated by the small Δ's and narrow FWHM's discussed in the previous section. This would result in an increase in the absorbed energy released via radiative pathways verses nonradiative pathways.

Reference

2. Burrows, P.E.; Shen, Z; Bulovic, V.; McCarty, D.M.; Forrest, S.R.; Cronin, J.A.; and Thompson, M.E. Relationship between electroluminescence and current

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CHAPTER 5

DEVICE FABRICATION AND ELECTROLUMINESCENCE

CHARACTERIZATION

5.1 Device Fabrication

Devices were fabricated and tested by Dr. Paul Burrows and Dr. Linda Sapochak at the Princeton University. All organic materials were purified by high-vacuum temperature-gradient sublimation prior to device fabrication. Devices were grown on glass slides precoated with indium tin oxide (ITO) with a sheet resistance of 15Ω/square. The ITO substrates were cleaned according to the following steps: 1) ultrasound treatment in water/detergent; 2) boiling in 1,1,1-trichloroethane; 3) rinsing with reagent grade acetone; 4) rinsing with methanol; 5) drying under pure nitrogen; and 6) plasma etching. After the cleaning treatment the substrates were loaded into a glove box immediately. All organic light-emitting devices were prepared according to the diagram shown in Figure 5.1. A 500 Å layer of the hole transporting material, N,N'-diphenyl-N,N'-bis(3-methyl phenyl) 1,1'-biphenyl-4,4'-diamine (TPD) or N,N'-diphenyl-N,N'-bis(1-naphthol) 1,1'-biphenyl-4,4'-diamine (NPD), was deposited on the ITO substrate by thermal evaporation from a baffled Mo crucible at a nominal rate of 2-4 Å/s under a base pressure of <2X10⁻⁶ Torr. A 550 Å layer of the electron-transporting (ETL) metal chelate Mq₃, 4Meq₃M, and 5Meq₃M for M = Al and Ga also serving as the emitter layer (EML),
was then deposited on the HTL. A top electrode consisting of 1 mm diameter circular contacts was subsequently deposited by thermal evaporation through a mask. Two different types of cathodes were utilized, LiF-Al and a Mg:Ag alloy. The LiF-Al cathode consisted of a 7 Å LiF layer deposited on the EML layer followed by a 1000 Å layer of Al metal. For the Mg:Ag cathode, a Mg:Ag alloy layer (1000 Å) was deposited by coevaporation of the two metals from separate Mo boats in a 10:1 Mg:Ag atomic ratio under a base pressure of 10⁻⁵ Torr, followed by a 300 Å Ag cap. For the systematic study, all HTL and cathode layers were deposited simultaneously and vacuum was never broken. Thus, devices produced from different metal chelate materials are identical in all respects. A quartz crystal oscillator placed near the substrate was used to measure the thickness of the films. Film thickness calibration was performed by ellipsometry measurements of films grown on silicon.

![Schematic representation of a device.](image)

**Figure 5.1. Schematic representation of a device.**

### 5.2 Device Testing

Electrical pressure contact to the device was made by means of a 25 μm diameter Au wire. Current-voltage characteristics were measured with a Hewlett-Packard HP4145 semiconductor parameter analyzer, and EL intensity was measured with a Newport 835 powermeter with a broad spectral bandwidth (400-1100 nm) photodetector placed
directly below the glass substrate, which gives an adequate measurement as materials under study exhibit a relatively narrow range of emission energies. This measurement underestimates the total power since much is lost by waveguiding to edges of the glass substrate. it nevertheless accurately measures the relative efficiency between devices. Electroluminescence spectra were recorded with an EG&G optical multichannel analyzer on a 0.25 focal length spectrograph.

5.3 Calculation of Electroluminescence and Power Efficiencies

Electroluminescent quantum efficiencies ($\phi_{EL} = \text{photons emitted} / \text{electrons injected}$) were calculated relative to devices prepared with Alq$_3$ as the EML. The applied voltage was increased gradually while measuring the light output and the current across the device. Data was collected for at least three pixels on each device. Electroluminescence and power efficiencies were calculated from the optical output power ($L$) at a moderate current of 100 $\mu$A (current density of 13 mA/cm$^2$) using equation (1).

$$\phi_x = \frac{\phi_x L_x}{L_r}$$  \hspace{1cm} (1)

The quantum efficiency of Alq$_3$ was assigned 1.00 for simplicity, and the quantum efficiency of the samples was calculated accordingly. The power efficiency (PE) is the amount of optical output power as a function required voltage, calculated from optical output power ($L$) and required voltage ($V$) using equation (2), the subscripts $x$ and $r$ correspond to the unknown sample and reference.

$$PE = \frac{L_x V_x}{L_r V_r}$$  \hspace{1cm} (2)
5.4 Electroluminescence Results

The device structures for the initial EL studies of the aluminum and gallium series of tris-quinolates consisted of NPD as the HTL and either Mg:Ag or LiF-Al as the cathode. All devices were fabricated during the same run. Therefore, the HTL and ETL layers were identical for all devices. The EL spectra are shown in Figure 5.2 and the EL emission maxima and FWHM data are outlined in Table 5.1.

![Figure 5.2](image)

**Figure 5.2.** Electroluminescence spectra for a) aluminum tris-quinolates; and b) gallium tris-quinolates from devices with a LiF-Al cathode.

The EL emission energy shifts are consistent with the energy shifts observed for the PL results. The 4-methyl-substituted derivatives are blue-shifted and the 5-methyl-substituted derivatives are red-shifted compared to the unsubstituted analogues. However, the EL emission energy of 4Meq₃Al is shifted much less from Alq₃ and the FWHM is broader than in the solution PL spectrum, whereas 4Meq₃Ga has the narrowest FWHM in the gallium series. The 5Meq₃Ga gives rise to an additional lower energy peak in the EL spectrum that is not observed in the solution PL spectra. This peak appears as a very weak shoulder in the PL spectrum of vapor-deposited films, and therefore it may be due to some type of dimer formation in the solid-state. The 3Meq₃Al was not included in

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this study. The EL emission spectral data included in Table 5.1 for this material was
determined from a device prepared in an experiment discussed later in this section. The
EL emission spectrum of the 3Meq\textsubscript{3}Al derivative was essentially identical to that of Alq\textsubscript{3}.

### Table 5.1 EL Spectral Data for Metal Tris-Quinolates

<table>
<thead>
<tr>
<th>Metal Chelate</th>
<th>Experimental $\lambda$(nm)</th>
<th>FWHM (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alq\textsubscript{3}</td>
<td>530</td>
<td>96</td>
</tr>
<tr>
<td>3Meq\textsubscript{3}Al</td>
<td>529</td>
<td>101</td>
</tr>
<tr>
<td>4Meq\textsubscript{3}Al</td>
<td>525</td>
<td>104</td>
</tr>
<tr>
<td>5Meq\textsubscript{3}Al</td>
<td>560</td>
<td>104</td>
</tr>
<tr>
<td>Gaq\textsubscript{3}</td>
<td>552</td>
<td>110</td>
</tr>
<tr>
<td>4Meq\textsubscript{2}Ga</td>
<td>537</td>
<td>105</td>
</tr>
<tr>
<td>5Meq\textsubscript{2}Ga</td>
<td>575, 690</td>
<td>110</td>
</tr>
</tbody>
</table>

A summary of the relative EL quantum efficiencies ($\phi_{EL}$), turn-on voltages, and
power efficiencies for devices prepared with different cathodes are shown in Table 5.2
(device set 1). Figure 5.3 shows the dependence of optical output power on drive current
for each of the devices made with LiF-Al as the cathode. The current vs. voltage plot is
shown in Figure 5.4.

It has been reported that the insertion of LiF between the EML and metal cathode
(Al) improves electron injection in OLEDs resulting in lower turn-on voltages and greater
EL efficiencies.\textsuperscript{(2)} In this study, no advantages were observed using LiF-Al over the more
commonly utilized cathodic material, Mg:Ag. Although the values for the relative EL
quantum efficiencies are similar for both types of devices prepared from the metal
chelates under study, there was a larger deviation in turn-on voltages. The film thickness
of the LiF layer is difficult to control and if it is too thick, the enhancement of electron
injection is diminished. This may be the explanation for the lack of enhancement of the EL properties of the devices discussed here.

Table 5.2  EL Device Data for Metal Tris-Quinolates Utilizing Different Cathodes.

<table>
<thead>
<tr>
<th>Emitter</th>
<th>LiF-Al / Emitter / NPD device</th>
<th>Mg:Ag / Emitter / NPD device</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Quantum Efficiency (Alq3 = 1)</td>
<td>Voltage (13mA/cm²)</td>
</tr>
<tr>
<td>Alq3</td>
<td>1.00</td>
<td>5.3</td>
</tr>
<tr>
<td>4Meq3Al</td>
<td>1.39</td>
<td>7.8</td>
</tr>
<tr>
<td>5Meq3Al</td>
<td>0.45</td>
<td>7.4</td>
</tr>
<tr>
<td>Gaq3</td>
<td>0.63</td>
<td>5.7</td>
</tr>
<tr>
<td>4Meq3Ga</td>
<td>1.00</td>
<td>7.6</td>
</tr>
<tr>
<td>5Meq3Ga</td>
<td>0.21</td>
<td>5.8</td>
</tr>
</tbody>
</table>

The relative EL quantum efficiencies are highest for the 4-methyl-substituted derivatives for both the aluminum and gallium chelates similar to the results for PL quantum efficiencies discussed in Chapter 4. However, all metal chelates except for 4Meq3Al exhibit a much higher relative $\phi_{EL}$ than $\phi_{PL}$ (see Table 4.4). The 4Meq3Al chelate exhibits approximately a 2 times lower $\phi_{EL}$ than $\phi_{PL}$. Even though the reported $\phi_{PL}$ for 4Meq3Al is lower in the solid-state as discussed earlier, if concentration quenching is the dominant factor affecting EL performance it might be expected that at least the 4Meq3Ga would be affected in the same way, but it is not.

Kido claimed that the 4Meq3Al exhibits a much larger enhancement in EL efficiency than observed in this study.\(^{(3,4)}\) Although Kido did not conduct a direct comparison to Alq3 (prepare identical devices during the same run) he did use a different HTL (TPD). Therefore, a second series of devices was prepared utilizing the aluminum tris-quinolates as the emitter materials, NPD and TPD as the HTL’s, and Mg:Ag as the
cathode. All devices were made identically during the same run as described previously.

The results are outlined in Table 5.3.

Figure 5.3 Optical Output Power of LiF/Alq/NPD devices.

Figure 5.4 Current vs. voltage curve of LiF/Alq/NPD devices.

Consistent with the previous study, devices prepared with 4Meq3Al as the emitter material, exhibited the highest EL quantum efficiencies compared to identical devices.
prepared with Alq₃. Although the differences are not as large as reported by Kido. However, the HTL did have an effect on the results. When TPD was utilized as the HTL \( \phi_{EL} \) increases for the 4Meq₃Al device relative to Alq₃, but with a corresponding increase in turn-on voltage. On the other hand, the 5Meq₃Al/TPD device also increased in \( \phi_{EL} \), but with a corresponding decrease in turn-on voltage. The Alq₃/TPD device exhibited slightly higher \( \phi_{EL} \) efficiencies and higher turn-on voltages compared to the same device made with NPD resulting in comparable power efficiencies.

Table 5.3 EL Device Data for Aluminum Tris-Quinolates Utilizing Different HTLs

<table>
<thead>
<tr>
<th>Metal Chelate /HTL</th>
<th>Voltage (at 13 mA/cm²)</th>
<th>(Alq₃/TPD = 1.00)</th>
<th>(Alq₃/NPD = 1.00)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Quantum Efficiency</td>
<td>Power Efficiency</td>
</tr>
<tr>
<td>Alq₃/NPD</td>
<td>6.3</td>
<td>0.94</td>
<td>1.06</td>
</tr>
<tr>
<td>4Meq₃Al/NPD</td>
<td>7.1</td>
<td>1.13</td>
<td>1.13</td>
</tr>
<tr>
<td>5Meq₃Al/NPD</td>
<td>6.9</td>
<td>0.37</td>
<td>0.38</td>
</tr>
<tr>
<td>Alq₃/TPD</td>
<td>7.1</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>4Meq₃Al/TPD</td>
<td>7.7</td>
<td>1.47</td>
<td>1.36</td>
</tr>
<tr>
<td>5Meq₃Al/TPD</td>
<td>6.2</td>
<td>0.45</td>
<td>0.51</td>
</tr>
</tbody>
</table>

A third set of devices was prepared with the aim of investigating whether the HTL affected the device properties of the gallium chelates similarly. Unfortunately several of the devices were not adequate for testing due to fabrication problems during the experiment. However, these problems did not affect all of the devices and data presented in Table 5.4 represents results that were obtainable, including data for a device utilizing 3Meq₃Al as the emitter layer. The EL efficiencies are reported relative to an identical device prepared during the same run with Alq₃ and TPD as the HTL.

The only material in this data series that the affect of changing the HTL can be evaluated is for Gaq₃. The EL quantum efficiency of Gaq₃/TPD device is higher and the
The turn-on voltage is lower compared to an identical device prepared with NPD as the HTL. The trends in EL efficiencies are similar to what is reported from data in device set 1 for this material, but the turn-on voltages are different. The Gaq\textsubscript{3}/NPD device exhibits a higher turn-on voltage in this set of devices. A possible explanation for these differences may be changes in substrate cleanliness during device fabrication that can cause variations in device properties between pixels on the same device.

### Table 5.4 Electroluminescence Quantum Efficiencies for Gallium Tris-Quinolates

<table>
<thead>
<tr>
<th>MQ\textsubscript{3}/HTL</th>
<th>Voltage (13 mA/cm\textsuperscript{2})</th>
<th>(Alq\textsubscript{3}/TPD = 1.00)</th>
<th>Quantum Efficiency</th>
<th>Power Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alq\textsubscript{3}/TPD</td>
<td>7.0</td>
<td>1.00</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>3Meq\textsubscript{3}Al/NPD</td>
<td>7.2</td>
<td>0.79</td>
<td>0.75</td>
<td></td>
</tr>
<tr>
<td>Gaq\textsubscript{3}/NPD</td>
<td>7.6</td>
<td>0.59</td>
<td>0.53</td>
<td></td>
</tr>
<tr>
<td>4Meq\textsubscript{3}Ga/NPD</td>
<td>6.4</td>
<td>1.04</td>
<td>1.12</td>
<td></td>
</tr>
<tr>
<td>Gaq\textsubscript{3}/TPD</td>
<td>6.2</td>
<td>0.70</td>
<td>0.78</td>
<td></td>
</tr>
<tr>
<td>5Meq\textsubscript{3}Ga/TPD</td>
<td>6.5</td>
<td>0.21</td>
<td>0.22</td>
<td></td>
</tr>
</tbody>
</table>

The preliminary device data for the 3Meq\textsubscript{3}Al suggests that similar to the 4Meq\textsubscript{3}Al derivative, \( \phi_{EL} \) is lower than the corresponding solution \( \phi_{PL} \). This may be a trend in the series of materials with methyl-substitution of the pyridyl ring. As discussed in the preceding paragraphs, materials with substitution on the phenoxyde ring (5-position) exhibited substantial increases in \( \phi_{EL} \) compared to the solution \( \phi_{PL} \). More detailed studies of the solid-state \( \phi_{PL} \) are necessary as well as analysis of other substitution positions of the phenoxyde ring of the ligand before a definite trend can be established.
References


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CHAPTER 6

CONCLUSIONS

It is well established that materials of high PL efficiency are good potential candidates for emitter materials in OLEDs. However, there are other material parameters that are also necessary, including: 1) volatility and good film forming ability; 2) adequate charge transport properties; 3) electronic compatibility with injection layers of a device; and 4) environmental and morphological stability. In order to establish design criteria for new emitter materials it is necessary to understand how to improve each of these parameters. In many cases, improvement in one parameter is achieved only by sacrificing another. For example, there are many organic dyes that have high PL quantum efficiencies in the solid-state. These materials however are often plagued by morphological instability because of their highly crystalline nature. PL quantum efficiencies can be adversely affected by intermolecular interactions of molecules via self-quenching, but intermolecular interactions are necessary for adequate charge-transport properties in solid-state films. The point is that the necessary parameters are all interrelated. The metal chelate, Alq₃, maintains the appropriate balance of these parameters and this is directly related to its unique molecular and electronic structure.

The purpose of this thesis was to conduct a systematic study of metal-tris quinolate derivatives of Alq₃ and to investigate how simple ligand and metal-ion substitutions affect the parameters necessary for optimal emitter materials. Extensive
physical, photophysical, and electroluminescence device studies were conducted on methyl-substituted and metal-ion substituted derivatives of the parent compound Alq₃. Major changes in the absorption energies, emission energies, and PL quantum efficiencies were observed for methyl-substitution on the pyridyl ring versus the phenoxide ring moieties of the 8-hydroxyquinoline ligand in all series of metal tris-chelates studied. In particular, methyl-substitution at the 4-position caused shifts to higher energy in absorption and emission, with corresponding enhancements in PL quantum efficiencies. On the other hand, shifts to lower energy and large decreases in PL quantum efficiencies were observed for derivatives with methyl-substitution at the 5-position. The fact that in all metal series the higher relative PL efficiencies of the 4-methyl-substituted derivatives were accompanied by the narrowest FWHM of emission and the smallest Franck-Condon shifts suggests that these derivatives may exhibit less vibrational distortion in the excited state. Furthermore, the 4-methyl-substituted derivatives exhibited the lowest melting point transitions. This is indicative of weaker intermolecular interactions between the molecules that can decrease the effect of PL self-quenching, but also can adversely affect charge-transport properties in OLEDs. This may be one of the explanations for the higher turn-on voltages for OLEDs composed with either 4Me₃Al or 4Me₃Ga.

The trends in EL emission energies and relative EL quantum efficiencies were similar to those observed for PL. However, 4Me₃Al exhibited lower relative EL efficiencies than that predicted by both solution ($\phi_{PL} = 3.0$) and solid-state ($\phi_{PL} = 1.6$) PL efficiencies (vs. $\phi_{EL} = 1.4$), whereas 5Me₃Al exhibited enhanced EL efficiency ($\phi_{EL} = 0.45$) compared to the solution PL ($\phi_{PL} = 0.29$). The EL efficiencies reported here for 4Me₃Al are not significantly greater than Alq₃ as reported by Kido. The major reason
for this difference is that in this thesis work, $4\text{Meq}_3\text{Al}$ and $\text{Alq}_3$ devices were prepared and tested identically. Previous studies compared quantum efficiencies of $\text{Alq}_3$ tested under different current driving conditions.\(^{(5)}\) Therefore, it is concluded that although $4\text{Meq}_3\text{Al}$ does indeed exhibit a higher relative EL efficiency than $\text{Alq}_3$, the magnitude is much smaller than previously reported. Furthermore, after taking into account that $4\text{Meq}_3\text{Al}$ OLEDs require higher drive voltages further suggests that it is not a better candidate than $\text{Alq}_3$ as an emitter material.

Upon metal-ion substitution, although the gallium tris-quinolate series exhibited an approximately four times decrease in relative PL quantum efficiencies compared to the aluminum chelate analogues, relative EL efficiencies are substantially larger than the respective solution PL quantum efficiencies for all methyl-substituted derivatives. The largest enhancement is observed for $5\text{Meq}_3\text{Ga}$. Preliminary results for indium tris-quinolates suggest the general trends in PL upon methyl substitution are similar to those reported for the gallium analogues. Characterization by NMR suggests that the facial isomer may be dominant in the indium tris-quinolate materials. Theoretical calculations indicate that the facial isomer is higher in energy than the meridinal isomer for $\text{Alq}_3$.\(^{(6,7)}\) This may not be the case for the gallium and indium chelates since there is more room in the coordination sphere of the larger metals. The effects of metal-ion substitution on the EL properties might be related to a different distribution of the two optical isomers in solid-state films compared to the $\text{Alq}_3$ materials. However, the ability to quantify the distribution of these isomers in solid-state films has been elusive. An investigation of the EL properties of the indium tris-chelates will be important to better understand the effects of metal-ion substitution.
The effect of methyl-substitution in the aluminum and gallium tris-quinolates on the charge injection and transport may be explained by the changes in the ability to stabilize the oxidized and reduced forms of the emitter materials upon charge injection. As discussed in this thesis, the ligand 8-hydroxyquinoline contains both electron-rich and electron deficient ring systems enabling the resulting metal chelates to transport both electrons and holes, more efficiently for the former. When electrons are injected into the LUMO of the electron deficient pyridyl ring the formation of the radical anion excited state may be adversely affected by methyl-substitution of the pyridyl ring. This increased electron density can act to destabilize the reduced excited state. On the other hand, the enhanced EL efficiencies of the 5-methyl substituted derivatives might be attributed to enhanced hole injection capabilities. Electron injection would be less affected by substitution of the phenoxide ring because the additional electron density is not centered on the pyridyl ring. However, hole injection would be enhanced because this additional electron density may act to stabilize the radical cation excited state formed upon injection of holes into the HOMO of the phenoxide ring. These results suggest that derivatives substituted on the pyridyl ring with electron withdrawing ability may improve electron injection. For example, replacement of the methyl group with a trifluoromethyl group may act to enhance electron injection, however the introduction of a halogenated substituent may also adversely affect the PL efficiency of the material. Therefore, introduction of a cyano-group may be a more practical choice.

Charge injection efficiencies are also dependent on the energy level matching of the emitter material with the other layers of the device. When the HTL layer was changed from NPD to TPD in a series of identically prepared devices it was shown that the EL efficiencies of Alq3, 4Meq3Al and 5Meq3Al were improved. Interestingly, only 5Meq3Al
exhibited a lower corresponding turn-on voltage when TPD was utilized as the HTL. Initial results for the gallium tris-quinolates suggest that EL efficiencies and driving voltages also change with different HTL materials.

A mapping of the electronic structure of both the emitter and HTL layers will aid in understanding the changes in charge injection at the material interfaces of these materials. This can be accomplished by a combination of x-ray absorption and x-ray emission spectroscopic data. In this thesis, x-ray absorption spectroscopy (XAS) was used to probe the unoccupied states (or LUMO's) of the metal tris-quinolate materials. The NEXAFS results for Alq₃ reported by Curioni (9,10) were successfully duplicated here. Those results were important for establishing confidence in our experimental procedure for conducting XAS of organic thin films. We showed significant changes in the C-edge NEXAFS spectra of metal tris-quinolates due to methyl-substitution and small changes due to metal-ion substitution. More subtle differences were observed in the N-edge spectra. These results suggest that there are observable differences in the electron density distributions in metal tris-quinolate derivatives and strengthens the necessity for obtaining the XES data, as well as a detailed theoretical treatment of these metal tris-quinolate derivatives of Alq₃. Once these important experiments and theoretical calculations are conducted a complete picture of the electronic structure of these materials will be obtained. This information will be crucial for aiding in establishing what additional substituents should be pursued to improve energy matching at the material interfaces, without sacrificing PL efficiencies and ultimately design better emitter materials.
References


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APPENDIX I

$^1$H NMR DATA
Figure A-1. $^1$H NMR spectrum of 3Meq

Figure A-2. $^1$H NMR spectrum of 4Meq
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Figure A-6. $^1$H NMR spectrum of 5Me$_3$Al
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Figure A-8. $^1$H NMR spectrum of 3Meq$_3$Ga

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Figure A-9. $^1$H NMR spectrum of 4Me$_3$Ga

Figure A-10. $^1$H NMR spectrum of 5Me$_3$Ga

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Figure A-11. $^1$H NMR spectrum of In$_3$

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Figure B-5  FT-IR Spectrum of 4Meq₃Al.

Figure B-6  FT-IR Spectrum of 5Meq₃Al.
Figure B-7  FT-IR Spectrum of GaQ₃.

Figure B-8  FT-IR Spectrum of 3Meq₃Ga.
Figure B-9 FT-IR Spectrum of 4Meq,Ga.

Figure B-10 FT-IR Spectrum of 5Meq,Ga.
Figure B-11  FT-IR Spectrum of Inq3.

Figure B-12  FT-IR Spectrum of 3Meq3In.
Figure B-13  FT-IR Spectrum of 4Me₃In.

Figure B-14  FT-IR Spectrum of 5Me₃In.

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Figure C-4  NEXAFS spectra at N-edge of 4Meq$_3$Al and 4Meq$_3$Ga.
Figure C-5  NEXAFS spectra at N-edge of 5Meq3Al and 5Meq3Ga.

Figure C-6  NEXAFS spectra at N-edge for In quinolate chelates.

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Figure C-7  NEXAFS spectra at C-edge for Ga quinolate chelates.

Figure C-8  NEXAFS spectra at C-edge of 3Meq_{3}Al and 3Meq_{3}Ga.
Figure C-9  NEXAFS spectra at C-edge of 4Meq₃Al and 4Meq₃Ga.

Figure C-10  NEXAFS spectra at C-edge of 5Meq₃Al and 5Meq₃Ga.

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Figure C-11 NEXAFS spectra at C-edge for In quinolate chelates.
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Figure D-6  Absorbance spectra of 4Meq₃In.

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E-2  I-L curves Device set 1, using Mg-Ag/Mq3/NPD, for Al quinolate chelates.

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E-3  I-V curves Device set 1, using Mg-Ag/Mqj/NPD, for Ga quinolate chelates.

E-4  I-L curves Device set 1, using Mg-Ag/Mqj/NPD, for Ga quinolate chelates.
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E-8  I-L curves Device set 2, using Mg-Ag/Mq3/TPD, for Al quinolate chelates.
E-9  I-V curves Device set 2, for Alq₃ using different HTL.

E-10  I-L curves Device set 2, for Alq₃ using different HTL.
E-11  I-V curves Device set 2, for 4Meq_{3}Al using different HTL.

E-12  I-L curves Device set 2, for 4Meq_{3}Al using different HTL.
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E-16  I-L curves Device set 3, for Mg-Ag/3Meq3Al/NPD.
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E-18  I-L curves Device set 3, for Mg-Ag/Gaq using different HTL.
APPENDIX VI

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Dr. Alessandro Curioni
Research Staff Member
Name (typed)

Computational material science group, IBM Research Division, Zurich Research Lab.
Representing

Signature
Date

11-04-2000
VITA

Graduate College
University of Nevada, Las Vegas

Asanga Bimalchandra Padmaperuma

Local Address:
4247 Cottage Circle, Apt No. 4
Las Vegas, Nevada 89119

Home Address:
69/9D Senanayake Avenue
Nawala, Sri Lanka

Degrees:
Bachelor of Science, Chemistry, 1996
University of Colombo, Sri Lanka

Special Awards:
Graduate Research Training Assistantship, University of Nevada, Las Vegas, 1999.
Justin Samarasekera Award for the Most Outstanding Student, University of Colombo, 1996.
Dr. C L De Silva Memorial Prize for Chemistry, University of Colombo, 1994.
The Studentship Award, University of Colombo, 1993.

Publications:

Thesis Title: Substitution Effects of Metal Quinolate Chelate Materials for Organic Electroluminescence Applications

Thesis Examination Committee:
Chairperson, Dr. Linda S. Sapochak, Ph.D.
Committee Member, Dr. Lydia McKinstry, Ph.D.
Committee Member, Dr. Kathleen A. Robins, Ph.D.
Graduate College Representative, Dr. David Shelton, Ph.D.