The Synthesis of Room-Temperature Ionic Liquids and Their Metathesis Reactions with Dilithium Phthalocyanine

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THE SYNTHESIS OF ROOM-TEMPERATURE IONIC LIQUIDS AND THEIR METATHESIS REACTIONS WITH DILITHIUM PHTHALOCYANINE

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science

By

ANDREW M. BEAUCHAMP
B.S., United States Air Force Academy, 2010

"The views expressed in this article are those of the author and do not reflect the official policy or position of the United States Air Force, Department of Defense, or the U.S. Government."

2012
Wright State University
I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Andrew M. Beauchamp ENTITLED The Synthesis of Room-Temperature Ionic Liquids and Their Metathesis Reactions with Dilithium Phthalocyanine, BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science.

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ABSTRACT

Beauchamp, Andrew M. M.S., Department of Chemistry, Wright State University, 2012. The Synthesis of Room Temperature Ionic Liquids and Their Metathesis Reactions with Dilithium Phthalocyanine.

A series of alkoxyalkylammonium salts has been synthesized for use in metathesis reactions with dilithium phthalocyanine. The salts, which were ionic liquids at or near room temperature, were synthesized by a nucleophilic substitution of tris[2-(2-methoxyethoxy)ethyl]amine and iodomethane, iodoethane, bromoethane, 1-bromo-propane, 1-bromo-2-(2-methoxyethoxy)ethane, and [2-[2-(2-methoxyethoxy)ethoxy]-ethoxy] p-toluenesulfonate in yields ranging from 67% - 88%. The methyl, ethyl, propyl, and tetra[2-(2-methoxyethoxy)ethyl]ammonium salts were obtained for use in metathesis reactions. The salts were liquid at room temperature, with the exception of tetra[2-(2-methoxyethoxy)ethyl]ammonium bromide which was found to melt at 46° and were thermally stable to approximately 200°. The four salts were used in metathesis reactions with dilithium phthalocyanine to produce an alkoxyalkylammonium cation lithium phthalocyanine anion complex in yields from 43% - 73%. The complex products were found to be thermally stable to approximately 300° with melting temperatures ranging from 118° - 160°. The structures of tris[2-(2-methoxyethoxy)ethyl]methylammonium lithium phthalocyanine, tris[2-(2-methoxyethoxy)ethyl]propylammonium lithium phthalocyanine, and tetra[2-(2-methoxyethoxy)ethyl]ammonium lithium phthalocyanine were determined by single crystal x-ray diffraction experiments.
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DEDICATION

I would like to dedicate this work to my family and friends and especially my girlfriend Keaira; for all of your love and support while I strived to reach and achieve my goals. I cannot thank you all enough.
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I would like to give thanks to my advisor, Dr. William Feld for allowing me the opportunity to work in his group. His instruction and guidance helped me to grow as both a student and a chemist. His willingness to share his knowledge made my time at Wright State a truly valuable experience.

Keaira, thank you for always being there for me and for all your support during my time here, you truly made my experience easier. To my parents, thank you for all of your support and encouragement, you made me the person I am today. To my brothers and sisters, thank you for all of your encouragement and for all the great times during my breaks.

To the undergraduate and graduate students in the WAF research group past and present: Jeff “Einstein” Fogle, Rachel “Quiet” Sayers, Sarah “the Fuzz” Bragg, Devin “Invisible” Anderson, Mark “Irish Shammrock’s” Duffy, Kristy “Muscles” Wickman, Dan “Blue” Greene, Joe “Story Time” Krol, Ryan “the Nose” Oostendorp, David “de Coen” de Oude, and Jeremy “Ole Man Jenkins” Lear; thanks for all of the discussions and laughs.

Finally, I would like to acknowledge the faculty, staff, and students of the Wright State Chemistry department for all that I have learned and the experiences we’ve had over the past nineteen months.
INTRODUCTION

Dilithium phthalocyanine (Li₂Pc) 1 is a metal complexed dianionic macrocycle. The phthalocyanine dianion is capable of complexing many metal cations, however, extensive research has been focused on the dilithium compound. It has had widespread use as a dye, and has been studied as a useful material in solid-state, lithium-ion batteries, and as a hydrogen-storage substrate.

An x-ray crystal structure revealed that in Li₂Pc 1, one of the lithium cations is centered in the ring, whereas the second lithium is coordinated outside the ring.

Exchange reactions have been performed which take advantage of the external lithium ion. Initially, tetrabutylammonium halides were used to generate the mixed cationic system 2. Later, 1,3-bis(1-adamantyl)imidazolium tetrafluoroborate and an extended series of tetraalkylammonium halides (R₄N⁺, R=1-8) were used as exchange agents. The inclusion of ether functionalities in the tetraalkylammonium cations was theorized to be a straightforward approach to change the physical properties of the final product.
The objectives of this research were 1) to develop a synthetic approach to a series of alkoxylalkylammonium cations, 2) to develop a reliable method for the metathesis reactions of those cations with Li₃Pc 1, and 3) evaluate the ammonium complexed lithium phthalocyanines by NMR, IR, thermal analysis, and single crystal x-ray analysis.
HISTORICAL

Dilithium Phthalocyanine: Synthesis

Dilithium phthalocyanine 1 has been extensively studied for numerous applications. Li$_2$Pc 1 can be used as a precursor for many other phthalocyanines (Pcs), both metal-free and other metal-ion-containing Pcs, due to its solubility and simple synthesis. The reaction of phthalonitrile 3 with lithium metal dissolved in pentanol (lithium pentyloxyde) at reflux yields Li$_2$Pc 1. This can undergo demetallation in dilute aqueous acid to synthesize the metal-free Pc 4.$^1$

![Chemical structures](image-url)
**Calculated Structure of Li$_2$Pc 1**

Using *ab initio* calculations, a structure of 1 was calculated. The lithium ions were predicted to be coordinated on either face of the opening of the ring as shown in **Figure 1**. Calculations were also performed to predict the alignment of multiple Pc rings. It was predicted that the rings would stack in a pattern with each ring shifted off-center from the ring below it, as shown in **Figures 2 and 3**. The predicted molecular self-assembly of 1 could form continuous “channels” created by the ring openings which would allow the transport of lithium ions through the solid matrix, presumably through the center of the ring.$^2$

![Figure 1](image-url1)

*Figure 1.* Calculated orientation of lithium ions relative to the phthalocyanine ring in Li$_2$Pc 1.

![Figure 2](image-url2)

*Figure 2.* Predicted packing of Li$_2$Pc 1.
Single Crystal X-Ray Diffraction of Li$_2$Pc 1

Crystals of 1 were grown for use in x-ray diffraction experiments to determine the validity of the calculated structure. Single crystal x-ray diffraction showed that the lithium ions were not centered in the opening on either face of the ring (Figure 4), as previously calculated. One lithium ion was centered in the plane of the ring, (a in Figure 4), while the second was external to the ring and coordinated to water and acetone molecules (b in Figure 4). The orientation of the rings was also different than predicted by calculations. The complex LiPc anion was found to be stacked in two pairs with spacing’s of 3.38(2) Å and 3.062(2) Å, between the rings respectively, (c and d in Figure 4). These pairs lie at a dihedral angle of 72.93(1)° to each other. The remaining lithium ions are also grouped in pairs, with one pair coordinating four waters and two acetone molecules and the other pair coordinating two waters and four acetone molecules (e and f in Figure 4). These sets, the LiPc pairs and lithium ion pairs, are linked by hydrogen bonding which creates channels within the structure.  

Figure 3. Side view of predicted packing of Li$_2$Pc 1.
Figure 4. Packing of Li$_2$Pc 1 from a single crystal x-ray diffraction experiment.

**Early Exchanges with Li$_2$Pc**

Prior to the report of the crystal structure, the mobility of one of the lithium ions in Li$_2$Pc was established by Homborg, et al.\textsuperscript{5,6} This investigation provided a useful model from which new exchanges were designed and carried out.

**Initial Tetraalkylammonium Halide Exchanges**

The exchange/metathesis reaction of Li$_2$Pc 1 with tetrabutylammonium bromide (TBA Br) 5 and tridodecylbutylammonium nitrate (TDBA NO$_3$) 6 provided the corresponding “onium” salts TBA LiPc 7 and TDBA LiPc 8.

These salts exhibit solubility in non-polar aprotic solvents in contrast to Li$_2$Pc 1. A crystal structure of 7 as the tetrahydrofuran solvate has been reported.\textsuperscript{6}
5, R = C₄H₉, X = Br⁻  
6, R = C₁₂H₂₅, X = NO₃⁻  
7, R = C₄H₉  
8, R = C₁₂H₂₅

1,3-Bis(1-adamantyl)imidazolium Tetrafluoroborate Exchanges

After Homborg, 1,3-disubstituted imidazolium cationic compounds were used in exchange reactions with Li₂Pc 1. Although several imidazoliums were investigated, 1,3-bis(1-adamantyl)imidazolium tetrafluoroborate (BAI BF₄) 9 was the only one that gave a good yield of an easily characterized product, 1,3-bis(1-adamantyl)imidazolium lithium phthalocyanine BAI LiPc 10.

A crystal of 10 suitable for x-ray crystal diffraction was isolated. It was found that both water and acetone (a and b in Figure 5) are included in the unit cell and participate in hydrogen bonding with complex anion (LiPc⁻) as well as the imidazolium cation. This is similar to the incorporation of water and acetone in 1. The complex anion
(LiPc) packs in symmetry related pairs that are not parallel but are offset by 2.39°. The distance between the rings in the pairs was found to be 10.10 Å, much larger than the distances found in 1. The complex anion packed in rows each offset from the other creating a staircase shape with each BAI cation “enclosed” by four anions. The product 10 exhibited good thermal stability with mass loss, other than solvent, starting between 350-357°C with an onset temperatures of 358-361°C by thermal gravimetric analysis.7,8

**Figure 5.** Packing of BAI LiPc 10 from single crystal x-ray experiment.

**Tetraalkylammonium Exchanges**

Homborg’s success synthesizing tetrabutylammonium lithium phthalocyanine suggested the used of other tetraalkylammonium bromides in exchange reactions. The
series consisting of symmetrical quaternary ammonium bromides 7, 11-16 having one to eight (except five) carbon chains was used.\textsuperscript{9,24}

\[
\begin{array}{ccc}
\text{7, } R=\text{C}_4\text{H}_9 & \text{1} & \text{8, } R=\text{C}_4\text{H}_9 \\
\text{11, } R=\text{CH}_3 & \text{17, } R=\text{CH}_3 \\
\text{12, } R=\text{C}_2\text{H}_5 & \text{18, } R=\text{C}_2\text{H}_5 \\
\text{13, } R=\text{C}_3\text{H}_7 & \text{19, } R=\text{C}_3\text{H}_7 \\
\text{14, } R=\text{C}_6\text{H}_{13} & \text{20, } R=\text{C}_6\text{H}_{13} \\
\text{15, } R=\text{C}_7\text{H}_{15} & \text{21, } R=\text{C}_7\text{H}_{15} \\
\text{16, } R=\text{C}_8\text{H}_{17} & \text{22, } R=\text{C}_8\text{H}_{17}
\end{array}
\]

The synthesis of the series of exchange products 8, 17-22 gave yields ranging from 54-64\%. The melting points of 8, and 17-22 decrease with increasing chain length with the exception of the tetrahexyl product. Proton spectra of the products 8, 17-22 in CDCl\textsubscript{3} showed chemical shifts of the cation chain protons which were observed far upfield relative to their positions in the spectra of the coordinating solvent, acetone-d\textsubscript{6}. This is believed to be caused by a sandwiching effect of the complex anion with the ammonium cations in the non-coordinating solvent. Powder XRD spectra showed that both the tetramethyl product 7 and tetraoctyl product 22 had significantly fewer peaks in their diffraction patterns relative to the rest of the series. This indicates that these products were less crystalline than the rest of the series.\textsuperscript{9}
Quaternary Ammoniums Containing Ether Functionalities

Quaternary ammoniums, QAs, that contain ether functionalities have been investigated by many groups for a wide-range of applications. They have been synthesized by different methods and can be cyclic, spiro cyclic, or straight-chained. These compounds have been used as solvents, surfactants, biocides, as ionic liquid (IL) electrolytes in electrochemical devices such as rechargeable lithium ion batteries, capacitors, and fuel cells, and many other applications.

Cyclic Quaternary Ammonium Salts

Zhou, Matsumoto, and Tatsumi created a series of low-viscosity, low-melting stable ionic liquid (IL) cyclic alkoxyalkylammonium compounds that could be used as electrolytes in high-energy devices such as lithium batteries, electrochemical capacitors, and fuel cells.\textsuperscript{10}

The cyclic quaternary ammonium salts 25, 28, 29, 32, and 33 were synthesized via a nucleophilic substitution by an N-methylheterocyclic 23, 26, 30, 31 on the appropriate bromoalkylether 24 or 27. Exchanges with the anions [CF$_3$BF$_3$]$^-$, [C$_2$F$_3$BF$_3$]$^-$, [nC$_3$F$_7$BF$_3$]$^-$, [nC$_4$F$_9$BF$_3$]$^-$, [BF$_4$]$^-$, and [TFSI]$^-$ created a large series of salts. It was found that the addition of the ether chain provided the best method to create low melting ILs compared to salts synthesized with alkyl bromides. Often the melting point was much lower than room temperature. The decrease in the melting temperature due to the incorporation of ether functionalities either in the side chain or in the heterocycle was accompanied by a decrease in short-term thermal stability of the salts.
While examining the electrochemical properties of the salts, viscosity was used as a tool to predict the performance of the compounds. In comparing compounds with the same anion, a trend in viscosity was found following the order 25 < 28 < 32 < 29 < 33. Conductivity measurements, on the other hand, gave rise to an opposite trend.\textsuperscript{10}

**Spiro Cyclic Quaternary Ammonium Salts**

Cyclic QA compounds that do not contain any side-chains can be spiro cyclic ammonium salts. One such salt, 8-oxa-5-azoniaspiro[4.5]-decane bromide 36 was reported in 1954, along with other similar compounds, as novel cholinergic agents.\textsuperscript{11} In 2002, Aitken, et. al.\textsuperscript{12} prepared this compound using the previously published procedure. A reaction of 1,4-dibromobutane 34 and morpholine 35 in aqueous base quaternized the amine via a nucleophilic substitution to provide 36.\textsuperscript{12}
Straight-Chain Alkoxyalkylammonium Compounds

Unlike the cyclic QA salts discussed previously, straight-chain QA compounds consist of a nitrogen atom with four separate chains. Like the cyclic salts, straight-chain alkoxyalkylammonium compounds use amines as their starting material. With a wide variety of possible starting amines and an even larger variety of alkyl halides and alkoxyalkyl halides a large number of compounds can be synthesized.

Synthesis of Trisalkoxyamines

In the process of creating new alkoxyalkylammonium salts, novel tertiary amines must be synthesized which then can be quaternized with a variety of side-chains.

Yokota, et. al. reported a useful synthesis of two trisalkoxyamines which were used as “open cryptands” to coordinate alkali and alkaline earth metals.\textsuperscript{13} The synthesis of tris(2-methoxyethyl)amine \textsuperscript{38} was carried out by two different procedures. In the first procedure, triethanolamine \textsuperscript{37} was reacted with metallic sodium followed by methyl iodide in a nucleophilic substitution to produce \textsuperscript{38}. In the second method, sodium hydride was used to deprotonate the alcohol instead of metallic sodium. The second procedure was also used in the synthesis of tris(2-ethoxyethyl)amine \textsuperscript{39}.\textsuperscript{13}

These trisalkoxyamines, \textsuperscript{38} and \textsuperscript{39}, were used in further reactions with numerous alkali and alkaline earth metal salts to form complexes such as \textsuperscript{41}. Reactions of \textsuperscript{38} and \textsuperscript{39} with hydrochloric, acetic, and p-toluene sulfonic acids provided quaternary salts.\textsuperscript{13}
Biofouling Control with Quaternary Ammonium Polyhalides

A 1988 patent by the Great Lakes Chemical Corporation represents a good example of the use of tertiary amines as starting materials for alkoxyalkylammonium salts. The patent covered the use of quaternary ammonium (QA) polyhalides as biocide agents. The QAs were used to deliver oxidizing polyhalide biocides and subsequently become non-oxidizing biocides. \(^{14}\)

The compounds of interest in this patent were based on alkyl ether containing quaternary ammonium halides, especially the intermediate product N-propyl-N,N,N-
Alkoxyalkylammonium Salts as Surfactants

Another biological application of alkoxyalkylammonium salts is as surfactants. In 2005, a group in India reported on the effect of surfactant head-group size and hydrophilicity on micelle enzyme activity. The reaction of the previously synthesized quaternary ammonium bromide $\text{47}$ with sodium hydride, followed by methyl iodide, and
an ion exchange to the bromide ion provided 48. Compounds 49 and 50 which had larger, more hydrophilic cationic “heads” were synthesized similarly.

![Chemical structures](image)

**Alkoxyalkylammonium Ionic Liquids**

In contrast to the biological uses discussed earlier many alkoxyalkylammonium salts have been synthesized in an attempt to create room temperature ionic liquids (ILs). Many groups published papers reporting IL syntheses and their possible uses in electrochemical devices such as secondary lithium batteries, electric double layer capacitors, and dye-sensitized solar cells. Low-melting and low-viscosity ILs were created by modifying the cation and exchanging the anionic species.

In 2004, Sato, Masuda, and Takagi reported novel ionic liquids for use in double layer capacitors. These ionic liquids were alkoxyalkylammonium compounds. The original focus was on imidazolium based ionic liquids, however, they found that aromatic quaternary ammonium cations had low cathodic stability making their use impractical.

Initially, methoxyethethyl chloride 51 was mixed with N,N-diethylamine 52 to produce solid N,N-diethylammonium chloride, which was filtered, and N,N-diethyl-N-2-methoxyethylamine 53. The new amine 53 was quaternized with methyl iodide 54 to give 55 which was exchanged with silver tetrafluoroborate 56 resulting in 57.
A second alkoxyalkylammonium compound was synthesized using \( \text{55} \) in an exchange with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) \( \text{58} \) resulting in the salt N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)imide \( \text{59} \).

Aliphatic quaternary ammonium ionic liquids were projected to have higher stability but at the cost of high melting points, removing the possibility of close-to-room temperature liquids. It was reported\(^{16}\) however, that asymmetric and short-chain alkyl ammonium cations with an ether functionalized chain on the nitrogen were liquid at or below room temperature.

**Quaternary Ammonium Salts in Capacitors**

A larger set of compounds which included more alkoxyalkylammonium salts was also reported.\(^{17}\) Anion exchange reactions were used to produce materials to examine the
differences in electrochemical properties of different anions. These compounds were tested as electrolytes in a fabricated electronic double layer capacitor (EDLC). Measurements of capacitance and resistance of the systems were compared as well as the stability of the electrolyte in the EDLC.

The synthesis of compounds 55 and 62 followed an earlier procedure. For the rest of the series, the appropriate amine was used in a nucleophilic substitution with methoxymethyl chloride 65 to form the chloride salts of the alkoxyalkylammoniums 66-68. These compounds were then used in exchanges with AgBF$_4$, LiPF$_6$, and LiTFSI to form the final salts.

\[
\begin{align*}
\text{Cl} & \quad \text{O} \quad + \quad \text{N} \quad \text{H} \quad \text{C} \quad \text{H} \quad \xrightarrow{\text{Mel}} \quad \text{N} \quad \text{C} \quad \text{H} \quad \text{O} \\
\text{51} & \quad \text{52} & \quad \text{53} & \quad \text{54} & \quad \text{55}
\end{align*}
\]

\[
\begin{align*}
\text{Cl} & \quad \text{O} \quad + \quad \text{N} \quad \text{H} \quad \text{C} \quad \text{H} \quad \xrightarrow{\text{Mel}} \quad \text{N} \quad \text{C} \quad \text{H} \quad \text{O} \\
\text{51} & \quad \text{60} & \quad \text{61} & \quad \text{54} & \quad \text{62}
\end{align*}
\]

\[
\begin{align*}
\text{R} & \quad \text{N} \quad \text{H} \quad \text{C} \quad \text{H} \quad \xrightarrow{\text{Cl} \quad \text{O}} \quad \text{R} \quad \text{N} \quad \text{H} \quad \text{C} \quad \text{H} \\
\text{63, R=CH}_3 & \quad \text{65} & \quad \text{66, R=CH}_3 & \quad \text{67, R=C}_2\text{H}_5
\end{align*}
\]

\[
\begin{align*}
\text{N} \quad \text{H} \quad \text{C} \quad \text{H} \quad \xrightarrow{\text{Cl} \quad \text{O}} \quad \text{N} \quad \text{H} \quad \text{C} \quad \text{H} \\
\text{23} & \quad \text{65} & \quad \text{68}
\end{align*}
\]

It was found that the electrolytes with the tetrafluoroborate anion had higher capacitance at room temperature. The synthesized salts that were liquids at room temperature were found to perform the best in the fabricated capacitor.
Novel Low Melting Point Ionic Liquids

A novel series of low-melting ILs was reported in 2009. This series contained twenty-one salts, eighteen new and three others that been previously reported but were further characterized by the group. Compounds 71 and 73 were synthesized as described by Ropponen.

\[
\text{H}_2\text{N} + \text{Br} - \text{O} \xrightarrow{\text{K}_2\text{CO}_3} \text{O} - \text{N}^+ \text{Br}^{-} \text{O} \text{N} \quad 69 \quad 70 \quad 71
\]

\[
\text{H}_2\text{N} + \text{Br} - \left(\text{aromatic} \right) \xrightarrow{\text{K}_2\text{CO}_3} \text{O} - \text{N}^+ \text{Br}^{-} \left(\text{aromatic} \right) \quad 69 \quad 72 \quad 73
\]

The remaining cations, 79-83, were prepared via nucleophilic substitution on 2-bromoethyl ethyl ether by five symmetrical trialkylamines 74-78. To create the rest of the series, the seven alkoxyalkylammonium bromides, 71, 73, 79-83, were used in metathesis reactions with HBF$_4$, and KPF$_6$.

\[
\begin{align*}
\text{R}^+\text{N}^-\text{R}^- + \text{Br} - \text{O} \xrightarrow{\text{Methanol}} \text{R}^+\text{N}^-\text{R}^- \text{O}^- \\
74, \text{R}=\text{C}_2\text{H}_5 & \quad 70 \\
75, \text{R}=\text{C}_3\text{H}_7 & \quad 79, \text{R}=\text{C}_2\text{H}_5 \\
76, \text{R}=\text{C}_4\text{H}_9 & \quad 80, \text{R}=\text{C}_3\text{H}_7 \\
77, \text{R}=\text{C}_5\text{H}_{11} & \quad 81, \text{R}=\text{C}_4\text{H}_9 \\
78, \text{R}=\text{C}_6\text{H}_{13} & \quad 82, \text{R}=\text{C}_5\text{H}_{11} \\
& \quad 83, \text{R}=\text{C}_6\text{H}_{13}
\end{align*}
\]

Multi-Methoxyethyl Substituted Quaternary Ammoniums

The synthesis and characterization of a series of multi-methoxyethyl alkoxyalkylammonium salts was reported in 2010. Incorporation of ether functionality
into the side-chains of quaternary ammonium salts had been used as a way to decrease the melting point and the viscosity of the compounds.\textsuperscript{10,16-19} It was concluded that the incorporation of ether functionalities also increased the ability of these compounds to solubilize lithium salts by coordinating lithium ions.

Nucleophilic substitutions by the tertiary amine starting materials 38 and 53 on the iodo compounds 54, 84, and 86 provided a series of multi-methoxyethyl compounds 85, 87-89. These were then used in metathesis reactions with KFSI and LiTFSI to create the IL series.\textsuperscript{20}

All compounds synthesized performed as expected with, lower melting points and viscosities, and better conductivity and solvating ability for lithium salts, relative to their alkylammonium counterparts.\textsuperscript{20}

**Quaternary Ammoniums with Three or Four Ether Groups**

In 2011, Fang, et. al. published their synthesis and characterization of thirteen ILs with three or four ether functionalized side-chains.\textsuperscript{21} Similar to the approach of Han\textsuperscript{20} the goal of these researchers was to attempt to alter the characteristics of QAs even more by adding more ether functionalities.
The synthesis of these multi-ether functionalized ILs started with the synthesis of the trisalkoxyamines 38 and 92, similar to the synthesis of tertiary amines with one ether group by Sato and Yuyama.\(^{16,17}\) The amines, 38 and 92, were then used in nucleophilic substitutions with different alkyl halides 93-96 as well as alkylether halides 27, 70, and 97 to form the ILs 98-110. An anion exchange was then performed with LiTFSI to form the TFSI anion form of the IL salts.\(^{21}\)

Several of the ILs were tested as electrolytes in a lithium battery cell, and showed good discharge capacity and electrochemical stability of the ILs.

**Alkoxyalkylammonium Halides as Counterions in Ionomers**
Wang, Liu, and Colby synthesized alkoxyalkylammonium cations for use as counterions in ionomers.\textsuperscript{22,23} The synthesis of alkoxyalkylammonium salts 111, 33, and 113 was carried out by nucleophilic substitution of the starting amine 31, 42 or imidazole 112 on methyl iodide 54 or bromoethyl methyl ether 27. The products were then used in ion exchange reactions with the ionomer 114 to form products with alkoxyalkylammonium counterions 115-117.

\begin{center}
\includegraphics[width=\textwidth]{chemical_diagram.png}
\end{center}

114, X = Na\textsuperscript{+}  
115, X = 111 cation  
116, X = 33 cation  
117, X = 113 cation
These ionomers were copolymers that provided physical strength and less rigid ion conductive regions making them useful lithium ion battery electrolytes. It was found that when large cations were used as counterions, many characteristics were altered that support higher ionic conductivities.

Alkoxyalkylammonium salts have been and continue to be investigated extensively. The inclusion of ether functionalities in the cation has been shown to alter many properties of their salts. The commercial availability of tris[2-(2-ethoxyethoxy)ethyl]amine 42 made it a good starting point for the generation of new alkoxyalkylammonium salts with unique physical properties.

The objectives of this research were 1) to develop a synthetic approach to a series of alkoxyalkylammonium cations, 2) to develop a reliable method for the metathesis reactions of those cations with Li$_2$Pc 1, and 3) evaluate the ammonium complexed lithium phthalocyanines by NMR, IR, thermal analysis, and single crystal x-ray analysis.
Experimental

**Instrumentation and Chemicals.** Melting points were obtained with a DigiMelt MPA-160 or TA DSC Q 200. Nuclear magnetic resonance (NMR) $^1$H and $^{13}$C spectra were obtained using a Bruker Avance 300 MHz NMR Spectrometer. The solvent for NMR was Acetone-d$_6$. Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) spectra were obtained with a TA TGA Q 500 and a TA DSC Q 200 both employing a N$_2$ atmosphere. Infrared (IR) spectra were recorded as thin films (NaCl) with a Nicolet 6700 FT-IR spectrometer. X-ray crystallographic data was obtained from the Bruker Smart X2S Single Crystal X-ray Diffractometer. Structures were solved using APEX 2 software package (Bruker AXS, 2011). Elemental analyses were obtained through Midwest Microlab, LLC, Indianapolis, IN. A 35 mL Q-tube™ (pressure tube reactor) was used for reactions involving volatile materials. Starting materials were purchased from Aldrich and used as received.

![Figure 6. Q-tube™ pressure reactors.](image-url)
Tris[2-(2-methoxyethoxy)ethyl]methylammonium Iodide (TAMe I) 111

Procedure A

Methyl iodide 54 was added to tris[2-(2-methoxyethoxy)ethyl]amine 42 in a Q-tube™ which was placed in an oil bath and heated. Molar ratios, temperatures, durations, and solvents are indicated in Table 1. The reaction mixture was allowed to cool to room temperature at which time solvent and excess 54 were evaporated to yield a dark-brown, viscous liquid. If the product was washed, diethyl ether or methyl tert-butyl ether (MTBE) was used. The product was dried under vacuum overnight. Product yields are indicated in Table 1.

Procedure B

Methyl iodide 54 (5.00 mL, 80.3 mmol) was placed in a three neck flask fitted with a drying tube and addition funnel and cooled in an ice bath. Tris[2-(2-methoxyethoxy)ethyl]amine 42 (10.0 mL, 29.7 mmol) was added dropwise with stirring. After the addition of 42 was complete, the reaction was stirred overnight as the ice bath slowly warmed to room temperature. Excess 54 was evaporated to yield a dark-brown viscous liquid in 55% yield. A sample was washed with diethyl ether and dried under vacuum.

IR (NaCl plate, cm⁻¹) 1112 C=O, 1458 C-C, 2883 C-H; ¹H NMR (acetone-d₆, δ) 3.33 (s, 9H, OCH₃), 3.46 (s, 3H, NCH₃), 3.54 (m, 6H, N(CH₂CH₂OCH₂CH₂OCH₃)₃), 3.70 (m, 6H, N(CH₂CH₂OCH₂CH₂OCH₃)₃), 4.04 (m, 12H, N(CH₂CH₂OCH₂CH₂OCH₃)₃); ¹³C NMR (300 MHz, acetone-d₆, ppm) 51.19, 58.84, 63.95, 65.53, 70.85, 72.36. Anal. Calcd. For C₁₆H₃₆INO₆: C, 41.29%; H, 7.80%; N, 3.01%. Found: C, 41.09%; H, 7.67%; N, 2.95%.
Tris[2-(2-methoxyethoxy)ethyl]ethylammonium Iodide (TAEt I) 118

Procedure A

A solution of tris[2-(2-methoxyethoxy)ethyl]amine 42 (3.2385 g, 9.512 mmol) and ethyl iodide 86 (1.5746 g, 10.10 mmol) in 10 mL of acetone was heated at 60° overnight in a round bottomed flask with attached condenser. On cooling the solvent and excess 86 were evaporated to obtain, in 87% yield, a dark-brown, viscous liquid.

Procedure B

Ethyl iodide 86 (0.86 mL, 25.51 mmol) was added to a solution of tris[2-(2-methoxyethoxy)ethyl]amine 42 (3.4351 g, 10.09 mmol) in 10 mL of acetone in a Q-tube™. The reaction was heated at 100° for 20 h. After cooling to room temperature, the solvent and excess 86 were evaporated to obtain, in 57% yield, a dark-brown, viscous liquid: Anal. Calcd. For C17H38INO6: C, 42.59%; H, 7.99%. Found: C, 42.49%; H, 7.88%.

Tris[2-(2-methoxyethoxy)ethyl]ethylammonium Bromide (TAEt Br) 119

Procedure A

In a round bottomed flask with condenser, a solution of tris[2-(2-methoxyethoxy)ethyl]amine 42 (3.8828 g, 11.40 mmol) and ethyl bromide 93 (1.460 g, 13.40 mmol) in 10 mL of acetone was heated at 55-60° overnight. Upon cooling, the solvent and excess 93 was evaporated to obtain a dark-brown, viscous liquid in 78% yield.

Procedure B

A solution of tris[2-(2-methoxyethoxy)ethyl]amine 42 (4.8564 g, 14.26 mmol) and ethyl bromide 93 (1.20 mL, 15.92 mmol) in 10 mL acetonitrile, in a Q-tube™, was
heated at 90° overnight. Upon cooling, the solvent and excess 93 were evaporated to
obtain a dark-brown, viscous liquid in 88% yield.

IR (NaCl plate, cm⁻¹) 1112 C-O, 1456 C-C, 2881 C-H; ¹H NMR (acetone-d₆, δ)
1.42 (t, 3H, NCH₂CH₃), 3.33 (s, 9H, OCH₃), 3.53 (m, 6H, N(CH₂CH₂OCH₂CH₂OCH₃)₃),
3.70 (m, 6H, N(CH₂CH₂OCH₂CH₂OCH₃)₃), 3.84 (q, 2H, NCH₂CH₃), 3.96 (m, 6H,
N(CH₂CH₂OCH₂CH₂OCH₃)₃), 4.05 (m, 6H, N(CH₂CH₂OCH₂CH₂OCH₃)₃); ¹³C NMR
(300 MHz, acetone-d₆, ppm) 8.82, 57.64, 58.80, 60.34, 65.34, 70.81, 72.37. Anal. Calcd.
For C₁₇H₃₈BrNO₆: C, 47.22%; H, 8.86%. Found: C, 47.01%; H, 8.73%.

Tris[2-(2-methoxyethoxy)ethyl]propylammonium Bromide (TAPr Br) 45

A solution of tris[2-(2-methoxyethoxy)ethyl]amine 42 and 1.1 molar equivalents
of bromopropane 94 was heated at 90° in a Q-tube™ for two to seven days depending on
the size of reaction. The crude dark-orange-brown product was cooled to room
temperature and washed with three to four aliquots of MTBE. The product was dried
under vacuum overnight to obtain a dark-orange-brown, viscous liquid: IR (NaCl plate,
cm⁻¹) 1112 C-O, 1458 C-C, 2880 C-H; ¹H NMR (acetone-d₆, δ) 0.98 (t, 3H,
NCH₂CH₂CH₃), 1.89 (m, 2H, NCH₂CH₂CH₃), 3.33 (s, 9H, OCH₃), 3.53 (m, 6H,
N(CH₂CH₂OCH₂CH₂OCH₃)₃), 3.65 (m, 8H, CH₃CH₂N(CH₂CH₂OCH₂CH₂OCH₃)₃), 3.94
(m, 6H, N(CH₂CH₂OCH₂CH₂OCH₃)₃), 4.03 (m, 6H, N(CH₂CH₂OCH₂CH₂OCH₃)₃); ¹³C
NMR (300 MHz, acetone-d₆, ppm) 10.67, 16.68, 58.80, 60.76, 63.60, 65.36, 70.78, 72.39.
Anal. Calcd. For C₁₈H₄₀BrNO₆: C, 48.43%; H, 9.03%; N, 3.14%. Found: C, 47.59%; H,
8.51%; N, 3.14%.
Tetra[2-(2-methoxyethoxy)ethyl]ammonium Bromide (TA$_4$ Br) 121

A solution of tris[2-(2-methoxyethoxy)ethyl]amine 42 (6.00 mL, 17.82 mmol) and 1-bromo-2-(2-methoxyethoxy)ethane 120 (2.60 mL, 18.35 mmol) was heated at 105-110° for five days. The crude product was washed with MTBE and dried under vacuum overnight to obtain, in 83% yield, a dark-brown-orange liquid that solidified to a brown wax: IR (NaCl plate, cm$^{-1}$) 1111 C-O, 1458 C-C, 2884 C-H; $^1$H NMR (acetone-d$_6$, $\delta$) 3.33 (s, 12H, OCH$_3$), 3.53 (m, 8H, N(CH$_2$CH$_2$OCH$_2$CH$_2$OCH$_3$)$_4$), 3.70 (m, 8H, N(CH$_2$CH$_2$OCH$_2$CH$_2$OCH$_3$)$_4$), 4.04 (m, 16H, N(CH$_2$CH$_2$OCH$_2$CH$_2$OCH$_3$)$_4$); $^{13}$C NMR (300 MHz, acetone-d$_6$, ppm) 58.79, 61.68, 65.41, 70.72, 72.37. Anal. Calcd. For C$_{20}$H$_{44}$BrNO$_8$: C, 47.43%; H, 8.76%; N, 2.77%. Found: C, 45.42%; H, 8.85%; N, 2.81%.

Tris[2-(2-methoxyethoxy)ethyl][2-[2-(2-methoxyethoxy)ethoxy]ethyl]ammonium tosylate (TA$_3$A Tos) 123

A solution of tris[2-(2-methoxyethoxy)ethyl]amine 42 (1.9995 g, 5.873 mmol) and [2-[2-(2-methoxyethoxy)ethoxy]ethoxy] $p$-toluenesulfonate 122 (2.0776 g, 5.873 mmol) in 20 mL acetonitrile was heated at 90° for 144 h. The crude product was dried under vacuum to obtain a dark-brown liquid in 67% yield: $^1$H NMR (acetone-d$_6$, $\delta$) 2.33 (s, 3H, ar-CH$_3$), 3.33 (m, 12H, OCH$_3$), 3.51 (m, 8H, NCH$_2$), 3.62 (m, 14H, CH$_3$OCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_2$CH$_2$N(CH$_2$CH$_2$OCH$_2$CH$_2$OCH$_3$)$_3$), 3.94 (m, 14H, CH$_3$OCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_2$CH$_2$N(CH$_2$CH$_2$OCH$_2$CH$_2$OCH$_3$)$_3$), 7.12 (d, 2H, ar), 7.70 (d, 2H, ar).
Tris[2-(2-methoxyethoxy)ethyl]methylammonium Lithium Phthalocyanine (TAMe LiPc) 124

Procedure A

To a slurry of Li$_2$Pc 1 (2.4071 g, 3.201 mmol) in 30 mL dichloromethane was added 111 (1.4925 g, 3.207 mmol) dissolved in 30 mL dichloromethane. The volume of dichloromethane was doubled and the mixture was stirred for 45 min. The mixture was filtered and the volume of the filtrate was reduced and cooled to 0°C to crystallize. The product was isolated by filtration in 61% yield. Anal. Calcd. For C$_{48}$H$_{52}$LiN$_9$O$_6$: C, 67.20%; H, 6.11%; N, 14.69%. Found: C, 65.99%; H, 4.50%; N, 17.01%.

Procedure B

To a solution of Li$_2$Pc 1 in acetone (20-25 mL for 1 g of Li$_2$Pc 1) was added a 0.70 molar equivalent of 111 dissolved in an equal volume of dichloromethane and the solution was stirred for 90 min. The solution was filtered and washed with DI water or brine and filtered. The product was obtained, in 73% yield, by one of the purification methods described in Figure 12.

IR (NaCl plate, cm$^{-1}$) 1111 C-O, 1451 C-C, 1581 C-C, 1603 C-N, 2886 C-H, 3051 C-H; $^1$H NMR (acetone-d$_6$, δ) 3.30 (s, 9H, OCH$_3$), 3.32 (s, 3H, NCH$_3$), 3.49 (m, 6H, N(CH$_2$CH$_2$OCH$_2$CH$_2$OCH$_3$)$_3$), 3.61 (m, 6H, N(CH$_2$CH$_2$OCH$_2$CH$_2$OCH$_3$)$_3$), 3.81 (m, 6H, N(CH$_2$CH$_2$OCH$_2$CH$_2$OCH$_3$)$_3$), 3.96 (m, 6H, N(CH$_2$CH$_2$OCH$_2$CH$_2$OCH$_3$)$_3$), 8.04 (m, 8H, ar), 9.39 (m, 8H, ar); $^{13}$C NMR (300 MHz, acetone-d$_6$, ppm) 50.18, 58.52, 63.16, 64.54, 70.37, 71.89, 122.65, 128.25, 141.71. Anal. Calcd. For C$_{48}$H$_{52}$LiN$_9$O$_6$: C, 67.20%; H, 6.11%; N, 14.69%. Found: C, 67.01%; H, 6.19%; N, 14.42%.
Tris[2-(2-methoxyethoxy)ethyl]ethylammonium Lithium Phthalocyanine (TAEt LiPc) 125

The product was prepared following Procedure B for 124 in 57% yield: IR (NaCl plate, cm\(^{-1}\)) 1110 C-O, 1451 C-C, 1583 C-C, 1604 C-N, 2887 C-H, 3052 C-H; \(^1\)H NMR (acetone-\(d_6\), \(\delta\)) 1.29 (t, 3H, NCH\(_2\)CH\(_3\)), 3.29 (s, 9H, OCH\(_3\)), 3.46 (m, 6H, N(CH\(_2\)CH\(_2\)OCH\(_2\)CH\(_2\)OCH\(_3\))\(_3\)), 3.56 (m, 6H, N(CH\(_2\)CH\(_2\)OCH\(_2\)CH\(_2\)OCH\(_3\))\(_3\)), 3.61 (q, 2H, CH\(_3\)CH\(_2\)N), 3.68 (m, 6H, N(CH\(_2\)CH\(_2\)OCH\(_2\)CH\(_2\)OCH\(_3\))\(_3\)), 8.04 (m, 8H, ar), 9.39 (m, 8H, ar); \(^{13}\)C NMR (300 MHz, acetone-\(d_6\), ppm) 7.60, 56.65, 58.53, 59.17, 64.26, 70.39, 71.91, 122.65, 128.27, 141.68, 155.60. Anal. Calcd. For C\(_{49}\)H\(_{54}\)LiN\(_9\)O\(_6\): C, 67.50%; H, 6.24%; N, 14.46%. Found: C, 67.37%; H, 6.22%; N, 14.47%.

Tris[2-(2-methoxyethoxy)ethyl]propylammonium Lithium Phthalocyanine (TAPr LiPc) 126

The product was prepared following Procedure B for 124 in 43% yield: IR (NaCl plate, cm\(^{-1}\)) 1109 C-O, 1450 C-C, 1582 C-C, 1604 C-N, 2891 C-H, 3051 C-H; \(^1\)H NMR (acetone-\(d_6\), \(\delta\)) 0.88 (t, 3H, NCH\(_2\)CH\(_2\)CH\(_3\)), 1.72 (m, 2H, NCH\(_2\)CH\(_2\)CH\(_3\)), 3.29 (s, 9H, OCH\(_3\)), 3.44 (m, 8H, CH\(_3\)CH\(_2\)CH\(_2\)N(CH\(_2\)CH\(_2\)OCH\(_2\)CH\(_2\)OCH\(_3\))\(_3\)), 3.54 (m, 6H, N(CH\(_2\)CH\(_2\)OCH\(_2\)CH\(_2\)OCH\(_3\))\(_3\)), 3.66 (m, 6H, N(CH\(_2\)CH\(_2\)OCH\(_2\)CH\(_2\)OCH\(_3\))\(_3\)), 3.84 (m, 6H, N(CH\(_2\)CH\(_2\)OCH\(_2\)CH\(_2\)OCH\(_3\))\(_3\)), 8.04 (m, 8H, ar), 9.39 (m, 8H, ar); \(^{13}\)C NMR (300 MHz, acetone-\(d_6\), ppm) 9.68, 15.30, 58.47, 59.22, 62.48, 64.02, 70.27, 71.82, 122.65, 128.29, 141.68, 155.60. Anal. Calcd. For C\(_{50}\)H\(_{56}\)LiN\(_9\)O\(_6\): C, 67.78%; H, 6.37%; N, 14.23%. Found: C, 67.61%; H, 6.54%; N, 14.14%.
Tetra[2-(2-methoxyethoxy)ethyl]ammonium Lithium Phthalocyanine (TA₄ LiPc)

The product was prepared following Procedure B for 124 in 51% yield: IR (NaCl plate, cm⁻¹) 1112 C-O, 1450 C-C, 1583 C-N, 2892 C-H, 3051C-H; ¹H NMR (acetone-d₆, δ) 3.26 (s, 12H, OCH₃), 3.40 (m, 8H, N(CH₂CH₂OCH₂CH₂OCH₃)₃), 3.44 (m, 8H, N(CH₂CH₂OCH₂CH₂OCH₃)₃), 3.52 (m, 8H, N(CH₂CH₂OCH₂CH₂OCH₃)₃), 3.68 (m, 8H, N(CH₂CH₂OCH₂CH₂OCH₃)₃), 8.05 (m, 8H, ar), 9.39 (m, 8H, ar); ¹³C NMR (300 MHz, acetone-d₆, ppm) 58.51, 60.25, 64.13, 70.20, 71.84, 122.67, 128.31, 141.67. Anal. Calcd. For C₅₂H₆₀Li₉N₉O₈: C, 66.02%; H, 6.39%; N, 13.33%. Found: C, 65.19%; H, 6.51%; N, 13.16%.
RESULTS AND DISCUSSION

Nucleophilic substitutions by tris[2-(2-methoxyethoxy)ethyl]amine 42 on assorted alkyl and alkoxyalkyl halides were used as a facile method to synthesize the alkoxyalkylammonium salts 45, 111, 119, and 121. These salts were then used in metathesis reactions with Li$_2$Pc 1 to synthesize salts composed of an ammonium cation and a LiPc complex anion.

Characterization of Starting Material

The starting amine 42 was characterized by $^1$H and $^{13}$C NMR (Figures 34 and 35). The $^1$H NMR exhibited a triplet absorption 2.74 $\delta$ which can be attributed to the NCH$_2$ protons (a). The singlet absorption at 3.30 $\delta$ attributed to the protons on the methoxy end-groups (e). The multiplet absorption at 3.51 $\delta$, including the corresponding triplet to the absorption at 2.74 $\delta$, can be attributed to the remaining protons (b-d).

![Diagram of 42](image)

The $^{13}$C NMR spectrum of 42 (Figure 35) exhibited four unique absorptions, of the five expected, corresponding to compound. The absorption at 55.81 ppm can be attributed to the carbons (a) adjacent to the nitrogen. The absorption due to CH$_3$ at 58.82 ppm can be attributed to the methoxy end-group carbons (e). The absorption at 70.96
ppm can be attributed to the carbons (b) and (c) on either side of the oxygen atom. The final absorption at 72.70 ppm can be attributed to the last CH<sub>2</sub> carbon (d) in the chain.

**Tris[2-(2-methoxyethoxy)ethyl]methylammonium Iodide (TAMe I) 111**

The ionic liquid tris[2-(2-methoxyethoxy)ethyl]methylammonium iodide 111, was obtained by the reaction of the tertiary amine 42 with methyl iodide 54 using two procedures. In the first procedure the reaction was carried out in a Q-tube™ pressure reactor. Several reactions were carried out using different conditions, as shown in Table 1. The second procedure used was a modified version of a previously published procedure.\(^{23}\)

![Chemical structure](image)

It was found that the Q-tube™ method did not require a solvent for the reaction. The reaction conditions indicated in experiment 5 in Table 1 proved to be the most efficient providing in high-yield a pure product. Drying the product under vacuum was found to be the only purification needed to be able to use the product in the subsequent metathesis reactions. A sample of 111 for characterization was obtained by washing the product with ether and drying the product in vacuo.
Table 1. Reaction conditions for quaternization reactions of 42 with methyl iodide 53.

<table>
<thead>
<tr>
<th>Exp #</th>
<th>Molar Ratio of 42 to 54</th>
<th>Solvent</th>
<th>Temp °C</th>
<th>Duration</th>
<th>Purification</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1 : 1.26</td>
<td>Acetone</td>
<td>50°C</td>
<td>24 hrs</td>
<td>Evaporated from a beaker over 36 hrs</td>
<td>98.49%</td>
</tr>
<tr>
<td>2</td>
<td>1 : 1.62</td>
<td>Methylene chloride</td>
<td>60°C</td>
<td>3 hrs</td>
<td>Dried under vacuum</td>
<td>90.94%</td>
</tr>
<tr>
<td>3</td>
<td>1 : 1.79</td>
<td>Chloroform</td>
<td>90°C</td>
<td>24 hrs</td>
<td>Dried under vacuum</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>1 : 1.50</td>
<td>Acetonitrile</td>
<td>90°C</td>
<td>24 hrs</td>
<td>Washed with diethyl ether, dried under vacuum</td>
<td>36.65%</td>
</tr>
<tr>
<td>5</td>
<td>1 : 1.23</td>
<td>-</td>
<td>90°C</td>
<td>72 hrs</td>
<td>Dried under vacuum, analytical sample washed with diethyl ether</td>
<td>91.1%</td>
</tr>
</tbody>
</table>

The infrared spectrum of 111 exhibited absorptions at 1112, 1458, 2883, cm\(^{-1}\) (Figure 36 and Table 2). The first absorption was attributed to the C-O ether bond stretching and the other two absorptions were attributed to the aliphatic C-C and C-H bond stretching, respectively.

The \(^1\)H NMR spectrum of 111 (Figures 7 and 37) exhibited singlet absorptions at 3.33 \(\delta\) and 3.46 \(\delta\) which can be attributed to the methyl protons from the three methoxy end groups (f) and N-methyl protons (a), respectively. The multiplet absorptions at 3.54 \(\delta\), 3.70 \(\delta\), and 4.04 \(\delta\) can be attributed to the alkoxy chain protons (b-e), respectively.
Figure 7. Portion of ¹H NMR spectrum of 111 with labeled structure.

The ¹³C NMR spectrum of 111 (Figure 38) exhibited the six unique absorptions expected for the product. The methyl absorption at 51.19 ppm can be attributed to the CH₃ (a) group. The absorption at 58.84 ppm can be attributed to the methoxy end-group (f). The remaining CH₂ absorptions 63.95 ppm, 65.53 ppm, 70.85 ppm, and 72.36 ppm can be attributed to carbons (b-e), respectively.

Table 2. IR, ¹H NMR, and ¹³C NMR spectral data of 111.

<table>
<thead>
<tr>
<th>TAMe Iodide, 111</th>
<th>IR (NaCl)</th>
<th>¹H NMR</th>
<th>¹³C NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>1112, C=O</td>
<td>1112, C-&lt;br&gt;1458, C-C</td>
<td>3.33 (s, 9H, OCH₃) 3.46 (s, 3H, NCH₃) 3.54 (m, 6H, NCH₂) 3.70 (m, 6H, CH₂O) 4.04 (m, 12H, OCH₂CH₂O)</td>
<td>51.19 &lt;br&gt;58.84 &lt;br&gt;63.95 &lt;br&gt;65.53 &lt;br&gt;70.85 &lt;br&gt;72.36</td>
</tr>
<tr>
<td>2883, C-H</td>
<td>2883, C-H</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Synthesis of Alkoxyalkylammonium Salts

The remaining alkoxyalkylammonium salts were prepared by the method found to be the most efficient for 111, experiment 5 in Table 1. Exceptions to the method were the use of different molar ratios and temperatures as shown in Table 3. Ethyl iodide 86 was used to quaternize 42 to obtain 118, however the product was not characterized and used in metathesis reactions; the bromide salt 119 was preferred.
The infrared spectrum of tris[2-(2-methoxyethoxy)ethyl]ethylammonium bromide (TAEt Br) 119 (Figure 39 and Table 4) exhibited characteristic absorptions at 1112, 1456, and 2881 cm\(^{-1}\). The absorption at 1112 cm\(^{-1}\) was attributed to the C-O ether bond stretching and the other two absorptions were attributed to the aliphatic C-C and C-H bond stretching, respectively.

The \(^1\)H NMR spectrum of 119 (Figures 8 and 40) exhibited a triplet and quartet pair at 1.42 \(\delta\), not shown in Figure 8, and 3.84 \(\delta\) which can be attributed to the protons (a) and (b), respectively, in the CH\(_2\)CH\(_3\) group. The singlet at 3.33 \(\delta\) can be attributed to the protons on the methoxy end-groups (g). The multiplets at 3.53 \(\delta\), 3.70 \(\delta\), 3.96 \(\delta\), and 4.05 \(\delta\) can be attributed to the CH\(_2\) protons (c-f) on the alkoxy chains, respectively.
Figure 8. Portion of $^1$H NMR spectrum of 119 with labeled structure.

The $^{13}$C NMR spectrum of 119 (Figure 41) showed seven unique absorptions.

The absorptions at 8.82 ppm and 57.64 ppm can be attributed to the carbons in the CH$_2$CH$_3$ (a,b) group, respectively. The absorption at 58.80 ppm can be attributed to the methoxy (g) end-groups on the alkoxy chain. The remaining absorptions at 60.34 ppm, 65.34 ppm, 70.81 ppm, 72.37 ppm can be attributed to carbons (c-f) in the alkoxy chain, respectively.

Table 4. IR, $^1$H NMR, and $^{13}$C NMR spectral data of 119.

<table>
<thead>
<tr>
<th>TAEt Bromide, 119</th>
<th>IR (NaCl)</th>
<th>$^1$H NMR</th>
<th>$^{13}$C NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1112, C-O</td>
<td>1.42 (t, 3H, CH$_3$)</td>
<td>8.82</td>
</tr>
<tr>
<td></td>
<td>3.33 (s, 9H, OCH$_3$)</td>
<td>57.64</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.53 (m, 6H, NCH$_2$)</td>
<td>58.80</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1456, C-C</td>
<td>3.70 (m, 6H, CH$_2$O)</td>
<td>60.34</td>
</tr>
<tr>
<td></td>
<td>3.84 (q, 2H, NCH$_2$)</td>
<td>65.34</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2881, C-H</td>
<td>3.96 (m, 6H, OCH$_2$)</td>
<td>70.81</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.05 (m, 6H, CH$_2$O)</td>
<td>72.37</td>
</tr>
</tbody>
</table>

Tris[2-(2-methoxyethoxy)ethyl]propylammonium Bromide (TAPr Br) 45

The infrared spectrum of tris[2-(2-methoxyethoxy)ethyl]propylammonium bromide 45 (Figure 42 and Table 5) showed three characteristic absorptions. The absorption at 1112 cm$^{-1}$ due to the C-O ether bond stretching and the other two
absorptions at 1458, and 2880 cm⁻¹ can be attributed to the C-C and C-H aliphatic bond stretching, respectively.

The \(^1\)H NMR spectrum of 45 (Figures 9 and 43) exhibited a triplet absorption at 0.98 \(\delta\), which can be attributed to the methyl protons (a) of the CH₂CH₂CH₃ group. The multiplet at 1.89 \(\delta\) can be attributed to the protons from (b) of the same group. Two of the protons from the multiplet absorption at 3.65 \(\delta\) are from the expected triplet which can be attributed to the protons from (c) of the CH₂CH₂CH₃ group. The singlet absorption at 3.33 \(\delta\) can be attributed to the methoxy (h) end-group protons. The multiplet absorptions at 3.53 \(\delta\), 3.65 \(\delta\), 3.94 \(\delta\), and 4.03 \(\delta\) can be attributed to the remaining protons (d-g), respectively.

![Figure 9](image)

**Figure 9.** Portion of \(^1\)H NMR spectrum of 45 with labeled structure.

The \(^{13}\)C NMR spectrum of 45 (Figure 44) exhibited eight unique absorptions as expected for the product. The absorption at 10.67 ppm can be attributed to the methyl from CH₂CH₂CH₃ (a). The absorptions at 16.68 ppm and 63.60 ppm can be attributed to the two methylenes (b) and (c) from the same propyl group. The absorption at 58.80 ppm can be attributed to the methoxy (h) end-groups. The absorptions at 60.76 ppm, 65.36 ppm, 70.78 ppm, and 72.39 ppm can be attributed to carbons (d-g) on the alkoxy chains, respectively.
Table 5. IR, $^1$H NMR, and $^{13}$C NMR spectral data of 45.

<table>
<thead>
<tr>
<th>TAPr Bromide, 45</th>
<th>IR (NaCl)</th>
<th>$^1$H NMR</th>
<th>$^{13}$C NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1112, C-O</td>
<td>0.98 (t, 3H, CH$_3$)</td>
<td>10.67</td>
</tr>
<tr>
<td></td>
<td>1458, C-C</td>
<td>1.89 (m, 2H, CH$_2$)</td>
<td>16.68</td>
</tr>
<tr>
<td></td>
<td>2880, C-H</td>
<td>3.33 (s, 9H, OCH$_3$)</td>
<td>58.80</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.53 (m, 6H, NCH$_2$)</td>
<td>60.67</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.65 (m, 8H, NCH$_2$, CH$_2$O)</td>
<td>63.60</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.94 (m, 6H, OCH$_2$)</td>
<td>65.36</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.03 (m, 6H, CH$_2$O)</td>
<td>70.78</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.70 δ</td>
<td>72.39</td>
</tr>
</tbody>
</table>

Tetra[2-(2-methoxyethoxy)ethyl]ammonium Bromide (TA$_4$ Br) 121

The infrared spectrum of 121 exhibited absorptions at 1111, 1458 and 2884 cm$^{-1}$ (Figure 45 and Table 6). The first absorption can be attributed to the C-O ether bond stretching and the other two absorptions can be attributed to the aliphatic C-C and C-H bond stretching, respectively.

The $^1$H NMR spectrum of 121 (Figures 10 and 46) exhibited a singlet absorption at 3.33 δ which can be attributed to the methyl protons from the four methoxy (e) end-groups. The multiplet absorption at 3.53 δ can be attributed to the protons from the NCH$_2$ (a). The multiplet absorption at 3.70 δ can be attributed to the protons of the OCH$_2$ (b). The remaining absorption at 4.04 δ can be attributed to the protons of OCH$_2$CH$_2$O (c) and (d).

Figure 10. Portion of $^1$H NMR spectrum of 121 with labeled structure.
The $^{13}$C spectrum of 121 (Figure 47) exhibited five unique absorptions expected for the product. The absorption at 58.79 ppm can be attributed to the methyl carbon from the methoxy (e) end-group. The remaining four absorptions at 61.68 ppm, 65.41 ppm, 70.72 ppm, and 72.37 ppm can be attributed to the carbons (a-d), respectively.

**Table 6.** IR, $^1$H NMR, and $^{13}$C NMR spectral data of 121.

<table>
<thead>
<tr>
<th>TA$_4$ Bromide, 121</th>
<th>IR (NaCl)</th>
<th>$^1$H NMR</th>
<th>$^{13}$C NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1111, C-O</td>
<td>3.33 (s, 12H, OCH$_3$)</td>
<td>58.79</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.53 (m, 8H, NCH$_2$)</td>
<td>61.68</td>
</tr>
<tr>
<td></td>
<td>1458, C-C</td>
<td>3.70 (m, 8H, CH$_2$O)</td>
<td>65.41</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.04 (m, 16H, OCH$_2$CH$_2$O)</td>
<td>70.72</td>
</tr>
<tr>
<td></td>
<td>2884, C-H</td>
<td></td>
<td>72.37</td>
</tr>
</tbody>
</table>

**Thermal Analysis of Salts**

This series of alkoxyalkylammonium salts, 45, 111, 119, and 121, were synthesized for use in metathesis reactions with Li$_2$Pc 1. The salts were found to be liquid at room-temperature with the exception of 121, which had a broad melting peak at 46.5°, as shown in Figure 48. The thermal stability of the products was examined via thermal gravimetric analysis (TGA) (Figure 49) under a nitrogen atmosphere using a 20°/min ramp. The four salts exhibited very similar decomposition temperatures with a sharp onset of weight loss just before 200° as shown in Figure 49.

**Tris[2-(2-methoxyethoxy)ethyl][2-[2-(2-methoxyethoxy)ethoxy]ethoxy]ethyl]ammonium tosylate (TA$_3$A Tos) 123**

The commercial availability of [2-[2-(2-methoxyethoxy)ethoxy]ethoxy] $p$-toluene sulfonate 122 made it a candidate for use in a nucleophilic substitution by 42. The quaternary ammonium product 123 was synthesized by a similar procedure to the
proceeding salts. The $^1$H NMR spectrum of 123 (Figure 50) exhibited singlet absorptions at 2.33 $\delta$ and 3.33 $\delta$ which can be attributed to the methyl protons (o) of the anion and the protons of the methoxy end-groups (e) and (l), respectively. The multiplet absorption at 3.51 $\delta$ can be attributed to the methylene protons (a) and (f) adjacent to the positively charged nitrogen. The two multiplets absorptions at 3.62 $\delta$ and 3.94 $\delta$ can be attributed to the remaining protons (b-d) and (g-k) on the alkoxy chains. The two doublet absorptions downfield at 7.70 $\delta$ and 7.12 $\delta$ can be attributed to the aromatic protons (m) and (n) of the anion, respectively.

![123](image)

The aromatic protons provided a simple feature of the spectrum which could be used to track the progress of the reaction, as shown in Figure 11. The peaks attributed to the formation of the product (p) grow relative to the peaks attributed to the reactant (r) as the reaction proceeds.

![Figure 11](image)

**Figure 11.** Aromatic peaks from $^1$H NMR spectra of 123 at 24, 48, 72 and 144 h.

**Attempted Alkoxyalkylammonium Salts Synthesis**
Other salts were also attempted to be synthesized for use in metathesis reactions with Li$_2$Pc 1. The tertiary amine 42 was used in nucleophilic substitutions on butyl, pentyl, heptyl, and octyl bromides using methods already discovered. The heptyl and octyl products were not obtained in any usable purity. The butyl and pentyl quaternized salts could be isolated but proved to be problematic in the metathesis reactions described later.

**Metathesis Reactions of Alkoxyalkylammonium Salts with Li$_2$Pc 1**

Metathesis/ion-exchange reactions with Li$_2$Pc 1 were carried out using the alkoxyalkylammonium salts 45, 111, 119, and 121. Two procedures were used for the reaction of 111 with 1 the more efficient of the two was used in later metathesis reactions.

The first method was a phase-transfer metathesis reaction. A solution of 111 dissolved in DCM was added to a slurry of 1 and DCM. After a stirring for 45 min the product was isolated by filtration and evaporation.

The second method, used in later metathesis reactions as well, involved mixing a solution of 1 in acetone and a solution of the appropriate ammonium salt in DCM. This provided a homogeneous solution. More involved purification was required for products made by this method.

Several methods used to purify products obtained by method two are shown in **Figure 12**. Each method began with a deionized water or brine wash followed by filtration. The brine wash provided a more distinct organic/aqueous separation. In the simpler procedure (A in **Figure 12**), the volume of the separated organic phase is reduced under vacuum and the solution is cooled to provide the product. This generally provided
product of unsuitable purity. The second option (B in Figure 12) involves the evaporation of the organic phase, dissolution of the residue in DCM and filtration to remove insoluble material. The product could be easily isolated by evaporation of the DCM (C in Figure 12). Alternately, the volume of the DCM phase was reduced under vacuum a two to three volume of toluene was added and crystallization was allowed to proceed at low temperature (D in Figure 12).

Figure 12. Purification methods for metathesis products.

Tris[2-(2-methoxyethoxy)ethyl]methylammonium Lithium Phthalocyanine (TAMe LiPc) 124

The infrared spectrum of 124 (Figure 51 and Table 7) exhibited characteristic absorptions at 1111, 1451, 1582, 1603, 2886, and 3051 cm$^{-1}$. The absorption at 1111 cm$^{-1}$ can be attributed to the C-O ether bond stretching. The absorptions at 1451 and 2886 cm$^{-1}$ can be attributed to the C-C and C-H aliphatic bond stretching, respectively. The absorption at 1582 cm$^{-1}$ can be attributed to the C-N bond stretching from the phthalocyanine ring. The absorptions at 1603 and 3051 cm$^{-1}$ can be attributed to the C-C and C-H aromatic bond stretching, respectively.
The $^1$H NMR spectrum of 124 (Figures 13 and 52) exhibited singlet absorptions at 3.30 δ and 3.32 δ which can be attributed to the protons of the methoxy end-groups (f) and the methyl protons of the NCH$_3$ group (a). The multiplet absorptions at 3.49 δ and 3.61 δ can be attributed to the protons from the NCH$_2$ group (b) and the CH$_2$O group (c), respectively. The multiplet absorption at 3.81 δ and 3.96 δ can be attributed to the CH$_2$ protons (d) and (e) between the ether groups on the chains. The multiplet absorptions at 8.04 δ and 9.39 δ can be attributed to the aromatic protons on (g) and (h).

Figure 13. Portion of $^1$H NMR spectrum of 124 with labeled structure.

The $^{13}$C NMR spectrum of 124 (Figure 53 and Figure 13 labels) exhibited nine unique absorptions of the ten absorptions expected for the product. The absorption at 50.18 ppm can be attributed to the carbon of the methyl group (a). The absorption at 58.52 ppm can be attributed to carbons of the methoxy end-groups (f). The absorptions
at 63.16 ppm, 64.54 ppm, 70.37 ppm, and 71.89 ppm can be attributed to the remaining carbons (b-e) on the alkoxy chains, respectively. The absorptions at 122.65 ppm and 128.25 ppm can be attributed to the carbons (g) and (h) in the phthalocyanine ring. The remaining absorption at 141.71 ppm can be attributed to the carbons (i) in the phthalocyanine ring. There is one absorption missing from the spectrum, around 155 ppm, that should be attributed to the remaining carbons of the anion (j).

**Table 7. IR, $^1$H NMR, and $^{13}$C NMR spectral data of 124.**

<table>
<thead>
<tr>
<th>TAMe LiPc, 124</th>
<th>IR (NaCl)</th>
<th>$^1$H NMR</th>
<th>$^{13}$C NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Structure" /></td>
<td>1111, C-O</td>
<td>3.30 (s, 9H, OCH$_3$)</td>
<td>50.18</td>
</tr>
<tr>
<td></td>
<td>1451, C-C</td>
<td>3.32 (s, 3H, NCH$_3$)</td>
<td>58.52</td>
</tr>
<tr>
<td></td>
<td>1582, ar C-N</td>
<td>3.49 (m, 6H, NCH$_2$)</td>
<td>63.16</td>
</tr>
<tr>
<td></td>
<td>1603, ar C-C</td>
<td>3.61 (m, 6H, CH$_2$O)</td>
<td>64.54</td>
</tr>
<tr>
<td></td>
<td>2886, C-H</td>
<td>3.81 (m, 6H, OCH$_2$)</td>
<td>70.37</td>
</tr>
<tr>
<td></td>
<td>3051, ar C-H</td>
<td>3.96 (m, 6H, CH$_2$O)</td>
<td>71.89</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.04 (m, 8H, ar)</td>
<td>122.65</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.39 (m, 8H, ar)</td>
<td>128.25</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>141.71</td>
</tr>
</tbody>
</table>

**Tris[2-(2-methoxyethoxy)ethyl]ethylammonium Lithium Phthalocyanine (TAEt LiPc) 125**

The infrared spectrum of **125** (**Figure 54 and Table 8**) exhibited characteristic absorptions at 1110, 1451, 1583, 1604, 2887, and 3052 cm$^{-1}$. The absorption at 1110 cm$^{-1}$ can be attributed to the C-O ether bond stretching. The absorptions at 1451 and 2887 cm$^{-1}$ can be attributed to the C-C and C-H aliphatic bond stretching, respectively, from the cation. The absorption at 1583 cm$^{-1}$ can be attributed to the C-N bond stretching from the phthalocyanine ring. The absorptions at 1604 and 3052 cm$^{-1}$ can be attributed to the C-C and C-H aromatic bond stretching from the anion.

The $^1$H NMR spectrum of **125** (**Figures 14 and 55**) exhibited a triplet absorption at 1.29 δ which can be attributed to the methyl protons (a). The expected quartet
absorption was found partially overlapped by a multiplet at 3.61 δ which can be attributed to the CH$_2$ protons (b) from the ethyl group. The singlet absorption at 3.29 δ can be attributed to the protons on the methoxy end-groups (g) of the alkoxy chains. The multiplets at 3.46 δ and 3.56 δ can be attributed to the protons from the NCH$_2$ (c) and the OCH$_2$ (d) groups, respectively. The multiplet absorptions at 3.68 δ and 3.86 δ can be attributed to the OCH$_2$CH$_2$O protons (e) and (f), respectively. The remaining absorptions at 8.04 δ and 9.39 δ can be attributed to the aromatic protons (h) and (i), respectively.

**Figure 14.** Portion of $^1$H NMR spectrum of 125 with labeled structure.

The $^{13}$C NMR spectrum of 125 (**Figure 56** and **Figure 14** labels) exhibited eleven unique absorptions corresponding to the product. The absorptions at 7.60 ppm and 56.65 ppm can be attributed to the carbons (a) and (b) on the ethyl group, respectively. The
absorption at 58.53 ppm can be attributed to the carbons on the methoxy end-groups (g). The absorptions at 59.17 ppm, 64.26 ppm, 70.39 ppm, and 71.91 ppm can be attributed to the carbons on the alkoxy chain (c-f), respectively. The absorptions at 122.65 ppm and 128.27 ppm can be attributed to the aromatic C-H carbons (h) and (i), respectively. The remaining absorptions 141.68 ppm and 155.60 ppm can be attributed to the aromatic carbons (j) and (k), respectively.

| Table 8. IR, $^1$H NMR, and $^{13}$C NMR spectral data of 125. |
|---|---|---|---|
|  | TAEt LiPc, 125 | IR (NaCl) | $^1$H NMR | $^{13}$C NMR |
|  | 1110, C-O 1451, C-C 1583, ar C-N 1604, ar C-C 2887, C-H 3052, ar C-H | 1110, C-O 1451, C-C 1583, ar C-N 1604, ar C-C 2887, C-H 3052, ar C-H | 1.29 (t , 3H, CH$_3$) 3.29 (s , 9H, OCH$_3$) 3.46 (m, 6H, NCH$_2$) 3.56 (m, 6H, CH$_2$O) 3.61 (q , 2H, NCH$_2$) 3.68 (m, 6H, OCH$_2$) 3.86 (m, 6H, CH$_2$O) 8.04 (m, 8H, ar) 9.39 (m, 8H, ar) | 7.60 56.65 58.53 59.17 64.26 70.39 71.91 122.65 128.27 141.68 155.60 |

Tris[2-(2-methoxyethoxy)ethyl]propylammonium Lithium Phthalocyanine (TAPr LiPc) 126

The infrared spectrum of 126 (Figure 57 and Table 9) exhibited characteristic absorptions at 1109, 1450, 1582, 1604, 2891, 3051 cm$^{-1}$. The absorption at 1109 cm$^{-1}$ can be attributed to the C-O ether bond stretching. The absorptions at 1450 and 2891 cm$^{-1}$ can be attributed to the C-C and C-H aliphatic bond stretching, respectively. The absorption at 1604 cm$^{-1}$ can be attributed to the C-N aromatic bond stretching. The absorptions at 1582 and 3051 cm$^{-1}$ can be attributed to the C-C and C-H aromatic bond stretching, respectively.
The $^1$H NMR spectrum of 126 (Figures 15 and 58) exhibited a triplet absorption at 0.88 δ which can be attributed to the protons (a) of the propyl group. The absorptions at 1.72 δ and 3.44 δ attributed to the two CH$_2$ groups (b) and (c), respectively, on the same chain. The singlet absorption at 3.29 δ can be attributed to the protons on the methoxy end-groups (h). The absorptions at 3.44 δ and 3.54 δ can be attributed to the protons on the NCH$_2$ (d) and the O CH$_2$ (e). The multiplet absorptions at 3.66 δ and 3.84 δ can be attributed to the remaining protons (f) and (g) on the alkoxy chains. The absorptions at 8.04 δ and 9.39 δ can be attributed to the aromatic CH groups (i) and (j), respectively, on the anion.

**Figure 15.** Portion of $^1$H NMR spectrum of 126 with labeled structure.
The $^{13}$C NMR spectrum of 126 (Figure 59 and Figure 15 labels) exhibited twelve unique absorptions that correspond to the product. The absorptions at 9.68 ppm, 15.30 ppm, and 62.48 ppm can be attributed to the carbons (a-c), respectively, on the propyl chain. The absorption at 58.47 ppm can be attributed to the carbon in the methoxy end-group (h). The absorptions at 59.22 ppm, 64.02 ppm, 70.27 ppm, and 71.82 ppm can be attributed to the remaining carbons on the alkoxy chain (d-g), respectively. The absorptions at 122.65 ppm and 128.29 ppm can be attributed to the CH groups (i) and (j), respectively, on the phthalocyanine ring. The absorptions at 141.68 ppm and 155.60 ppm can be attributed to the unassigned carbons (k) and (l), respectively, on the phthalocyanine ring.

**Table 9.** IR, $^1$H NMR, and $^{13}$C NMR spectral data of 126.

<table>
<thead>
<tr>
<th>TAPr LiPc, 126</th>
<th>IR (NaCl)</th>
<th>$^1$H NMR</th>
<th>$^{13}$C NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Tetra[2-(2-methoxyethoxy)ethyl] ammonium Lithium Phthalocyanine (TA4 LiPc)" /></td>
<td>1109, C-O 1450, C-C 1582, ar C-N 1604, ar C-C 2891, C-H 3051, ar C-H</td>
<td>0.88 (t, 3H, CH$_3$) 1.72 (m, 2, CH$_2$) 3.29 (s, 9H, OCH$_3$) 3.44 (m, 8H, NCH$_2$) 3.54 (m, 6H, CH$_2$O) 3.66 (m, 6H, OCH$_2$) 3.84 (m, 6H, CH$_2$O) 8.04 (m, 8H, ar) 9.39 (m, 8H, ar)</td>
<td>9.68 15.30 58.47 59.22 62.48 64.02 70.27 71.82 122.65 128.29 141.68 155.60</td>
</tr>
</tbody>
</table>

127

The infrared spectrum of 127 (Figure 60 and Table 10) exhibited characteristic absorptions at 1112, 1450, 1583, 1604, 2892, 3051 cm$^{-1}$. The absorption at 1112 cm$^{-1}$ can be attributed to the C-O ether bond stretching. The absorptions at 1450 and 2892 cm$^{-1}$ can be attributed to the C-C and C-H aliphatic bond stretching, respectively. The
absorption at 1583 cm\(^{-1}\) can be attributed to the C-N aromatic stretching in the anion. The absorptions at 1604 and 3051 cm\(^{-1}\) can be attributed to the C-C and C-H aromatic bond stretching.

The \(^1\)H NMR spectrum of 127 (Figures 16 and 61) exhibited a singlet absorption at 3.26 \(\delta\) which can be attributed to the protons on the methoxy end-groups (e). The absorptions at 3.40 \(\delta\) and 3.44 \(\delta\) can be attributed to the NCH\(_2\) (a) and O CH\(_2\) (b) groups. The absorptions at 3.52 \(\delta\) and 3.68 \(\delta\) can be attributed to the remaining protons (c) and (d) on the alkoxy chains. The absorptions at 8.05 \(\delta\) and 9.39 \(\delta\) can be attributed to the protons from the CH groups (f) and (g), respectively, on the phthalocyanine ring.

Figure 16. Portion of \(^1\)H NMR spectrum of 127 with labeled structure.

The \(^{13}\)C NMR spectrum of 127 (Figure 62 and Figure 16 labels) exhibited eight of nine expected absorptions corresponding to the product. The absorption at 58.51 ppm
can be attributed to the methoxy (e) end-groups. The absorptions at 60.25 ppm, 64.13 ppm, 70.20 ppm, and 71.84 ppm can be attributed to the CH$_2$ carbons (a-d), respectively, on the alkoxy chains. The absorptions at 122.67 ppm and 128.31 ppm can be attributed to the aromatic CH carbons (f) and (g), respectively, in the phthalocyanine ring. The remaining absorption at 141.67 ppm can be attributed to the aromatic carbon (h) on the phthalocyanine structure while the absorption due to (i) did not appear, approximately at 155 ppm, as expected.

**Table 10.** IR, $^1$H NMR, and $^{13}$C NMR spectral data of 127.

<table>
<thead>
<tr>
<th>TA$_4$ LiPc, 127</th>
<th>IR (NaCl)</th>
<th>$^1$H NMR</th>
<th>$^{13}$C NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Structure" /></td>
<td>1112 C-O 1450, C-C 1583, ar C-N 1604, ar C-C 2892, C-H 3051, ar C-H</td>
<td>3.26 (s , 12H, OCH$_3$) 3.40 (m, 8H, NCH$_2$) 3.44 (m, 8H, CH$_3$O) 3.52 (m, 8H, OCH$_2$) 3.68 (m, 8H, CH$_2$O) 8.05 (m, 8H, ar) 9.39 (m, 8H, ar)</td>
<td>58.51 60.25 64.13 70.20 71.84 122.67 128.31 141.67</td>
</tr>
</tbody>
</table>

**Concentration Effects in $^1$H NMR Spectra of Metathesis Products**

While characterizing the metathesis products, the position of the proton absorptions of the alkoxyalkylammonium ion were sensitive to concentration of the sample. Spectra of 124, 125, and 126 (Figures 17-19 and 63-65) were obtained using 1, 5, 10, and 25 mg of the product, 126 was only analyzed with 1, 5, and 10 mg. In all three products as the concentration was increase the absorptions attributed to the protons on the alkoxy and alkyl chains of the cations were shifted up-field relative to their positions to the residual solvent peak. This indicates that with increasing concentration the protons are being shielded resulting in an up-field shift. It is noted that the absorptions attributed to the aromatic protons on the anion do not shift with increasing concentration.
Figure 17. Cation absorptions of 124 from ^1H NMR spectra of 1, 5, 10, and 25 mg samples.

Figure 18. Cation absorptions of 125 from ^1H NMR spectra of 1, 5, 10, and 25 mg samples.
Figure 19. Cation absorptions of $^{126}$ from $^1$H NMR spectra of 1, 5, and 10 mg samples.

Thermal Analysis of Metathesis Products $^{124-127}$

The thermal properties of the alkoxyalkylammonium lithium phthalocyanine products $^{124-127}$ were examined by thermal gravimetric analysis (TGA) (Figures 20 and 66) and differential scanning calorimetry (DSC) (Figures 67-70). Thermal stability was determined by TGA, using a 20°/min ramp. While phase transitions were examined by DSC, using a 20°/min ramp for the initial heating and a 10°/min ramp for the subsequent cooling and heating. All experiments were performed under a nitrogen atmosphere.

Thermal Gravimetric Analysis

The thermal stability (Figures 20 and 66) of the metathesis products $^{124-127}$ were similar, with the exception of $^{124}$. TAMe LiPc $^{124}$ exhibits a more pronounced mass loss from room temperature to about 300° than $^{125-127b}$. At 300° weight loss of $^{124}$ sharply increases to approximately 61% of its original mass. That mass loss can be
attributed to the loss of the ammonium cation which comprises approximately 40% of the total weight of the compound.

The other three LiPcs show much more similar profiles until approximately 300°, with TAPr LiPc 126 showing slightly more stability. After 300°, the products all sharply lose approximately 40-45% of their masses, approximately equivalent to the coordinated ammonium cation.

![Trisalkoxyalkylammonium LiPcs](image)

**Figure 20.** Weight % vs. temperature TGA trace of 124-127.

**Differential Scanning Calorimetry**

The DSC traces of the products 124-127 (Figures 67-70) showed interesting transitions in the products and provided some initial information on the crystallinity of the compounds. The initial heating scan of 124 (Figure 67) shows two endothermic transitions at 81° and 150°. The first transition at 81° can be attributed to a solid-solid transition while the endotherm at 150° can be attributed to the sample melting. On the
cooling scan an exotherm, attributed to crystallization, was seen at 118°. On a second heating scan, at a slower heating rate, only one endothermic peak was seen at 147°, which was attributed to the melting point.

The DSC trace of 125 (Figure 68) exhibited only one peak at 118° in the initial heating scan, attributed to the product melting. The cooling and second heating scan showed no endo- or exothermic peaks indicating that the product did not re-crystallize and melt.

The DSC trace of 126 (Figure 69) exhibits an endothermic peak at 126° attributed to the product melting during the initial heating. During the cooling scan, an exothermic peak at 83° was observed attributed to the crystallization of the product. On the second, slower heating scan the endothermic peak attributed to the melting point was seen at 124°.

The DSC trace of 127 (Figure 70) exhibits two endothermic peaks at 106° and 160° during the initial heating. The first was attributed to a solid-solid transition while the second at 160° was attributed to the melting point of the product. During the cooling scan, an exothermic, crystallization peak was observed at 146°. During the second, slower heating a broader endothermic peak, attributed to the melting point, was seen at 158°.

**Single Crystal X-ray Diffraction Experiments**

Crystals suitable for single-crystal x-ray diffraction experiments of 124, 126, and 127 were grown and analyzed. While the structural details obtained were useful in determining LiPc anion spacing and relative cation position, the crystal structures of these compounds all exhibited disorder due to the alkoxyalkyl chains.
Tris[2-(2-methoxyethoxy)ethyl]methylammonium Lithium Phthalocyanine (TAMe LiPc) 124

The crystal structure of TAMe LiPc 124 was found to crystallize in a monoclinic lattice with $P2_1$ symmetry. It contains a repeating pair of rings, at an angle of 85.9°, with their respective cations (Figure 21). The alkoxyalkylammonium cation was determined to coordinate to the anion with its alkoxy chains spread over the face of the macrocycle (a and b in Figure 21). The center chain appears to coordinate through an oxygen atom with the lithium ion centered in the Pc ring on one of the anions (c in Figure 21). The cations were not fully resolved, with several bonds and atoms not fully delineated.

Figure 21. Coordination between LiPc complex anion and ammonium cation in 124.

The perpendicular rings were found to be approximately 4.0 Å apart, as shown in Figure 21. The parallel ring pairs created by the repeated units were offset in three dimensions with a 1.92 Å distance between the mean planes of the rings, as shown in Figure 21. The distance between the ring centers, shown in Figure 22, was calculated to
be 14.5 Å at an approximate angle of 24° from a centerline through the rings. The packing pattern of 124, shown in Figure 23 and 24, is comprised of the asymmetric units with a symmetry operator of a two-fold screw axis along the b-axis.

**Figure 22.** Separation of parallel rings created by symmetry pairs in 124.

**Figure 23.** View of packing pattern of 124 down vector between a- and c-axes.
Figure 24. View of packing pattern of 124 down b-axis of unit cell.

Tris[2-(2-methoxyethoxy)ethyl]propylammonium Lithium Phthalocyanine (TAPr
LiPc) 126

Crystals of 126 were found to crystallize in a monoclinic lattice with P2₁/c
symmetry. The asymmetric unit was found to be an ammonium cation/LiPc complex
anion complex, as shown in Figure 25. One alkoxy chain was found to lie across the
face of the Pc ring where the terminal ether group coordinated the lithium ion centered in
the macrocycle (a in Figure 25). The remaining alkoxy chains were positioned around
the outside of the ring with the propyl group also extended over the ring.
Figure 25. Determined structure of 126 from single crystal x-ray diffraction experiment.

The symmetry equivalents created a pair of rings that were found to have a 68.8° angle between their mean planes and were approximately 3.5 Å apart, as shown in Figure 26. The pairs of parallel rings created by the symmetry operations were offset in three dimensions with a 0.716 Å distance between the mean planes of the rings, as shown in Figure 27. The distance between these ring centers, shown in Figure 26, was calculated to be 14.07 Å at an approximate angle of 25.5° from a centerline through the rings. The packing pattern of 126 shown in Figure 28 is the result of three symmetry operations, a two-fold screw axis, an inversion center, and a glide plane perpendicular to the screw axis.
Figure 27. Side view of parallel rings in 126.

Figure 26. View of the face of parallel rings in 126.
Figure 28. Packing pattern of 126.

Tetra[2-(2-methoxyethoxy)ethyl] ammonium Lithium Phthalocyanine (TA₄ LiPc) 127

Compound of 127 was found to form a monoclinic crystalline lattice with P2₁/c symmetry. The asymmetric unit was found to be one ammonium cation and LiPc complex anion complex, as shown in Figure 29. One alkoxy chain was found to lie across the face of the LiPc ring where the terminal ether group is coordinated with the lithium ion centered in the macrocycle (a in Figure 29). The remaining alkoxy chains were positioned off-center above the ring mostly off of the edge of the LiPc ring. The macrocycle was found to have an approximately 17° distortion, away from the coordinated cation.
Figure 29. Determined structure of 127 from single crystal x-ray diffraction experiment.

Figure 30. Side-view of parallel rings in 127.
Figure 31. Face-view of parallel rings in 127.

The symmetry equivalent molecules create a pair of rings that were found to have a 71.05° angle between their mean planes and were approximately 3.6 Å apart, as shown in Figure 30. The pairs of parallel rings created by the symmetry operations were offset in three dimensions with a 6.425 Å distance between the mean planes of the rings, as shown in Figure 30. The distance between these ring centers, shown in Figure 31, was calculated to be 10.5 Å. The packing pattern of 127 shown in Figures 32 and 33 is the result of three symmetry operations, a two-fold screw axis, an inversion center, and a glide plane perpendicular to the screw axis.
Figure 32. View of packing pattern of 127 down the c-axis of unit cell.

Figure 33. View of packing pattern of 127.
Conclusions

A series of alkoxyalkylammonium salts was successfully synthesized via nucleophilic substitution of alkylhalides by 42 and purified. The salts 45, 111, 119, and 121 were later used in metathesis reactions with Li₂Pc 1. The proposed series, methyl to heptyl substituted, was not completed due to problematic metathesis reactions using tris[2-(2-methoxyethoxy)ethyl]butylammonium bromide and tris[2-(2-methoxyethoxy)ethyl]pentylammonium bromide.

The metathesis products 124-127 resulting from the salts 45, 111, 119, and 121 were successfully synthesized and purified in acceptable yields from 43%-73%. The products were found to be thermally stable to 300°, with the exception of 124 which was found to be stable to 250°. The melting points of the products were found to range from 118°-160°.

Suitable crystals of 124, 126, and 127 were obtained and examined by single crystal x-ray diffraction. Though general structural information of these compounds was found, disorder due to the alkoxyalkyl chains in the cations prevented complete structural resolution.
Future Work

- Synthesize the remaining ammonium salts in the series using butyl, pentyl, hexyl, and heptyl bromide
- Demonstrate that current purification techniques can be applied to entire series
- Synthesize metathesis products for remainder of the series
- Further examine and resolve crystal structures of the metathesis products and attempt new crystallization techniques for 125
Figure 34. 300 MHz $^1$H NMR spectrum (acetone-d$_6$) of 42.

Figure 35. 300 MHz $^{13}$C NMR spectrum (acetone-d$_6$) of 42.
Figure 36. IR (NaCl plate) spectrum of 111.

Figure 37. 300 MHz $^1$H NMR spectrum (acetone-d$_6$) of 111.
Figure 38. 300 MHz $^{13}$C and DEPT 135 NMR spectrum (acetone-$d_6$) of 111.

Figure 39. IR (NaCl plate) spectrum of 119.
Figure 40. 300 MHz $^1$H NMR spectrum (acetone-$d_6$) of 119.

Figure 41. 300 MHz $^{13}$C and DEPT 135 NMR spectrum (acetone-$d_6$) of 119.
Figure 42. IR (NaCl plate) spectrum of 45.

Figure 43. 300 MHz $^1$H NMR spectrum (acetone-d$_6$) of 45.
Figure 44. 300 MHz $^{13}$C and DEPT 135 NMR spectrum (acetone-d$_6$) of 45.

Figure 45. IR (NaCl plate) spectrum of 121.
Figure 46. 300 MHz $^1$H NMR spectrum (acetone-d$_6$) of 121.

Figure 47. 300 MHz $^{13}$C and DEPT 135 NMR spectrum (acetone-d$_6$) of 121.
Figure 48. DSC trace of 121.

Figure 49. TGA overlay of 45, 111, 119, and 121.
Figure 50. 300 MHz $^1$H NMR spectra overlay (acetone-$d_6$) of 123 at 24, 48, 72, and 144 h (top to bottom).

Figure 51. IR (NaCl plate) spectrum of 124.
Figure 52. 300 MHz $^1$H NMR spectrum (acetone-d$_6$) of 124.

Figure 53. 300 MHz $^{13}$C NMR spectrum (acetone-d$_6$) of 124.
Figure 54. IR (NaCl plate) spectrum of 125.

Figure 55. 300 MHz $^1$H NMR spectrum (acetone-d$_6$) of 125.
Figure 56. 300 MHz $^{13}$C NMR spectrum (acetone-$d_6$) of 125.

Figure 57. IR (NaCl plate) spectrum of 126.
Figure 58. 300 MHz $^1\text{H}$ NMR spectrum (acetone-$d_6$) of 126.

Figure 59. 300 MHz $^{13}\text{C}$ NMR spectrum (acetone-$d_6$) of 126.
Figure 60. IR (NaCl plate) spectrum of 127.

Figure 61. 300 MHz $^1$H NMR spectrum (acetone-$d_6$) of 127.
Figure 62. 300 MHz $^{13}$C NMR spectrum (acetone- $d_6$) of 127.
Figure 63. 300 MHz $^1$H NMR spectra (acetone-d$_6$) of 124 at 1, 5, 10 and 25 mg.
Figure 64. 300 5MHz $^1$H NMR spectra (acetone-d$_6$) of 125 at 1, 5, 10 and 25 mg.
Figure 65. 300 MHz $^1$H NMR spectra (acetone-d$_6$) of 126 at 1, 5, and 10 mg.

Figure 66. TGA overlay of 124, 125, 126, and 127.
Figure 67. DSC trace of 124.

Figure 68. DSC trace of 125.
Figure 69. DSC trace of 126.

Figure 70. DSC trace of 127.
REFERENCES


24. Unpublished results
VITAE

Andrew Michael Beauchamp was born in Manchester, NH. He graduated from Dartmouth High School in 2006. After high school he joined the US Air Force and attended the United States Air Force Academy where he earned his Bachelor of Science in biochemistry. He was commissioned as a 2\textsuperscript{nd} Lt in the U.S. Air Force in May of 2010. He entered Wright State as a graduate student in the fall of 2010 and expects to receive his Master of Science Degree in Chemistry in March 2012.