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The establishment of the oligomeric purity and molecular structure for n-methylated bis(8-hydroxyquinoline) zinc (n = 0, 2, 4, and 5)

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THE ESTABLISHMENT OF THE OLIGOMERIC PURITY AND MOLECULAR
STRUCTURE FOR NMEQ₂ZN (N = 0, 2, 4, & 5)

by

Anna R. Falkowitz

Bachelor of Science
North Central College
1998

A thesis submitted in partial fulfillment
of the requirements for the

Master of Science Degree
Department of Chemistry
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Graduate College
University of Nevada, Las Vegas
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Anna R. Falkowitz

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The Establishment of the Oligomeric Purity and Molecular Structure

for nMeq₂2n (n = 0, 2, 4, & 5)

is approved in partial fulfillment of the requirements for the degree of

Masters of Science


Examination Committee Chair


Dean of the Graduate College


Examination Committee Member


Examination Committee Member


Graduate College Faculty Representative

ABSTRACT

The Establishment of the Oligomeric Purity and Molecular Structure for $n\text{Meq}_2\text{Zn}$ ($n = 0, 2, 4, \& 5$)

by

Anna R. Falkowitz

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

Znq_2 has been studied as electroluminescent material. However, no correlation of the structure of Znq_2 to resulting device properties has been established. Most reports of Znq_2 as an electroluminescent material have not considered the impact of higher order molecular structures on the device properties. By utilization of size exclusion chromatography it has been determined that the dominant species of $n\text{Meq}_2\text{Zn}$ ($n = 0, 4, 5$) is tetrameric in crystalline form dissolved in chloroform, in thermally vapor deposited films, and in crystalline form dissolved in chloroform and DMSO. The $2\text{Meq}_2\text{Zn}$ was determined to be solely monomeric under the previously mentioned condition. The significance of this work is that it provides the oligomeric structure(s) of the methylated zinc chelates, and the data reveals that the process of thermal vapor deposition, which is used to create organic light emitting devices, do not break up the higher molecular order oligomer.

TABLE OF CONTENTS

ABSTRACT.....	iii
LIST OF FIGURES	vi
ACKNOWLEDGEMENTS	vii
CHAPTER 1 ELECTROLUMINESCENCE AND ORGANIC-LIGHT EMITTING DEVICES.....	1
1.1 Introduction.....	1
1.2 Alq ₃	4
1.3 Znq ₂ and Its Methylated Derivatives	7
1.4 The Purpose of This Thesis.....	12
1.5 Technique.....	12
1.6 References.....	13
CHAPTER 2 EXPERIMENTAL METHODS.....	16
2.1 Introduction.....	16
2.2 Materials	19
2.3 Apparatus	19
2.4 Sample Preparation	20
2.5 Sample Analysis Via Size Exclusion Chromatography.....	20
2.6 References.....	21
CHAPTER 3 RESULTS OF THE SIZE EXCLUSION CHROMATOGRAPHY.....	22
3.1 Comparison of Area and Volume of Metal (8-hydroxyquinoline) Chelates	22
3.2 SEC Results	23
3.3 Discussion of the Oligomeric Purity and Stability of nMeq ₂ Zn Chelates.....	30
3.4 References.....	33
CHAPTER 4 CONCLUSION.....	35
VITA.....	42

LIST OF FIGURES

1.1	Aluminum (III) tris(8-hydroxyquinoline) (Alq ₃).....	3
1.2	Common organic light emitting device.....	3
1.3	Electroluminescent effect.....	4
1.4	Meridional (mer) and facial (fac) geometric isomers of Alq ₃	5
1.5	Possible oligomers of zinc (8-hydroxyquinoline) and the calculated dipole moments ⁴	8
1.6	Orbital amplitude Plots	10
3.1	Structures, formula weights, and dimensions of Alq ₃ and (Znq ₂) _n (n = 1, 2, & 4).....	24
3.2	Chromatograms of ST760, ST2330, Alq ₃ and 8-hydroxyquinoline (q) dissolved in CHCl ₃ showing the utility of SEC for differentiating between the sizes and MW's of the metal chelate and ligand.	25
3.3	Chromatogram for 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (Aldrich) dissolved in CHCl ₃ showing minimal tailing effects.	26
3.4	Size exclusion chromatograms for the crystalline nMeq ₂ Zn chelates dissolved CHCl ₃	27
3.5	Size exclusion chromatography results for the standards and vapor deposited zinc chelate series	29
3.6	Size exclusion chromatography results for the standards and crystalline zinc chelate series with DMSO.....	30

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CHAPTER 1

ELECTROLUMINESCENCE AND ORGANIC-LIGHT EMITTING DEVICES

1.1 Introduction

In the past decade there has been a push to replace traditional television sets and computer monitors with less bulky, more energy efficient, flat panel displays.

Anticipated market interest in flat panel displays and competition from plasma and liquid crystal displays have catalyzed development in organic light-emitting devices (OLED's). The other advantageous properties of OLED's are the synthetic flexibility of organic materials for achieving a wide range of emission colors, high brightness with low drive voltage¹.

The key process for OLED operation is based on organic electroluminescence (EL). The first report of efficient EL using an organic material was reported by Kodak researchers, Tang and Van Slyke in 1987². The important breakthrough from this work was the use of aluminum tris (8-hydroxyquinoline) (Alq_3) as the active EL material and the unique device architecture composed of very thin layers of materials (see Fig. 1.1)².

The device was fabricated on indium tin oxide (ITO, serving as the anode) coated glass by thermal vapor deposition of a preferentially hole transporting layer (HTL) composed of a tertiary aromatic amine followed by deposition of the preferentially electron transporting material (ETL), Alq₃, which also serves as the emissive layer (EML). A top cathode usually composed of a low work function metal or alloy (i.e., Mg:Ag) is then deposited through a shadow mask to complete the OLED³ (see figure 1.2). The desired electroluminescent effect occurs when under an applied voltage electrons from the cathode and holes from the anode are injected and transported through the organic layers where excitons are formed near the organic heterojunction (ETL/HTL interface), which decay to give light emission (see Figure 1.3)⁴. The very thin layers and appropriate choice of organic materials for the ETL/EML and HTL resulted in the first efficient OLED.

The EL light emission energy from an OLED is usually similar to the emission energy achieved by photoluminescence (PL); suggesting that the molecular excited state and relaxation processes leading to light emission are similar for EL and PL, where the difference lies in how the excited state species is formed, either by electrical excitation in the former or by light excitation in the latter. Optimization of PL efficiency in organic molecules requires high extinction coefficient of absorption and favorable radiative relaxation verses nonradiative relaxation processes. However, optimization of EL efficiency is more complicated, and depends on a combination of efficient charge injection, charge transport of both holes and electrons, exciton formation, and finally exciton relaxation to give light emission^{5 & 14}. The appropriate choice of organic materials serving as the HTL and ETL are required in order to provide confinement of

charges in the active EML/HTL interface for efficient formation and relaxation of the molecular exciton.

The utilization of tertiary aromatic amines for the HTL was a result of prior successful applications of this class of molecules for xerography applications. There are fewer organic materials that preferentially transport electrons for serving as the ETL. Although there have been many organic materials studied for EL applications over the last decade, Alq₃ is still the archetypal molecule used for the ETL/EML in OLEDs. The unique properties of this molecule that render it preferentially electron transporting and advantageous as the ETL/EML in OLED's are discussed in the next section.

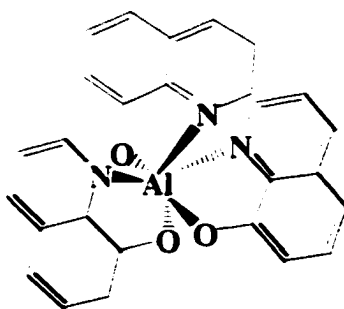


Figure 1.1 Aluminum (III) tris(8-hydroxyquinoline) (Alq₃)

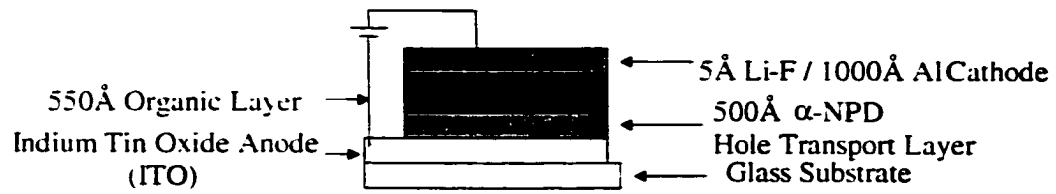


Figure 1.2 Common Organic Light Emitting Device

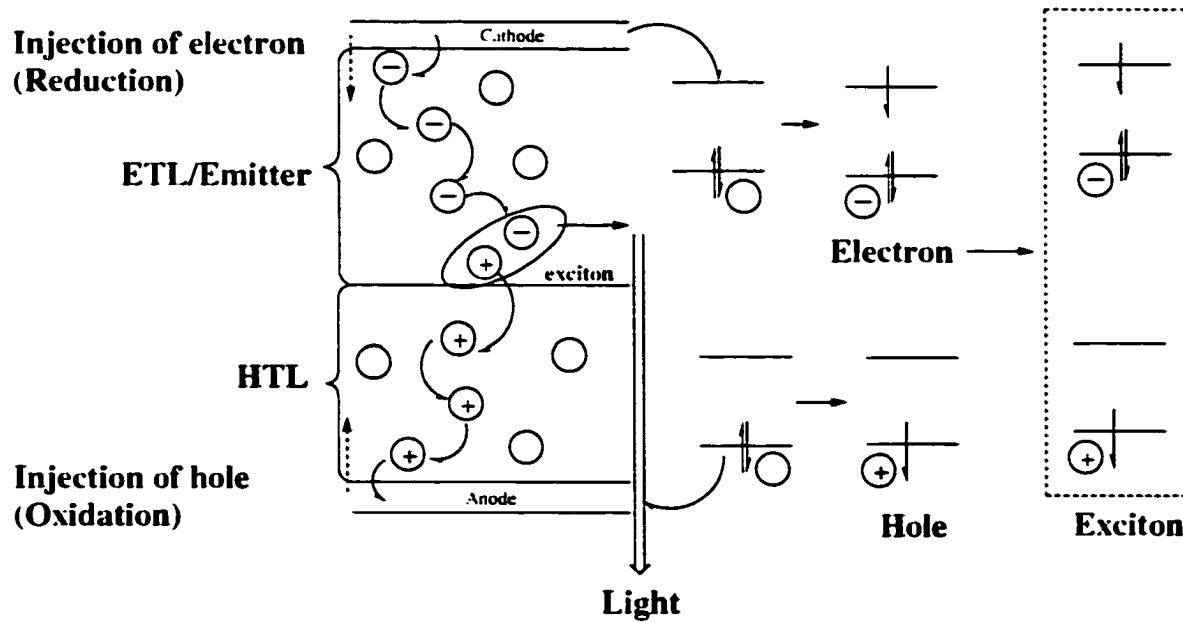


Figure 1.3 Electroluminescent Effect

1.2 Alq₃

1.2.1 Unsubstituted

The most studied organic EL molecule is Alq₃. Alq₃ is composed of a single Al³⁺ metal center surrounded by three 8-hydroxyquinoline ligands resulting in a spherically shaped molecule. The ligands are composed of an electron deficient pyridyl ring fused to an electron rich phenoxide ring, where two geometric isomers are possible upon chelation with Al³⁺, meridional (*mer*) and facial (*fac*) (See figure 1.4).

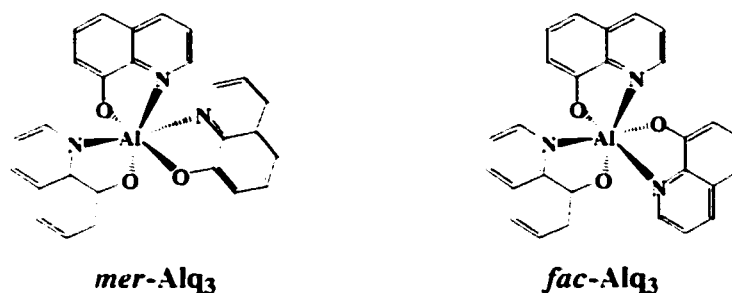


Figure 1.4 Meridional (*mer*) and Facial (*fac*) Geometric Isomers of Alq₃

The structural stability of Alq₃ has been attributed to the proposed presence of the *mer* and *fac* isomers, which, according to Chen et. al. may hinder recrystallization of Alq₃ films¹, because of strong dipole interactions⁶. Based on theoretical calculations, the more symmetrical *fac* isomer has a higher dipole moment and is higher in energy than the *mer* isomer by 4 kcal/mol⁸. If the *fac* isomer is present, even in a very small amount it could significantly change charge conduction mechanisms. This is because, although in the neutral *fac*-Alq₃ is 4kcal/mol higher in energy than *mer*-Alq₃, calculations of the energies of the radical anions indicate that the *fac*-Alq₃ radical anion, formed upon “injection” of

an extra electron, is lower in energy by 0.4 kcal/mol and therefore could act as an electron trap⁸. However, only the *mer* isomer has been observed experimentally^{6&7}, but there is still some question in regards to isomeric purity of vapor deposited films of Alq₃.

It is most likely that the ability of *mer*-Alq₃ to transport electrons may be due to the preferential pyridyl/pyridyl ring overlap identified in at least 3 polymorphic phases of the molecule⁶. The lowest unoccupied molecular orbital (LUMO) is concentrated on the pyridyl ring and is the most likely location for injected electrons, whereas the highest occupied molecular orbital (HOMO) is concentrated on the phenoxide ring, which is the most likely location of the holes created by the removal of an electron⁹. However, the question of Alq₃ isomeric purity and the effect on the overall EL process is still not established. Regardless, most discussions of structure function relationships of Alq₃ in OLEDs usually refer to the *mer*-isomer only.

1.2.2 Affect of Methylation Upon Alq₃

The methylated derivatives of Alq₃, aluminum tris(8-hydroxy-*n*-methylquinoline) (*n*Meq₃Al: *n* = 3, 4, 5) have been shown to have significantly different PL and EL properties. Substitution of the pyridyl ring giving 3Meq₃Al and 4Meq₃Al results in an increase in absorption and emission energies in both polar nonpolar solvents, as well as an enhanced PL efficiency, which is greater for the latter⁹. In contrast, substitution of the phenoxide ring giving 5Meq₃Al decreases the absorption and emission energies accompanied by a substantial decrease in PL efficiency compared to the unsubstituted analogue. The EL efficiencies of identically prepared OLEDs follow similar trends⁹. However, although all methylated derivatives required higher

device operating voltages compared to Alq₃, the 4Meq₃Al exhibited the highest operating voltage, offsetting the higher EL efficiency suggesting that Alq₃ is a superior EL material overall.

Since all nMeq₃Al were shown to be meridinal by ¹H NMR similar to Alq₃, the higher operating voltage for 4Meq₃Al was proposed to be a consequence of decreased pyridyl/pyridyl ring overlap, because the pyridyl ring is the location of the LUMO and the likely site for electron injection⁹. Although the molecular crystal structure and packing preferences have not been determined for the nMeq₃Al chelates, thermal analysis results showed that 4Meq₃Al had a significantly lower melting point (~60°C), suggesting that intermolecular interactions were weaker compared to Alq₃⁹.

1.3 Znq₂ and Its Methylated Derivatives

1.3.1 Znq₂ Vs. Alq₃

The zinc chelate of 8-hydroxyquinoline (Znq₂)₄ has also been studied as an EL material, but not as extensively as Alq₃. Endrino and Sapochak reported photophysical studies of Znq₂ and showed that unlike Alq₃, the absorption and emission properties of Znq₂ are strongly influenced by solvents¹⁰. For example, no differences were observed between the absorption spectra of Alq₃ in CH₂Cl₂ and the more polar solvent, DMF¹⁰. However, Znq₂ exhibited a large red shift of the longest wavelength band. Furthermore, in MeOH, Alq₃ exhibited a small shift to higher energy of absorption, attributed to stabilization of the ground state molecule via H-bonding of the phenolato oxygens of the ligand¹¹. In contrast, Znq₂ exhibited a small shift to lower energy in MeOH, suggesting

that the phenolato oxygens are not available for H-bonding in Znq_2 . These results suggested that the structure of Znq_2 may not be the simple bis-chelate as supposed by most researchers. In fact, Kai et al. showed that anhydrous Znq_2 crystals grown from the vapor phase have a tetrameric structure $(\text{Znq}_2)_4$ composed of two distinct Zn^{+2} ion centers with six- and five-coordinate geometry respectively¹¹. In the tetrameric structure, six of the eight ligands are involved in bridging of the four zinc ions via the phenolato oxygens, rendering the oxygens unavailable for H-bonding interactions in protic solvent.¹¹ This suggests that unlike Alq_3 , where there is concern in regards to 'isomeric' purity, for Znq_2 , one must be concerned about 'oligomeric' purity. However, only recently has the effect of oligomerization of Znq_2 on electroluminescent properties been considered.

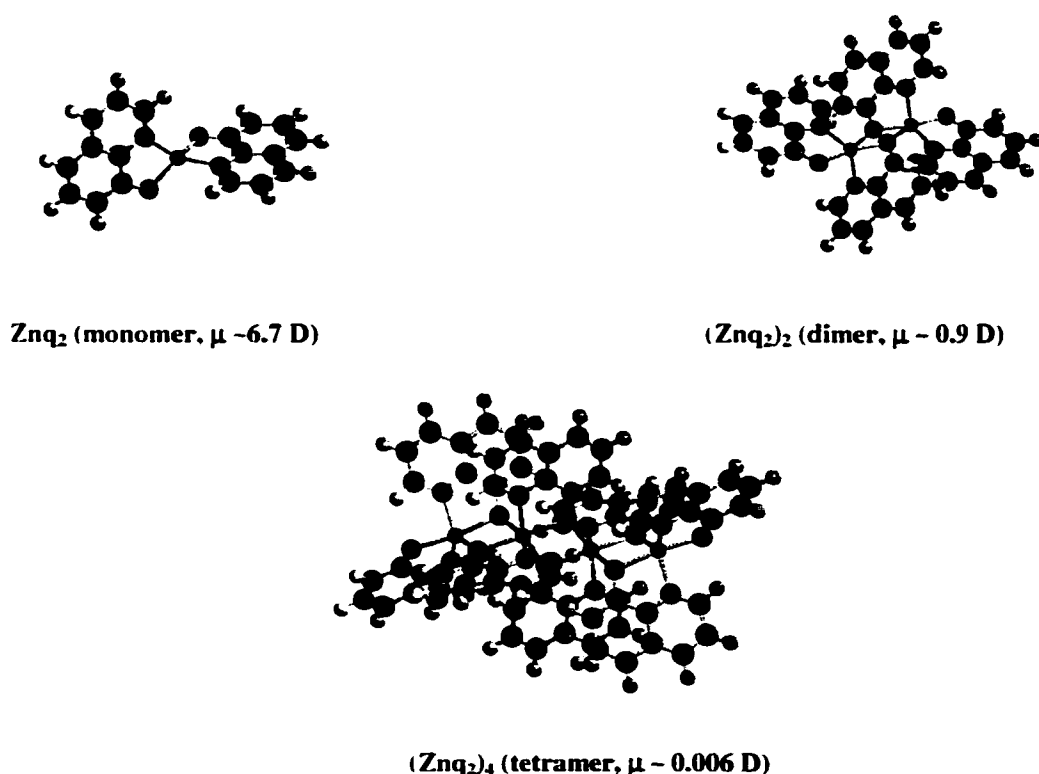


Figure 1.5 Possible oligomers of zinc (8-hydroxyquinoline)
and the calculated dipole moments⁴

Sapochak, et al. showed that Znq_2 purified by high vacuum gradient temperature sublimation, the common technique used for purifying EL materials, was indeed tetrameric by x-ray diffraction studies⁴. The sole presence of the tetramer $[(\text{Znq}_2)_4]$ over smaller oligomers, such as a dimer $[(\text{Znq}_2)_2]$ or monomer Znq_2 was evaluated experimentally and theoretically (see Fig. 1.5). Since there are differences in both the sizes and polarities of the Znq_2 monomer, dimer, and tetramer, based on calculated dipole moments, different melting points for these oligomers would be expected. Thermal analysis of crystalline $(\text{Znq}_2)_4$ by differential scanning calorimetry (DSC) showed a single endothermic transition at several heating rates. They concluded that if smaller oligomeric species were present or formed by molecular rearrangement during fusion of $(\text{Znq}_2)_4$, additional enthalpic transitions would be expected to become resolved at slower heating rates. Furthermore, thermal analysis of the material after sublimation under similar conditions used to fabricate OLEDs also resulted in a single melting peak⁴. These results suggest that the supramolecular $(\text{Znq}_2)_4$ is stable to sublimation and is most likely the sole species in vapor deposited films used in OLEDs.

However, Hopkins et al, reported that the ^1H NMR spectrum of Znq_2 in CDCl_3 showed a single set of aromatic resonances, but upon addition of the polar solvent, DMSO- d_6 , a second set of aromatic resonances was observed. They concluded that the nonpolar tetramer was stable in CDCl_3 , but was disassociated to the monomer by the nucleophilic DMSO solvent¹². Additional studies are necessary to establish the stability of this supramolecular structure both in solution and especially in vapor deposited films.

1.3.2 The Structure of Tetrameric Znq_2 and the Structural Affects on Electronic Properties

The overall structure of $(\text{Znq}_2)_4$ is quite different than Alq_3 . $(\text{Znq}_2)_4$ as explained by Kai et al. is comprised of two types of Zn^{2+} , which include the two central hexacoordinate atoms which causes a highly distorted octahedral geometry, and two terminal pentacoordinate zinc atoms which cause distorted trigonal bipyramidal geometry (see Figure 1.5)¹¹. $(\text{Znq}_2)_4$ is symmetrical with 9 centers of inversion and a dipole moment almost equal to zero. These centers of inversions include one at the middle of the tetramer and one on each of the terminal ends. The two centers of symmetry at the terminal ends of the structure forces the intermolecular π - π stacking of the terminal ligands of adjacent tetrameric units. The π - π stacking of adjacent tetramers occurs through the pyridyl and phenolato rings, which is significantly different than the preferred pyridyl/pyridyl ring stacking of mer- Alq_3 . Furthermore, $(\text{Znq}_2)_4$ also exhibits intramolecular π - π stacking with the central ligands of the tetrameric structure. The tetramers electronic structure is directly effected by the molecular symmetry where the (HOMO) is located on the two nonbridging terminal ligands (See figure 1.6a) and the LUMO is located at the site of Π - Π stacking interactions, the two bridging terminal ligands⁴(See figure 1.6b).

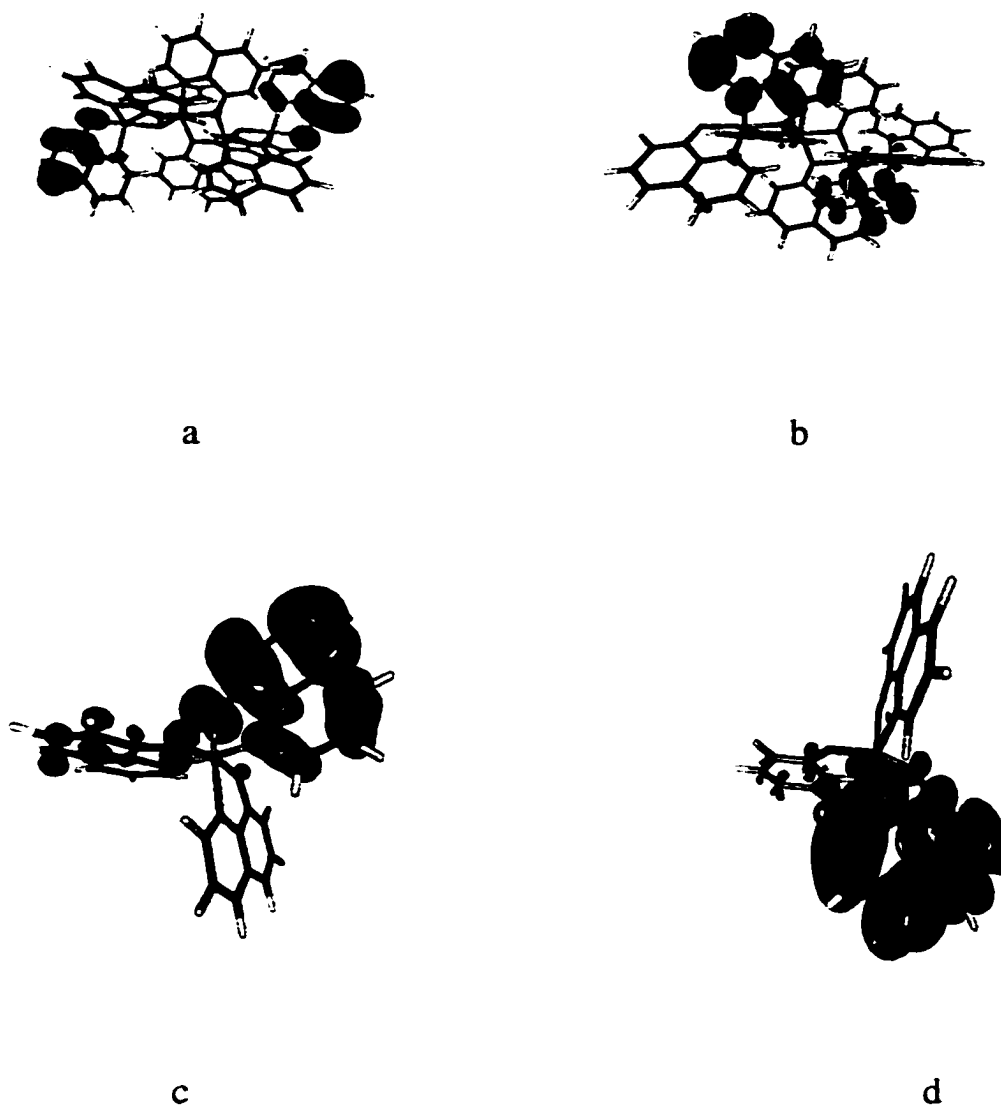


Figure 1.6 Orbital amplitude plots of a). HOMO $(\text{Znq}_2)_4$ (tetramer), b). LUMO $(\text{Znq}_2)_4$ (tetramer), c). HOMO *mer*-Alq₃ and Lumo *mer*-Alq₃

A comparison of identically prepared OLEDs utilizing the EL materials $(\text{Znq}_2)_4$ and Alq₃ showed that the operating voltage was lower for the $(\text{Znq}_2)_4$ -based OLEDs⁹. It was proposed that the strong π - π stacking interactions in $(\text{Znq}_2)_4$ provides a more efficient electron transport pathway compared to Alq₃ and may be the reason for lower device operating voltage.

3.1.3 Methylated Derivatives of Znq_2

Originally Znq_2 and its methylated derivatives ($2\text{Meq}_2\text{Zn}$, $4\text{Meq}_2\text{Zn}$, $5\text{Meq}_2\text{Zn}$) were thought to be monomeric, however, the absorption and emission properties of the $4\text{Meq}_2\text{Zn}$ and $5\text{Meq}_2\text{Zn}$ in photophysical studies mirror that of tetrameric Znq_2 with large red shifts of the longest wavelength band between the absorption spectra in CH_2Cl_2 and the more polar solvent, DMF^{14} , and a small shift to lower energy in MeOH^{14} . For the $2\text{Meq}_2\text{Zn}$ the absorption and emission spectra mirrored Alq_3 . In the case of the $4\text{Meq}_2\text{Zn}$, this chelate gives the highest EL efficiency for the Znq_2 series but also the lowest operating voltage. This is different from $4\text{Meq}_3\text{Al}$ which also gives higher EL efficiency compared to the unsubstituted analogue (Alq_3) but at a higher operating voltage,⁵ as discussed previously. It is more likely that the $4\text{Meq}_2\text{Zn}$ and $5\text{Meq}_2\text{Zn}$ exist as higher oligomers, such as the tetrameric structure reported by Kai¹¹. However, the nature of the oligomeric structure(s) must be dependent on the position of methylation of the ligand as suggested by the differences in photophysical properties exhibited by $2\text{Meq}_2\text{Zn}$ compared to Znq_2 and its other methylated derivatives³. Therefore, an explanation for the solvent dependent photophysical properties, the voltage requirements, and the EL efficiency of $n\text{Meq}_2\text{Zn}$ chelates requires determination of their molecular structure.

1.4 The Purpose of This Thesis

The purpose of this thesis is to investigate the oligomeric purity of the $n\text{Meq}_2\text{Zn}$ chelates ($n = 0, 2, 4, 5$), which is essential for establishing structure/function relationships in OLED performance. As shown by previous studies the molecular structure confers

upon the $(\text{Znq}_2)_4$ symmetry that becomes a critical factor in intermolecular interactions and might account for the differences in the behavior of Znq_2 and Alq_3 as EL materials in OLEDs.

Although photophysical and thermal analysis results suggest that $4\text{Meq}_2\text{Zn}$ and $5\text{Meq}_2\text{Zn}$ are tetrameric and $2\text{Meq}_2\text{Zn}$ monomeric, additional information is necessary to confirm this supposition. However, all zinc chelates have only limited solubility in organic solvents and are difficult to analyze by NMR spectroscopy – only giving broad peaks as discussed by Endrino (2001). However, since the tetrameric structure has been confirmed for the unsubstituted material, $(\text{Znq}_2)_4$ it can be used as a standard in size exclusion chromatography studies to determine if indeed the methylated derivatives are also large supramolecular structures. This information will be important for better understanding the significantly different EL performance of the $n\text{Meq}_2\text{Zn}$ chelates compared to the corresponding $n\text{Meq}_3\text{Al}$ materials.

1.5 Technique

The purpose of this thesis work was to use gel permeation chromatography, GPC, (size exclusion chromatography) to investigate the oligomeric purity of Znq_2 and its methylated derivatives. This technique was used because the column packing is made up of chemically inert polystyrene “beads” that contain pores and allows for the separation of molecular species based on size rather than chemical interactions with the column. Larger molecular weight structures will interact with the column less and exhibit a shorter retention time as compared to lower molecular weight molecules, which will interact with the column more and have a longer retention times.

Three types of samples were analyzed to access the stability of the tetrameric structure and/or presence of other oligomers (dimer or monomer) in different solvents and after thermal evaporation: 1) crystalline material dissolved in a nonpolar solvent (CHCl_3); 2) crystalline material dissolved in CHCl_3 with the addition of polar DMSO added; and 3) amorphous material formed by thermal vapor deposition dissolved in CHCl_3 . The experimental setup for these studies is presented in Chapter 2 and results are presented in Chapter 3. A discussion of the implications of this work on understanding the properties of nMeq_2Zn chelates as EL materials and conclusions of these studies will be presented in Chapter 4.

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CHAPTER 2

EXPERIMENTAL METHODS

2.1 Introduction

Size exclusion chromatography (SEC), also known as gel permeation chromatography (GPC) was used to investigate the oligomeric purity of zinc (8-hydroxyquinoline) chelates. Separation of different size oligomers can be achieved because larger molecular species will elute off the column at faster retention times, whereas smaller molecular species will enter the pores of the column and elute off at slower retention times. The stationary column used in this work was composed of porous, chemically inert polystyrene beads allowing for separation of molecular species based on size rather than chemical interactions with the column. The mobile phase in SEC must be a solvent that is compatible with the column and pumping system, as well as provide adequate solubility of test samples.

Determining the appropriate solvent system was the biggest challenge. Three important factors were considered when choosing the appropriate solvent for the mobile phase: 1) sufficient solubility of metal chelates; 2) good stability of metal chelates; and 3) no swelling of the polystyrene column. The known structure for the unsubstituted Znq_2 is the symmetrical tetramer, which is nonpolar (dipole moment ~ 0.006 D), and therefore should have better solubility in less polar solvents. In fact, all $nMeq_2Zn$

chelates have only limited solubility in both polar and nonpolar solvents. Previously, Hopkin's proposed based on ¹HNMR spectroscopic studies that the Znq₂ was stable as the tetramer in chloroform, but was disassociated to the monomeric species in the polar, nucleophilic solvent dimethylsulfoxide⁵. Therefore, for both solubility and stability purposes only low polarity solvents, such as dichloromethane, chloroform, benzene, tetrahydrofuran, and combinations of these solvents were considered. The nMeq₂Zn chelates exhibited the greatest solubility in benzene, but this solvent swelled the polystyrene column and no separation was achieved.

Dichloromethane was tested as the mobile phase solvent, but was too volatile and caused the pump to cavitate. Tetrahydrofuran (THF) did not provide sufficient solubility of the standards or metal chelates and therefore was not an appropriate solvent for these studies. Mixtures of tetrahydrofuran and dichloromethane were tested unsuccessfully due to the refractive index detecting a peak and flat lining at the maximum response units. The optimum solvent tested was chloroform, which provided adequate solubility of both the standards and metal chelates and did not swell the polystyrene column. However, the volatility of chloroform resulted in loss of solvent during filtration and injection of the samples and some precipitation on the guard column. Therefore, the procedure presented here is not quantitative because only an approximate concentration of sample injected on the column is unknown.

Two polystyrene standards with molecular weights 2330 and 760 amu were chosen because the molecular weight of the tetramer (1414/1526 unmethylated/methylated tetramer amu) falls between the standards. The molecular weight of the dimer (763 – 707 amu) and monomer (382-354 amu) falls below the

standards. However, it must be noted that the molecular weights of the standards cannot be accurately compared to the zinc chelates because they are different types of materials. The polystyrene standard is a chain and therefore might undergo some folding and therefore the possibility of size not corresponding to molecular weight is a factor. Based on the separation of the two standards the flow rate of the solvent system was established.

Next, Alq_3 was run through the column in order to insure that metal chelates were not falling apart. It has been well established that only one oligomeric form of Alq_3 exists⁴ and therefore only one peak should be present on the column if the molecule has not dissociated. The tris-chelate, Alq_3 was also used as a way to compare sizes of the zinc chelates. The tetramer and the dimer would be bigger and have a shorter retention time than Alq_3 , and the monomer would be smaller and therefore have a longer retention time than Alq_3 . So both the size and molecular weights are significantly different to allow for separation on the SEC column. Third, Gaq_3 and Inq_3 were chosen to better establish that the column was not causing a metal surrounded by ligands of 8-hydroxyquinoline to molecule to dissociate. Also, gallium and indium which are found in the same family of the periodic table as aluminum have different molecular sizes due to the metal ion (Al^{+3} (~0.5 Å), Ga^{+3} (~0.65 Å), In^{+3} (0.8 Å)), and therefore running them through the column will allow for the confirmation of separation based on size. Alq_3 , Gaq_3 , and Inq_3 were used to determine if a metal surrounded by ligands of 8-hydroxyquinoline would dissociate, if separation based on size was following expected patterns, and as comparison molecules for the zinc chelate series. Finally, the 8-hydroxyquinoline ligand was tested to see where the ligands would elute if any of the chelates dissociated. The 2, 4, and 5 methylated ligands were not tested because the

equipment and technique being used was not sensitive enough to separate a compound based on one additional methyl group.

Once appropriate experimental conditions were worked out, the following samples of $n\text{Meq}_2\text{Zn}$ chelates were tested: 1) crystalline sample dissolved in chloroform; 2) amorphous sample formed by thermal vapor deposition and dissolved in chloroform; and 3) crystalline sample dissolved in chloroform (CH_2Cl_2) with the addition of polar dimethylsulfoxide (DMSO). These three sets of conditions were chosen to establish the stability of the Znq_2 tetramer in the presence of nonpolar versus polar solvent and to thermal vapor deposition.

2.2 Materials

The metal chelates, Alq_3 and $(\text{Znq}_2)_4$ were obtained from Aldrich Chemical, Co. and synthesis and characterization of $(n\text{Meq}_2\text{Zn})_4$ chelates ($n = 2, 4, \& 5$) have been reported previously^{2,3,4}. All metal chelates were purified by high vacuum gradient temperature sublimation using zone controlled heating under pressure to achieve separation of metal chelate from impurity.

2.3 Apparatus

Size exclusion chromatography was performed using high performance liquid chromatography (HPLC) equipment consisting of a B-100-S pump (Eldex Laboratories, Inc.), a 50 μL injector loop, a guard column (Alltech Associates), a 300mm x 7.8 mm polystyrene size exclusion 100Å column (Jordi Gel) (Alltech Associates, Inc.), a refractive index detector (Shodex RI-71), and an IBM 286 computer with "Simple Peak" software (SRD). The mobile phase was amylene stabilized high performance liquid

chromatography (HPLC) grade chloroform (Aldrich). The DMSO was high purity solvent from Burdick & Jackson Brand[™]. Polystyrene molecular weight (MW) standards (760 and 2330 amu) were obtained from Aldrich Chemical, Co..

2.4 Sample Preparation

For each sample, 5 mg was weighed into a 5 ml volumetric flask and dissolved in chloroform. The ligands, Alq₃, and the polystyrene standards dissolved completely in chloroform giving known concentrations of 1mg/mg. However, the exact concentration of the nMeq₂Zn chelates was not known because samples did not dissolve completely in chloroform and had to be filtered through a 0.2 µm filter before injecting on the column. Samples run in chloroform/DMSO mixtures were prepared in the same manner described above, except 10 µl of DMSO was added to each sample prior to injection on the column. Note that the zinc chelates were filtered prior to addition of DMSO. Finally, amorphous samples were prepared as films on quartz slides by resistive thermal vapor deposition of the crystalline powder from a baffled Ta crucible at a nominal deposition rate of 1-3 Å/s under a base pressure of $< 5 \times 10^{-7}$ Torr. Films were dissolved off the slide with 5 ml of CH₃Cl and filtered through a 0.2 µm filter before injection on the column. No attempt was made to determine the concentration of these samples. Each sample was run at least several times to insure reproducibility of the results.

2.5 Sample Analysis Via Size Exclusion Chromatography

For each sample, 25 µL was injected into the injection port and monitored for up to 25 minutes. The sample was pumped through the HPLC at a pressure of between 850

PSI and 900 PSI (a flow rate of .8ml/min). After passing through the refractive index detector the sample was collected in a waste container. The computer program, "Simple Peak", displayed and stored the data from the refractive index detector. The data was transferred to "Microsoft Excel" and then put into "Origin" software where it will be graphically displayed in the results section of this thesis.

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CHAPTER 3

RESULTS OF THE SIZE EXCLUSION CHROMATOGRAPHY

3.1 Comparison of Area and Volume of Metal (8-hydroxyquinoline) Chelates

Since the utility of size exclusion chromatography is to separate chemical species according to their size, a discussion of the differences in sizes between the metal (8-hydroxyquinoline) chelates studied is presented. The area and volume of mer-Alq₃ and (Znq₂)₄ (tetramer), (Znq₂)₂ (dimer), and Znq₂ (monomer) were calculated using *ab initio* Hartree-Fock (HF) calculations performed using the PC version of the GAMESS and Spartan systems of electronic structure programs as reported previously.³ Molecular geometries were force optimized at the SCF level using the 3-21G* basis set using C₁ symmetry. Starting geometries for these optimizations were derived from the x-ray crystal structures for mer-Alq₃ and (Znq₂)₄ reported by Brinkman, et al.¹, and Kai et al.², respectively.

The molecular structures including molecular weight (MW), area, and volumes are shown in Fig. 3.1 and a comparison of the magnitude of the size differences based on area, volume, and MW are shown in Table 3.1. Based on these comparisons, the differences in sizes are similar regardless of which parameter is used for the comparison. For example, the calculated areas and volumes of the Znq₂ monomer and dimer are ~2X

and 4X smaller than the tetramer, which corresponds well with their differences in MW. The difference between mer-Alq₃ and the smallest zinc oligomer (Znq₂), shows that the tris-chelate is ~ 1.3X larger in size than the bis-chelate. These results suggest that separation of these metal chelates according to size should be feasible.

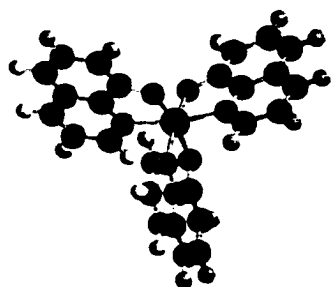
Table 3.1 Size Comparisons of Metal (8-hydroxyquinoline) Chelates

Size Comparison	Ratio of Volumes	Ratio of Areas	Ratio of MW's
(Znq ₂) ₄ / (Znq ₂) ₂	1.8	1.5	2.0
(Znq ₂) ₂ /Znq ₂	1.8	1.6	2.0
(Znq ₂) ₂ /Alq ₃	1.4	1.2	1.4
Alq ₃ /Znq ₂	1.3	1.3	1.3

3.2 SEC Results

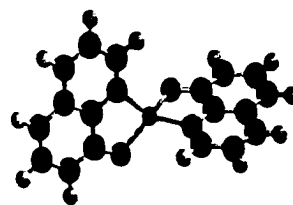
3.2.a Results for Reference Samples in CHCl₃

The size exclusion chromatograms for ST760, ST2330, Alq₃, and 8-hydroxyquinoline (q) obtained in CH₃Cl as the mobile phase are shown in Fig 3.2. A single peak was observed for both Alq₃ and 8-hydroxyquinoline (q) with retention times longer (15.1 minutes and 20.3 min, respectively) than the smaller MW standard ST760 (13.1 minutes) indicating a good correspondence to the smaller size and MW's (459.4 and 145.16, respectively) of these reference materials. The MW standard ST2330 appeared at the shortest retention time (8.05 minutes) and gave a broader peak because of a larger polydispersity compared to ST760⁴



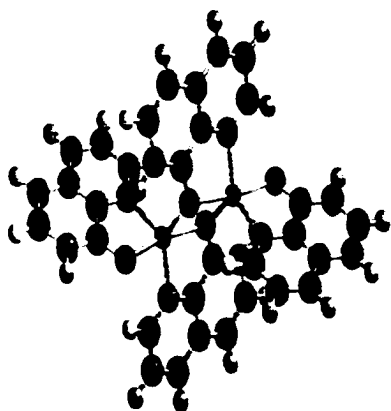
mer-Alq₃ FW = 496 AMU

Area = 656.65 Å² & Volume = 1154.91 Å³



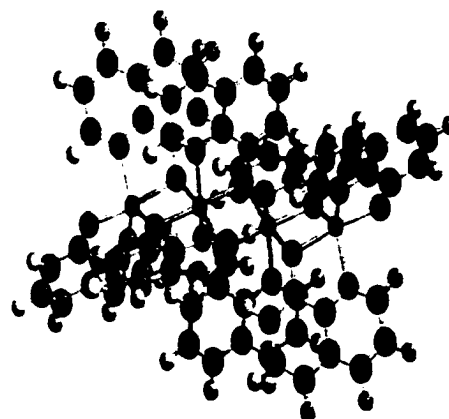
Znq₂ -Bisquinolate FW = 381.6 amu

Area = 511.58 Å² & Volume = 847.65 Å³



Znq₂ -Dimer FW = 707 amu

Area = 820.64 Å² & Volume 1528.72 Å³



Znq₂-Tetramer FW = 1414 amu

Area = 1239.37 Å² & Volume = 2717.29 Å³

Figure 3.1 Structures, formula weights, and dimensions of Alq₃ and (Znq₂)_n (n = 1, 2, & 4)

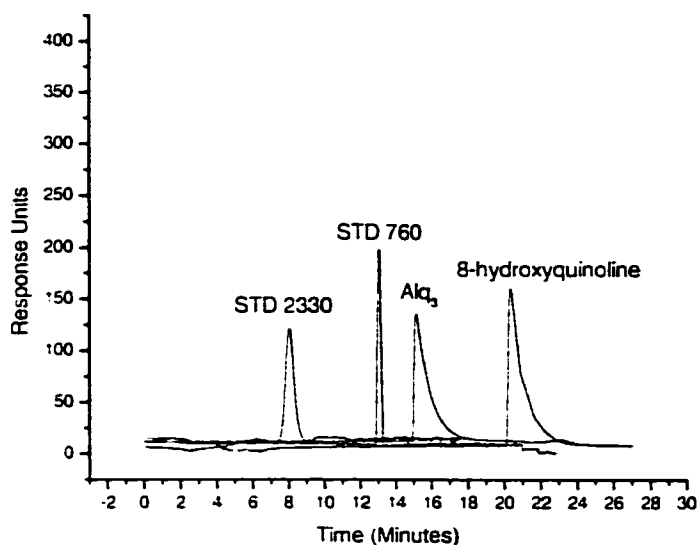


Figure 3.2 Chromatograms of ST760, ST2330, Alq₃ and 8-hydroxyquinoline (q) dissolved in CHCl₃ showing the utility of SEC for differentiating between the sizes and MW's of the metal chelate and ligand.

Although “tailing” of both Alq₃ and q peaks was observed there was no evidence for decomposition of the metal chelate on the column. According to Strobel and Heineman, “asymmetry in a peak cannot be related directly to a specific process”⁵. However, there are certain phenomena that will influence the shape of the peaks. This includes basic principles of chromatography where the sample will only flow through the column in the mobile phase, but if a sample is caught in the stationary phase it will not flow through the column and produce a lagging effect⁵. A reason the sample might lag and briefly get caught in the stationary phase is due to surface interactions with the beads of the column. In manufacturing a polystyrene column some compounds with functional groups are used that cannot be completely removed and interact with the injected sample thus causing a tailing effect⁶. The oxygen atom of the 8-hydroxyquinoline ligand is a possible site of interaction with the column. To test this possibility 2,9-dimethyl-4,7-

diphenyl-1,10-phenanthroline (360.46 amu), which does not have any oxygen atoms, was tested on the column and the chromatogram is shown in Fig. 3.3. This sample gave a single peak with very little tailing compared to Alq₃ or the ligand, suggesting that the oxygen might chemically interact with the column slightly.

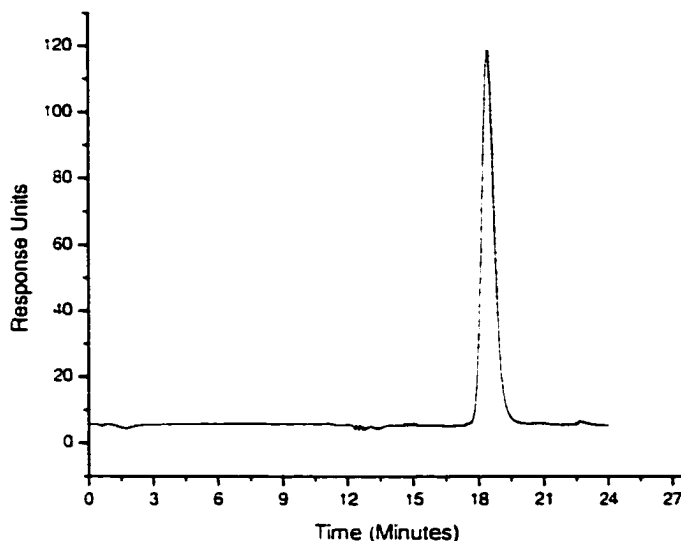


Figure 3.3 Chromatogram for 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (Aldrich) dissolved in CHCl₃ showing minimal tailing effects.

3.2.b Results for Crystalline nMeq₂Zn Chelates in CHCl₃

The size exclusion chromatograms for crystalline nMeq₂Zn chelates ran in CHCl₃ are shown in Fig. 3.4. The unsubstituted Znq₂ has already been shown to be tetrameric (MW = 1414 amu) in the solid state¹, and indeed a single chromatographic peak with a retention time of 11.6 minutes was observed, which falls at a retention time between ST2330 and ST760. Single peaks were also observed for crystalline 4Meq₂Zn and 2Meq₂Zn at 11.6 minutes and 18.5 minutes, respectively. The retention time for 4Meq₂Zn was identical to (Znq₂)₄, suggesting that 4Meq₂Zn is similar in size and likely

tetrameric. In contrast, the much longer retention time observed for $2\text{Meq}_2\text{Zn}$ falling between the retention times for Alq_3 and q , suggests that $2\text{Meq}_2\text{Zn}$ is monomeric ($\text{MW} = 381.6$). The $5\text{Meq}_2\text{Zn}$ chelate was unique in the zinc chelate series because three peaks (11.1 minutes, 16.1, and 18.1 minutes) were detected, suggesting that more than one oligomeric species was present. The first peak eluted off the column near the retention time for the tetramer and was the most prominent peak, indicating a greater concentration of this oligomeric species. The third peak was detected at a retention time similar to the retention time for $2\text{Meq}_2\text{Zn}$. The second peak was the smallest eluting from the column at 16.1 minutes between the tetramer and monomer suggesting that it might be a dimer. However, it has a longer retention time than Alq_3 which is opposite of what is expected, therefore the possibility of an impurity of a transitional zinc chelate species cannot be ruled out. $5\text{Meq}_2\text{Zn}$ is composed of a mixture of tetrameric and monomeric structures, and a third species that's nature is not exactly clear.

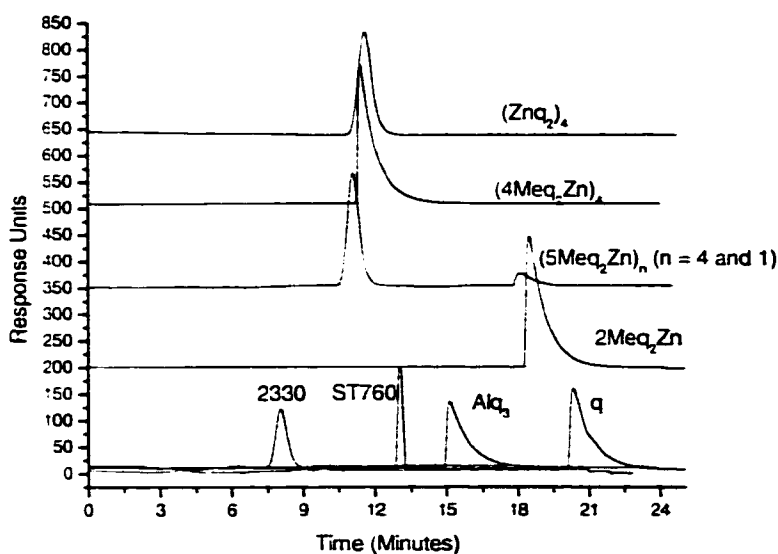


Figure 3.4 Size exclusion chromatograms for the crystalline $n\text{Meq}_2\text{Zn}$ chelates dissolved CHCl_3 .

3.2.c Amorphous (Vapor Deposited Films) of nMeq₂Zn Chelates in CHCl₃

It is noted that the solubility of the vapor deposited films was significantly higher compared to the crystalline materials, where all material dissolved in CHCl₃ and filtration of the solution was not necessary prior to injection on the column. The SEC results for the vapor deposited film samples are shown in Fig. 3.5. There was no difference in the number of peaks and retention times between the crystalline and vapor deposited film samples for Alq₃, (Znq₂)₄, and 4Meq₂Zn. These results suggest that upon thermal vapor deposition no deleterious changes in the structure of these materials occurred. However, small changes in the retention times between the crystalline and vapor deposited samples was observed for 2Meq₂Zn and 5Meq₂Zn, but the number of peaks for the 2Meq₂Zn did not change. The 5Meq₂Zn sample exhibited the most change with disappearance of the second peak previously observed at 16.1 minutes and differences were largest for the retention times increased for both peaks by 0.7 minutes for the tetramer o and 0.3 minutes for the monomer.

3.2.d Crystalline nMeq₂Zn Chelates in CHCl₃/DMSO

The polar solvent, dimethyl sulfoxide (DMSO) was added to the filtered crystalline solutions and the SEC results are shown in Fig. 3.6. Upon addition of DMSO a dip in the spectra was detected at approximately 24 minutes, which corresponded to DMSO coming off the column and the void volume. The unsubstituted (Znq₂)₄ showed a predominant peak eluted off the column at 11.5 minutes. However, with the addition of the polar DMSO solvent a second much smaller peak eluted from the column at 18.4 minutes between Alq₃ and 8-hydroxyquinoline which was similar to the retention time for monomeric Znq₂ ran in CHCl₃ only. The behavior of the 4Meq₂Zn in the presence of

DMSO was identical to the unsubstituted zinc chelate where a prominent peak at 11.7 minutes and a second smaller peak at 18.4 minutes were observed. The number of peaks in the chromatograms for $2\text{Meq}_2\text{Zn}$ were not affected by the presence of DMSO. Similar to the results observed in CHCl_3 , three peaks for $5\text{Meq}_2\text{Zn}$ (11.5 minutes, 16.7, and 18.5 minutes) were observed. The peaks for the $5\text{Meq}_2\text{Zn}$ are consistent with the tetramer, monomer, and a third species that's nature is not determined.

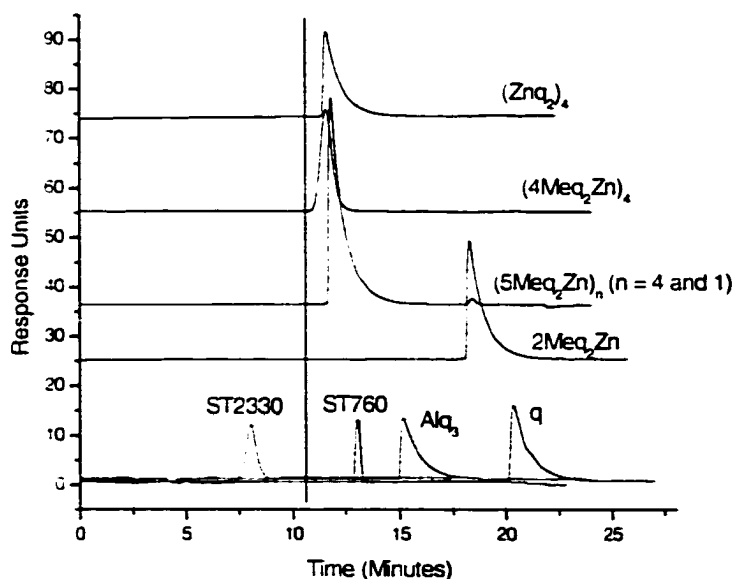


Figure 3.5 Size exclusion chromatography results for the standards and vapor deposited zinc chelate series

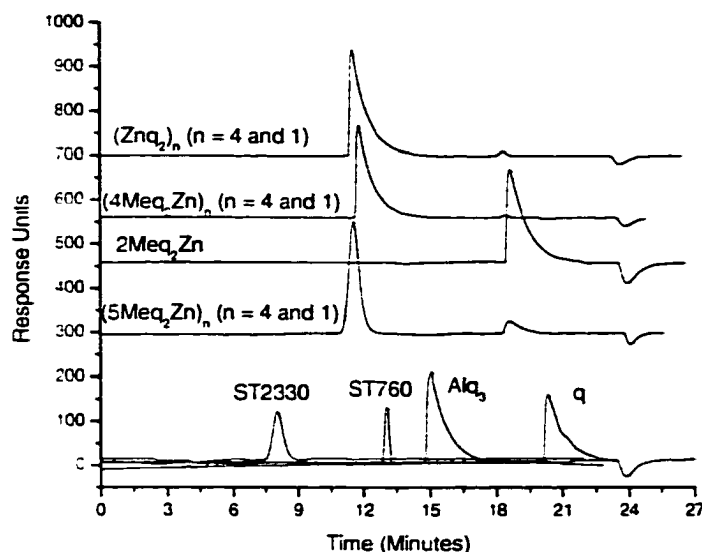


Figure 3.6 Size exclusion chromatography results for the standards and crystalline zinc chelate series with DMSO

3.3 Discussion of the Oligomeric Purity and Stability of $nMeq_2Zn$ Chelates

The tetrameric structure of crystalline Znq_2 was previously established by both single crystal² and powder x-ray diffraction studies³. The SEC results reported here showed a single peak in the MW range between the two polystyrene standards at a retention time 1.3X shorter than the smaller Alq_3 molecule for both the crystalline material and sample after thermal vapor deposition for both $(Znq_2)_4$ and $4Meq_2Zn$. These results suggest that the tetrameric structure is stable in nonpolar solvents and after thermal vapor deposition.

However, SEC results for $(Znq_2)_4$ and $4Meq_2Zn$ in the presence of DMSO showed an additional smaller peak at a retention time 1.2X *longer* compared to Alq_3 , but still at a retention time shorter than the ligand itself, suggesting that the tetramer begins to disassociate to smaller oligomeric species in the presence of polar solvents. Based on the

SEC results for $2\text{Meq}_2\text{Zn}$ the likely form of this new oligomeric species is monomeric. Because of steric hindrance effects caused by methylation at the C2 position of the ligand and resulting differences in photophysical and thermal analysis data it was previously proposed that $2\text{Meq}_2\text{Zn}$ was monomeric. The SEC results for crystalline $2\text{Meq}_2\text{Zn}$ in both CHCl_3 and $\text{CHCl}_3/\text{DMSO}$ showed a single peak eluting at approximately the *same* retention time as the smaller peak observed for $(\text{Znq}_2)_4$ in the presence of DMSO. Since the dimer would be expected to elute at a shorter retention time than Alq_3 , based on the difference in sizes as discussed in Section 3.1, $2\text{Meq}_2\text{Zn}$ must be monomeric and stable in this form even in the presence of a polar solvent. These results suggest that the $(\text{Znq}_2)_4$ (tetramer) disassociates in the presence of a polar solvent *directly* to the monomer without showing evidence for any other oligomeric species, such as the dimer. The mechanism for the disassociation of the tetramer is not known, but it is speculated to start at the two central hexacoordinated zinc atoms because they have the longest bond lengths. The $5\text{Meq}_2\text{Zn}$ exhibited the most dynamic behavior of all the chelates. The crystalline $5\text{Meq}_2\text{Zn}$ dissolved in chloroform and dissolved in chloroform and DMSO had three peaks which correspond to the tetramer, monomer, and a third species that has not been identified. The unidentified species might be the dimer, however, it has a longer retention time than Alq_3 which indicates that it is smaller than Alq_3 which is inconsistent with the size of the dimer (see figure 3.1). It is possible that the unidentified species is an impurity or some type of transitional zinc chelate. In the thermally vapor deposited $5\text{Meq}_2\text{Zn}$ only has two peaks which are consistent with the tetramer and monomer.

Table 3.2 Summary of Retention Times Under Different Sampling Conditions

Metal Chelate	Cryst. Material Retention Time (CHCl ₃)	Vap. Dep. Material Retention Time	Cryst. Material Retention Time (CHCl ₃ /DMSO)
ST2330	8.0	----	8.0
ST760	13.1	----	13.1
Q	20.3	----	20.3
Alq ₃	15.1	15.1	15.1
(Znq ₂) ₄	11.6	11.6	11.5, 18.3
(4Meq ₂ Zn)	11.4	11.6	11.8, 18.4
(2Meq ₂ Zn)	18.5	18.3	18.6
(5Meq ₂ Zn)	11.1, 16.1, 18.1	11.8, 18.4	11.5, 16.7, 18.5

Throughout the crystalline, vapor deposited films, and crystalline with DMSO samples tailing was observed for the chelates with some inconsistency. For crystalline zinc chelates in chloroform the unsubstituted and the 5methylsubstituted (tetramer) did not posses the tail like that of the 2Meq₂Zn, 4Meq₂Zn, Alq₃ and q (see figure 3.5). For the vapor deposited films all the zinc chelates had a tail except the 4Meq₂Zn. Finally for the samples in CHCl₃/DMSO tailing is present for Alq₃, q, and all of the zinc chelates except for 5Meq₂Zn (tetramer), which looks like crystalline 5meq₂Zn in CHCl₃ (see figures 3.4 & 3.7). No one reason is the known cause of tailing³, but in this cause it might be due to a cumulative effect of interaction with the column and concentration. In manufacturing a polystyrene column some compounds with functional groups are used that cannot be completely removed and interact with the injected sample thus causing a tailing effect⁴. The metal chelates oxygen atom on the 8-hydroxyquinoline ligand is a possible site of interaction with the column. To test that possibility 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (360.46 amu), which does not have any oxygen atoms, was run through the column (see figure 3.3). and does not show tailing. This suggests that the oxygen atoms can be part of the reason for the tailing seen for Alq₃, q, and the zinc

chelates. The concentration argument being part of the cause for tailing is harder to make because the volume of zinc detected was not possible to obtain because not all the crystalline chelates did not dissolve completely in chloroform, the volatile nature of chloroform, and the precipitate build up on the guard column. The fact that all the vapor deposited thin film chelates dissolved completely in chloroform and the fact that the crystalline material had to be filtered does not add anything to the argument of concentration because it is not known how much of each type of material precipitated out on the column and reach the detector. At this point further experimentation is necessary to come up with a satisfactory explanation for the tailing observed in the zinc chelate series.

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CHAPTER 4

CONCLUSION

The purpose of this thesis was two fold, first to investigate the “oligomeric purity” of the $n\text{Meq}_2\text{Zn}$ chelates ($n = 0, 2, 4, \& 5$), which is essential for establishing structure/function relationships in OLED performance, and second investigate the structural stability of the $n\text{Meq}_2\text{Zn}$ chelates ($n = 0, 2, 4, 5$). By utilizing size exclusion chromatography the “oligomeric purity” of the crystalline and vapor deposited zinc chelates in a virtually nonpolar solvent (chloroform) has been determined. Size exclusion chromatography has also allowed for the determination that thermal vapor deposition process on the zinc chelate series has no effect on the materials. This is the most important finding of this research because the process by which OLEDs are made utilized thermal vapor deposition, In addition, the effect of a polar solvent (DMSO) upon the crystalline zinc chelates have been determined. Finally, from this research there is now a better understanding of the molecular structure(s) of each of the $n\text{Meq}_2\text{Zn}$ chelates ($n = 0, 2, 4, 5$).

First, the presence of a single oligomeric species for crystalline and vapor deposited Znq_2 , $2\text{Meq}_2\text{Zn}$, and $4\text{Meq}_2\text{Zn}$ has been detected by size exclusion chromatography (see previous chapter). Znq_2 and $4\text{Meq}_2\text{Zn}$ both have a single peak, which is detected at a shorter retention time than Alq_3 and is therefore larger than the Alq_3 and a 760 amu polystyrene standard. However, because the polystyrene standards

are not the same “type” of material the molecular weights of the compounds and the standards cannot be compared due the concern that the polystyrene might “fold”. However, the 1414 amu tetramer does fall between the 2330 and 760 am molecular weight standards. Based on previous research, the unsubstituted $(\text{Znq}_2)_4$ has been determined to be tetrameric from the x-ray diffraction pattern for the structural parameters of Znq_2 taken from Kai et al.¹ has good correspondence to the calculated pattern for tetrameric Znq_2 ², theoretical calculations show that the tetramer is energetically preferred over both the monomer and dimer². Therefore, it can be concluded that the tetramer is the dominant species for Znq_2 , $4\text{Meq}_2\text{Zn}$. However, due to the limited solubility of the zinc chelates in chloroform the presence of other oligomers cannot be ruled out.

Unlike Alq_3 , the absorption and emission properties of the zinc chelates, with the exception of $2\text{Meq}_2\text{Zn}$ are strongly influenced by solvents. For example, no differences were observed between the absorption spectra of Alq_3 and its methylated derivatives in CH_2Cl_2 and the more polar solvent, DMF ³. However, the $n\text{Meq}_2\text{Zn}$ chelates exhibited large red shifts to the longest wavelength band. Furthermore, in MeOH , Alq_3 exhibited a small shift to higher energy of absorption, attributed to stabilization of the ground state molecule via H-bonding of the phenolato oxygens of the ligand¹. In contrast, the $n\text{Meq}_2\text{Zn}$ chelates exhibited a small shift to lower energy in MeOH . This suggests that the phenolato oxygens are not available for H-bonding or that the MeOH oxygen atoms have a higher affinity for interaction with the Zn^{2+} metal ion. Based on size exclusion chromatography we see that the zinc chelates are not simple monomers, which explains the differences in behavior between 2, 4, & 5 Meq_2Zn as compared to Alq_3 .

The $2\text{Meq}_2\text{Zn}$ showed a single peak detected at ~ 18 minutes in both chloroform and vapor deposited film. This detection time of is longer then Alq_3 and shorter than the 8-hydroxyquinoline. Therefore, $2\text{Meq}_2\text{Zn}$ is proposed to be monomeric.

The only zinc chelate that exhibited multiple oligomeric species was $5\text{Meq}_2\text{Zn}$. The presence of the first peak is detected at approximately the same time as Znq_2 and $4\text{Meq}_2\text{Zn}$ (see chapter 3), and therefore it is concluded that it is tetrameric. The second much smaller peak is detected at approximately the same time as the monomeric $2\text{Meq}_2\text{Zn}$. The nature third much smaller peak detected between 16 and 17 minutes is somewhat harder to explain than the other two peaks. If it were the dimeric species, it would be expected to be eluted from the column before the Alq_3 , which is not the case. However, we cannot rule out the possibility that it is some sort of impurity, or a transitional species between the monomer and tetramer. Absorption spectra for $5\text{Meq}_2\text{Zn}$ exhibit a small shift to lower energy in MeOH. This supports the tetramer being the majority of the material as exhibited by SEC spectra because the phenolato oxygens are not available for H-bonding or that the MeOH oxygen atoms have a higher affinity for interaction with the Zn^{2+} metal ion³. In addition, the PL emission of the full-width-at-half-maximum (FWHM) for the $5\text{Meq}_2\text{Zn}$ are wider (134 nm & 169) compared to $(\text{Znq}_2)_4$ (111 & 110), $(4\text{Meq}_2\text{Zn})_4$ (102 & 103), $2\text{Meq}_2\text{Zn}$ (116 & 112), and Alq_3 (105 & 102) in CH_2Cl_2 and DMF respectively^{3 & 4}. The wider FWHM might in part be due to two overlapping peaks in the spectra (the tetramer and the monomer). However, FWHM broadening is also present in $5\text{Meq}_3\text{Al}$ and $5\text{Meq}_3\text{Ga}$ in DMF that is only one oligomeric species, but the FWHM is not as large as that of $5\text{Meq}_2\text{Zn}$ ³. This indicates that the larger FWHM might be the results of both substitution at the five position and multiple

oligomers being present. Finally, $5\text{Meq}_2\text{Zn}$ was the only zinc chelate to exhibit an additional endothermic transition prior to T_m that is suggestive of more than one species⁴. Based upon SEC results $5\text{Meq}_2\text{Zn}$ is the only zinc chelate with multiple oligomers which is supportive of some of the results of previous studies reported about the zinc chelates.

Running the crystalline form of ($n\text{Meq}_2\text{Zn}$ $n = 0, 1, 2, 4, \& 5$) was essential to this research because it revealed the oligomeric nature of the chelates before the thermal vapor deposition process. The thermal vapor deposition process is utilized to make OLEDs. Therefore, the comparison of the vapor deposited samples to the crystalline material sheds light on the question if thermal vapor deposition causes the dissociation of higher ordered molecular structures. In the comparing these two forms for Znq_2 , $4\text{Meq}_2\text{Zn}$, and $5\text{Meq}_2\text{Zn}$ the higher molecular ordered tetramer remains intact. The intact tetramer is important because it confers a lower operating voltage due to more efficient electron transport. Thus the single most important finding of this thesis is that higher molecular ordered structures (tetrameric $n\text{Meq}_2\text{Zn}$ ($n = 0, 2, 4, \& 5$)) that confer favorable voltage properties do not dissociate using the typical processes by which OLEDs are produced. Whether this can be applied to other higher ordered molecular structures is not known because only the zinc chelates have been examined.

The only physical change we detected between the crystalline to the thermally vapor deposited form is found in the $5\text{Meq}_2\text{Zn}$. The peak that falls between 16-17 minutes in both crystalline sample dissolved in chloroform and the crystalline sample in chloroform with DMSO is not detected in the $5\text{Meq}_2\text{Zn}$ that has undergone vapor deposition. One possibility is that the peak (represents an adduct of the monomer with

excess quinolate or solvent) that inhibits the formation of the energetically more favorable dimer. This subtle change may be the result of a more electron rich phenoxide ion. Thus it might be possible, that a more electron poor phenoxide ion is necessary for making a higher molecular structure as indicated by the presence of the monomer in samples of crystalline $5\text{Meq}_2\text{Zn}$.

Thus far it has been mentioned that the chelates are stable in the virtually nonpolar solvent chloroform and that thermal vapor deposition does not break up the tetramer. However, Hopkins et al.⁴ suggested that the tetrameric structure may be unstable, due to the appearance one set of ^1H resonances in chloroform and upon addition of DMSO a second set of resonances was observed⁴. To test the stability of the tetramer with the addition of a polar solvent, DMSO was added to the chloroform solution of crystalline zinc chelates, and a second peak in the bisquinolate region was observed for the Znq_2 and $4\text{Meq}_2\text{Zn}$. Therefore higher order molecular structures can dissociate into monomers with the addition of a polar solvent.

From the results of SEC chromatography it is known that the tetramer is the prevalent species for the $n\text{Meq}_2\text{Zn}$ ($n = 0, 4, \& 5$). However, due to the low solubility of the zinc chelates in chloroform and the small amount of zinc chelates used on the vapor deposited films (1500 Å) it is possible that other species are present, but found in such low concentrations that they are not detected. Therefore, higher concentrations of amorphous zinc chelates should be tested in chloroform by quickly subliming the sample in order to break up the packing structure that hinders the chelates from dissolving. In addition, the undissolved chelates could be dissolved with the addition of more chloroform and analyzed on the SEC to see if there are any differences in oligomeric

structure or purity. Finally, X-ray diffraction studies on each of the methylated substituted zinc chelates is currently being completed.

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