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

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North Central College
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A thesis submitted in partial fulfillment of the requirements for the

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

Masters of Science

Examination Committee Chair

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ABSTRACT

The Establishment of the Oligomeric Purity and Molecular Structure for nMeq₂ZN (n = 0, 2, 4, & 5)

by

Anna R. Falkowitz

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

Znq₂ has been studied as electroluminescent material. However, no correlation of the structure of Znq₂ to resulting device properties has been established. Most reports of Znq₂ 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 nMeq₂ZN (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 2Meq₂ZN 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.
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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 voltage\(^1\).

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 1987\(^2\). 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 emission⁵ & 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, Alq$_3$ 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.

![Aluminum (III) tris(8-hydroxyquinoline) (Alq$_3$)](image)

Figure 1.1 Aluminum (III) tris(8-hydroxyquinoline) (Alq$_3$)
Figure 1.2 Common Organic Light Emitting Device

Figure 1.3 Electroluminescent Effect
1.2 Alq$_3$

1.2.1 Unsubstituted

The most studied organic EL molecule is Alq$_3$. Alq$_3$ is composed of a single Al$^{3+}$ 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 Al$^{3+}$, meridional (mer) and facial (fac) (See figure 1.4).

\[ \text{mer-Alq}_3 \quad \text{fac-Alq}_3 \]

Figure 1.4 Meridional (mer) and Facial (fac) Geometric Isomers of Alq$_3$

The structural stability of Alq$_3$ has been attributed to the proposed presence of the mer and fac isomers, which, according to Chen et. al. may hinder recrystallization of Alq$_3$ films$^1$, because of strong dipole interactions$^6$. 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/mol$^8$. 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-Alq$_3$ is 4kcal/mol higher in energy than mer-Alq$_3$, calculations of the energies of the radical anions indicate that the fac-Alq$_3$ 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 trap\(^8\). However, only the \textit{mer} isomer has been observed experimentally\(^6\&^7\). but
there is still some question in regards to isomeric purity of vapor deposited films of Alq\(_3\).

It is most likely that the ability of \textit{mer}-Alq\(_3\) to transport electrons may be due to
the preferential pyridyl/pyridyl ring overlap identified in at least 3 polymorphic phases of
the molecule\(^6\). 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 electron\(^9\). However, the
question of Alq\(_3\) isomeric purity and the effect on the overall EL process is still not
established. Regardless, most discussions of structure function relationships of Alq\(_3\) in
OLEDs usually refer to the mer-isomer only.

1.2.2 Affect of Methylation Upon Alq\(_3\)

The methylated derivatives of Alq\(_3\), aluminum tris(8-hydroxy-n-methylquinoline)
(\textit{nMeq}\(_3\)Al: \textit{n} = 3, 4, 5) have been shown to have significantly different PL and EL
properties. Substitution of the pyridyl ring giving 3Meq\(_3\)Al and 4Meq\(_3\)Al 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 latter\(^9\). In contrast,
substitution of the phenoxide ring giving 5Meq\(_3\)Al 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 trends\(^9\). However, although all methylated derivatives required higher
device operating voltages compared to Alq$_3$, the 4Meq$_3$Al exhibited the highest operating voltage, offsetting the higher EL efficiency suggesting that Alq$_3$ is a superior EL material overall.

Since all nMeq$_3$Al were shown to be meridinal by 1H NMR similar to Alq$_3$, the higher operating voltage for 4Meq$_3$Al 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 injection$^9$. Although the molecular crystal structure and packing preferences have not been determined for the nMeq$_3$Al chelates, thermal analysis results showed that 4Meq$_3$Al had a significantly lower melting point (~60°C), suggesting that intermolecular interactions were weaker compared to Alq$_3$.$^9$

1.3 Znq$_2$ and Its Methylated Derivatives

1.3.1 Znq$_2$ Vs. Alq$_3$

The zinc chelate of 8-hydroxyquinoline (Znq$_2$)$_4$ has also been studied as an EL material, but not as extensively as Alq$_3$. Endrino and Sapochak reported photophysical studies of Znq$_2$ and showed that unlike Alq$_3$, the absorption and emission properties of Znq$_2$ are strongly influenced by solvents$^{10}$. For example, no differences were observed between the absorption spectra of Alq$_3$ in CH$_2$Cl$_2$ and the more polar solvent, DMF$^{10}$. However, Znq$_2$ exhibited a large red shift of 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 ligand$^{11}$. In contrast, Znq$_2$ exhibited a small shift to lower energy in MeOH, suggesting
that the phenolato oxygens are not available for H-bonding in Znq₂. These results suggested that the structure of Znq₂ may not be the simple bis-chelate as supposed by most researchers. In fact, Kai et al. showed that anhydrous Znq₂ 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 respectively. 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. This suggests that unlike Alq₃, where there is concern in regards to 'isomeric' purity, for Znq₂, one must be concerned about 'oligomeric' purity. However, only recently has the effect of oligomerization of Znq₂ on electroluminescent properties been considered.

\[(\text{Znq}_2)\text{ (monomer, } \mu \approx 6.7 \text{ D)}\]
\[(\text{Znq}_2)_2 \text{ (dimer, } \mu \approx 0.9 \text{ D)}\]
\[(\text{Znq}_2)_4 \text{ (tetramer, } \mu \approx 0.006 \text{ D)}\]

Figure 1.5 Possible oligomers of zinc (8-hydroxyquinoline) and the calculated dipole moments
Sapochak, et al. showed that Znq₂ 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 [(Znq₂)₄] over smaller oligomers, such as a dimer [(Znq₂)₂] or monomer Znq₂ was evaluated experimentally and theoretically (see Fig. 1.5). Since there are differences in both the sizes and polarities of the Znq₂ monomer, dimer, and tetramer, based on calculated dipole moments, different melting points for these oligomers would be expected. Thermal analysis of crystalline (Znq₂)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 (Znq₂)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 (Znq₂)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 Znq₂ in CDCl₃ showed a single set of aromatic resonances, but upon addition of the polar solvent, DMSO-d₆, a second set of aromatic resonances was observed. They concluded that the nonpolar tetramer was stable in CDCl₃, 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 Znq₂ and the Structural Affects on Electronic Properties

The overall structure of (Znq₂)₄ is quite different than Alq₃. (Znq₂)₄ as explained by Kai et al. is comprised of two types of Zn²⁺, 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). (Znq₂)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 tetraromers occurs through the pyridyl and phenolato rings, which is significantly different than the preferred pyridyl/pyridyl ring stacking of mer-Alq₃. Furthermore, (Znq₂)₄ also exhibits intremolecular 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 ligands (See figure 1.6b).
Figure 1.6 Orbital amplitude plots of a). HOMO (Znq$_2$)$_4$ (tetramer), b). LUMO (Znq$_2$)$_4$ (tetramer), c). HOMO mer-Alq$_3$, and Lumo mer-Alq$_3$

A comparison of identically prepared OLEDs utilizing the EL materials (Znq$_2$)$_4$ and Alq$_3$ showed that the operating voltage was lower for the (Znq$_2$)$_4$-based OLEDs$^9$. It was proposed that the strong $\pi-\pi$ stacking interactions in (Znq$_2$)$_4$ provides a more efficient electron transport pathway compared to Alq$_3$ and may be the reason for lower device operating voltage.
3.1.3 Methylated Derivatives of Znq₂

Originally Znq₂ and its methylated derivatives (2Meq₂Zn, 4Meq₂Zn, 5Meq₂Zn) were thought to be monomeric, however, the absorption and emission properties of the 4Meq₂Zn and 5Meq₂Zn in photophysical studies mirror that of tetrameric Znq₂ with large red shifts of the longest wavelength band between the absorption spectra in CH₂Cl₂ and the more polar solvent, DMF¹⁴, and a small shift to lower energy in MeOH¹⁴. For the 2Meq₂Zn the absorption and emission spectra mirrored Alq₃. In the case of the 4Meq₂Zn, this chelate gives the highest EL efficiency for the Znq₂ series but also the lowest operating voltage. This is different from 4Meq₃Al which also gives higher EL efficiency compared to the unsubstituted analogue (Alq₃) but at a higher operating voltage,⁵ as discussed previously. It is more likely that the 4Meq₂Zn and 5Meq₂Zn 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 2Meq₂Zn compared to Znq₂ and its other methylated derivatives³. Therefore, an explanation for the solvent dependent photophysical properties, the voltage requirements, and the EL efficiency of nMeq₂Zn 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 nMeq₂Zn 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 \(\text{Znq}_2\) and \(\text{Alq}_3\) 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 \(\text{Znq}_2\) 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 (CHCl₃); 2) crystalline material dissolved in CHCl₃ with the addition of polar DMSO added; and 3) amorphous material formed by thermal vapor deposition dissolved in CHCl₃. 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 nMeq₂Zn chelates as EL materials and conclusions of these studies will be presented in Chapter 4.

References


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 Znq₂ 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 nMeq₂Zn
chelates have only limited solubility in both polar and nonpolar solvents. Previously, Hopkin’s proposed based on 1H NMR spectroscopic studies that the Znq₂ was stable as the tetramer in chloroform, but was disassociated to the monomeric species in the polar, nucleophilic solvent dimethysulfoxide⁵. 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, Alq₃ 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 Alq₃ exists⁴ and therefore only one peak should be present on the column if the molecule has not dissociated. The tris-chelate, Alq₃ 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 Alq₃, and the monomer would be smaller and therefore have a longer retention time than Alq₃. So both the size and molecular weights are significantly different to allow for separation on the SEC column. Third, Gaq₃ and Inq₃ 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 (Al³⁺ (~0.5 Å), Ga³⁺ (~0.65Å), In³⁺ (0.8 Å), and therefore running them through the column will allow for the confirmation of separation based on size. Alq₃, Gaq₃, and Inq₃ 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\(_3\)Cl) 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 verses 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 preformed using high performance liquid chromatography (HPLC) equipment consisting of a B-100-S pump (Eldex Laboratories, Inc.), a 50 \( \mu \)L 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 R I-71), and an IBM 286 computer with “Simple Peak” software (SRI). The mobile phase was amylyne 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 1 mg/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 ran 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 x 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 were it will be graphically displayed in the results section of this thesis.

References

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 \textit{ab initio} Hartree-Fock (HF) calculations performed using the PC version of the GAMESS and Spartan systems of electronic structure programs as reported previously. 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

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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

<table>
<thead>
<tr>
<th>Size Comparison</th>
<th>Ratio of Volumes</th>
<th>Ratio of Areas</th>
<th>Ratio of MW's</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Znq₂)₄/ (Znq₂)₂</td>
<td>1.8</td>
<td>1.5</td>
<td>2.0</td>
</tr>
<tr>
<td>(Znq₂)₂/Znq₂</td>
<td>1.8</td>
<td>1.6</td>
<td>2.0</td>
</tr>
<tr>
<td>(Znq₂)₂/Alq₃</td>
<td>1.4</td>
<td>1.2</td>
<td>1.4</td>
</tr>
<tr>
<td>Alq₃/Znq₂</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
</tr>
</tbody>
</table>

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 CHCl₃ 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.
Figure 3.1 Structures, formula weights, and dimensions of Alq$_3$ and (Znq$_2$)$_n$ (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". 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 effect. 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 tailsing effect. 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.

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

**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 state, 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 2Meq$_2$Zn falling between the retention times for Alq$_3$ and q, suggests that 2Meq$_2$Zn is monomeric (MW = 381.6). The 5Meq$_2$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 2Meq$_2$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. 5Meq$_2$Zn is composed of a mixture of tetrameric and monomeric structures, and a third species that’s nature is not exactly clear.

![Size exclusion chromatograms for the crystalline nMeq$_2$Zn chelates dissolved CHCl$_3$.](image-url)

Figure 3.4  Size exclusion chromatograms for the crystalline nMeq$_2$Zn chelates dissolved CHCl$_3$. Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
3.2.c Amorphous (Vapor Deposited Films) of nMeq-Zn 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 4Meq-Zn. 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 2Meq-Zn and 5Meq-Zn, but the number of peaks for the 2Meq-Zn did not change. The 5Meq-Zn 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 0 and 0.3 minutes for the monomer.

3.2.d Crystalline nMeq-Zn 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 4Meq-Zn 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 2Meq\textsubscript{2}Zn were not affected by the presence of DMSO. Similar to the results observed in CHCl\textsubscript{3}, three peaks for 5Meq\textsubscript{2}Zn (11.5 minutes, 16.7, and 18.5 minutes) were observed. The peaks for the 5Meq\textsubscript{2}Zn are consistent with the tetramer, monomer, and a third species that's nature is not determined.

![Size exclusion chromatography results for the standards and vapor deposited zinc chelate series](image)

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

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3.3 Discussion of the Oligomeric Purity and Stability of nMeq2Zn Chelates

The tetrameric structure of crystalline Znq₂ was previously established by both single crystal and powder x-ray diffraction studies. The SEC results reported here showed a single peak in the MW range between the two polystryene standards at a retention time 1.3X shorter than the smaller Alq₃ molecule for both the crystalline material and sample after thermal vapor deposition for both (Znq₂)₄ and 4Meq₂Zn. These results suggest that the tetrameric structure is stable in nonpolar solvents and after thermal vapor deposition.

However, SEC results for (Znq₂)₄ and 4Meq₂Zn in the presence of DMSO showed an additional smaller peak at a retention time 1.2X longer compared to Alq₃, 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

Figure 3.6 Size exclusion chromatography results for the standards and crystalline zinc chelate series with DMSO.
SEC results for 2Meq: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 2Meq:Zn was monomeric. The SEC results for crystalline 2Meq:Zn in both CHCl₃ and CHCl₃/DMSO showed a single peak eluting at approximately the *same* retention time as the smaller peak observed for (Znq₂)₄ in the presence of DMSO. Since the dimer would be expected to elute at a shorter retention time than Alq₃, based on the difference in sizes as discussed in Section 3.1, 2Meq:Zn must be monomeric and stable in this form even in the presence of a polar solvent. These results suggest that the (Znq₂)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 5Meq:Zn exhibited the most dynamic behavior of all the chelates. The crystalline 5Meq: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 Alq₃ which indicates that it is smaller than Alq₃ 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 5Meq:Zn only has two peaks which are consistent with the tetramer and monomer.
Table 3.2 Summary of Retention Times Under Different Sampling Conditions

<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>ST2330</td>
<td>8.0</td>
<td>----</td>
<td>8.0</td>
</tr>
<tr>
<td>ST760</td>
<td>13.1</td>
<td>----</td>
<td>13.1</td>
</tr>
<tr>
<td>Q</td>
<td>20.3</td>
<td>----</td>
<td>20.3</td>
</tr>
<tr>
<td>Alq₃</td>
<td>15.1</td>
<td>15.1</td>
<td>15.1</td>
</tr>
<tr>
<td>(Znq₂)₄</td>
<td>11.6</td>
<td>11.6</td>
<td>11.5, 18.3</td>
</tr>
<tr>
<td>(4Meq:Zn)</td>
<td>11.4</td>
<td>11.6</td>
<td>11.8, 18.4</td>
</tr>
<tr>
<td>(2Meq:Zn)</td>
<td>18.5</td>
<td>18.3</td>
<td>18.6</td>
</tr>
<tr>
<td>(5Meq:Zn)</td>
<td>11.1, 16.1, 18.1</td>
<td>11.8, 18.4</td>
<td>11.5, 16.7, 18.5</td>
</tr>
</tbody>
</table>

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 2Meq:Zn, 4Meq:Zn, Alq₃ and q (see figure 3.5). For the vapor deposited films all the zinc chelates had a tail except the 4Meq:Zn. Finally for the samples in CHCl₃/DMSO tailing is present for Alq₃, q, and all of the zinc chelates except for 5Meq:Zn (tetramer), which looks like crystalline 5meq:Zn in CHCl₃ (see figures 3.4 & 3.7). No one reason is the known cause of tailing, but in this case 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 effect. 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 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.

References


4. Aldrich web site certificate of analysis for the lot.

5. Heineman, W.R.; and Strobel H.A. Chemical Instrumentation: A Systematic

CHAPTER 4

CONCLUSION

The purpose of this thesis was two fold, first to investigate the "oligomeric purity" of the nMeq^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 nMeq^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 nMeq^Zn chelates (n = 0, 2, 4, 5).

First, the presence of a single oligomeric species for crystalline and vapor deposited Znq, 2Meq,Zn, and 4Meq,Zn has been detected by size exclusion chromatography (see previous chapter). Znq and 4Meq,Zn both have a single peak, which is detected at a shorter retention time than Alq3 and is therefore larger than the Alq3 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 \(\text{Znq}_2\) taken from Kai et al.\(^1\) has good correspondence to the calculated pattern for tetrameric \(\text{Znq}_2\), theoretical calculations show that the tetramer is energetically preferred over both the monomer and dimer.\(^2\) Therefore, it can be concluded that the tetramer is the dominant species for \(\text{Znq}_2, 4\)Meq\(_2\)Zn. However, due to the limited solubility of the zinc chelates in chloroform the presence of other oligomers cannot be ruled out.

Unlike \(\text{Alq}_3\), the absorption and emission properties of the zinc chelates, with the exception of 2Meq\(_2\)Zn are strongly influenced by solvents. For example, no differences were observed between the absorption spectra of \(\text{Alq}_3\) and its methylated derivatives in CH\(_2\)Cl\(_2\) and the more polar solvent, DMF.\(^3\) However, the nMeq\(_2\)Zn chelates exhibited large red shifts to the longest wavelength band. Furthermore, in MeOH, \(\text{Alq}_3\) 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 ligand.\(^4\) In contrast, the nMeq\(_2\)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\(_2\)Zn as compared to Alq\(_3\).
The 2Meq\(_2\)Zn showed a single peak detected at \(\sim 18\) minutes in both chloroform and vapor deposited film. This detection time is longer than Alq\(_3\) and shorter than the 8-hydroxyquinoline. Therefore, 2Meq\(_2\)Zn is proposed to be monomeric.

The only zinc chelate that exhibited multiple oligomeric species was 5Meq\(_2\)Zn. The presence of the first peak is detected at approximately the same time as Znq\(_2\) and 4Meq\(_2\)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 2Meq\(_2\)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 5Meq\(_2\)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 ion\(^3\). In addition, the PL emission of the full-width-at-half-maximum (FWHM) for the 5Meq\(_2\)Zn are wider (134 nm & 169) compared to (Znq\(_2\))\(_4\) (111 & 110), (4Meq\(_2\)Zn)\(_4\) (102 & 103), 2Meq\(_2\)Zn (116 & 112), and Alq\(_3\) (105 & 102) in CH\(_2\)Cl\(_2\) 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 5Meq\(_3\)Al and 5Meq\(_3\)Ga in DMF that is only one oligomeric species, but the FWHM is not as large as that of 5Meq\(_2\)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 Tm that is suggestive of more than one species. 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 $\text{Znq}_2$, $4\text{Meq}_2\text{Zn}$, 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 ($\text{tetrameric nMeq}_2\text{Zn}$ $(n = 0, 2, 4, \& 5)$) 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 5Meq₂Zn.

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 Znq₂ and 4Meq₂Zn. 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 nMeq₂Zn (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.

3.1 References


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