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Progress towards a model compound for the active site of sulfite reductase. Part I. Synthesis of tetrathiol porphyrin ligands. Part II. Reaction of a tetrathiol porphyrin with the iron-sulfur cubane cluster

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Rice University, 1993
RICE UNIVERSITY

PROGRESS TOWARDS A MODEL COMPOUND FOR
THE ACTIVE SITE OF SULFITE REDUCTASE

PART I: SYNTHESIS OF TETRATHIOL PORPHYRIN LIGANDS
PART II: REACTION OF A TETRATHIOL PORPHYRIN WITH
THE IRON-SULFUR CUBANE CLUSTER

by

THEODORE C. ARNST

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
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DOCTOR OF PHILOSOPHY

APPROVED, THESIS COMMITTEE

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Progress Towards a Model Compound for
the Active Site of Sulfite Reductase

Part I - Synthesis of Tetrathiol Porphyrin Ligands
Part II - Reaction of a Tetrathiol Porphyrin Ligand
with an Iron-Sulfur Cubane Cluster

ABSTRACT

Part I

Novel mercaptoethoxy and mercaptoxyleneoxy derivatives of meso-
tetraphenylporphyrin, H₂TPP, and meso-tetranaphthalporphyrin, H₂TNPP, with the
potential for coordinating an iron-sulfur cubane cluster, have been synthesized and
characterized. The thiol function is guarded during synthesis by an acetate protecting
group, which is removed quantitatively by an acid-catalyzed hydrolysis reaction in the final
workup step. The four "thiol-arms" on these light-sensitive porphyrins allows for the
presence of atropisomers which have been observed and, in the case of the tetranaphthal-
porphyrin derivative, separated. The atropisomers of the acetylmercaptoxyleneoxy
derivatized tetraphenylporphyrin, H₂TAMXPP, interconvert at a rapid rate and are only
observable by \(^1\text{H}\) NMR spectroscopy at \(-70^\circ\text{C}\). The free-base porphyrins, in the thiol-
protected form, are easily metallated by literature procedures and the zinc(II) and iron(III)
chloro derivatives of these new porphyrin compounds have been synthesized and
characterized.
Part II

The thiol functionality of the mercaptoxylyleneoxy derivative of tetraphenylporphyrin, H$_2$TAMXPP, readily exchanges for ethanethiol when H$_2$TAMXPP is reacted with [Fe$_4$S$_4$(SEt)$_4$]$^{2-}$. The dioxygen and light sensitive product, (cation)$_2$[Fe$_4$S$_4$(H$_2$TMXPP)] has been isolated and characterized. Mössbauer and $^1$H NMR spectroscopy provide evidence for the successful synthesis of the desired porphyrin/iron-sulfur cluster compound. As such, this compound is the first example for the synthesis and isolation of a 1:1 porphyrin/iron-sulfur cluster compound and provides as a first generation model compound for the siroheme/iron-sulfur cluster structural unit found at the active site of sulfite reductase.
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Introduction

Sulfite reductase is a multi-metal enzyme that catalyses the extraordinary six-electron reduction of sulfite to sulfide:

\[ \text{SO}_3^{2-} + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{S}^2- + 3\text{H}_2\text{O}. \]

Sulfite reductase is diversely distributed in nature and has been broadly categorized as either an "assimilatory" or "dissimilatory" type enzyme. The assimilatory enzyme, found in plants and many microorganisms, is used to procure reduced sulfur for biosynthetic purposes. Dissimilatory sulfite reductase is commonly found in chemolithotrophs, an unusual group of organisms, where sulfite is used as a terminal electron acceptor in their anaerobic metabolic processes (producing \( \text{H}_2\text{S} \)), akin to the manner in which aerobic organisms use \( \text{O}_2 \) as a terminal electron acceptor.

Assimilatory sulfite reductase is vital in the acquisition of inorganic sulfur for incorporation into important biological components, such as, amino acids (cysteine and methionine), vitamins (biotin), coenzymes (acetyl CoA), and enzymes (ferredoxins, nitrogenases, fatty acid synthase, etc.). This bioincorporation of inorganic sulfur by plants and microorganisms is crucial because higher levels of the food chain lack the ability to assimilate inorganic sulfur from their surroundings and are therefore dependent upon diet to provide bio-sulfur in a metabolically acceptable form.

Amongst evolutionary biologists, microbial inorganic sulfur metabolism is viewed as the anaerobic predecessor to aerobic respiration and photosynthesis. An example of these types of organisms is seen in the phototrophic bacterium, \textit{Chromatium vinosum}. This bacterium when grown autotrophically (no immediate "food" source present, reduced sulfur and inorganic carbon available) in a sulfide/bicarbonate medium, produces a significant quantity of sulfite reductase. However, when the bacterium was grown
heterotrophically (readily metabolizable "food" source present) in a malate/sulfate medium, sulfite reductase could not be isolated, even at the detection level. It is proposed that this enzyme serves as a "reverse sulfite reductase", in that during the process of photosynthesis, the organism uses sulfite reductase to anaerobically oxidize sulfide to sulfate.¹

Sulfite reductase was isolated from a variety of sources (bacteria, fungi, algae, and higher plants) during the 1960's and early 1970's.² Despite the diversity of these sources, the purified sulfite reductases demonstrated remarkable similarities. Their electronic absorption spectra had a very intense absorption in the 385-410 nm region and a strong absorption in the 582-589 nm region. The electronic spectrum was subject to considerable change when the enzyme was treated with strong heme binding ligands such as CO or CN⁻, and upon such treatment, enzymatic activity was significantly reduced. Another intriguing feature of these sulfite reductases was that during the catalytic conversion of sulfite to sulfide, no other sulfur species were detected.

There are overt differences in the enzymes isolated from these different sources. Sulfite reductase from *Escherichia coli* has a mass of 685 kD.³ The enzyme from spinach leaves has a mass of 270 kD that readily disassociates into identical subunits with masses of 69-71 kD each.⁴,⁵ In fungi and aerobic bacteria the electron donor utilized by the enzyme is NADPH, while in anaerobes and photosynthetic organisms, the electron donor is ferredoxin.²,⁴

Despite the gross differences between the various sulfite reductases, the active site of these enzymes appears to be the same. Research has shown that there are two prosthetic groups found at the active site of sulfite reductase. The first feature to be recognized was the iron porphyrin derivative, now designated as siroheme.⁶,⁷ Present along with the siroheme in a 1:1 ratio is a four-iron, four-sulfur cubane cluster.⁸
It should also be noted that sulfite reductase is closely related to nitrite reductase which catalyzes the six-electron reduction of nitrite to ammonia:

\[
\text{NO}_2^- + 8 \text{H}^+ + 6 \text{e}^- \rightarrow \text{NH}_4^+ + 2 \text{H}_2\text{O}.
\]

In vitro experiments have demonstrated that the substrates, sulfite and nitrite, are interchangeable for spinach and *E. coli* sulfite reductase.\(^8,9\) Despite the active-site similarities between assimilatory sulfite and nitrite reductases and the fact that the substrates are interchangeable for sulfite reductase, spinach nitrite reductase cannot reduce sulfite, although it does bind sulfite. A second difference between the two reductases is that the oxidized form of nitrite reductase will form complexes with cyanide, hydroxylamine, nitrite, or sulfite, while, sulfite reductase must first be reduced before this complex formation will take place.

The heme prosthetic group has been extruded from both sulfite and nitrite reductases by extraction of the enzyme with an acetone/HCl mixture.\(^5,7\) The isolated porphyrin derivative is classified as an isobacteriochlorin, that is, two of the adjacent pyrrole rings are reduced, as shown in Figure 1. A unique feature of siroheme is that it is not derived metabolically from protoporphyrin IX as are all other biologically active hemes, but instead it is an intermediate from the biosynthesis of corrins (vitamin B\(_{12}\)).\(^2,10\)

On the basis of spectroscopic changes observed in the enzyme upon the addition of substrate or inhibitors (typical heme ligands; CO, CN\(^-\)), siroheme has been proposed as the binding site for the substrate. Furthermore, extruded siroheme has been demonstrated to be catalytically active, reducing sulfite to thiosulfate, trithionate, tetrathionate, and sulfide with a hydrogen-hydrogenase-methyl viologen system as the electron source.\(^11\)
Figure 1  The Structure of Siroheme

The sulfite reductase from *Escherichia coli* (EC 1.8.1.2) is one of the more fully-characterized enzymes of the assimilatory sulfite reductases. The purified enzyme (685 kD) is composed of disassociateable subunits, with an overall composition of α8β4. The α subunit (59 kD) is referred to as the "flavoprotein" and is the binding site for NADPH. The β subunit (54 kD) is referred to as the "hemoprotein" which sequesters the siroheme and Fe4S4 cluster prosthetic groups.

The *E. coli* hemoprotein has been crystallized and characterized by x-ray crystallography at a 3 Å resolution.12 The siroheme and iron-sulfur cubane cluster are in close proximity of one another, with possibly a bridging ligand linking the siroheme iron and one of the cluster irons. The distance between the siroheme iron and the center of the cluster is 5.5 Å, and the separation between the siroheme iron and the nearest cluster iron is 4.4 Å. A cubane sulfur atom appears to be within Van der Waals contact of the siroheme ligand. The side of the siroheme opposite the cluster is left exposed by the protein.
structure, which leaves it available as a binding site for the substrate. This structure agrees with the multitude of spectroscopic evidence that indicates that the siroheme iron and the iron-sulfur cluster have physical contact that leads to the "exchange coupling" that has been observed with EPR and Mössbauer spectroscopy.3,13

The true nature of the coupling between these two prosthetic groups has not been firmly established. The bridging ligand is thought to be a sulfur or oxygen atom. The sulfur atom could be either sulfide or the thiolate terminus of cysteine, while an oxygen atom would be derived from a serine.14 This proposed atom-bridging structure is shown in Figure 2. In addition to the outright bulk of the protein backbone, a significant impediment to the elucidation of the mechanism of electron transfer between these prosthetic groups and the substrate is the lack of conformational homogeneity in the active site of the enzyme.15 With regards to the iron-sulfur cluster, research with synthetic [Fe₄S₄(SR)₄]²⁻ derivatives has demonstrated that by itself the cluster shows little or no catalytic activity.16

Synthesis of the iron-sulfur cubane cluster, [Fe₄S₄(SR)₄]²⁻, was first reported in 1972 by Herskovitz et al.17 Since that time many derivatives of the cubane cluster have been synthesized and characterized using monodentate or bidentate ligands. More recently, a tridentate ligand derivative has been developed18-20 and there are a limited number of reports of quadridentate thio ligand derivatives.21 As of yet, there has been no successful report in the literature of a covalent coupling of an iron-sulfur cubane cluster with an isobacteriochlorin or with a porphyrin molecule. An early attempt to connect these two fragments was based on combining the [Fe₄S₄(S-Phenyl)₄]²⁻ cluster with 2,3,7,8,12,13,17,18-octaethylporphyrinatoiron(III) perchlorate, in the hopes of producing a thermodynamic affinity between the two prosthetic groups.22 These experiments, however, resulted in decomposition of the iron-sulfur cluster.
Figure 2 The Proposed Coupling of Siroheme and the Iron-Sulfur Cluster

The initial approach taken here to the modelling of the active site of sulfite reductase involves first synthesizing an appropriate tetrathiol-armed porphyrin. This tetrathiol ligand is then reacted with an iron-sulfur cubane cluster in a thiol ligand exchange experiment to yield the desired product, as envisioned in Figure 3. An R'SH ligand exchange hierarchy in \([\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}\) clusters has been previously established\(^{23}\), and by starting with a volatile, low affinity ligand on the cluster it was thought possible to drive the equilibrium of ligand exchange reaction to completion, when attempting to create the tetrathiol-armed porphyrin/cluster compound.
Figure 3  A Proposed Model for the Active Site of Sulfite Reductase
Obtained by Reacting a Tetrathiol-armed Porphyrin with a [Fe₄S₄(SR)₄]²⁻
Cluster

\[ \text{M} = 2\text{H}^+, \text{Zn}^{2+}, \text{or Fe}^{3+} \]

This approach does not attempt to produce a ligand bridged structure, Fe–X–Fe, as
depicted in Figure 2 but, on the other hand, it does possess the potential for systematically
varying the distance between the iron-sulfur cluster and the porphyrin metal center by
changing the length of the thiol arms. In this way, it should be possible to test the effect of
distance on the electronic communication ("exchange coupling") between the cluster and the
porphyrin metal center. However, a pitfall in this approach is the possibility of forming a
porphyrin/cluster oligomer instead of the discrete molecular unit depicted in Figure 3.

Figure 3 shows an idealized structure for one of the two [Fe₄S₄]²⁻-porphyrin
structures sought in this work. The structure shown is derived from 5,10,15,20-tetrakis[3-
(p-mercaptoxylyleneoxy)phenyl]porphyrin and [Fe₄S₄(SR)₄]²⁻, while the second structure is derived from 5,10,15,20-tetrakis[2-(2-mercaptoethoxy)phenyl]porphyrin and the same [Fe₄S₄(SR)₄]²⁻ cluster. Although these [Fe₄S₄]²⁻-porphyrins and their related Zn(II) and Fe(III) metalloporphyrins were the ultimate goal of this research, the tetrathio-armed porphyrin intermediates of Figure 4 have been synthesized, characterized, and studied in detail in order to gain general insight into synthetic approaches toward the targeted [Fe₄S₄]²⁻-porphyrin molecules.
Figure 4  A) Mercaptoxylyleneoxy- and B) Mercaptoethoxy-
Armed Porphyrins

A.

\[ \text{H}_2\text{TMXPP} \]

B.

\[ \text{H}_2\text{TMEPP} \]
Part I

Synthesis of the Tetrathiol-Armed Porphyrin Ligands
Introduction

The conceptual considerations for the synthesis and purification of a tetrathiol-armed porphyrin capable of ligating an iron-sulfur cubane cluster in the manner depicted in Figure 3 are straightforward. The thiol arms need to be of a suitable length and configuration to coordinate the cluster with minimal strain or steric hindrance, while permitting the iron-sulfur cluster to reside above and near the porphyrin. The synthesis of the porphyrin ligand can be simplified by having all of the thiol arms equivalent, and the use of an appropriate protecting group on the thiol prevents disulfide formation during preliminary synthetic and subsequent purification sequences. Finally, it is desirable to have a procedure for quantitative cleavage of the protecting group to yield the tetrathiol porphyrin for reaction with the $[\text{Fe}_4\text{S}_4(\text{SR})_4]^2^-$ cluster.

*Meso*-tetr phenylporphyrins and substituted tetr phenylporphyrins are used extensively in modelling bioporphyrinic molecules because they are relatively simple to synthesize, purify and characterize. A simple thiol-substituted tetr phenylporphyrin with the potential for ligating the cubane iron-sulfur cluster is 5,10,15,20-tetrakis-[2-(2-mercaptoethoxy)phenyl]porphyrin, shown in Figure 4B. A ball and stick model of a $[\text{Fe}_4\text{S}_4]^2^-$ porphyrin molecule derived from this porphyrin indicates that the iron-sulfur cluster can be ligated with only a slight strain on the planar porphyrin system with the center of the iron-sulfur cubane cluster approximately 5 Å from the center of the porphyrin. A minimum energy configuration also seems to place one of the cubane sulfur atoms in near Van der Waals contact of the porphyrin π system. This closely approximates the situation and the 5.5 Å distance observed crystallographically for the sulfite reductase active site. An increase of the arm length by substituting a propoxy moiety in place of the ethoxy
moiety, results in a 6 to 7 Å distance between the cubane and porphyrin centers. Any further lengthening of the thiol arms results in a model with demanding steric restrictions. Additionally, while there are no reports of synthetic tetrathioporphyrins in the extensive literature of porphyrin and porphyrin derivatives, there are reports of tetraphenylporphyrin derivatives with thiolate "tails", as efforts towards modelling the heme site of cytochrome P-450.24,25

A problem with the tetrakis-[2-(2-mercaptoethoxy)phenyl]porphyrin ligand or any alternate ortho- substituted phenyl porphyrin is the existence of atropisomers. These positional isomers, caused by restricted rotation about the meso-carbon–phenyl bond, were first reported in tetrakis-o-methoxyphenyl porphyrin by Gottwald and Ullmann.26 The nomenclature and configuration of the four atropisomers are shown in Figure 5. When attempting to ligate the iron-sulfur cluster, the α,α,α,α-isomer could well yield the desired product, while the other three atropisomers are more likely to promote the formation of a porphyrin/cluster oligomer.

Figure 5 also relates the configuration of the atropisomers to their statistical distribution. Starting with the α,α,α,α-isomer, the rotation of any one of the four phenyl rings results in the formation of the α,α,α,β-isomer. In the α,α,α,β-isomer, the rotation of either phenyl adjacent to the β-phenyl results in the formation of the α,α,β,β-isomer, while rotation of the opposite phenyl results in the α,β,α,β- isomer. Meanwhile, the rotation of any one of the phenyl rings in either α,α,β,β-isomer or the α,β,α,β- isomer restores the α,α,α,β-isomer. This process of intraconversion allows for the statistical mixture of the atropisomers, 1:4:2:1, that is most commonly seen in freely-rotating ortho-substituted tetraphenyl porphyrins.
Figure 5  Statistical Ratios and Intraconversion of the

*ortho*-Substituted Tetraphenylporphyrin Atropisomers

\[ \alpha,\alpha,\alpha,\alpha \text{- atropisomer} \]

\[ \alpha,\alpha,\alpha,\beta \text{- atropisomer} \]

\[ \alpha,\alpha,\beta,\beta \text{- atropisomer} \]

\[ \alpha,\beta,\alpha,\beta \text{- atropisomer} \]
The rate of the interconversion of porphyrin atropisomers is dependent largely upon the steric size of the phenyl ring ortho substituents.\textsuperscript{27} As a phenyl ring begins to rotate about the meso-carbon bond the ortho substituents begin to encroach upon the β-pyrrole hydrogens. When the porphyrin core and the phenyl ring are co-planar the steric interactions are maximized, as depicted in Figure 6. Crossley et al. derived a geometric parameter, \( \Sigma r^* \), which relates to the deformation of bond angles and bond lengths that occurs during this rotational transition state. \( \Sigma r^* \) is defined as the sum of "apparent overlap" of the ortho-phenyl substituents with the β-pyrrole hydrogens in the transition state. More precisely, the "apparent overlap" of two atoms, \( r^* \), is defined as the sum of those interacting atoms' Van der Waals radii, minus their internuclear distance. Using a series of ortho-substituted porphyrins and experimentally determining the rate of atropisomer interconversion, the relationship \( \Delta G^+_{340} = 45.1 \Sigma r^* - 65.0 \text{kJ}\text{-mol}^{-1} \) was determined.

**Figure 6** A Depiction of the Rotational Transition State for a Tetr phenylporphyrin
The existence of porphyrin atropisomers creates multiple approaches towards the pursuit of a tetrathiol ligand suitable for coordinating the iron-sulfur cubane cluster. *Meta* or *para* substituted tetraphenylporphyrins have minimal energy barriers to rotation and for practical purposes, the phenyl groups are "free" to rotate. The *ortho* substituted, 5,10,15,20-tetakis[2-(2-hydroxyethoxy)phenyl] porphyrin has a modest energy barrier for phenyl rotation. The rotation is "hindered" at temperatures < 25°C, but the atropisomers rapidly interconvert at = 50°C.\(^{28}\) The rotation of the phenyl ring can be "blocked" by placing a methyl group in the "6" position of the *ortho*-ethoxy compound or by utilizing a substituted naphthalene in place of the phenyl substituent. These three possible rotational modes "free", "hindered", and "blocked" are shown in Figure 7.

**Figure 7** Potential Tetrathiol Porphyrin Ligands

"Free" Rotation  "Hindered" Rotation  "Blocked" Rotation

This work has considered all four of these meso-porphyrin derivatives. It was anticipated that the dynamically rotating phenyl ring (with its thiol arm) could possibly influence the outcome of the reaction for forming discrete \([\text{Fe}_4\text{S}_4]\)^{2−}-porphyrin molecules. For this reason, the "dynamics" of porphyrin ring rotation have been carefully evaluated for the free and hindered rotation forms of the armed porphyrins studied in this work.
I.A. Experimental Section

I.A.1.a Materials

Solvents for synthesis were reagent grade (Burdick & Jackson, EM Science, Mallinckrodt), unless noted otherwise. When specified as dry, the solvents were dried by standard laboratory methods.\textsuperscript{29,30} In general, solvents were dried by refluxing with, then distilling from an appropriate drying agent as follows: acetone (anhydrous calcium sulfate (Drierite)), diethyl ether (LiAlH\textsubscript{4}), methanol (Na metal (NaOMe)), methylene chloride (CaH\textsubscript{2}), tetrahydrofuran (LiAlH\textsubscript{4}), triethylamine (CaH\textsubscript{2}), trifluoroacetic acid (P\textsubscript{2}O\textsubscript{5}). Deoxygenated solvents and solutions were prepared by purging the solvent with O\textsubscript{2}-free nitrogen or argon, unless noted otherwise.

Chloroform (EM Science, reagent grade) was obtained with 0.75% ethanol as the stabilizing agent. This low level of ethanol increases the eluting power of chloroform in silica gel and alumina column chromatography. Additionally, the ethanol preservative performs as a co-catalyst in the Lindsey porphyrin synthesis procedure.\textsuperscript{31,32} Chloroform was dried by stirring with anhydrous CaCl\textsubscript{2} for a minimum of eight hours, decanting, and then distilling from CaH\textsubscript{2} under a nitrogen blanket. Ethanol-free chloroform was obtained by washing the chloroform with water, pre-drying the organic layer with anhydrous CaCl\textsubscript{2}, and distilling from CaH\textsubscript{2}.

Commercial reagents, inorganic and organic, were "reagent" grade and were used without further purification unless noted otherwise: anhydrous ferrous chloride (Johnson Mattey Electronics), anhydrous magnesium sulfate (Mallinckrodt), anhydrous potassium carbonate (Mallinckrodt), anhydrous calcium chloride (EM Science), anhydrous sodium sulfate (EM Science), salicylaldehyde (Aldrich), α,α-dibromo-\textit{p}-xylene (Aldrich),
2-chloroethanol (Aldrich), Darco G-60 activated carbon (Baker), ethanol (Aaper Alcohol & Chemical), thiolacetic acid (Aldrich), 3-hydroxybenzaldehyde (Aldrich), 2-hydroxy-1-naphthaldehyde (Fluka), methanesulfonyl chloride (Aldrich), sodium chloride (Baker), sodium hydroxide (EM Science), triethyl orthoformate (Aldrich).

Silica gel (Aldrich, grade 62, 60-200 mesh, 150 Å) and aluminum oxide (Aldrich, activated, neutral, Brockman I, ~150 mesh, 58 Å, surface area, 155 m²/g) were heated in a 130°C oven for a minimum of 8 hours and then cooled in a desiccator just prior to use. Unless noted otherwise, chromatography columns were slurry packed and run at atmospheric pressure.

Pyrrole (Aldrich) was dried with CaH₂ and vacuum distilled.²⁹ A pyrrole solution for porphyrin synthesis was prepared by diluting freshly distilled pyrrole with dry methylene chloride 1:9 (v/v). This solution was stored desiccated in the freezer and was discarded when it turned yellow.

Boron trifluoride diethyl etherate (Aldrich) was distilled from CaH₂ under reduced pressure.²⁹ A BF₃-etherate catalyst solution (1.25 M) was prepared by diluting freshly distilled BF₃-etherate (3.85 ml) with dry methylene chloride (21.15 ml). This solution remained viable for > 5 weeks when stored refrigerated in a desiccator.

Argon and nitrogen gases were dried through a column of Drierite and then passed through a column of R3-11 catalyst (Chemical Dynamics, Inc.) to remove traces of dioxygen.

I.A.1.b Physical and Spectroscopic Measurements

Proton NMR and ¹³Carbon NMR were obtained on an IBM/Bruker AF-300 NMR spectrometer or an IBM/Bruker AF-250 NMR spectrometer. Infrared spectra were
collected on a Perkin-Elmer 1600 Series FT-IR spectrometer. Mass spectra were obtained on a Finnigan 9500 Automated Gas Chromatograph/Mass Spectrometer with solid probe inlet. Fast-atom bombardment mass spectra were obtained on a Kratos MS50TC mass spectrometer, calibrated with cesium iodide. UV-visible spectra were collected using matched cuvettes on a Cary model 17 spectrometer with an Compaq DeskPro 286 computer system, running Cary 17 Data Acquisition System Version 2.1 (Compaq-VGA) Software. Mössbauer spectra were acquired on a Ranger Scientific MS-900 spectrometer with a Cryo Industries Model 8CC variable temperature Mössbauer cryostat and a TRI Research Model T-200 cryogenic controller; manipulation of the resultant spectral data was performed on an IBM clone computer using the Ranger Scientific Mössbauer curve fitting program Mossfit version 1.0. X-band Electron Paramagnetic Resonance spectra were recorded as frozen solutions at \( \approx 11 K \) on a Varian E-Line EPR spectrometer (Varian E-101 microwave bridge). Elemental analyses were done on a Carlo Erba Instruments NA 1500 series 2 Analyzer (C, H, N, S), Perkin-Elmer Model 60 Atomic Absorption Spectrometer (Zn), Perkin-Elmer Plasma 400 Emission Spectrometer (Fe), or were performed by Galbraith Laboratories.

I.A.2 Syntheses

I.A.2.a A "Free" Rotation Armed Phenyl Porphyrin

5,10,15,20-Tetrakis[2-(2-mercaptoxylyleneoxy)phenyl]porphyrin was synthesized from pyrrole and \( \alpha \)-acetylmercapto,\( \alpha' \)-(3-formylphenoxy)-p-xylene using a modification of the Lindsey procedure. The following intermediates were synthesized and isolated. Refer to Figure 8 for the reaction schematic.
Figure 8  The Synthetic Scheme for Tetraxylylenoxyphenyl Porphyrin, H$_2$TAMXPP

\[ \text{H}_2\text{O} + \text{BrCH}_2\text{Br} \rightarrow \text{BrCH}_2\text{Br} \]

\[ \text{K}_2\text{CO}_3, \text{refluxing acetone} \]

\[ \text{H}_2\text{O} + \text{CH}_3\text{COSH} \rightarrow \text{H}_2\text{O} + \text{S}_2\text{CO}_3, \text{refluxing acetone} \]

\[ 4 \text{H}_2\text{O} + 4 \text{N} \rightarrow \text{H}_2\text{TAMXPP} \]

1) BF$_3$•OEt$_2$, EtOH, CHCl$_3$, RT, no O$_2$, no light.
2) p-chloranil, reflux.
I.A.2.a.1

\(\alpha\text{-Bromo,}\alpha'\text{-}(3\text{-formylphenoxy})-p\text{-xylene}\)

\(\alpha\text{-Bromo,}\alpha'\text{-}(3\text{-formylphenoxy})-p\text{-xylene}\) was synthesized by aryloxyalkylation of 3-hydroxybenzaldehyde. 3-Hydroxybenzaldehyde (3.05 g, 25 mmol), \(\alpha,\alpha'\text{-dibromo-}p\text{-xylene}\) (6.60 g, 25 mmol), potassium carbonate (3.60 g, 26 mmol), and 250 ml of acetone were placed in a round bottom flask. The flask was fitted with a condenser and the reaction mixture was refluxed for 3 hours. The acetone was removed from the resultant mixture by rotary evaporation. The residues were taken up in diethyl ether (100 ml) and water (200 ml). The layers were separated and the aqueous layer was extracted with an additional portion of diethyl ether (50 ml). The ether layers were combined, then washed with aqueous potassium carbonate (2x 200 ml, 1% w/v) and again with aqueous sodium chloride (200 ml, 5% w/v). The diethyl ether solution was dried with anhydrous magnesium sulfate, filtered and rotary evaporated to dryness to yield a pale yellow oil that solidified upon standing. The recovered material (7.3 g) contained the desired compound (50%) mixed with a by-product, \(\alpha,\alpha'\text{-bis}(3\text{-formylphenoxy})-p\text{-xylene}\) (30%), and residual \(\alpha,\alpha'\text{-dibromo-}p\text{-xylene}\) (20%), as ascertained by integration of the \(^1\text{H}\) NMR spectrum.

This mixture was used as is in the next synthetic step, however, the components of the mixture can be separated chromatographically on silica gel. With methylene chloride as the eluant, \(\alpha,\alpha'\text{-dibromo-}p\text{-xylene}\) is not retained by the adsorbent, while \(\alpha\text{-Bromo,}\alpha'\text{-}(3\text{-formylphenoxy})-p\text{-xylene}\) is weakly retained. \(\alpha,\alpha'\text{-Bis}(3\text{-formylphenoxy})-p\text{-xylene}\) is retained on the column, but can be eluted from the column using ethanol-stabilized chloroform.

\(\alpha\text{-Bromo,}\alpha'\text{-}(3\text{-formylphenoxy})-p\text{-xylene}, \text{mp 48-49 °C, m/z 304, 306; Figure MS-1;}\)
\(^1\)H NMR (CDCl\(_3\), 298 K, 300 MHz, reference TMS \(\delta=0.0\), see Figure \(^1\)H-1): \(\delta=4.51\) (s, CH\(_2\)), \(\delta=5.12\) (s, CH\(_2\)), \(\delta=7.23-7.27\) (m, 1H, phenyl), \(\delta=7.43\) ("s", 4H, xylyl), \(\delta=7.48-7.50\) (m, 3H, phenyl), \(\delta=9.98\) (s, CHO);

\(^{13}\)C NMR (CDCl\(_3\), 298 K, 300 MHz, reference CDCl\(_3\) \(\delta=77.0\), see Figure \(^{13}\)C-1):

\(\delta=33.05\) (CH\(_2\)), 69.64 (CH\(_2\)), 112.94 (CH), 122.16 (CH), 123.88 (CH), 127.86 (2CH), 129.34 (2CH), 130.14 (C), 136.54 (C), 137.71 (2C), 159.07 (C), 192.06 (CHO);

IR (neat, KBr plates, Figure IR-1) \(\nu_{C=O}\) 1697 cm\(^{-1}\), \(\nu_{asym\ Ph-O-C}\) 1261 cm\(^{-1}\),

\(\nu_{sym\ Ph-O-C}\) 1020 cm\(^{-1}\);


\(\alpha,\alpha'^{-}\text{Bis}(3\text{-formylphenoxy})-p\text{-xylene, mp 124-125 C, } m/z 346; \text{ Figure MS-2;}

\(^1\)H NMR (CDCl\(_3\), 298 K, 300 MHz, reference TMS \(\delta=0.0\), see Figure \(^1\)H-2): \(\delta=5.13\) (s, 2CH\(_2\)), \(\delta=7.24\) (m, 2H phenyl), \(\delta=7.48\) (s, 4H, xylyl), \(\delta=7.4\) (m, 6H, phenyl), \(\delta=9.96\) (s, 2CHO);

\(^{13}\)C NMR (CDCl\(_3\), 298 K, 300 MHz, reference CDCl\(_3\) \(\delta=77.0\), see Figure \(^{13}\)C-2):

\(\delta=69.77\) (2CH\(_2\)), 112.97 (2CH), 122.20 (2CH), 123.87 (2CH), 127.83 (4CH, xylyl), 130.14 (2CH), 136.28(2C), 137.73 (2C), 192.10 (2CHO);

IR (solid, KBr disc, Figure IR-2) \(\nu_{C=O}\) 1686 cm\(^{-1}\), \(\nu_{asym\ Ph-O-C}\) 1261 cm\(^{-1}\),

\(\nu_{sym\ Ph-O-C}\) 1015 cm\(^{-1}\);

**Anal. Calculated** for C\(_{22}\)H\(_{18}\)O\(_4\): C, 76.29; H, 5.24. **Found**: C, 75.94; H, 5.41.

**I.A.2.a.2**

\(\alpha\text{-Acetylmercapto,}\alpha'^{-}(3\text{-formylphenoxy})-p\text{-xylene}

\(\alpha\text{-Acetylmercapto,}\alpha'^{-}(3\text{-formylphenoxy})-p\text{-xylene was synthesized by acyloxy-de-
halogenation of }\alpha\text{-Bromo,}\alpha'^{-}(3\text{-formylphenoxy})-p\text{-xylene with thiolacetic acid. The}
mixture of α-Bromo,α'-(3-formylphenoxy)-p-xylene, α,α'-bis(3-formylphenoxy)-p-xylene, and α,α'-dibromo-p-xylene (7.3 g) was dissolved in dry acetone (250 ml). Potassium carbonate (4.15 g, 30 mmol) and thiolacetic acid (2.46 ml, 30 mmol) were added and the flask was fitted with a condenser. The magnetically-stirred mixture was refluxed for one hour and then the solvent was removed by rotary evaporation. The residues were taken up in diethyl ether (100 ml) and water (200 ml). The layers were separated and the aqueous layer was extracted with an additional portion of diethyl ether (50 ml). The ether layers were combined and washed with aqueous sodium chloride (3x 200 ml, 5% w/v). The diethyl ether solution was dried with anhydrous magnesium sulfate, filtered, and rotary evaporated to dryness to yield a varying yellow/red oil that would solidify upon standing. The mixture was chromatographed on 30 g of silica gel in a 3 cm id chromatography column using methylene chloride as the eluant. α-Acetylmercapto,α'-(3-formylphenoxy)-p-xylene and α,α'-bis(acetylmercapto)-p-xylene were poorly resolved, while α,α'-bis(3-formylphenoxy)-p-xylene was retained on the column. Complete resolution of the first two components was unnecessary because α,α'-bis(acetylmercapto)-p-xylene does not adversely affect the condensation of the pyrrole and aldehyde moieties in the porphyrin synthesis reaction. Removal of solvent by rotary evaporation under reduced pressure left 4.7 g of a mixture that was 60 mol % product (64% by mass), as ascertained by integration of the $^1$H NMR spectrum.

$\alpha$-Acetylmercapto,α'-(3-formylphenoxy)-p-xylene, mp 40-41 °C, m/z 300; Figure MS-3;  $^1$H NMR (CDCl$_3$, 298 K, 300 MHz, reference TMS δ=0.0, see Figure $^1$H-3): δ= 2.34 (s, CH$_3$), 4.12 (s, CH$_2$), 5.08 (s, CH$_2$), 7.22-7.25 (m,1H, phenyl), 7.29-7.39 (m, 4H, xylyl), 7.43-7.49 (m, 3H, phenyl), 9.97 (s, CHO);
$^{13}$C NMR (CDCl$_3$, 298 K, 300 MHz, reference CHCl$_3$ $\delta$=77.0, see Figure $^{13}$C-3):
$\delta$= 30.35 (CH$_3$), 33.09 (CH$_2$), 69.83 (CH$_2$), 113.02 (CH), 122.19 (CH), 123.79 (CH),
127.87 (2CH), 129.14 (2CH), 130.13 (CH), 135.30 (C), 137.70 (C), 137.71 (C),
159.18 (C), 192.06 (CHO), 195.05 (C=O);
IR (neat, KBr plates, Figure IR-3) $\nu_{C=O}$ 1695 cm$^{-1}$, $\nu_{asym\,Ph-O-C}$ 1262 cm$^{-1}$;
Anal. Calculated for C$_{17}$H$_{16}$O$_3$S:  C, 67.98; H, 5.37; S, 10.67.  Found:  C, 66.92;
H, 5.47; S, 11.82.

$\alpha,\alpha'$-Bis(acetylmercapto)-p-xylene, mp 91-92 C, m/z 254; Figure MS-4;
$^1$H NMR (CDCl$_3$, 298 K, 300 MHz, reference TMS $\delta$=0.0, see Figure $^1$H-4):  $\delta$= 2.34 (s,
2CH$_3$), 4.07 (s, 2CH$_2$), 7.20 (s, 4H, xylyl);
$^{13}$C NMR (CDCl$_3$, 298 K, 300 MHz, reference CDCl$_3$ $\delta$=77.0, see Figure $^{13}$C-4):
$\delta$= 30.32 (2CH$_3$), 33.02 (2CH$_2$), 129.06 (4CH), 136.64 (2C), 195.12 (2C=O);
IR (solid, KBr disc, Figure IR-4) $\nu_{C=O}$ 1682 cm$^{-1}$, $\delta_{C-S-C=O}$ 1132 and 626 cm$^{-1}$;
Anal. Calculated for C$_{12}$H$_{14}$O$_2$S$_2$:  C, 56.66; H, 5.55; S, 25.21.  Found:  C, 56.19;
H, 5.55; S, 24.82.

I.A.2.a.3

$^{5,10,15,20}$-Tetrakis[3-(p-acetylmercaptoxylyleneoxy)phenyl]porphyrin,
$^{2}$H$_2$TAMXPP

$^{5,10,15,20}$-Tetrakis[3-(p-acetylmercaptoxylyleneoxy)phenyl]porphyrin was
synthesized by condensation of $\alpha$-acetylmercapto,$\alpha'$-(3-formylphenoxy)-p-xylene with
pyrrole.  $\alpha$-Acetylmercapto,$\alpha'$-(3-formylphenoxy)-p-xylene (4.69 g previous mixture =
3.00 g aldehyde, 10 mmol) was dissolved with dry chloroform (1000 ml) in an 2L three
neck flask fitted with a reflux condenser, magnetic stir bar, rubber septum, and glass
stopper. The flask was wrapped with aluminum foil, the solution was purged with nitrogen, and dry pyrrole solution (6.9 ml of a 1/10 dilution, 10 mmol) was added to the aldehyde solution using a syringe. After a 10-15 minute purge, the N2 cannula was removed from the septum and inserted into the top of the condenser to maintain a dry, O2 free "blanket" over the top of the solution. The acid catalyst, 1.25M boron trifluoride etherate solution (2.6 ml, 3.25 mmol) was added to the stirring solution using a syringe. After 45 minutes, triethyl orthoformate (1.67 ml, 10 mmol) and an additional portion of 1.25M boron trifluoride etherate solution (2.6 ml) were added to the solution with a syringe. After a second 45 minute period, p-chloranil (1.85 g, 7.5 mmol) was added through the stoppered opening, the N2 cannula removed from the reflux condenser and the entire flask assembly placed in a hot water bath (50-60°C). After one hour, the flask was removed from the water bath and the solvent was removed using reduced-pressure rotary evaporation. The black residue demonstrated a blue-purple sheen to reflected light. Hereafter, the porphyrin was handled with minimal exposure to light. This black residue was redissolved in methylene chloride and vacuum filtered using a medium porosity glass fritted filter. The solid retained in the filter frit was washed with small portions of methylene chloride until the filtrate was no longer intensely colored. The silver-grey solid retained on the filter frit was predominantly tetrachlorodihydroquinone. Heptane (30 ml) was added to the filtrate and the volume was reduced to approximately 20 ml with reduced-pressure rotary evaporation. The precipitate was filtered and washed several times with hexanes to remove a yellow alkane soluble impurity. The remaining solid was dissolved in methylene chloride (30 ml), ethanol (30 ml) was added to the solution, and the solution volume was reduced to 10-15 ml with reduced-pressure rotary evaporation. The precipitate was filtered and washed with ethanol (2x 20 ml) to remove a yellow-brown ethanol soluble impurity. The resultant solid was dried in vacuo. The dried solid (3.8 g) was mixed
thoroughly with celite filter aid (8 g), slurried with ethyl acetate (30 ml), and filtered through a medium pore glass fritted funnel. The solid was extracted with ethyl acetate until the filtrate was no longer intensely colored (5x 30 ml). The combined filtrate was reduced to a small volume and then chromatographed on 10 g of silica gel in an aluminum foil wrapped column, using ethyl acetate as the eluate and a modest pressure (5 psi) to speed the flow rate. The eluted purple solution was evaporated to dryness, the residue redissolved in methylene chloride and chromatographed on 20 g of silica gel in an aluminum foil wrapped column. Minor traces of impurities eluted with the initial methylene chloride eluate. The pure product was eluted from the column with 2% diethyl ether in methylene chloride. The solvent was removed from the collected eluate using reduced-pressure rotary evaporation and the product was further dried in vacuo to recover 0.84 g of H$_2$TAMXPP for a yield of 24%.

H$_2$TAMXPP

FABMS (3-nitrobenzyl alcohol), m/z 1391.8 (M+H$^+$); Figure MS-5;

$^1$H NMR (CDCl$_3$, 298 K, 300 MHz, reference TMS δ=0.0, see Figure $^1$H-5): δ= -2.85 (br s, 2NH), 2.32 (4CH$_3$), 4.11 (4CH$_2$), 5.21 (4CH$_2$), 7.23-7.45 (m, 20H), 7.64 ("r", 4H), 8.2-8.4 (m, 8H), 8.85 (s, 8H);

$^{13}$C NMR (CDCl$_3$, 298 K, 300 MHz, reference CDCl$_3$ δ=77.0, see Figure $^{13}$C-5):

δ= 30.32 (4CH$_3$), 33.10 (4 CH$_2$), 69.81 (4CH$_2$), 114.45 (4CH), 119.72 (4C), 121.36 (4CH), 127.57 (4CH), 127.96 (4CH,8CH), 129.09 (8CH), 131.18 (br, 8CH), 135.88 (4C), 137.45 (4C), 143.38 (4C), 156.95 (4C), 195.11 (4 C=O);

IR (solid, KBr disc, Figure IR-5) ν$_{\text{C=O}}$ 1688 cm$^{-1}$, ν$_{\text{aromatic C-C}}$ 1595, 1574 cm$^{-1}$;

Anal. Calculated for C$_{84}$H$_{70}$N$_4$O$_8$S$_4$: C, 72.49; H, 5.07; N, 4.03; S, 9.21. Found: C, 72.04; H, 4.96; N, 3.91; S, 9.72.
I.A.2.a.4

5,10,15,20-Tetrakis[3-(p-mercaptoxylyleneoxy)phenyl]porphyrin,
H₂TMXPP

The deprotected-tetrathiol porphyrin, H₂TMXPP was prepared from H₂TAMXPP using an acid-catalyzed hydrolysis reaction. In an aluminum foil wrapped Schlenk flask fitted with a reflux condenser and oil bubbler, 5,10,15,20-Tetrakis[3-(p-acetylmercaptoxylyleneoxy)phenyl]porphyrin (420 mg, 30 mmole) was dissolved in deoxygenated THF (30 ml). Deoxygenated 1M HCl-methanol (50 ml) was added to the flask and the resultant solution was refluxed for three hours. An additional portion of 1M HCl-methanol (50 ml) was added and the solution was allowed to reflux overnight. The solvent was removed in vacuo (using a DMSO/NaOH trap to neutralize HCl gas), the residue was redissolved in deoxygenated chloroform and washed with deoxygenated aqueous sodium bicarbonate/sodium sulfate buffer (0.5 g NaHCO₃, 2.0 g Na₂SO₄, 200 ml water). Working in a darkened room, the chloroform layer was transferred with a cannula to a second Schlenk flask assembly containing anhydrous sodium sulfate. The Schlenk flask assembly was then inverted to filter the dried porphyrin solution and the solvent was removed in vacuo to recover 340 mg (0.28 mmole), a 93% yield.

H₂TMXPP

FABMS (3-nitrobenzyl alcohol), m/z 1391.8 (M+H⁺); Figure MS-6;

¹H NMR (CDCl₃, 293 K, 250 MHz, reference TMS δ=0.0, see Figure ¹H-6): δ= 1.74 (t, J = 7.6, 4SH), 3.74 (d, J = 7.6, 4CH₂), 5.23 (s, 4CH₂), 7.29-7.47 (m, 16H), 7.40 (dd, J= 1.5, 8.0, 4H), 7.65 (t, J = 8.0, 7.2, 4H), 7.81 (d, J = 7.2, 4H), 7.83 (d, J = 1.5, 4H), 8.83 (s, 8H);
\textsuperscript{13}C NMR (CDCl\textsubscript{3}, 298 K, 250 MHz, reference CDCl\textsubscript{3} \( \delta = 77.0 \), see Figure \textsuperscript{13}C-6):
\( \delta = 28.52 \) (4CH\textsubscript{2}), 69.72 (4CH\textsubscript{2}), 114.44 (4CH), 119.74 (4C), 121.44 (4CH), 127.54 (4CH), 127.83 (4CH, 8CH), 128.18 (8CH), 131.15 (br, 8CH), 135.53 (4C), 140.82 (4C), 143.31 (4C), 156.90 (4C);
IR (solid, KBr disc, Figure IR-6) \( \nu_{\text{aromatic C-C}} \) 1595, 1573 cm\textsuperscript{-1}, \( \delta_{\text{pyrrole C\textbeta-H}} \) 803 cm\textsuperscript{-1};
\textbf{Anal. Calculated} for C\textsubscript{76}H\textsubscript{62}N\textsubscript{4}O\textsubscript{4}S\textsubscript{4} \cdot H\textsubscript{2}O: C, 73.52; H, 5.20; N, 4.51; S, 10.33.
\textbf{Found}: C, 73.39; H, 5.33; N, 4.69; S, 10.25.

\textbf{I.A.2.a.5}

5,10,15,20-Tetrakis[3-(p-acetylmercaptoxylyleneoxy)phenyl]porphyrinato-zinc(II), [Zn\textsuperscript{II}(TAMXPP)]

The zinc derivative of H\textsubscript{2}TAMXPP was synthesized using the standard zinc acetate method.\textsuperscript{33} The free base porphyrin (100 mg, 0.072 mmole) was transferred to an aluminum foil wrapped, 100 ml round bottom flask and 50 ml of deoxygenated chloroform was added. The flask was fitted with a reflux condenser, stirred magnetically, and heated to reflux. A 10-fold excess of zinc acetate dihydrate (0.15 g, 0.7 mmole) dissolved in 5 ml of deoxygenated methanol was added to the refluxing solution and a pseudo-dioxygen-free atmosphere was maintained by using a nitrogen blanket over the top of the condenser. After refluxing the mixture for 45 minutes, the solvent was removed with reduced-pressure rotary evaporation. The dry residue was dissolved in a small portion of methylene chloride and applied to an aluminum foil wrapped, slurry packed column of activated silica gel (15 g, 2 cm id). The column was eluted first with 100 ml of methylene chloride, then the eluate polarity was increased by using 2% diethyl ether / 98% methylene chloride. The eluate was collected with minimal exposure to light, however in a brief observation, the zinc porphyrin solution demonstrated a brilliant pink-purple color. The eluting solvent was removed with
reduced-pressure rotary evaporation to recover 99 mg (0.068 mmole) of [ZnII(TAMXPP)] for a 95% yield.

[ZnII(TAMXPP)]

FABMS (3-nitrobenzyl alcohol), m/z 1454.3 (M+); Figure MS-7;

1H NMR (CDCl3, 298 K, 300 MHz, reference TMS δ=0.0, see Figure 1H-7): δ= 2.20 (s, 4CH3), 3.99 (s, 4CH2), 5.11 (s, 4CH2), 7.20-7.38 (m, 20H), 7.62 (t, J= 7.7, 4H), 7.81 (s, 4H), 7.82 (d, J = 7.5, 4H), 8.93, 8.94 (2s, 8H);

13C NMR (CDCl3, 298 K, 300 MHz, reference CDCl3 δ=77.0, see Figure 13C-7):
δ= 30.19 (4CH3), 33.02 (4CH2), 69.78 (4CH2), 114.32 (4CH), 120.68 (4C), 121.19 (4CH), 127.39 (4CH), 127.93 (8CH), 129.03 (8CH), 131.95 (8CH), 135.87 (4C), 137.37 (4C), 144.09 (4C), 149.97 (8C), 156.61 (4C), 195.16 (4 C=O);

IR (solid, KBr disc, Figure IR-7) νC=O 1689 cm⁻¹, νaromatic C=C 1595, 1574 cm⁻¹, vpyrrole 1001 cm⁻¹;

Anal. Calculated for C₈₄H₆₈N₄O₈S₄Zn: C, 69.34; H, 4.71; N, 3.85; S, 8.81;
Zn, 4.49. Found: C, 69.12; H, 4.56; N, 3.70; S, 9.18; Zn 4.32.

I.A.2.a.6

5,10,15,20-Tetrakis[3-(p-acetylmercaptoxylyleneoxy)phenyl]porphyrinato-iron(III) Chloride, [FeIII(TAMXPP)Cl]

The ferric chloride derivative of H₂TAMXPP was synthesized using a permutation of the literature methodology.34-37 The free-base porphyrin (310 mg, 0.22 mmole) and anhydrous ferrous chloride (110 mg, 0.87 mmole) were placed in a nitrogen-filled, aluminum-foil-wrapped 100 ml Schlenk flask. Approximately 30 ml of dry, deoxygenated tetrahydrofuran was added to the flask using a cannula. The Schlenk flask was fitted with
a reflux condenser and oil bubbler. The magnetically-stirred solution was refluxed overnight, while maintaining a positive pressure nitrogen atmosphere on the apparatus. While maintaining minimal light conditions, the hot solution was poured into a polypropylene beaker containing 10 ml of 6N hydrochloric acid. The resultant mixture was stirred for 30 seconds, diluted with 100 ml of water, and placed in a freezer for 24 hours. The frozen mixture was thawed and the precipitate was collected by filtration using glass fritted filter. The precipitate was washed two times with water then dried in vacuo. The brown solid was redissolved in an small amount of chloroform, precipitated with heptane and the precipitate was collected by filtration. The solid was reprecipitated a second time in the same manner. Residual heptane was removed from the solid in vacuo to recover 260 mg (0.17 mmole), a 79% yield.

[Fe$^{III}$](TAMXPP)Cl]
FABMS (3-nitrobenzyl alcohol), $m/z$ 1480.2 (M$^+$); Figure MS-8;
$^1$H NMR (CDCl$_3$, 298 K, 300 MHz, reference TMS δ=0.0, see Figure $^1$H-8): δ= 2.30 (s, 4CH$_3$), 4.02, 4.20 (2s, 4CH$_2$), 5.54, 6.10 (2s, 4CH$_2$), 6.8-7.9 (m, 7CH), 11.58, 12.85 (2s, 4CH), 81.8 (s, 8CH);
IR (solid, KBr disc, Figure IR-8) $\nu_{C=O}$ 1689 cm$^{-1}$, $\nu_{\text{aromatic } C-C}$ 1595, 1574 cm$^{-1}$,
$\nu_{\text{pyrrole}}$ 1001 cm$^{-1}$;

**Anal. Calculated** for C$_{84}$H$_{68}$ClFeN$_4$O$_8$S$_4$: C, 68.12; H, 4.63; N,3.78; S, 8.66; Fe, 3.77.
**Found:** C, 67.53; H, 4.74; N, 3.80; S, 8.45; Fe, 3.96.
I.A.2.a.7

μ-Oxo-bis[5,10,15,20-Tetrakis[3-(p-acetylmercaptopyrroleoxy)phenyl]porphyrinatoiron(III)], [Fe^{III}(TAMXPP)]_2O

μ-Oxo-bis[5,10,15,20-Tetrakis[3-(p-acetylmercaptopyrroleoxy)phenyl]porphyrinatoiron(III)] was synthesized from [Fe^{III}(TAMXPP)Cl] using the general procedure outlined by Dolphin et al.\(^{38}\) With minimal exposure to light, the iron chloro porphyrin derivative (0.1 g, 0.07 mmole) was dissolved in 25 ml of methylene chloride, 50 ml of 1N aqueous NaOH was added, and the two-phase mixture was stirred vigorously for 20 minutes. The mixture was transferred to a separatory funnel, the organic layer was drawn off, dried with anhydrous potassium carbonate, filtered, and the solvent was removed. The brownish-purple solid was redissolved in methylene chloride and applied to an aluminum foil-wrapped silica gel chromatography column (10 g silica). The unreacted [Fe^{III}(TAMXPP)Cl] was removed from the column with a 4% diethyl ether/96% methylene chloride eluant, while the μ-oxo-derivative was eluted from the column with a 2% methanol/98% methylene chloride mixture. Removal of the solvent, allowed for the recovery of 32 mg of product (0.01 mmole), a 16% yield.

[Fe^{III}(TAMXPP)]_2O

FABMS (3-nitrobenzyl alcohol), \(m/z\) 2906.8 (M\(^+\)); Figure MS-21;

\(^1\)H NMR (CDCl\(_3\), 298 K, 300 MHz, reference TMS \(δ=0.0\), see Figure \(^1\)H-21): \(δ=\);

IR (solid, CsI disc, Figure IR-21) \(ν_{C=O}\) 1691 cm\(^{-1}\), \(ν_{aromatic C-C}\) 1597, 1576 cm\(^{-1}\),

\(ν_{pyrrole}\) 1002 cm\(^{-1}\), \(ν_{Fe-O-Fe}\) 878 cm\(^{-1}\);

Anal. Calculated for C\(_{168}H_{136}Fe_{2}N_{8}O_{17}S_{8}\): C, 69.41; H 4.72; N, 3.85; S, 8.82; Fe, 3.84.

Found: C, 69.48; H, 4.74; N, 3.80; S, 9.18; Fe, 3.55.
I.A.2.a.8

5,10,15,20-Tetrakis[3-(p-bromoxyleneoxy)phenyl]porphyrin, $H_2TBrxPP$

5,10,15,20-Tetrakis[3-(p-bromoxyleneoxy)phenyl]porphyrin was synthesized by condensation of $\alpha$-Bromo,$\alpha'$-(3-formylphenoxy)-$p$-xylene with pyrrole. $\alpha$-Bromo,$\alpha'$-(3-formylphenoxy)-$p$-xylene (1.88 g mixture, 19 wt % $\alpha,\alpha'$-dibromo-$p$-xylene, 5 mmol aldehyde) was dissolved with dry chloroform (500 ml) in an 1L three neck flask fitted with a reflux condenser, magnetic stir bar, rubber septum and glass stopper. The flask was wrapped with aluminum foil, the solution purged with nitrogen and a dry pyrrole solution (3.46 ml of a 1/10 dilution , 5 mmol) added to the aldehyde solution using a syringe. After a 10-15 minute purge, the $N_2$ cannula was removed from the septum and inserted into the top of the condenser to maintain a dry, $O_2$ free "blanket" over the top of the solution. The acid catalyst, 1.25M boron trifluoride etherate solution (1.3 ml, 2.7 mmol) was added to the stirring solution using a syringe. After 45 minutes, triethyl orthoformate (0.83 ml, 5 mmol) and an additional portion of 1.25M boron trifluoride etherate solution (1.3 ml) were added to the solution with a syringe. After a second 45 minutes, $p$-chloranil (0.92 g, 3.75 mmol) was added through the stoppered opening, the $N_2$ cannula removed from the reflux condenser, and the entire flask assembly placed in a hot water bath (50-60°C). After one hour, the flask was removed from the water bath and the solvent removed using reduced-pressure rotary evaporation. The black residue demonstrated a blue-purple sheen to reflected light. This black residue was redissolved in methylene chloride and vacuum filtered, using a medium porosity glass fritted filter. The solid retained in the filter frit was washed with small portions of methylene chloride until the filtrate was no longer intensely colored. The silver-grey solid retained on the filter frit was predominantly tetrachlorodihydroquinone. Heptane (30 ml) and triethylamine (25 ul) were added to the solution and the volume was reduced to 15-20 ml using reduced-pressure rotary
evaporation. The resultant precipitate was filtered and washed several times with hexanes to remove a yellow alkane soluble impurity. The solid was dissolved in 30 ml methylene chloride, 30 ml of ethanol added to the solution, and the mixture reduced to a volume of 15-20 ml with reduced-pressure rotary evaporation. The precipitate was filtered and washed with ethanol (2x 20 ml) to remove a yellow-brown ethanol-soluble impurity. The resultant solid was dried in vacuo to recover 2 g of a purple solid. Portions of the crude purple product (0.25 to 0.5 g) were dissolved in methylene chloride and chromatographed on 10 g of silica gel in an aluminum foil wrapped column. Minor traces of impurities elute with the initial methylene chloride eluate. The pure product was eluted from the column with 2% diethyl ether in methylene chloride. The solvent was removed with reduced-pressure rotary evaporation and the solid was further dried under vacuum. The yield based on the portion purified with the optimized chromatographic procedure was 48%.

H₂TBₐXPP

FABMS (3-nitro benzyl alcohol), overlapping Br isotope patterns at m/z 1410.7, 1411.7 (M⁺, M+H⁺), Figure MS-9;

¹H NMR (CDCl₃, 298 K, 250 MHz, reference TMS δ=0.0, see Figure ¹H-9): δ= -2.85 (br s, 2NH), 4.48 (s, 4CH₂), 5.23 (s, 4CH₂), 7.36-7.48 (m, 20H), 7.64 ("t", J = 8.1, 4H), 7.81 (m, 8H), 8.82 (s, 8H);

¹³C NMR (CDCl₃, 298 K, 300 MHz, reference CDCl₃ δ=77.0, see Figure ¹³C-8):
δ= 33.10 (4CH₂), 69.68 (4CH₂), 114.58 (4CH), 119.72 (4C), 121.46 (4CH), 127.63 (4CH), 127.89 (8CH), 128.05 (4CH), 129.33 (8CH), 131.01 (br, 8CH), 137.25 (4C), 137.51 (4C), 143.43 (4C), 156.90 (4C);

IR (solid, KBr disc, Figure IR-9) νaromatic C-C 1595, 1574 cm⁻¹, νpyrrole Cβ-H 803 cm⁻¹;
**Anal. Calculated** for C$_{76}$H$_{58}$Br$_4$N$_4$O$_4$: C, 64.70; H, 4.14; N, 3.97. **Found**: C, 64.52; H, 4.19; N, 4.06.

**I.A.2.b**

**A "Hindered" Rotation Thiol "Armed" Phenyl Porphyrin**

5,10,15,20-Tetrakis[2-(2-mercaptoethoxy)phenyl]porphyrin was synthesized from pyrrole and 2-(2-acetylmercaptoethoxy)benzaldehyde using a modification of the Lindsey procedure. The following intermediates were synthesized and isolated. Figure 9 displays the reaction scheme.
Figure 9  The Synthetic Scheme for Tetraethoxyphenyl Porphyrin, H$_2$TAMEPP

H$_2$COO + Cl-CH$_2$-CH$_2$OH $\xrightarrow{\text{aqueous NaOH}}$ H$_2$COO-CH$_2$OH

H$_2$COO-CH$_2$OH + Cl-SO$_3$CH$_3$ $\xrightarrow{\text{Et$_3$N, MeCl$_2$, 0°C}}$ H$_2$COO-SO$_2$CH$_3$

H$_2$COO-SO$_2$CH$_3$ + CH$_3$COSH $\xrightarrow{\text{K$_2$CO$_3$, refluxing acetone}}$ H$_2$COO-SCH$_3$

H$_2$COO-SCH$_3$ + 4 H$_2$N$\equiv$N $\xrightarrow{\text{1) CF$_3$COOH, MeCl$_2$, RT, no O$_2$, no light, 2) p-chloranil, reflux}}$ H$_2$TAMEPP
I.A.2.b.1

2-(2-Hydroxyethoxy)benzaldehyde

2-(2-Hydroxyethoxy)benzaldehyde was synthesized by alkoxyalkylation of salicylaldehyde with chloroethanol as outlined in the procedure of Almog et al.\textsuperscript{28} Fresh vacuum distilled salicylaldehyde (100 g, 0.82 mol) was added to an aqueous solution (600 ml) of NaOH (32.8 g, 0.82 mol) in a three necked flask fitted with a reflux condenser and a mechanical stirrer. 2-Chloroethanol (53.6 ml, 0.80 mol) was added dropwise to the stirred solution over a 90 minute period. After the addition was complete, the reaction mixture was heated on a steambath for 18 hours. The resultant mixture was cooled, made basic with aqueous NaOH (20% w/v, pH>10) and extracted with methylene chloride (4 x 150 ml). The combined organic layers were washed with aqueous sodium carbonate (4 x 150 ml, 5% w/v), aqueous NaCl (1 x 150 ml, 7.5% w/v), dried with anhydrous magnesium sulfate, filtered, treated with Darco G-60 activated carbon, filtered, and rotary evaporated to a reddish yellow oil. Residual solvent was removed in vacuo to recover 93.6 g, 0.56 mole. The yield based on the limiting reagent 2-chloroethanol was 70%. Further purification of the product was effected by recrystallization from methylene chloride with the addition of hexanes.

2-(2-Hydroxyethoxy)benzaldehyde, mp 43 °C, (literature 46 °C), m/z 166; Figure MS-10;\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 298 K, 250 MHz, reference TMS δ=0.0, see Figure \textsuperscript{1}H-10): δ= 2.1 ± .1 (br s, OH), 4.04 (m, CH\textsubscript{2}), 4.22 (m, CH\textsubscript{2}), 7.02 (d 1H, J= 8.3), 7.08 (t, 1H, J= 7.8), 7.56 (td, 1H, J= 1.8 , 7.8, 8.3), 7.83 (dd, 1H, J= 1.8, 7.8), 10.47 (s, CHO);\textsuperscript{13}C NMR (CDCl\textsubscript{3}, 298 K, 300 MHz, reference CDCl\textsubscript{3} δ=77.0, see Figure \textsuperscript{13}C-9): δ= 61.14 (CH\textsubscript{2}), 70.14 (CH\textsubscript{2}), 112.95 (CH), 121.17 (CH), 125.06 (C), 129.63 (CH), 135.95 (CH), 160.77 (C), 189.88 (CHO);
IR (neat, KBr plates, Figure IR-10) $\nu_{\text{O-H}}$ 3432, 3376, 3256 cm$^{-1}$, $\nu_{\text{C=O}}$ 1679, 1660 cm$^{-1}$; 

**Anal. Calculated** for C$_9$H$_{10}$O$_3$ • H$_2$O: C, 58.69; H, 6.57. **Found**: C, 58.42; H, 6.59.

**I.A.2.b.2**

2-(2-Methanesulfonateethoxy)benzaldehyde

2-(2-Methanesulfonateethoxy)benzaldehyde was synthesized by nucleophilic substitution on an inorganic acid halide, using 2-(2-hydroxyethoxy)benzaldehyde and methanesulfonyl chloride. 2-(2-Hydroxyethoxy)benzaldehyde (16.6 g, 0.1 mol) was dissolved in dry methylene chloride (250 ml) in a 1000 ml round bottom flask fitted with a rubber septum. Dry triethylamine (18.1 ml, 0.13 mol) was added with a syringe to the magnetically stirred solution. The resulting solution was cooled in an ice bath for 10 minutes before the dropwise addition of methanesulfonyl chloride (9.3 ml, 0.12 mol). The solution was stirred in the ice bath for one hour, then allowed to warm to room temperature. The resultant slurry was filtered to remove the bulk of the triethylamine hydrochloride byproduct. The methylene chloride filtrate was then washed with water (3 x 100 ml), dried with anhydrous magnesium sulfate, and rotary evaporated to dryness. Residual solvent was removed in vacuo to recover 21.1 g, 0.86 mole. The yield based on the limiting reagent 2-(2-hydroxyethoxy)benzaldehyde was 86%. Further purification of the product was effected by recrystallization from methylene chloride with the addition of hexanes.

2-(2-Methanesulfonateethoxy)benzaldehyde, mp 65-66 °C, $m/z$ 244; Figure MS-11; 

$^1$H NMR (CDCl$_3$, 298 K, 250 MHz, reference TMS $\delta$=0.0, see Figure $^1$H-11): $\delta$=3.09 (s, CH$_3$) $\delta$=4.39 (m, CH$_2$), $\delta$=4.64 (m, CH$_2$), $\delta$=6.98 (d, J=8.4, 1H), $\delta$=7.10 (t, J=7.5, 1H), $\delta$=7.57 (dt, J=1.8, 7.9, 1H), $\delta$=7.86 (dd, J=1.8, 7.7, 1H), $\delta$=10.50 (s, 1H);
$\text{^{13}C NMR (CDCl}_3$, 298 K, 300 MHz, reference CDCl$_3$ $\delta=77.0$, see Figure $\text{^{13}C-10}$): $\delta= 37.79$ (CH$_3$), 66.37 (CH$_2$), 67.01 (CH$_2$), 112.50 (CH), 121.72 (CH), 125.17 (C), 129.01 (CH), 135.92 (CH), 160.12 (C), 189.30 (CHO); IR (solid, KBr disc, Figure IR-11) $\nu_{\text{O=S=O}}$ 1349, 1179 cm$^{-1}$, $\nu_{\text{C=O}}$ 1681 cm$^{-1}$; Anal. Calculated for C$_{10}$H$_{12}$O$_5$S: C, 49.17; H, 4.95; S, 13.13. Found: C, 48.95; H, 4.82; S, 12.85.

I.A.2.b.3

2-(2-Acetylmercaptoethoxy)benzaldehyde

2-(2-Acetylmercaptoethoxy)benzaldehyde was synthesized by acetylmercapto-de-sulfonyloxy-substitution of 2-(2-methanesulfonateethoxy)benzaldehyde with thiolacetic acid. 2-(2-Methanesulfonateethoxy)benzaldehyde (71.4 g, 0.29 mol) was dissolved in dry acetone (1000 ml) in a 2000 ml three neck flask fitted with a mechanical stirrer and condenser. To this solution, anhydrous potassium carbonate (48.4 g, 0.35 mol) and thiolacetic acid (24.8 ml, 0.35 mol) were added. The mixture was stirred and refluxed for two hours, during which time a reddish/orange color appeared. The reaction mixture was cooled and the resultant suspension was filtered. The solid residues were washed with methylene chloride (3 x 200 ml), the organic extracts were combined, and evaporated to near dryness. The red oil was redissolved in 250 ml of chloroform and washed with water (5 x 150 ml). The organic layer was dried with anhydrous sodium sulfate, filtered, and the solvent was removed with reduced-pressure rotary evaporation. The product was recovered as 63.7 g of a yellow-red oil, a yield of 97%.\textsuperscript{39,40}

2-(2-Acetylmercaptoethoxy)benzaldehyde, viscous oil that decomposes before bp, $m/z$ 224; Figure MS-12;
$^1$H NMR (CDCl$_3$, 298 K, 250 MHz, reference TMS $\delta$=0.0, see Figure $^1$H-12): $\delta$= 2.39 (s, CH$_3$), 3.34 (t, J= 6.3, CH$_2$), 4.23 (t, J=6.3, CH$_2$), 6.99 (d, J= 8.0, 1H), 7.04 (t, J= 7.7, 7.8, 1H), 7.54 (dt, J= 1.8, 7.7, 8.0, 1H), 7.84 (dd, J= 1.8, 7.8, 1H), 10.49 (s, CHO);

$^{13}$C NMR (CDCl$_3$, 298 K, 300 MHz, reference CDCl$_3$ $\delta$=77.0, see Figure $^{13}$C-11):

$\delta$= 28.25 (CH$_2$), 30.51 (CH$_3$), 66.90 (CH$_2$), 112.51 (CH), 121.11 (CH), 124.93 (C), 128.31 (CH), 135.87 (CH), 160.62 (C), 189.56 (CHO), 195.17 (C=O);

IR (neat, KBr disc, Figure IR-12) $v_{C=O}$ 1688 cm$^{-1}$, $v_{aromatic C-C}$ 1599 cm$^{-1}$;

Anal. Calculated for C$_{11}$H$_{12}$O$_3$S:  C, 58.91; H, 5.39; S, 14.30. Found: C, 58.49; H, 5.46; S, 14.36.

**I.A.2.b.4**

**5,10,15,20-Tetrakis[2-(2-acetylimercaptoethoxy)phenyl]porphyrin, H$_2$TAMEPP**

2-(2-Acetylimercaptoethoxy)benzaldehyde (3.1 g, 13.8 mmol) was dissolved with dry methylene chloride (1000 ml) in an 2L three neck flask fitted with a reflux condenser, magnetic stir bar, rubber septum, and glass stopper. The flask was wrapped with aluminum foil, the solution was purged with nitrogen, and freshly distilled pyrrole (0.96 ml, 13.8 mmol) was added to the aldehyde solution using a syringe. After a 10-15 minute purge, the N$_2$ cannula was removed from the septum and inserted into the top of the condenser to maintain a dry, dioxygen-free "blanket" over the top of the solution. The acid catalyst, trifluoroacetic acid (1.0 ml, 13 mmol), was added to the stirring solution using a syringe. After 60 minutes, $p$-chloranil (2.55 g, 10.4 mmol) was added through the stoppered opening, the N$_2$ cannula was removed from the reflux condenser and the entire flask assembly was placed in a hot water bath (40°C). After one hour, the flask was
removed from the water bath and the solvent was removed using a rotary evaporator. The black residue demonstrated a blue-purple sheen to reflected light. This black residue was redissolved in methylene chloride and vacuum filtered using a medium porosity glass fritted filter. The solid retained in the filter frit was washed with small portions of methylene chloride until the filtrate was no longer intensely colored. The silver-grey solid retained on the filter frit was predominantly tetrachlorodihydroquinone. A few drops of triethylamine was added to the filtrate and then the solvent was removed with reduced-pressure rotary evaporation to recover 5.4 g of crude porphyrin. This material was dissolved in a small portion of methylene chloride and the porphyrin was precipitated with the addition of hexanes. The brown-green solution was discarded and the purple-black solid (4.7 g) was dried in vacuo. Portions of the solid (0.5 g) were dissolved in a minimal amount of methylene chloride and chromatographed on silica gel (30 g) in an aluminum foil wrapped column. An early faint yellow band in the methylene chloride eluant was discarded, while, a variable purple band which appeared after 200-300 ml of eluate was collected. The solvent strength was increased by switching to ethanol-stabilized chloroform and this solvent eluted an intense purple band. A further increase in solvent strength (5% methanol in chloroform or methylene chloride) would elute additional porphyrin that was highly contaminated with polypyrrolic by-products. The solvent was removed from the solutions containing the first two purple bands using reduced-pressure rotary evaporation to recover purple products that had identical spectroscopic characteristics. On the basis of the batch with optimal chromatographic isolation, the yield was 23%.

H₂TAMEPP
FABMS (3-nitrobenzyl alcohol), m/z 1087.0 (M+H⁺); Figure MS-13;
$^1$H NMR (CDCl$_3$, 298 K, 300 MHz, reference TMS $\delta=0.0$, see Figure $^1$H-13):
$\delta=$ -2.61 (br s, 2NH), 1.68-1.78 (m, 4CH$_3$), 2.44-2.53 (m, 4CH$_2$), 3.86-3.97 (m,
4CH$_2$), 7.29-7.37 (m, 8CH), 7.66-7.71 (m, 4CH), 7.96-8.07 (m, 4CH), 8.74-8.79 (m,
8CH);
$^{13}$C NMR(CDC$_3$, 298 K, 300 MHz, reference CDC$_3$ $\delta=77.0$, see Figure $^{13}$C-12):
$\delta=$ 27.61 (4CH$_2$), 29.91 (4CH$_3$), 67.13 (4CH$_2$), 112.77 (4CH), 115.38 (4C), 119.96
(4CH), 129.75 (4CH), 131.? (4CH), 131.72 (4C), 135.84 (4CH), 158.09 (4C), 195.10
(4C=O);
IR (solid, KBr disc, Figure IR-13) $\nu_{C=O}$ 1688 cm$^{-1}$, $\delta_{pyrrole}$ C=H 801 cm$^{-1}$;
Anal. Calculated for C$_{60}$H$_{54}$N$_4$O$_8$S$_4$ • 0.5 H$_2$O: C, 65.74; H, 5.06; N, 5.11; S, 11.70.
Found: C, 65.97; H, 5.10; N, 5.38; S, 11.54.

I.A.2.b.5

5,10,15,20-Tetrakis[2-(2-mercaptoethoxy)phenyl]porphyrin, H$_2$TMEPP

The deprotected tetrathiol porphyrin, H$_2$TMEPP was prepared from H$_2$TAMEPP
using an acid-catalyzed hydrolysis reaction. In an aluminum foil-wrapped Schlenk flask
fitted with a reflux condenser and oil bubbler, 5,10,15,20-tetrakis[2-(2-acetylmercapto-
ethoxy)phenyl]porphyrin (150 mg, 0.14 mmole) was dissolved in 100 ml of deoxygenated
1M HCl-methanol and the resultant solution was refluxed for six hours. The solvent was
removed in vacuo (using a DMSO/NaOH trap to neutralize HCl gas), the residue was
redissolved in deoxygenated chloroform and washed with deoxygenated aqueous buffer
(0.5 g NaHCO$_3$, 2.0 g Na$_2$SO$_4$, 200 ml water). Working in a darkened room, the
chloroform layer was transferred with a cannula to a second Schlenk flask assembly
containing anhydrous sodium sulfate. The Schlenk flask assembly was then inverted to
filter the anhydrous porphyrin solution, and the solvent was removed in vacuo to recover 110 mg (0.12 mmole) for a 86% yield.

H₂TMEPP

FABMS (3-nitrobenzyl alcohol), m/z 919.3 (M+H⁺), Figure MS-14;

¹H NMR (CDCl₃, 298 K, 300 MHz, reference TMS δ=0.0, see Figure ¹H-14): δ = -2.64 (br s, 2NH), 0.51-0.66 (m, 4SH), 2.01-2.14 (m, 4CH₂), 3.97-4.02 (m, 4CH₂), 7.27-7.38 (m, 8CH), 7.71-7.76 (m, 4CH), 7.98-8.03 (m, 4CH), 8.75 (s, 8CH);

¹³C NMR (CDCl₃, 298 K, 300 MHz, reference CDCl₃ δ=77.0, see Figure ¹³C-13):

δ = 23.56 (4CH₂), 70.19 (4CH₂), 112.05 (CH), 115.56 (C), 119.91 (CH), 129.78 (CH), 130.52 (CH), 131.37 (C), 135.87 (CH), 158.15 (C);

IR (solid, KBr disc, Figure IR-14) δ_methylene C-H 1490, 1444 cm⁻¹,

ν_C-phenyl-O-C 1234, 1048 cm⁻¹, δ_N-H 966 cm⁻¹;

Anal. Calculated for C₅₂H₄₆N₄O₄S₄·H₂O: C, 66.64; H, 5.16; N, 5.98; S, 13.68.

Found: C, 66.97; H, 5.10; N, 5.76; S, 14.04.

I.A.2.b.6

5,10,15,20-Tetrakis[2-(2-acetylmercaptoethoxy)phenyl]porphyrinato-zinc(II), [Zn²⁺(TAMEPP)]

The zinc(II) derivative of H₂TAMEPP was synthesized using the standard zinc acetate method.³³ The free base porphyrin (0.5 g, 0.46 mmole) was transferred to an aluminum foil-wrapped, 100 ml round bottom flask and 50 ml of deoxygenated chloroform was added. The was fitted with a reflux condenser, stirred magnetically, and heated to reflux. A 5-fold excess of zinc(II) acetate dihydrate (0.51 g, 2.3 mmole) dissolved in 5 ml of deoxygenated methanol was added to the refluxing solution and a pseudo dioxygen-free
atmosphere was maintained by using a nitrogen blanket over the top of the condenser. After refluxing the mixture for 45 minutes, the solvent was removed with rotary evaporation. The dry residue was dissolved in a small portion of methylene chloride and applied to an aluminum foil-wrapped, slurry packed column of activated silica gel (25 g, 2 cm id). The column was eluted first with 100 ml of methylene chloride, then the eluate strength was increased to 2% diethyl ether / 98% methylene chloride. The zinc porphyrin solution presented a brilliant pink-purple color when it was briefly viewed in normal fluorescent lighting conditions. The eluting solvent was removed with reduced-pressure rotary evaporation to recover (0.51 g, 0.44 mmole) of [ZnII(TAMEPP)] for a yield of 96%.

[ZnII(TAMEPP)]

FABMS (3-nitrobenzyl alcohol), m/z 1150.1 (M+); Figure MS-15;

$^1$H NMR (CDCl$_3$, 298 K, 300 MHz, reference TMS δ=0.0, see Figure $^1$H-15): δ= 1.68-1.78 (m, 4CH$_3$), 2.32-2.47 (m, 4CH$_2$), 3.79-3.96 (m, 4CH$_2$), 7.25-7.36 (m, 8CH), 7.68-7.74 (m, 4CH), 7.96-8.03 (m, 4CH), 8.74-8.79 (m, 8CH);

$^{13}$C NMR (CDCl$_3$, 298 K, 300 MHz, reference CDCl$_3$ δ=77.0, see Figure $^{13}$C-14): δ= 27.63 (4CH$_2$), 29.67 (4CH$_3$), 67.11 (4CH$_2$), 112.56 (4CH), 116.06 (4C), 119.80 (4CH), 129.34 (4CH), 131.28 (4C), 132.58 (8CH), 135.86 (4CH), 149.95 (8C), 158.04 (4C), 195.41 (4C=O);

IR (solid, KBr disc, Figure IR-15) ν$_{C=O}$ 1689 cm$^{-1}$, ν$_{pyrrole}$ 997 cm$^{-1}$;

Anal. Calculated for C$_{60}$H$_{52}$N$_4$O$_8$S$_4$Zn $\cdot$ H$_2$O: C, 61.66; H, 4.66; N, 4.79; S, 10.97; Zn, 5.59. Found: C, 61.96; H, 4.86; N, 4.71; S, 10.70; Zn, 5.47.
I.A.2.b.7

5,10,15,20-Tetrakis[2-(2-acetylmercaptoethoxy)phenyl]porphyrinato-iron(III) Chloride, [FeIII(TAMEPP)Cl]

The ferric chloride derivative of H2TAMEPP was synthesized using a permutation of the literature methodology.34-37 The free base porphyrin (300 mg, 0.22 mmole) and anhydrous ferrous chloride (150 mg, 1.2 mmole) were placed in a nitrogen filled, aluminum foil wrapped, 100 ml Schlenk flask. Approximately 30 ml of dry, deoxygenated tetrahydrofuran was added to the flask using a cannula. The Schlenk flask was fitted with a reflux condenser and oil bubbler. The magnetically stirred solution was refluxed overnight, while maintaining a positive pressure nitrogen atmosphere on the apparatus. While maintaining minimal light conditions, the hot solution was poured into a polypropylene beaker containing 10 ml of 6N hydrochloric acid. The resultant mixture was stirred for 30 seconds, diluted with 100 ml of water, and placed in a freezer for 24 hours. The frozen mixture was thawed and the precipitate was collected by filtration using glass fritted filter. The precipitate was washed two times with water then dried in vacuo. The brown solid was redissolved in an small amount of chloroform, precipitated with heptane, and the precipitate was collected by filtration. The solid was reprecipitated a second time in the same manner. Residual heptane was removed from the solid in vacuo to recover 280 mg (0.19 mmole) for a 86% yield.

[FeIII(TAMEPP)Cl]

FABMS (3-nitrobenzyl alcohol), m/z 1175.1 (M+); Figure MS-16;

1H NMR (CDCl3, 298 K, 300 MHz, reference TMS δ=0.0, see Figure 1H-16): δ= 1.42-2.30 (m, 4CH3), 3.41-4.15 (m, 4 CH2), 5.22-5.85 (m, 4CH2), 7.15-9.2 (m, 8CH), 12.00, 12.93, 13.19, 14.76 (br s, 8CH), 80.9 (br s, 8CH);
IR (solid, KBr disc, Figure IR-16) \( \nu_{C=O} \) 1689 cm\(^{-1}\), \( \nu_{\text{pyrrole}} \) 997 cm\(^{-1}\).

**Anal. Calculated** for C\(_{60}H_{52}ClFeN_4O_8S_4 \cdot \text{H}_2\text{O} \): C, 60.32; H, 4.56; N, 4.69; S, 10.74; Fe, 4.67. **Found**: C, 59.82; H, 4.74; N, 4.55; S, 10.63; Fe, 4.46.

**I.A.2.c**

**A "Blocked" Rotation Thiol "Armed" Porphyrin**

5,10,15,20-Tetrakis[2-(2-mercaptoethoxy)naphthyl]porphyrin was synthesized from pyrrole and 2-(2-acetylmercaptoethoxy)-1-naphthaldehyde using a modification of the Lindsey procedure. The following intermediates shown in Figure 10 were synthesized and isolated.
Figure 10  The Synthetic Scheme for Tetraethoxynaphthyl Porphyrin,

\( \text{H}_2\text{TAMENP} \)
I.A.2.c.1

2-(2-Hydroxyethoxy)-1-naphthaldehyde

2-(2-Hydroxyethoxy)-1-naphthaldehyde was synthesized by aryloxyalkylation of 2-hydroxy-1-naphthaldehyde with 2-chloroethanol. 2-Hydroxy-1-naphthaldehyde (34.4 g, 0.2 mol) dissolved in (100 ml) was added over a twenty minute period to mechanically stirred slurry of sodium hydroxide (8.0 g, 0.2 mol, 250 ml dimethyl sulfoxide) in a 1 L, three neck round bottom flask fitted with a reflux condenser. A slight excess of 2-chloroethanol (14 ml, 0.21 mol) was mixed with DMSO (30 ml) and this solution was added to the naphthaldehyde solution over a fifteen minute period. The resultant mixture was stirred and heated on a steam bath for 18 hours. The mixture was cooled, diluted with aqueous sodium hydroxide (400 ml, 0.5% w/v) and extracted with chloroform (1x 250 ml, 2x 50 ml). The combined organic layer was washed first with aqueous sodium hydroxide (3x 400 ml, 0.25% w/v) and then with aqueous sodium chloride (400 ml, 5% w/v). The organic layer was dried with anhydrous sodium sulfate, filtered, and evaporated under reduced-pressure to a volume of approximately 100 ml. Fifty ml of heptane was added to the solution and reduced-pressure rotary evaporation was continued until only 15-20 ml of heptane remained. The brown precipitate was filtered, washed with small portions of hexanes and dried in vacuo to recover 24.8 g (0.12 mol) for a 57% yield.

2-(2-Hydroxyethoxy)-1-naphthaldehyde, mp 108-109 C, m/z 216; Figure MS-17;
$^1$H NMR (CDCl$_3$, 298 K, 300 MHz, reference TMS $\delta$=0.0, see Figure $^1$H-17): $\delta$= 2.19 (br s, OH), 4.09 (m, CH$_2$), 4.37 (m, CH$_2$), 7.31 (d, J=9.1), 7.45 ("t", J=8.0, ~7.8), 7.65 ("t", J=8.7, ~7.8), 7.80 (d, J=8.0), 8.08 (d, J=9.1), 9.23 (d, J=8.7), 10.97(s, CHO);
$^{13}$C NMR (CDCl$_3$, 298 K, 300 MHz, reference CDCl$_3$ δ=77.0, see Figure $^{13}$C-15): δ =
61.39 (CH$_2$), 71.09 (CH$_2$), 113.76 (CH), 117.13 (C), 124.72 (CH), 124.98 (CH),
128.28 (CH), 128.73 (C), 129.89 (CH), 131.57 (C), 137.58 (CH), 162.98 (C), 191.73
(CH$_3$);
IR (solid, KBr disc, Figure IR-17) ν$_{O-H}$ 3458, 3278 cm$^{-1}$, ν$_{C=O}$ 1666, 1650 cm$^{-1}$;
Anal. Calculated for C$_{13}$H$_{12}$O$_3$: C, 72.21; H, 5.59. Found: C, 71.89; H, 5.69.

I.A.2.c.2

2-(2-Methanesulfonateethoxy)-1-naphthaldehyde

2-(2-Methanesulfonateethoxy)-1-naphthaldehyde was synthesized by the reaction of
2-(2-hydroxyethoxy)-1-naphthaldehyde with methanesulfonyl chloride in the presence of
triethylamine. 2-(2-hydroxyethoxy)-1-naphthaldehyde (10.81 g, 0.05 mol) and
triethylamine (9.05 ml, 0.065 mol) were dissolved with dry methylene chloride (150 ml) in
a 500 ml round bottom flask. The magnetically stirred solution was placed in an ice bath
and cooled before beginning the dropwise addition of a methanesulfonyl chloride solution
(4.65 ml, 0.06 mol, in 20 ml of dry methylene chloride). The reaction mixture was left in
the ice bath for after the addition was complete and it was allowed to warm to room
temperature over night. The solution was evaporated to dryness, the residue redissolved in
dry methylene chloride and filtered to remove most of the triethylamine hydrochloride. The
filtrate was washed with aqueous sodium bicarbonate (5% w/v, 2x 200 ml), dried with
anhydrous sodium sulfate, filtered and evaporated with reduced-pressure to yield a red-
brown oil. This oil was further dried in vacuo to yield a brown solid (14.1 g, 0.048 mol,
96%). Recrystallization from THF/heptane gave clear needles.
2-(2-Methanesulfonateethoxy)-1-naphthaldehyde, mp.110-112 °C, m/z 294; Figure MS-18; 1H NMR (CDCl3, 298 K, 300 MHz, reference TMS δ=0.0, see Figure 1H-18): δ=3.10 (s, CH3), δ=4.54 (m, CH2), δ=4.66 (m, CH2), δ=7.27 (d, J=9.1), δ=7.46 ("t", J=8.1, 7.8), δ=7.65 ("t", J=8.7, 7.8), δ=7.80 (d, J=8.1), δ=8.09 (d, J=9.1), δ=9.26 (d, J=8.7), δ=10.94 (s, CHO);

13C NMR (CDCl3, 298 K, 300 MHz, reference CDCl3 δ=77.0, see Figure 13C-16):
δ= 37.79 (CH3), 67.02 (CH2), 67.48 (CH2), 113.36 (CH), 117.47 (C), 124.99 (CH), 125.25 (CH), 128.27 (CH), 129.00 (C), 130.09 (CH), 131.37 (C), 137.61 (CH), 162.18 (C), 191.61 (CHO);

IR (solid, KBr disc, Figure IR-18) νC=O 1672 cm⁻¹, νO=S=O 1356, 1180 cm⁻¹,
δO=S=O 1035 cm⁻¹;

Anal. Calculated for C14H14O5S: C, 57.13; H, 5.12; S, 10.86. Found: C, 57.13; H, 4.98; S, 10.78.

I.A.2.c.3

2-(2-Acetylmercaptoethoxy)-1-naphthaldehyde

2-(2-Acetylmercaptoethoxy)-1-naphthaldehyde was synthesized by acetylmercapto-de-sulfonyloxy-substitution of 2-(2-methanesulfonateethoxy)-1-naphthaldehyde with thioacetic acid. 2-(2-Methanesulfonateethoxy)-1-naphthaldehyde (14.1 g, 0.048 mol) was dissolved in dry acetone (500 ml). Anhydrous potassium carbonate (8.29 g, 0.06 mol) and thioacetic acid (4.25 ml, 0.06 mol) were added and the resultant mixture was stirred and heated to reflux for 1.5-2 hours. The solution was cooled to room temperature, filtered, and the filtrate was evaporated to dryness. The residue was redissolved in methylene chloride, treated with activated carbon, filtered, and evaporated with reduced-pressure to a small volume (= 50 ml). The concentrated solution was diluted with 8 volumes of diethyl
ether and filtered to remove an insoluble impurity. The red filtrate was subjected to
reduced-pressure rotary evaporation yielding a red oil which crystallized upon
standing. (11.4 g, 0.04 mol, 86% yield). Recrystallization from methylene chloride and
hexanes yielded clear needles.

2-(2-Acylmercaptoethoxy)-1-naphthaldehyde, mp 106-107 °C, m/z 274; Figure MS-19;
$^1$H NMR (CDCl$_3$, 298 K, 300 MHz, reference TMS $\delta$=0.0, see Figure $^1$H-19): $\delta$=2.40
(s, CH$_3$), 3.37 (m, CH$_2$), 4.36 (CH$_2$), 7.29 (d, $J$=9.2), 7.44 ("t", $J$=8.0, $\sim$7.5), 7.64
("t", $J$=8.6, $\sim$7.5), 7.78 (d, $J$=8.0), 8.06 (d, $J$=9.2), 9.28 (d, $J$=8.6), 10.91 (s, CHO);
$^{13}$C NMR (CDCl$_3$, 298 K, 300 MHz, reference CDCl$_3$ $\delta$=77.0, see Figure $^{13}$C-17):
$\delta$= 28.49 (CH$_2$), 29.94 (CH$_3$), 67.85 (CH$_2$), 113.33 (CH), 116.89 (C), 124.95 (2CH),
128.21 (C), 128.67 (C), 129.94 (CH), 131.43 (C), 137.60 (CH), 162.73 (C), 192.00
(CH$_2$), 195.35 (C=O);
IR (solid, KBr disc, Figure IR-19) $\nu_{C=O}$ 1693, 1673 cm$^{-1}$, $\nu_{C-S-C=O}$ 1135, 627 cm$^{-1}$;
Anal. Calculated for C$_{15}$H$_{14}$O$_3$S: C, 65.67; H, 5.14; S, 11.69. Found: C, 65.13;
H, 5.16; S, 11.71.

I.A.2.c.4

5,10,15,20-Tetrakis[2-(2-acetylmercaptoethoxy)naphthyl]porphyrin
H$_2$TAMENP

2-(2-Acetylmercaptoethoxy)-1-naphthaldehyde (2.74 g, 10 mmol) was dissolved
with dry chloroform (1000 ml) in an 2L three neck flask fitted with a reflux condenser,
magnetic stir bar, rubber septum, and glass stopper. The flask was wrapped with
aluminum foil, the solution was purged with nitrogen, and freshly distilled pyrrole (0.69
ml, 10 mmol) was added to the aldehyde solution using a syringe. After a 10-15 minute
purge, the N₂ cannula was removed from the septum and inserted into the top of the condenser to maintain a dry, dioxygen-free "blanket" over the top of the solution. The boron trifluoride etherate acid catalyst solution (2.6 ml, 3.3 mmol), was added to the stirring solution using a syringe. After 60 minutes, p-chloranil (1.84 g, 7.5 mmol) was added through the stoppered opening, the N₂ cannula was removed from the reflux condenser and the entire flask assembly was placed in a hot water bath (50-60 °C). After one hour, the flask was removed from the water bath and the solvent was removed using a rotary evaporator. The black residue demonstrated a blue-purple sheen to reflected light. Subsequent purification of the porphyrin product was performed with minimal exposure to light. This black residue was redissolved in methylene chloride and vacuum filtered using a medium porosity glass fritted filter. The solid retained in the filter frit was washed with small portions of methylene chloride until the filtrate was no longer intensely colored. The silver-grey solid retained on the filter frit was predominantly tetrachlorodihydroquinone. The filtrate was rotary evaporated to dryness to recover 4.5 g of crude reaction mixture. A 1.5 g portion of this crude mixture was ground to a fine powder and mixed with 1.5 g of celite filter aid. The dry mixture was applied to the top of an aluminum foil wrapped, ethyl acetate slurry packed, silica gel chromatography column (20 g silica gel, 2 cm id). The column was eluted with 200 ml of ethyl acetate to remove a faint yellow impurity. The solvent composition was changed to 25% methylene chloride / 75% ethyl acetate which eluted a dark purple/brown band. The solvent from the purple/brown colored eluate was removed with reduced-pressure evaporation to recover 0.45 g of semi-pure free base porphyrin. The semi-pure H₂TAMENP was dissolved in a minimal portion of methylene chloride and applied to an aluminum foil wrapped, methylene chloride slurry packed, silica gel column (20 g silica gel, 2 cm id). This column was eluted with 150 ml methylene chloride, then the solvent polarity was increased to 1% diethyl ether / 99% methylene
chloride (100 ml), and the faint purple band was collected. The solvent polarity was further increased to 5% diethyl ether/95% methylene chloride. When a second, more intensely colored band began to elute, the collection receivers were switched. Evaporation of the solvent from the second band yielded 0.12 g of purple solid. The 0.12 g of H$_2$TAMENP was dissolved in a minimal amount of methylene chloride and applied to an aluminum foil wrapped, methylene chloride slurry packed, silica gel column (12 g silica gel, 1 cm id). This column was eluted with 250 ml methylene chloride, the solvent polarity was then increased to 1% diethyl ether/99% methylene chloride (100 ml), and the faintly colored eluate was discarded. When the color intensity of the eluate increased collection was begun. The eluate was evaporated to recover 0.02 g of the $\alpha,\alpha,\alpha,\beta$-atropisomer of H$_2$TAMENP. Removal of the aluminum foil from the column revealed that another band, the $\alpha,\alpha,\alpha,\alpha$-atropisomer, still remained on the column. The silica gel was removed from the column, the portion containing this final band was isolated and then extracted with 20% diethyl ether/80% toluene. The solvent was removed by reduced-pressure rotary evaporation, the residue was dissolved in a small amount of methylene chloride and the material was rechromatographed in 10 g of silica gel using 2% diethyl ether/98% methylene chloride as the eluting solvent. The recovered $\alpha,\alpha,\alpha,\alpha$-atropisomer band was minute, yet sufficient for spectral analysis.

H$_2$TAMENP

FABMS (3-nitrobenzyl alcohol), m/z 1287.1(M+H$^+$); Figure MS-20;
$\alpha,\alpha,\alpha,\beta$ atropisomer

$^1$H NMR (CDCl$_3$, 298 K, 300 MHz, reference TMS $\delta$=0.0, see Figure $^1$H-20): $\delta$ = -2.14 (2NH), 1.67 (CH$_3$), 1.70 (3CH$_3$), 2.43 (t, CH$_2$, J= ), 2.52 (m, CH$_2$), 4.01 (m, 3CH$_2$),
4.08 (t, CH$_2$, J= ), 6.97 (m, 8CH), 7.32 (m, 4CH), 7.69 (d, 4CH, J= ), 8.01 (d, 4CH, J= ), 8.26 (d, 4CH, J= ), 8.44 (s, 2CH), 8.46 (s, 6CH);

$\alpha,\alpha,\alpha,\alpha$ atropisomer

$^1$H NMR (CDCl$_3$, 298 K, 300 MHz, reference TMS δ=0.0): δ=-2.16 (2NH), 1.70 (4CH$_3$), 2.47 (m, 4CH$_2$), 2.52 (m, CH$_2$), 4.00 (m, 4CH$_2$), 6.98 (m, 8CH), 7.32 (m, 4CH), 7.72 (d, 4CH, J= ), 8.01 (d, 4CH, J= ), 8.26 (d, 4CH, J= ), 8.45 (s, 8CH);

$\alpha,\alpha,\alpha,\beta$ atropisomer

$^{13}$C NMR (CDCl$_3$, 298 K, 300 MHz, reference CDCl$_3$ δ=77.0, see Figure $^{13}$C-18):

δ= 28.12 (4CH$_2$), 29.94 (4CH$_3$), 66.07 & 66.27 (4CH$_2$), 112.92 (4C), 114.80 & 115.15 (4CH), 123.59 & 123.69 (4CH), 125.83 (4C), 126.48 (4CH), 127.47 (4CH), 127.60 (4CH), 128.77 (4C), 130.50 (4CH), 130.70 (br, 8CH), 137.85 (4C), 156.19 & 156.32 (4C), 195.21 & 195.36 (4C=O);

IR (solid, KBr disc, Figure IR-20) ν$_{C=O}$ 1686 cm$^{-1}$, δ$_{\text{pyrrole C$\beta$-H}}$ 802 cm$^{-1}$;

**Anal. Calculated** for C$_{76}$H$_{62}$N$_4$O$_8$S$_4$·H$_2$O: C, 69.92; H, 4.94; N, 4.29; S, 9.82.

**Found:** C, 69.32; H, 4.92; N, 4.23; S, 10.19.
I.B. Spectroscopic Results

I.B.1 NMR Spectrometry

The proton and carbon nuclear magnetic resonance spectra of the these new tetrathioloporphyrins, their derivatives, and their precursor aldehydes have been acquired and interpreted in detail. These results are most easily presented as groups of related compounds with the systematic progression through each series providing clarity and support for the chemical shift assignments of the individual compounds. The results are also presented in tabular form to simplify the comparison of members of a chemical series. The experimental spectra, Figures $^1$H-1 – $^1$H-21 and Figures $^{13}$C-1 – $^{13}$C-18 are located in the appendix of this work.

The Substituted Xylyleneoxy-benzaldehyde Series, $^1$H NMR Spectra

The proton NMR spectrum of \( \alpha\)-Bromo,\( \alpha'\)-(3-formylphenoxy)-\( p\)-xylene, Figure $^1$H-1, provides for a fairly simple interpretation. The two singlets at 4.15 and 5.12 ppm are the \( p\)-xylene methylene groups, with the ether methylene being shifted further downfield than the bromo methylene owing to the higher electronegativity of the oxygen atom. The singlet furthest downfield, 9.98 ppm is the aldehydic proton. The tall singlet in the phenyl region, 7.43 ppm integrates for four protons and is assigned as the xylene protons. The multiplet 7.22-7.26 integrates for one proton and is assigned as proton \( H_4\), while the multiplet 7.46-7.50 ppm integrates for three protons and is assigned as protons \( H_2, H_5, \) and \( H_6\). These assignments of the phenyl ABCD spin system are based on the
assignments determined for the compound \(\alpha\)-acetylmercapto,\(\alpha\)\(^{\prime}\)-(3-formylphenoxy)-p-xylene.

The proton NMR spectrum of \(\alpha,\alpha^{\prime}\)-Bis(3-formylphenoxy)-p-xylene, Figure 1H-2, has an equally simple interpretation. The singlet at 5.14 ppm represents the xylene methylene groups, while the singlet farthest downfield (9.98 ppm) is the aldehydic protons. The large singlet in the phenyl region, 7.49 ppm represents the four xylene protons. The multiplet at 7.24-7.28 ppm integrates for two protons (when allowing for residual CHCl\(_3\) in the NMR solvent) and is assigned as the \(\text{H}_4\) protons. The remaining protons, two \(\text{H}_2\)'s, two \(\text{H}_5\)'s, and two \(\text{H}_6\)'s are in the multiplet 7.44-7.51 ppm.

The proton NMR of \(\alpha\)-acetylmercapto,\(\alpha\)\(^{\prime}\)-(3-formylphenoxy)-p-xylene, Figure 1H-3, is easy to interpret where the singlets are concerned. The singlets in this spectrum 2.35, 4.13, 5.09, and 9.98 ppm are assigned as the acetate methyl group, the thioacetate methylene group, the ether methylene group, and the aldehydic proton, respectively. However, the deceptively simple singlet of the xylene spin system is gone, yielding a weakly 2nd order AA'BB' spin system that gives the appearance of an AB spin system with the predominant signals at 7.31, 7.34, 7.37, and 7.40 ppm. The phenyl ABCD spin system is strongly 2nd order with three of the protons in the multiplet at 7.45-7.49 ppm and the remaining proton in the multiplet at 7.21-7.26 ppm. Using the Jackman-Sternhell substituted benzene estimate tables,\(^{41}\) the calculated chemical shifts are proton \(\text{H}_2\) \(\delta=\) 7.36 ppm, proton \(\text{H}_4\) \(\delta=\) 7.09 ppm, proton \(\text{H}_5\) \(\delta=\) 7.38 ppm, and proton \(\text{H}_6\) \(\delta=\) 7.39 ppm. Adjusting these estimates to reflect the ranges of the experimental multiplets (7.44, 7.23, 7.46, 7.47 ppm) and using the approximate coupling constants (\(J_{24}=2\) Hz, \(J_{25}=0.2\) Hz, \(J_{26}=2\) Hz, \(J_{45}=8\) Hz, \(J_{46}=2\) Hz, \(J_{56}=8\) Hz)\(^{42}\) the calculated spectrum shown in Figure 11 was generated using the PANIC program.\(^{43}\) Further confirmation of this proton assignment was derived from heteronuclear correlation experiments, \textit{vide post}.  


Figure 11 The Experimental $^1$H NMR Spectra of the Phenyl Protons of $\alpha$-Acetylmercapto,$\alpha'$-(3-formylphenoxy)-$p$-xylene (a) and $\alpha$-Bromo,$\alpha'$-(3-formylphenoxy)-$p$-xylene (b) and the Calculated Spectrum for the 3-Formylphenoxy ABCD Spin-System (c)
The proton assignment for $\alpha,\alpha'$-Bis(acetylmercapto)-$p$-xylene, Figure $^1$H-4, is trivial. The thioacetate methyl signal is observed at 2.34 ppm, the methylene group at 4.08 ppm, and the xylene protons are at 7.22 ppm.

**The Substituted Xylyleneoxy-benzaldehyde Series, $^{13}$C NMR Spectra**

The broad band decoupled $^{13}$Carbon NMR spectra of these intermediates, Figures $^{13}$C-1 to $^{13}$C-4, were assigned by calculating the estimated chemical shifts using the $^{13}$C estimate tables$^{44}$, comparing the $^{13}$C spectra across this series of compounds, and using single frequency on-resonance decoupling experiments to confirm key assignments in this series. These assignments are compared in Table 1.

The simplest spectrum of this series is $\alpha,\alpha'$-bis(acetylmercapto)-$p$-xylene, Figure $^{13}$C-4, which has five resonances. The aliphatic region contains the acetate methyl carbon at 30.32 ppm and the methylene carbon at 33.02 ppm. The acetate carbonyl is found at 195.12 ppm. The phenyl region contains the two xylene quaternary carbons at 136.64 ppm and the four protonated xylene carbons at 129.06 ppm.

The spectrum of $\alpha,\alpha'$-bis(3-formylphenoxy)-$p$-xylene, Figure $^{13}$C-2, is slightly more complex with ten signals. The aliphatic ether methylene at 69.77 ppm, the aldehydic carbon at 192.10 ppm, and the four protonated xylene carbons at 127.83 ppm are easily assigned. The two xylene quaternary carbons are assigned to the signal at 136.28 ppm on the basis of the single frequency on-resonance decoupling experiments performed on $\alpha$-acetylmercapto,$\alpha'$-(3-formylphenoxy)-$p$-xylene. The four protonated benzaldehyde
carbons can be distinguished from the two remaining quaternary carbons by their signal intensity. Using the $^{13}$C chemical shift estimate tables the following chemical shifts are predicted for the benzaldehyde ring carbons:

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Estimate</th>
<th>Assigned</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_1$</td>
<td>138.4</td>
<td>137.71</td>
</tr>
<tr>
<td>$C_2$</td>
<td>115.0</td>
<td>112.97</td>
</tr>
<tr>
<td>$C_3$</td>
<td>159.9</td>
<td>159.13</td>
</tr>
<tr>
<td>$C_4$</td>
<td>119.8</td>
<td>122.20</td>
</tr>
<tr>
<td>$C_5$</td>
<td>130.6</td>
<td>130.14</td>
</tr>
<tr>
<td>$C_6$</td>
<td>121.6</td>
<td>123.87</td>
</tr>
</tbody>
</table>

The carbon NMR spectra of $\alpha$-bromo,$\alpha'$-(3-formylphenoxy)-$p$-xylene and $\alpha$-acetylmercapto,$\alpha'$-(3-formylphenoxy)-$p$-xylene, Figures $^{13}$C-1 and $^{13}$C-3, are quite similar with the chemical shifts of the former compound based on the assignments of the later. In the aliphatic region, the thioacetate methyl resonance is found at 30.32 ppm, while the thioacetate methylene signal is at 33.02 ppm. The distinction between these two signals was ascertained using a DEPT experiment (Distortionless Enhancement by Polarization Transfer - a spectral editing sequence that allows for the determination of quaternary, methine, methylene, and methyl carbon resonances). The bromo methylene resonance is found at 33.05 ppm. The ether methylene signal is found at 69.83 ppm (69.64 in the bromo compound), while the aldehydic carbon resonance is at 192.10 (192.06 in the bromo compound). Single frequency on-resonance decoupling is an experiment wherein a particular proton is decoupled which leads to signal enhancement of the adjoining carbons, akin to the manner in which broad band decoupling is used to
enhance $^{13}$C spectra. This signal enhancement is transferred to neighboring atoms in a diminishing manner. Using this technique, it was possible to irradiate the aldehydic proton and determine that the quaternary carbon, C$_1$, has a chemical shift of 137.71 ppm. Irradiation of the thioacetate methylene at 4.08 ppm identifies carbon C$_4$ at 137.70 ppm, while irradiation of the ether methylene identifies carbon C$_1'$ at 135.25 ppm and carbon C$_3$ at 159.13 ppm. The results of a heteronuclear correlation experiment shown in Figure 12 lends confirmation to the assignment of carbon C$_4$ $\delta$= 122.14 ppm and the proton H$_4$ $\delta$= 7.24 ppm. The lack of resolution in the proton dimension hinders further confirmation of the benzaldehyde carbons, but does confirm the assignment of the protons H$_2$, H$_5$, and H$_6$ as the multiplet at 7.44-7.47 ppm.

In comparing the effect of substitution of thioacetate for bromine, the $^{13}$C and $^1$H chemical shifts of the terminal methylene group ,"b", are nearly identical which indicates that these functional groups have similar short-range inductive effects (electronegativity). These two functional groups do have different long-range effects as evidenced by the modest change in chemical shift in the xylene skeletal carbons C$_1$ and C$_3'$ = C$_5'$. This difference is also observed in the porphyrin derivatives, *vide post*. 
Figure 12  The Heteronuclear Correlation Spectrum

of 3-(p-Acetylmercaptoxylyleneoxy)benzaldehyde
The Xylyleneoxy-porphyrin Series, $^1$H NMR Spectra

The proton NMR spectrum of H$_2$TAMXPP, Figure $^1$H-5, shows little change in the aliphatic region and slightly more resolution in the phenyl ABCD spin system, when compared with the precursor aldehyde, Figure $^1$H-3. The singlets 2.32 ppm, 4.11 ppm, and 5.21 ppm are assigned as the thioacetate methyl group, the thioacetate methylene group, and the ether methylene group, respectively. The downfield aldehydic signal is replaced by a singlet at 8.85 ppm, which integrates for the eight β-pyrrole protons. A broad singlet at -2.85 ppm integrates for the two exchangeable pyrrole nitrogen protons, the upfield shift being due to the strong porphyrin ring current effect.$^{45}$

This xylene AA'BB' spin system shows more 2nd order effects than the precursor aldehyde, although portions of the "deceptively simple" AB pattern, 7.30-5.45 ppm can be picked out when this spectrum is compared to the spectrum of α-acetylmercapto,α′-(3-formylphenoxy)-p-xylene. The phenyl ABCD spin system has less 2nd order effects than the starting aldehyde with the assignments; proton H$_2$ as a singlet at 7.84 ppm, proton H$_4$ as a doublet of doublets buried in the AA'BB' resonance at 7.38 ppm, proton H$_5$ as a triplet centered at 7.64 ppm, and proton H$_6$ as a doublet centered at 7.83 (half of the doublet overlaps proton H$_2$). The proton chemical shifts of H$_2$TAMXPP and the other xylyleneoxy substituted porphyrins are summarized along with the precursor aldehydes in Table 2.

The proton spectrum of H$_2$TMXPP, Figure $^1$H-6, exhibits changes in the aliphatic region associated with the deprotection of the thiol and minor shifts in the positions of the aromatic resonances. The thiol proton is observed as a triplet at 1.74 ppm with a coupling constant of 7.6 Hz and the thiol methylene group is visible as a doublet at 3.73 ppm. The ether methylene remains constant at 5.23 ppm. The porphyrin resonances remain
essentially unchanged, with the pyrrole NH signal at -2.85 ppm and the β-pyrrole protons at 8.83 ppm. The aromatic region alters slightly, but the overall positioning is the same; the proton H2 singlet is observed at 7.83 ppm, the proton H4 doublet is centered at 7.39 ppm, the proton H5 triplet is at 7.66 ppm, and the proton H6 doublet is centered at 7.82 ppm. In this porphyrin, the proton H4 doublet is cleanly centered in the AA'BB' simplistic AB pattern and can be observed as a doublet. In one particular sample, the spin-spin coupling between protons H2 and H4 was observed and a J value of 1.5 Hz was measured. The resonances at 8.16 ppm and 8.43 ppm are the result of a trace of the porphyrin dication (the acidic form of the porphyrin) still present after considerable attempts at neutralization.

The proton spectrum of [ZnII(TAMXPP)], Figure 1H-7, demonstrates modest changes from the unmetallated porphyrin. All of the aliphatic resonances are shifted slightly upfield, the thioacetate methyl signal being observed at 2.14 ppm, the thioacetate methylene group is observed at 3.91 ppm, and the ether methylene group is found at 5.06 ppm. The porphyrin signal presents an interesting surprise, the β-pyrrole resonance is observed as either a doublet or a pair of equal-intensity singlets situated at 8.93 and 8.94 ppm, a feature that will be addressed fully in the discussion section. The aromatic resonances have the same general appearance as the other porphyrins of this series. The proton H2 singlet is observed at 7.81 ppm, but this time it overlaps the upfield half of the proton H6 doublet, which is centered at 7.82 ppm. The proton H5 triplet centered at 7.62 ppm indicates an average coupling constant of 7.5-8 Hz. The proton H4 doublet centered at ~7.32 ppm is partially obscured in the highly 2nd order xylene AA'BB' spin system, 7.16-7.38 ppm.

The proton NMR spectrum of H2TBrXPP, Figure 1H-9, has a spectrum similar to that of the thioacetate derivative. The aliphatic region changes slightly due to the electronegativity difference between bromine and the thioacetate group, with the bromo
methylene group shifting to slightly lower field, 4.48 ppm. The ether methylene group resonance is found at 5.24 ppm. The porphyrin signals do not change significantly, with the pyrrole NH resonance being found at -2.85 ppm and the \( \beta \)-pyrrole protons at 8.82 ppm. The proton \( H_2 \) singlet and the proton \( H_6 \) doublet overlap at 7.82 ppm while the proton \( H_5 \) triplet remains at 7.64 ppm. The proton \( H_4 \) doublet at 7.39 ppm alters what would otherwise be a simplistic AB pattern of the xylene AA'BB' spin system, 7.38, 7.41, 7.45, and 7.48 ppm.

The proton NMR spectrum of [Fe\( \text{III} \)(TAMXPP)Cl], Figure 1H-8, presents an entirely different spectrum because of the paramagnetic iron metal center. The most striking feature is the extreme downfield shift of the \( \beta \)-pyrrole protons, 81.8 ppm. This is congruent with the literature values for a high-spin (\( S = 5/2 \)) iron(III) porphyrin. There is no evidence of a resonance at -15 to -20 ppm which would be indicative of a low-spin (\( S = 1/2 \)) Fe(III) porphyrin. The \( H_5 \) proton is seen as a pair of singlets at 11.58 and 12.85 ppm, a consequence of the displacement of the high-spin iron atom from the plane of the porphyrin ligand.\(^{46}\) The remaining aromatic protons fall in a multiplet 6.8-7.9 ppm. The ether methylene resonance is shifted downfield and split into two broad signals at 5.54 and 6.10 ppm. As in the case of the \( H_5 \) proton, the presence of two signals is due to the out-of-plane displacement of the five coordinate iron atom. The thioacetate methylene group resonance, 4.02 and 4.20 ppm is far enough removed from the paramagnetic metal center that the linewidth has narrowed to nearly half that of the ether methylene group and the thioacetate methyl group is observed as a singlet at 2.30 ppm.
The Xylyleneoxy-porphyrin Series, $^{13}$C NMR Spectra

The broad-band decoupled $^{13}$Carbon NMR spectra of the xylyleneoxy-substituted tetraphenylporphyrins, Figures $^{13}$C-5--$^{13}$C-8, were assigned by comparing the spectra across the series, comparing these spectra with those of the precursor aldehydes, and by comparison with the literature and experimental values for unsubstituted tetraphenyl porphyrins. The assignments are summarized in Table 3, which lends itself to the discussion of these $^{13}$C chemical shifts on the basis of skeletal position.

The chemical shift of the ether methylene carbon, "a" is strongly influenced by the electronegativity of the ether oxygen atom and is practically invariant across the series. In the same manner, the chemical shift of the other methylene group, "b" is influenced by the electronegativity of the "R" group. The difference between the bromine and thioacetate substituents is not noticeable, while the less electronegative thiol group produces a slight upfield chemical shift in the adjoining methylene group. The chemical shifts of the thioacetate carbonyl and methyl carbons are invariant in this series, as well as in the ethoxyphenyl series of compounds, with the methyl carbon at 30.3 ppm and the carbonyl carbon at 195.1 ppm.

The phenyl ring carbons demonstrate a substantial change in chemical shift with the conversion of the formyl group into the porphyrin meso-carbon and a smaller, yet significant change when the porphyrin ring is metallated with the diamagnetic zinc atom. The skeletal position C$_1$ is strongly influenced by the inductive effect of the formyl or porphyrin group, with the porphyrin exerting a stronger effect and hence creating a greater downfield shift.

The C$_2$ skeletal position is ortho to the phenyl ether functionality which provides a strong shielding effect on carbon C$_2$, the formyl and porphyrin groups have only a slight or
moderate deshielding influence with the end result being the upfield shift of this carbon (112.9 or 121.4 ppm).

The highly deshielding influence of the ether functional group is observed in the extreme downfield chemical shift of carbon C3, \( \delta = 156.9 \) or 159.1 ppm. The ring current effects of the aromatic porphyrin molecule provide for the \( \pm 3 \) ppm upfield difference observed between the aldehyde and porphyrin structures.

The C4 skeletal position is similar to the C2 carbon in that it is ortho to the strongly shielding phenyl ether functionality. However, in this case, the magnitude of the deshielding influence of the para formyl and porphyrin groups is reversed, such that the porphyrin carbon C4 is found at higher field (114.4 ppm).

The C5 carbon exhibits a downfield chemical shift (\( \pm 3 \) ppm) with the conversion of the formyl to porphyrin that can be attributed to the ring current effects of the porphyrin, akin to carbon C3. However, in this case the skeletal carbon is meta to the phenyl ether and experiences only a slight deshielding effect from that functional group, resulting in \( \delta = 130.1 \) or 127.5 ppm.

The aldehyde C6 phenyl carbons are para to the ether functionalities which produces a moderate shielding effect, this effect is weakly countered by the deshielding ortho-formyl group resulting in a chemical shift \( \delta = 123.8 \) ppm. In these porphyrins, the shielding effect of the ether is more strongly countered by the porphyrin ring current effect. The ring current effect is in turn influenced by the presence or absence of a metal ion, the net result being a chemical shift for the free-base porphyrins \( \delta = 127.6 \) to 128.1 ppm and for the zinc porphyrin \( \delta = 131.9 \) ppm.

The xylene skeletal carbons are assigned on the basis of the assignments determined for the precursor aldehydes. It is interesting to note again that the change from bromine to thioacetate has only a minimal short-range effect, but a larger influence on the more distant
C1' carbon. A plausible explanation for this phenomenon is that the electronegativities of these two substituents are very similar allowing for the equivalent short-range effect, yet the thioacetate carbonyl group has a ring current effect that may be positioned in space so as to influence the more remote location.

The assignments of the two equivalent sets of xylene carbons, C2', C6' and C3', C5' is based on the premise that the particular alkyl substituents (CH2Br, CH2SH, CH2OPh, and CH2SAc) are ortho-para directing functionalities, and as such, they will have a much smaller effect on the meta position that they have on the ipso, ortho, and para positions. The phenyl ether substituent is a constant factor in this series and the chemical shifts δ = 127.83 - 127.96 display a similar consistency, therefore these chemical shifts are assigned to the carbons C2' and C6'.

The rapidly exchanging pyrrole-nitrogen protons allow for a C4v symmetry of the porphyrin macrocycle, which in turn provides for the three porphyrin carbon resonances, the meso-carbon, the Cα-carbon and the Cβ-carbon. The meso-carbon is in the shielding zone of the porphyrin ring current effect and is found upfield at 119.7 ppm. The α-pyrrole carbon resonance is generally found near 145 ppm but suffers from extreme line broadening a consequence of the rapid exchange of the nitrogen protons.45 The β-pyrrole carbon experiences a moderate line-broadening effect from the N-H tautomerism in the free-base porphyrins, with this resonance being found at 131.1 ppm in these porphyrins. Metallation of the porphyrin with diamagnetic zinc(II) removes the effects of the N-H exchange and sharpens the carbon Cα δ = 149.97 ppm and Cβ δ = 131.95 ppm resonances.
The Substituted Ethoxy-phenyl Series of Compounds, \(^1\text{H} \) NMR Spectra

The proton NMR spectrum of 2-(2-hydroxyethoxy)benzaldehyde, Figure \(^1\text{H}-10\), provides the basis for assigning the ortho-ethoxy substituted benzaldehyde series. The proton chemical shifts of this series are listed in Table 4. The experimental values obtained for this compound closely match the literature values\(^28\) with the exception of the hydroxyl proton, which is not surprising for an exchanging alcohol proton. The experimental results in this lab showed the hydroxyl chemical shift to routinely vary between 2.0 and 2.2 ppm. The ethoxy arm methylene groups form a 2nd order AA'BB' spin system. The upfield multiplet centered at 4.04 ppm is assigned to the alcohol end of the substituent on the basis of residual coupling to the alcohol proton that was occasionally observed. The multiplet centered at 4.23 ppm is assigned to the ether end of the ethoxy group. The aldehydic proton resonance is observed far downfield at 10.47 ppm. An expansion of the aromatic portion of the spectrum containing the ABCD spin system is shown in Figure 13. The initial assignments were based on calculated chemical shifts using the Jackman-Sternhell Table for Aromatic Protons: \(^41\)

<table>
<thead>
<tr>
<th>Proton</th>
<th>Estimate (ppm)</th>
<th>Assigned (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_3)</td>
<td>7.02</td>
<td>7.01</td>
</tr>
<tr>
<td>H(_4)</td>
<td>7.45</td>
<td>7.56</td>
</tr>
<tr>
<td>H(_5)</td>
<td>7.05</td>
<td>7.08</td>
</tr>
<tr>
<td>H(_6)</td>
<td>7.72</td>
<td>7.84</td>
</tr>
</tbody>
</table>
Figure 13  The $^1$H NMR Spectral Region for the Phenyl Protons
of ortho-Substituted Benzaldehydes

The weak "W" coupling of the $H_6$ and $H_4$ protons is readily apparent from the expanded view of the aromatic region of the spectrum. Further confirmation of the assignment ordering was obtained using selective proton decoupling experiments. In this set of experiments; irradiation of the $H_6$ proton (7.84 ppm) produced a "clean" triplet at 7.57 ppm and a doublet at 7.08 ppm; irradiation of proton $H_4$ (7.56 ppm) produced a "clean" doublet at 7.85 ppm, a doublet at 7.08 ppm, and a singlet at 7.00 ppm; and irradiation of protons $H_3$ and $H_5$ (7.08 ppm) produced two weakly coupled "singlets" at 7.55 and 7.85 ppm.

The proton NMR spectrum of 2-(2-methanesulfonateethoxy)benzaldehyde, Figure $^1$H-11, has proton chemical shifts very similar to its precursor benzaldehyde, especially in the phenyl ABCD spin system. These protons were assigned $H_3$ $\delta= 6.98$ ppm, $H_4$ $\delta= 7.57$ ppm, $H_5$ $\delta= 7.10$ ppm, and $H_6$ $\delta= 7.86$ ppm. The aldehydic proton
resonance is located at 10.50 ppm, while the new methanesulfonate methyl group resonance is the upfield signal at 3.09 ppm. The ethoxy AA'BB' spin system, shown with greater detail in Figure 14, presents a spectral pattern typical of two pairs of chemically equivalent yet magnetically inequivalent nuclei. Analysis of this 2nd order spectrum suggests that ν_A = 1391.7 Hz (4.64 ppm) and ν_B = 1316.2 Hz (4.39 ppm), along with J values; J_{AA'} = 114 Hz, J_{AB} = 7 Hz, J_{AB'} = 2 Hz, and J_{BB'} = 10 Hz. These values were input into the spectral modelling program, PANIC,\textsuperscript{43} which produced the calculated spectrum also shown in Figure 14. The upfield resonance 4.39 ppm is assigned to the ether methylene group and the resonance at 4.64 ppm is assigned to the mesylate methylene group on the basis of the comparatively stronger chemical shift effect of the OSO₂R functional group.\textsuperscript{44}

The proton NMR of 2-(2-acetylmercaptoethoxy)benzaldehyde, Figure 1\textsuperscript{H}-12, has chemical shifts that essentially duplicates those found in the previous compounds. The substitution of the thioacetate group in place of the methanesulfonate diminishes the downfield shift of the ethoxy methylene groups, this effect being most pronounced in the neighboring methylene group at 3.34 ppm. The ether methylene group is observed at 4.23 ppm and the chemical shift difference of these two resonances (δν = 220 Hz) is large enough that a 1st order A₂X₂ spin system is observed. The two methylene groups are spin-spin coupled with a coupling constant of J_{AX} = 6.4 Hz.
Figure 14  The Ethoxy-arm AA'BB' Spin-System of
2-(2-Methanesulfonateethoxy)benzaldehyde in CDCl₃
at 300 MHz: (a) Experimental and (b) Calculated Spectrum.
The proton NMR spectrum of $\text{H}_2\text{TAMEPP}$, Figure $^1\text{H}-13$ differs significantly from the precursor aldehyde because of the ring current effects of the porphyrin macrocycle. The spectrum is further complicated with the overlapping resonances of the different atropisomers, which is most evident in the multiplicity of the methyl signals at $\delta = 1.68 - 1.78$ ppm. The thioacetate methylene resonance is the multiplet $\delta = 2.44 - 2.53$ ppm while the ether methylene resonance is in the region $3.86 - 3.97$ ppm. The calculated and assigned phenyl proton resonances are as tabulated:

<table>
<thead>
<tr>
<th>Proton</th>
<th>Estimate (ppm)</th>
<th>Assignment (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H3</td>
<td>7.34</td>
<td>7.3</td>
</tr>
<tr>
<td>H4</td>
<td>7.70</td>
<td>7.7</td>
</tr>
<tr>
<td>H5</td>
<td>7.37</td>
<td>7.3</td>
</tr>
<tr>
<td>H6</td>
<td>8.2</td>
<td>8.0</td>
</tr>
</tbody>
</table>

These phenyl proton assignments are further confirmed by a heteronuclear correlation experiment, *vide post*. The broad resonance at -2.61 ppm integrates for the two exchanging pyrrole nitrogen protons with the extreme upfield shift being a result of the porphyrin ring current effect. While the downfield resonance at 8.76 ppm integrates for the eight $\beta$-pyrrole protons.

The proton NMR spectrum of $\text{H}_2\text{TMEPP}$, Figure $^1\text{H}-14$, shows the loss of the thioacetate signal and the appearance of the thiol multiplet at $\delta = 0.51-0.66$ ppm. The methylene group ($\delta = 2.01-2.14$ ppm) nearest to the thiol demonstrates an upfield shift, additional multiplicity, and some broadening due to the inductive effects and spin-spin coupling of the thiol proton. The ether methylene, $\delta = 3.97-4.02$ ppm shows only a slight downfield shift, upon cleavage of the acetate protecting group. The phenyl proton
resonances suffer little or no effect with the deprotection of the thiol, protons H₃ δ = 7.27-7.38 ppm; H₄ δ = 7.71-7.76 ppm; H₅ δ = 7.27-7.38 ppm; and H₆ δ = 7.98-8.03 ppm. The porphyrin β-pyrrole proton resonance δ = 8.75 ppm is unchanged and in this particular sample the N-H resonance shows resolution of two groups of atropisomers, δ = -2.64 and -2.67 ppm.

The proton NMR spectrum of [Zn²⁺(TAMEPP)], Figure ¹H-15, differs from the free-base porphyrin not in terms of chemical shift, but on increased resolution of the different atropisomer resonances, particularly noticeable is the multiplicity of the thioacetate methyl resonances δ = 1.68-1.78 ppm and the β-pyrrole proton resonances δ = 8.74-8.79 ppm. Occasionally, an NMR spectrum of this compound would offer evidence for one of the thioacetate arms being positioned over the metal center, however, this phenomenon was not reproducible.

The proton NMR spectrum of [Fe³⁺(TAMEPP)Cl], Figure ¹H-16, provides a much different set of resonances due to the paramagnetic iron(III) metal center. The extreme downfield shift of the β-pyrrole protons δ = 80.9 ppm is consistent with the literature value for a high-spin (S = 5/2) iron(III) porphyrin.⁴⁶ There is no evidence of a resonance at -15 to -20 ppm which would be indicative of a low-spin (S = 1/2) iron(III) porphyrin. The H₃ and H₅ protons are observed as a series of resonances δ = 12.00, 12.93, 13.19, and 14.76 ppm. The H₄ and H₆ protons provide for the signals in the range 7.15-9.2 ppm, while the thioacetate methyl, thioacetate methylene and ether methylene present the signals 1.42-2.30, 3.41-4.15, and 5.22-5.85 ppm.

The Substituted Ethoxy-phenyl Series of Compounds, ¹³C NMR Spectra
The broad-band decoupled $^{13}$C NMR spectra of the ethoxyphenyl series of aldehydes and porphyrin, Figures $^{13}$C-9–$^{13}$C-14, were assigned by comparison of the members of the series, calculation of chemical shift estimates, heteronuclear correlation experiments on key compounds, and comparison with literature and experimental values for unsubstituted tetraphenyl porphyrins. The assignments are summarized in Table 5 which affords the mechanism for discussing the chemical shifts of portions of this series on the basis of skeletal position.

The highly electronegative ether oxygen atom produces a deshielding effect on the adjoining methylene group, "a" and provides for the downfield chemical shifts ranging from 67.02 to 70.19 ppm.

The other methylene group, "b" demonstrates a variability in its chemical shift that is dependent upon the nature of the attached "R" group. The hydroxyl and methanesulfonate functionalities are strongly deshielding ($\delta = 61.14$ and $67.48$ ppm), while the thioacetate and thiol groups are only moderately deshielding ($\delta = 28.3$ to 23.6 ppm).

The phenyl $^{13}$C chemical shifts were initially assigned on the basis of calculated chemical shifts as herein tabulated:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Aldehyde Convert</th>
<th>Porphyrin Convert</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>Estimate</td>
<td>Assigned</td>
</tr>
<tr>
<td>C1</td>
<td>122.8</td>
<td>124.93</td>
</tr>
<tr>
<td>C2</td>
<td>159.9</td>
<td>160.62</td>
</tr>
<tr>
<td>C3</td>
<td>115.0</td>
<td>112.51</td>
</tr>
<tr>
<td>C4</td>
<td>135.7</td>
<td>135.87</td>
</tr>
<tr>
<td>C5</td>
<td>121.6</td>
<td>121.11</td>
</tr>
<tr>
<td>C6</td>
<td>135.4</td>
<td>128.31</td>
</tr>
</tbody>
</table>
The correlation between the estimated and assigned values for the aldehyde C₅-carbon is weak. This poor correlation is most likely due to "electronic field effects" between the two ortho functional groups. The carbon assignments are buttressed by interpretation of the individual spectra and a heteronuclear correlation experiment on the free-base porphyrin, H₂TAMEPP.

The phenyl carbons of the aldehyde series is typified by the spectrum of 2-(2-acetyl mercaptoethoxy)benzaldehyde, Figure 13C-11. The four protonated carbons tower above the two quaternary carbons, C₁ δ = 124.93 and C₂ δ = 160.62 ppm, the downfield shift of carbon C₂ being a result of the highly deshielding ether oxygen atom. The carbons C₃ and C₅ are assigned on the basis of correlation with the estimated chemical shift. This leaves the question of the assignment of carbons C₄ and C₆, which is resolved by reviewing the chemical shifts of protons H₄ and H₆. The proton H₄ resonance is upfield of the proton H₆ resonance and the carbons are thereby similarly assigned.

The porphyrin phenyl carbon resonances again demonstrate the powerful influence of the porphyrin ring current effect. The results of a heteronuclear correlation experiment, shown in Figure 15, gives credence to the ¹H and ¹³C assignments previously reported. Starting with the upfield phenyl resonances, proton H₃ δ = 7.3 ppm correlates with carbon C₃ δ = 112.77 ppm, proton H₅ δ = 7.3 ppm correlates with carbon C₅ δ = 119.96 ppm, proton H₄ δ = 7.7 ppm correlates with carbon C₄ δ = 129.75 ppm, proton H₆ δ = 8.0 ppm correlates with carbon C₆ δ = 135.84 ppm, and proton H₇ δ = 8.76 ppm correlates with carbon C₇ δ = 131.7 ppm.
Figure 15  
The Heteronuclear Correlation of  
5,10,15,20-Tetrakis[2-(2-acetylmercaptoethoxy)phenyl]porphyrin
As in the case of the xylyleneoxyphenylporphyrins, the rapidly exchanging pyrrole-nitrogen protons allow for a $C_{4v}$ symmetry of the porphyrin macrocycle, which in turn provides for the three porphyrin carbon resonances, the meso-carbon, the $C_\alpha$-carbon and the $C_\beta$-carbon. The meso-carbon is in the shielding zone of the porphyrin ring current effect and is found upfield at 115.38 ppm. The $\alpha$-pyrrole carbon is generally found near 145 ppm but suffers from extreme line broadening a consequence of the rapid exchange of the nitrogen protons.$^{45}$ The $\beta$-pyrrole carbon ($=131$ ppm) experiences a moderate line-broadening effect from the N-H tautomerism in the free-base porphyrins, while metallation of the porphyrin with diamagnetic zinc(II) removes the effects of the N-H exchange and sharpens the $C_\alpha$ ($\delta= 149.95$ ppm) and $C_\beta$ ($\delta= 132.58$ ppm) resonances.

The Substituted Ethoxy-Naphthalene Series, $^1$H NMR Spectra

This series of aldehydes and the resultant porphyrin is similar to the previous substituted ethoxy-phenyl series, the primary difference being the obvious naphthalene/phenyl switch. The second difference being the characterization of an individual atropisomer of the ethoxy-naphthyl-porphyrin, as opposed to the mixture of ethoxy-phenyl-porphyrin atropisomers. The $^1$H chemical shifts of the ethoxy-naphthalene series of compounds are summarized in Table 6.

The proton NMR spectrum of 2-(2-hydroxyethoxy)-1-naphthaldehyde, Figure $^1$H-17, shows a deceptively simple spectrum for the naphthalene protons and a slightly 2nd order spectral pattern for the ethoxy-methylene protons. The aldehyde proton resonance is furthest downfield at 10.97 ppm, while the exchangeable alcohol proton at 2.19 ppm demonstrates the variability previously seen in 2-(2-hydroxyethoxy) benzaldehyde (Figure $^1$H-10, Table 4). The methylene protons nearest to the alcohol
functionality have a chemical shift, 4.09 ppm, practically identical to the chemical shift demonstrated by that related benzaldehyde compound. Comparison of the chemical shifts of the ethoxy-naphthaldehyde with those of the ethoxy-benzaldehyde indicates that the naphthalene ring has a stronger ring current effect, as witnessed by the slightly stronger downfield shift of the ether methylene protons. The increased downfield shift of these methylene protons is a consistent 0.14 ppm throughout the series; hydroxy, methanesulfonate, acetylmercaptop. The naphthalene ring protons are invariant in this same series of compounds and are summarized in Table 6. The assignment of these chemical shifts is based on structural interpretation, coupling constants, and single-frequency decoupling experiments performed on the hydroxyethoxy-member of the series. The protons H₃ and H₄ present a pair of doublets with identical coupling constants (J = 9.1 Hz). The upfield resonance, proton H₃ (δ = 7.27 ppm) is the result of the inductive effects of the ether oxygen, while the proton H₄ (δ = 8.08 ppm) experiences a downfield shift due to the para-aldehyde functional group. The protons H₅ and H₈ give doublets while protons H₆ and H₇ provide deceptively simple triplets. (Close inspection of the triplets reveals an asymmetry in the spectral pattern that would not be present in the case of a 1st order triplet) The proton H₈ can be assigned to the doublet centered at 9.23 ppm due to the strong deshielding ring current effect of the peri-aldehyde carbonyl group. Single-frequency decoupling of the resonance at 9.23 ppm creates a doublet out of the triplet centered at 7.64 and this resonance is assigned as proton H₇. The remaining triplet at 7.45 ppm is assigned as proton H₆, while the doublet centered at 7.80 ppm is assigned as proton H₅. The coupling constants of the doublets can be determined directly from the spectrum, however, the coupling between protons H₆ and H₇ are not discernable by simple inspection. Spectral modeling using the computer program PANIC⁴ suggests that this coupling constant is on the order of 7.8 Hz.
The proton NMR spectrum of 2-(2-methanesulfonateethoxy)-1-naphthaldehyde, Figure 1H-18, is simple to interpret by extension of the previous naphthalene analysis and review of the assignments for the ethoxy substituent of 2-(2-methanesulfonateethoxy) benzaldehyde (Table 4). The consistent 0.14 ppm downfield shift of the ether methylene protons, position "a", in the naphthaldehyde series (Table 6) lends further confirmation to the previous assignment of the methylene protons in the related compound, 2-(2-methane sulfonateethoxy)benzaldehyde.

The proton NMR spectrum of 2-(2-acetylmercaptoethoxy)-1-naphthaldehyde, Figure 1H-19, is nearly identical to the two previous naphthaldehyde compounds. The preceding comments about the ethoxy substituent behaving as the benzaldehyde series holds true for this compound as well. The chemical shifts are listed in Table 6.

The proton NMR spectrum of H$_2$TAMENP, Figure 1H-20, is inherently different from its precursor aldehyde. The most dramatic change is the upfield shift of proton H$_8$ from 9.28 ppm to $\approx$7.0 ppm. The original downfield position was promoted by the strong deshielding influence of the aldehyde carbonyl group. In the porphyrin that deshielding functionality is gone, furthermore, the positioning of the proton H$_8$, with respect to the porphyrin macrocycle, places it in a shielding zone of the aromatic ring current. Proton H$_7$ also experiences the shielding effect of the porphyrin ring current demonstrating an upfield shift from 7.64 ppm to 6.97 ppm, while proton H$_6$ experiences only a small upfield shift to 7.32 ppm. Proton H$_3$ is positioned in the deshielding zone of the porphyrin ring current and is shifted downfield accordingly, now centered at 7.69 ppm. Protons H$_4$ and H$_5$ experience smaller downfield shifts moving from 8.06 ppm to 8.26 ppm and 7.78 ppm to 8.01 ppm, respectively.
The Substituted Ethoxy-Naphthalene Series, $^{13}$C NMR Spectra

The broad-band decoupled $^{13}$C NMR spectra of the substituted ethoxynaphthalene series of aldehydes and porphyrin, Figures $^{13}$C-15--$^{13}$C-18, were assigned by comparison of the members of the series, comparison with the members of the ethoxynaphthalene series, heteronuclear correlation experiments on 2-(2-acetylmercaptoethoxy)-1-naphthaldehyde, and comparison with literature values for tetrathylporphyrins. These assignments are summarized in Table 7 which provides a vehicle for presenting the chemical shifts on the basis of skeletal position.

The chemical shifts of the naphthyl-ethoxy "arm" nearly match the chemical shifts previously reported for the ethoxynaphthalene series of compounds, Table 5. The highly electronegative ether oxygen atom provides for a downfield shift (67.02 to 71.16 ppm) on methylene carbon "a". The chemical shift of methylene carbon "b" is dependent upon the nature of the attached "R" group, with the hydroxyl and methanesulfonate functional groups being the more strongly deshielding groups producing chemical shifts of 61.37 ppm and 67.48 ppm, respectively. As before, the thioacetate group is only moderately deshielding producing a chemical shift of 28.49 ppm in the naphthaldehyde compound and 28.12 ppm in the porphyrin derivative. The thioacetate carbonyl carbon demonstrates a far downfield shift with $\delta = 195.35$ ppm.

The alteration of the terminal "R" group in the naphthaldehyde compounds has very minimal effects upon the chemical shifts observed in the naphthaldehyde ring carbons. A quick glance at the naphthaldehyde spectra, Figures $^{13}$C-15--$^{13}$C-17, allows for an immediate distinction between the more intense signal of the protonated carbons (shorter $T_1$ times) and the weaker signal of the more slowly relaxing quaternary carbons. Of the four quaternary carbons, carbon C2 is the furthest downfield (162.18 - 162.98 ppm) as a result
of the strongly deshielding influence of the electronegative ether oxygen. The upfield shift of quaternary carbon C₁ (116.89 - 117.47 ppm) is a combinational effect of the mildly deshielding ipso-aldehyde and the more strongly shielding ortho-ether oxygen. The two remaining quaternary carbons C₉ and C₁₀ are assigned as δ = 131.37 - 131.57 ppm and δ = 128.67 - 129.00 ppm, respectively. The assignments of carbons C₉ and C₁₀ are based on the literature assignments for 1-isopropenyl-2-methoxynaphthalene⁴⁸ and these assignments are supported by the minor but significant chemical shift changes of carbon C₁₀ which is located para to the ethoxy arm.

Of the six methine carbons, C₃ (δ = 113.33 - 113.76 ppm) and C₄ (δ = 137.58 - 137.61 ppm) can easily be assigned on the basis of the shielding effects of the ether oxygen and the deshielding effects of the para carbonyl. The remaining protonated carbons depend upon heteronuclear correlation experiments to confer the following assignments; carbon C₅ (δ = 128.21 - 128.28 ppm), carbon C₆ (δ = 124.95 - 124.99 ppm) carbon C₇ (δ = 129.89 - 130.09 ppm),and carbon C₈ (δ = 124.72 - 125.25 ppm).
Table 1  The $^{13}$C Chemical Shifts of the Xylene Derivatives

1 R = Br  
2 R = OPhCHO  
3 R = SAc  
4 Bis(acetyl mercapto)-p-xylene

<table>
<thead>
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<th>Skeletal position</th>
<th>cmpd 1</th>
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<th>cmpd 3</th>
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<td>33.02</td>
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<tr>
<td>b</td>
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<td>33.09</td>
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</tr>
<tr>
<td>R (methyl)</td>
<td>-</td>
<td>-</td>
<td>30.35</td>
<td>30.32</td>
</tr>
<tr>
<td>(carbonyl)</td>
<td>-</td>
<td>-</td>
<td>195.10</td>
<td>195.12</td>
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Table 4  $^1$H Chemical Shifts of the Ethoxyphenyl Series of Compounds

1 R = OH  \hspace{1cm} R' = CHO
2 R = OSO$_2$CH$_3$  \hspace{1cm} R' = CHO
3 R = SC(O)CH$_3$  \hspace{1cm} R' = CHO
4 R = SC(O)CH$_3$  \hspace{1cm} R' = porphyrin
5 R = SC(O)CH$_3$  \hspace{1cm} R' = Zn porphyrin
6 R = SH  \hspace{1cm} R' = porphyrin

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Table 5  $^{13}$C Chemical Shifts of Ethoxyphenyl Series of Compounds

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Table 6  $^1$H Chemical Shifts of the Ethoxynaphthyl Series of Compounds

1 $R = \text{OH}$ $R' = \text{CHO}$
2 $R = \text{OSO}_2\text{CH}_3$ $R' = \text{CHO}$
3 $R = \text{SC(O)CH}_3$ $R' = \text{CHO}$
4 $R = \text{SC(O)CH}_3$ $R' = \text{porphyrin}$

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Table 7  $^{13}$C Chemical Shifts of the Ethoxynaphthyl Series of Compounds

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<td>b</td>
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<td>( \text{R} (\text{CH}_3) )</td>
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<td>( \text{R'} - \text{Porphyrin} - \alpha )</td>
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<td>-</td>
<td>-</td>
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<tr>
<td>- ( \beta )</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>-meso</td>
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<td>112.92</td>
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</table>
I.B.2 Mass Spectrometry

α-Brorno,α′-(3-formylphenoxy)-p-xylene

The mass spectrum of this compound, Figure MS-1, shows the molecular ions at m/z 304 and 306, a result of the isotopic abundance of bromine (79Br - 100%, 81Br - 98%). The loss of the bromine (-79 or -81amu) results in an ion at m/z 225, while the cleavage of the ether bond with loss of -O-phenyl-CHO as a neutral (-121amu) leads to the fragments at m/z 183 and 185. The combination of these two losses leads to the xylene version of a tropilium ion at m/z 104. A small amount of the CHO-phenyl-O fragment can be observed at m/z 121.

α,α′-Bis(3-formylphenoxy)-p-xylene

The mass spectrum of this compound, Figure MS-2, shows the molecular ion at m/z 346. The loss of a CHO-phenyl-O fragment (-121 amu) results in an ion at m/z 225, while the cleavage of the second ether bond with loss of an identical fragment leads to the xylene version of a tropilium ion at m/z 104. A small amount of the CHO-phenyl-O fragment can be observed at m/z 121.

α-Acetylmercapto,α′-(3-formylphenoxy)-p-xylene

The mass spectrum of this compound, Figure MS-3, shows the molecular ion at m/z 300. The loss of a thioacetate fragment (-75 amu) results in an ion at m/z 225, while the cleavage of the ether bond with loss of -O-phenyl-CHO as a neutral leads to the fragment at m/z 179. The combination of these two losses leads to the xylene version of a tropilium ion at m/z 104. In this compound, the fragment at m/z 121 is not observed.
\(\alpha,\alpha'-\text{Bis(acetylmercapto)-p-xylene}\)

The mass spectrum of this compound, Figure MS-4, shows the molecular ion at \(m/z\) 254. The loss of a thioacetate fragment (-75 amu) results in an ion at \(m/z\) 179. The loss of the second thioacetate leads to the formation of the xylene version of the tropillium ion at \(m/z\) 104. A significant fragment at \(m/z\) 136 appears to be the result of the combinational loss of acetate and thioacetate.

\(5,10,15,20\)-Tetrakis[3-(\(p\)-acetylmercaptoxyleneoxy)phenyl]porphyrin, \(\text{H}_2\text{TAMXPP}\)

The FAB mass spectrum of this compound, Figure MS-5, was obtained using 3-nitrobenzyl alcohol as the matrix and shows the quasi-molecular ion (M+H\(^+\)) at \(m/z\) 1391.8. The loss of an acetate or a thioacetate provides for the ions at \(m/z\) 1348.3 and 1316.2, respectively.

\(5,10,15,20\)-Tetrakis[3-(\(p\)-mercaptoxyleneoxy)phenyl]porphyrin, \(\text{H}_2\text{TMXPP}\)

The FAB mass spectrum of this compound, Figure MS-6, was obtained using 3-nitrobenzyl alcohol as the matrix and shows the quasi-molecular ion (M+H\(^+\)) at \(m/z\) 1223.4. The loss of -SH provides for the ion at \(m/z\) 1191. The loss of the fragment -CH\(_2\)PhCH\(_2\)SH (-137 amu) corresponds to the ion at \(m/z\) 1087 and further loss of -SH from another arm on this fragment provides the ion at \(m/z\) 1054. The loss of two -CH\(_2\)PhCH\(_2\)SH fragments leads to the ion at \(m/z\) 949 and the additional loss of -SH provides for the fragment at \(m/z\) 917. The ion at \(m/z\) 943, as well as the other less intense ions are either artifacts of the nitrobenzyl alcohol matrix or are the products of molecular rearrangement of the parent ion.
5,10,15,20-Tetrakis[3-(p-acetylmercaptoxylyleneoxy)phenyl]porphyrinato-
zn{eq}^{II}\text{}} \text{(TAMXPP)\text{}}

The FAB mass spectrum of this compound, Figure MS-7, was obtained using
3-nitrobenzyl alcohol as the matrix and shows the molecular ion \(\text{(M}^{+}\text{)}\) at \(m/z\) 1454.3. The
loss of acetate provides for the ion observed at \(m/z\) 1411. Any other fragmentation
products are obscured in the baseline noise. The expanded view of the molecular ion
cluster provides for a comparison of the experimental and calculated isotopic distribution of
\[\text{Zn}^{II}\text{(TAMXPP)\text{}}\].\text{\textsuperscript{49}}

5,10,15,20-Tetrakis[3-(p-acetylmercaptoxylyleneoxy)phenyl]porphyrinato-
iron(III) Chloride, \[\text{Fe}^{III}\text{(TAMXPP)Cl}\]

The FAB mass spectrum of this compound was obtained with the addition of the
solid porphyrin directly to a 3-nitrobenzyl alcohol matrix. The spectrum, Figure MS-8,
shows the molecular ion cluster \(m/z\) 1480 amu. However, the predominant ion is the
molecular ion less chloride, \(\text{(M-Cl)}^{+}\) at \(m/z\) 1445. There is an ion cluster at \(m/z\) 1461
which corresponds to the molecular ion minus a chlorine atom plus an oxygen atom,
\(\text{(M-Cl+O)}^{+}\). This particular ion could possibly be a fragment of an \(\mu\)-oxo dimer
contaminant in the iron(III)-chloro product.

\mu-Oxo-bis\{5,10,15,20-tetrakis[3-(p-acetylmercaptoxylyleneoxy)phenyl]-
porphyrinatoiron(III)\}, \[\text{Fe}^{III}\text{(TAMXPP)\text{}}\text{\textsubscript{2}O}\]

The FAB mass spectrum obtained using 3-nitrobenzyl alcohol as the matrix,
Figure MS-21 shows the quasi-molecular ion, \(\text{(M+H)}^{+}\) at \(m/z\) 2906.8. Most of the
smaller fragments can be explained in terms of combinational losses of acetate and
thioacetate. The expansion of the molecular ion-cluster shows the isotope distribution.\text{\textsuperscript{49}}
5,10,15,20-Tetrakis[3-(p-bromoxyleneoxy)phenyl]porphyrin, H₂TBrXPP

The FAB mass spectrum of this compound obtained using 3-nitrobenzyl alcohol as the carrier, Figure MS-9, shows the molecular ion cluster at \( m/z \) 1410.8. The loss of a bromine leads to the ion cluster at \( m/z \) 1330.9, while loss of a second bromine combined with rearrangement lead to the ion clusters at \( m/z \) 1256.7 and 1227.2. The expansion of the mass spectrum to reveal higher resolution detail of the molecular ion cluster shows the \((M^+)^n \) pattern for four bromine atoms overlapping with the quasi-molecular ion, \((M+H)^+\) pattern for four bromine atoms. The classical pattern for four bromine atoms (mass 79 and 81 amu, isotopic abundance 1 to 0.98) would be a multiplet of five signals in a ratio of 1:4:6:4:1, with two mass unit separation between the signals. This distribution pattern is seen in the calculated isotope distribution⁴⁹ and, with mental compensation for the overlapping molecular ion and quasi-molecular ion, the experimental isotope distribution is consistent for four bromine atoms.

2-(2-Hydroxyethoxy)benzaldehyde

The mass spectrum of this compound, Figure MS-10, has a molecular ion at \( m/z \) 166. Loss of water (-18 amu) which is typical for alcohols results in the fragment at \( m/z \) 148. The loss of the aldehyde functionality (-29 amu) results in the fragment at \( m/z \) 137. The predominant fragments \( m/z \) 121, 122 are the result of rearrangements after loss of the ethylhydroxide substituent (-45 amu). A smaller fragment at \( m/z \) 105 is the result of the loss of the entire ethoxyhydroxy substituent.

2-(2-Methanesulfonateethoxy)benzaldehyde

The mass spectrum of this compound, Figure MS-11, has a molecular ion at \( m/z \) 244. Loss of CO (-28 amu) from the aldehyde functionality gives a small ion at \( m/z \) 216.
The loss of $-\text{SO}_2\text{CH}_3$ (-79 amu) gives a small ion at $m/z$ 165. A major fragment at $m/z$ 148 is from the loss of $-\text{OSO}_2\text{CH}_3$ (-96 amu), while the predominant fragment cluster is from the loss of $-\text{EtOSO}_2\text{CH}_3$. This observed cluster of fragments is represented by both the phenyl fragment and the ethylmesylate fragment with their concurrent rearrangements. One other notable fragment is the loss of $-\text{OEtOSO}_2\text{CH}_3$ (-139 amu) resulting in the fragment at $m/z$ 105.

2-(2-Acetylmercaptoethoxy)benzaldehyde

The mass spectrum of this compound, Figure MS-12, has a molecular ion at $m/z$ 224. The loss of acetate (-43 amu) results in the fragment at $m/z$ 181, while the loss of thioacetate (-75 amu) provides for the fragment at $m/z$ 149. The loss of ethylthioacetate (-103 amu) along with rearrangements gives the series of fragments at $m/z$ 121, and the ethylthioacetate fragment itself is observed at $m/z$ 103.

5,10,15,20-Tetrakis[2-(2-acetylmercaptoethoxy)phenyl]porphyrin, $\text{H}_2\text{TAMEPP}$

The FAB mass spectrum obtained using 3-nitrobenzyl alcohol as the matrix, Figure MS-13, shows an overlapping molecular ion and quasi-molecular ion ($\text{M}^+$, $\text{M}+\text{H}^+$) at $m/z$ 1087.1. The ratio of molecular ion to quasi-molecular ion is approximately 2:1 as ascertained by comparison$^{49}$ of the experimental isotopic distribution and the calculated isotopic distribution for the quasi-molecular ion ($\text{M}+\text{H}^+$).

5,10,15,20-Tetrakis[2-(2-mercaptopethoxy)phenyl]porphyrin, $\text{H}_2\text{TMEPP}$

The FAB mass spectrum of this compound obtained using 3-nitrobenzyl alcohol as the matrix, Figure MS-14, shows the quasi-molecular ion ($\text{M}+\text{H}^+$) at $m/z$ 919.3. The ion
signal at \( m/z 977.4 \) (+58 amu) might be dismissed as ion-molecule reactions taking place in the ion source \( ^{50} \), except for the unusually large intensity. The differential mass, 58 amu, does not match the mass of acetate or thioacetate, but the neutralization step during synthesis allows for speculation that sodium chloride maybe contaminating this particular sample and forming an ion pair with the ionized porphyrin. A high resolution expansion of this ion cluster would have allowed for confirmation of this hypothesis, but that information was not provided for this sample.

\( 5,10,15,20 \)-Tetrakis[2-(2-acetylmercaptoethoxy)phenyl]porphyrinato-zinc(II), \([\text{Zn}^{II}(\text{TAMEPP})]\)

The FAB mass spectrum of this compound was obtained using 3-nitrobenzyl alcohol as the matrix. Figure MS-15 shows the molecular ion isotope cluster (M\(^{+}\)) at \( m/z \) 1150, and a comparison \( ^{49} \) of the experimental isotopic distribution with the calculated isotopic distribution for the quasi-molecular ion (M+H\(^{+}\)) shows that ionization of this compound is preferentially towards the molecular ion (M\(^{+}\)).

\( 5,10,15,20 \)-Tetrakis[2-(2-acetylmercaptoethoxy)phenyl]porphyrinato-iron(III) Chloride, \([\text{Fe}^{III}(\text{TAMEPP})\text{Cl}]\)

The FAB mass spectrum obtained using 3-nitrobenzyl alcohol as the matrix, Figure MS-16, shows the molecular ion isotope cluster at \( m/z \) 1175. The predominant feature of this spectrum is the molecular ion minus the chloride at 1140 amu. The initial attempts to obtain a spectrum of \([\text{Fe}^{III}(\text{TAMEPP})\text{Cl}]\) was made by dissolving the solid porphyrin in methylene chloride and adding this to the 3-nitrobenzyl alcohol matrix. The resulting spectrum was nearly devoid of the molecular ion. The successful attempt was made by adding the solid porphyrin directly to the 3-nitrobenzyl alcohol matrix, this
produced the spectrum in Figure MS-16. The remaining fragmentation pattern of this spectrum can be ascribed to the loss of acetate or thioacetate from one or more of the "arms" of the porphyrin. The ion clusters at mass greater than the molecular ion are mostly likely a result of ion-molecule reactions taking place within the ion source. An expansion of the molecular ion portion of the spectrum shows the isotopic pattern anticipated for the porphyrin containing one iron atom and one chlorine atom, at 1175 amu. A similar expansion of the isotope pattern at 1140 amu reflected the absence of the chlorine isotope contributions. The isotope cluster at 1157 amu represent the molecular ion less chlorine plus an oxygen atom, conceivably this is a fragment of a μ-oxo dimer of the iron porphyrin.

2-(2-Hydroxyethoxy)-1-naphthaldehyde

The mass spectrum of this compound, Figure MS-17, shows a molecular ion at m/z 216. Loss of the alcohol group as water (-18 amu) leads to the fragment at m/z 198, while loss of CHO (-29 amu) or CO (-28 amu) result in the fragments at m/z 187 and 188. Loss of the ethylhydroxide fragment (-45 amu) along with rearrangements leads to a series of fragments centered on m/z 171. Loss of the ethoxyhydroxide fragment (-61 amu) results in the fragment at m/z 155. The series of fragments at m/z 126 to 128 represent the bare naphthalene core.

2-(2-Methanesulfoateethoxy)-1-naphthaldehyde

The mass spectrum of this compound, Figure MS-18, shows the molecular ion at m/z 294. The base peak at m/z 171 is the consequence of the loss of the entire methanesulfoateethoxy arm and the fragment at m/z 123 presumably is the arm fragment. The small ion cluster at m/z 198 is the result of rearrangement after the loss of CH₃SO₂OH.
2-(2-Acetylmercaptoethoxy)-1-naphthaldehyde

The mass spectrum of this compound, Figure MS-19, shows the molecular ion at
m/z 274. The base peak at m/z 171 is the consequence of the loss of the entire
acetylmercaptoethoxy arm and the fragment at m/z 103 presumably is the arm fragment.
The fragment at m/z 144, also seen in the previous spectrum, can best be explained by a
McLafferty rearrangement between the aldehyde and ethoxy arm resulting in a naphthalene
ring with a hydroxyl group (C_{10}H_{2}O f.wt. 144.16).

5,10,15,20-Tetrakis[2-(2-mercaptoethoxy)naphthyl]porphyrin, \text{H}_{2}\text{TAMENP}

The FAB mass spectrum of this compound, Figure MS-20, was obtained using 3-
nitrobenzyl alcohol as the matrix and shows the quasi-molecular ion (M+H^+) at m/z
1287.1. The low intensity fragment cluster are the result of combinational losses of acetate
and thioacetate, the more intense fragment at m/z 1031.4 can only be attained by
rearrangement, while the ion cluster at m/z 1303 is most likely the result of molecule-ion
reactions taking place in the source.
I.B.3 Infrared Spectrometry

The majority of the compounds examined were solids once they were purified. These samples were prepared by thoroughly grinding a portion of the compound (= 1 mg) and anhydrous KBr (= 100 mg) with an agate mortar and pestle, transferring the solid mixture to a die set, and compressing the mixture in vacuo with a hydraulic press (12,000 psi). This procedure resulted in a nearly transparent disc for the aldehyde precursors and an translucent brown-tinted disc for the porphyrin compounds. Liquid samples were examined neat, as a thin film pressed between KBr salt plates.

All of these compounds exhibited the typical aromatic and aliphatic carbon-hydrogen stretches in the region 3060-3020 cm\(^{-1}\) and 2980-2840 cm\(^{-1}\), as well as the various C–H bending modes. These absorptions have not been listed unless they are especially intense or are otherwise unique. The tabulated absorptions are reported along with the relative intensity (s-strong, m-moderate, w-weak, vw-very weak), the type of vibration (v-stretching, δ-bending), and the functionality associated with the absorption.

The infrared spectra of the xylyleneoxy series of compounds were interpreted by comparison between members of the series, comparison with simpler related compounds (benzyl chloride and benzyl thioacetate), and with the aid of literature descriptions of characteristic infrared absorption frequencies.\(^{44,51}\)

\textit{α-Bromo,α'-\(3\)-formylphenoxy)-\(p\)-xylene}

The infrared spectrum of this compound shown in Figure IR-1 was collected as a neat oil on KBr plates. The predominant absorption is that of the carbonyl stretch \(\nu_{C=O}\) 1697 cm\(^{-1}\). The other readily definable absorptions include:
\( \alpha, \alpha'-\text{Bis(3-formylphenoxy)}-p\)-xylene

The infrared spectrum of this compound shown in Figure IR-2 was collected as a solid in a KBr disc. The intensity and narrow band width of the majority of the absorptions momentarily distracts attention from the carbonyl stretch a 1686 cm\(^{-1}\). The other readily definable absorptions include:

\[
\begin{array}{cccc}
\text{cm}^{-1} & \text{intensity} & \text{type} & \text{functional group} \\
2813, 2730 & w & v & \text{aldehyde C-H} \\
1697 & s & v & \text{carbonyl} \\
1595, 1586 & m & v & \text{aromatic C-C} \\
1382 & m & \delta & \text{aldehyde C-H} \\
1261 & s & \nu_{\text{asym}} & \text{phenyl-O-C} \\
1020 & m & \nu_{\text{sym}} & \text{phenyl-O-C} \\
\end{array}
\]

\( \alpha\text{-Acetylmercapto} \ \alpha'-\text{(3-formylphenoxy)}-p\)-xylene

The infrared spectrum of this compound shown in Figure IR-3 was collected as a
neat oil on KBr plates. The predominant features are the carbonyl stretch (1695 cm\(^{-1}\)) and the asymmetric stretching mode of the phenyl-O-C bonds (1262 cm\(^{-1}\)). The other readily definable absorptions include:

<table>
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<tr>
<th>cm(^{-1})</th>
<th>intensity</th>
<th>type</th>
<th>functional group</th>
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</thead>
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<tr>
<td>2729</td>
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<td>v</td>
<td>aldehyde C-H</td>
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<tr>
<td>1695</td>
<td>s</td>
<td>v</td>
<td>carbonyl</td>
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<tr>
<td>1596, 1589</td>
<td>m</td>
<td>v</td>
<td>aromatic C-C</td>
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<tr>
<td>1385</td>
<td>w</td>
<td>δ</td>
<td>aldehyde C-H</td>
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<tr>
<td>1262</td>
<td>s</td>
<td>(\nu_{asym})</td>
<td>phenyl-O-C</td>
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<tr>
<td>1134, 627</td>
<td>m</td>
<td>v</td>
<td>C-S-C=O</td>
</tr>
<tr>
<td>1020</td>
<td>w</td>
<td>(\nu_{sym})</td>
<td>phenyl-O-C</td>
</tr>
</tbody>
</table>

\(\alpha,\alpha'-\text{Bis(acetylmercapto)-p-xylene}\)

The infrared spectrum of this compound shown in Figure IR-4 was collected as a solid in a KBr disc. The spectrum was also collected as a nujol mull and as a thin film on KBr plates, as a demonstration that the broadness of the absorptions is a result of the compound not experimental technique. The predominant feature of this spectrum is the broad unsymmetrical absorption of the carbonyl group (1682 cm\(^{-1}\)). The other readily definable absorptions include:
<table>
<thead>
<tr>
<th>cm⁻¹</th>
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<th>functional group</th>
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<tr>
<td>3338</td>
<td>w</td>
<td>v</td>
<td>overtone of C=O</td>
</tr>
<tr>
<td>1904</td>
<td>w</td>
<td></td>
<td>overtone of 963 cm⁻¹</td>
</tr>
<tr>
<td>1682</td>
<td>s</td>
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<td>carbonyl</td>
</tr>
<tr>
<td>1512</td>
<td>m</td>
<td>v</td>
<td>aromatic C-C</td>
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<tr>
<td>1132, 626</td>
<td>s</td>
<td>v</td>
<td>C-S-C=O</td>
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<tr>
<td>963</td>
<td>m</td>
<td></td>
<td>associated with S-(C=O)-CH₃</td>
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</table>

The infrared spectra of the xylyleneoxy series of porphyrins were interpreted by comparison of the members of the series with the precursor aldehydes, comparison with unsubstituted tetraphenyl porphyrins (H₂TPP Figure IR-22, [ZnⅡ(TPP)] Figure IR-23) and literature descriptions of characteristic porphyrin infrared absorption frequencies.\(^\text{52,53}\) The distinctive absorptions of the free-base tetraphenyl porphyrin (H₂TPP) are the N-H stretching (3317 cm⁻¹) and bending modes (966 and 699 cm⁻¹) and the pyrrole Cβ-H bending modes (1072 and 799 cm⁻¹). Seeking out these vibrations in the substituted porphyrins highlights the fact that the substituent absorptions predominate the spectrum.

5,10,15,20-Tetrakis[3-(p-acetylmercaptoxylyleneoxy)phenyl]porphyrin, H₂TAMXPP

The infrared spectrum of this compound shown in Figure IR-5 was collected as a solid in a KBr disk. The predominant absorption is that of the carbonyl group stretch (1688 cm⁻¹). The other readily definable absorptions include:
<table>
<thead>
<tr>
<th>cm$^{-1}$</th>
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<th>type</th>
<th>functional group</th>
</tr>
</thead>
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<tr>
<td>3314</td>
<td>vw</td>
<td>v</td>
<td>N-H</td>
</tr>
<tr>
<td>1688</td>
<td>s</td>
<td>v</td>
<td>carbonyl</td>
</tr>
<tr>
<td>1594, 1574</td>
<td>s</td>
<td>v</td>
<td>aromatic C-C</td>
</tr>
<tr>
<td>1130, 625</td>
<td>m</td>
<td>v</td>
<td>C-S-C=O</td>
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<tr>
<td>975</td>
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<td>N-H</td>
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<tr>
<td>802</td>
<td>m</td>
<td>δ</td>
<td>pyrrole C$_{\beta}$-H</td>
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<tr>
<td>698</td>
<td>m</td>
<td>δ</td>
<td>N-H, porphyrin ring</td>
</tr>
</tbody>
</table>

5,10,15,20-Tetrakis[3-(p-mercaptoxylyleneoxy)phenyl]porphyrin,

$\text{H}_2\text{TMXPP}$

The infrared spectrum of this compound shown in Figure IR-6 was collected as a solid in a KBr disc. The important feature of this spectrum is the lack of the acetate carbonyl group. The readily definable absorptions include:

<table>
<thead>
<tr>
<th>cm$^{-1}$</th>
<th>intensity</th>
<th>type</th>
<th>functional group</th>
</tr>
</thead>
<tbody>
<tr>
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<td>vw</td>
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<td>N-H</td>
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<td>2563</td>
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<td>v</td>
<td>S-H</td>
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<td>1595, 1573</td>
<td>s</td>
<td>v</td>
<td>aromatic C-C</td>
</tr>
<tr>
<td>974</td>
<td>w</td>
<td>δ</td>
<td>N-H</td>
</tr>
<tr>
<td>803</td>
<td>s</td>
<td>δ</td>
<td>pyrrole C$_{\beta}$-H</td>
</tr>
<tr>
<td>698</td>
<td>vw</td>
<td>δ</td>
<td>N-H, porphyrin ring</td>
</tr>
</tbody>
</table>

5,10,15,20-Tetrakis[3-(p-bromoxylyleneoxy)phenyl]porphyrin, $\text{H}_2\text{TBrXPP}$

The infrared spectrum of this compound shown in Figure IR-9 was collected as a
solid in a KBr disc. In comparison with the previous spectra the obvious feature is the lack of the carbonyl absorption. The readily definable absorptions include:

<table>
<thead>
<tr>
<th>cm⁻¹</th>
<th>intensity</th>
<th>type</th>
<th>functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>3318</td>
<td>v</td>
<td>v</td>
<td>N-H</td>
</tr>
<tr>
<td>1595, 1574</td>
<td>s</td>
<td>v</td>
<td>aromatic C-C</td>
</tr>
<tr>
<td>1262</td>
<td>w</td>
<td>v_{asym}</td>
<td>phenyl-O-C</td>
</tr>
<tr>
<td>1020</td>
<td>w</td>
<td>v_{sym}</td>
<td>phenyl-O-C</td>
</tr>
<tr>
<td>975</td>
<td>m</td>
<td>δ</td>
<td>N-H</td>
</tr>
<tr>
<td>803</td>
<td>m</td>
<td>δ</td>
<td>pyrrole C\textsubscript{β}-H</td>
</tr>
<tr>
<td>698</td>
<td>w</td>
<td>δ</td>
<td>N-H and porphyrin ring</td>
</tr>
</tbody>
</table>

The infrared spectra of the ethoxy benzaldehyde series of compounds were interpreted by comparison between members of the series and with the aid of literature descriptions of characteristic infrared absorption frequencies.⁴⁴,⁵¹

2-(2-Hydroxyethoxy)benzaldehyde

The infrared spectrum of this compound shown in Figure IR-10 was obtained as a neat oil on KBr plates. The predominant features are the "free" O-H stretch (3432 cm⁻¹), the hydrogen-bonded O-H stretch (3376 and 3256 cm⁻¹), the "free" carbonyl stretch (1679 cm⁻¹), and the hydrogen-bonded carbonyl stretch (1660 cm⁻¹). The other readily definable absorptions include:
2-(2-Methanesulfonateethoxy)benzaldehyde

The infrared spectrum of this compound shown in Figure IR-11 was obtained as a solid in a KBr disc. The predominant features include the SO$_2$ stretches (1349 and 1179 cm$^{-1}$) and the carbonyl stretch (1681 cm$^{-1}$). The other readily definable absorptions include:

<table>
<thead>
<tr>
<th>cm$^{-1}$</th>
<th>intensity</th>
<th>type</th>
<th>functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>3030-3012</td>
<td>vw-m</td>
<td>v</td>
<td>aromatic C-H</td>
</tr>
<tr>
<td>2950-2867</td>
<td>w-m</td>
<td>v</td>
<td>alkyl C-H</td>
</tr>
<tr>
<td>2768</td>
<td>w</td>
<td>v</td>
<td>aldehyde C-H</td>
</tr>
<tr>
<td>1681</td>
<td>s</td>
<td>v</td>
<td>carbonyl</td>
</tr>
<tr>
<td>1599</td>
<td>s</td>
<td>v</td>
<td>aromatic C-C</td>
</tr>
<tr>
<td>1349, 1179</td>
<td>vs</td>
<td>v</td>
<td>O=S=O</td>
</tr>
<tr>
<td>1031</td>
<td>s</td>
<td>δ</td>
<td>O=S=O</td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th>cm$^{-1}$</th>
<th>intensity</th>
<th>type</th>
<th>functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>3432</td>
<td>s</td>
<td>v</td>
<td>O-H</td>
</tr>
<tr>
<td>3376, 3256</td>
<td>w</td>
<td>v</td>
<td>O-H</td>
</tr>
<tr>
<td>1679, 1660</td>
<td>s</td>
<td>v</td>
<td>carbonyl</td>
</tr>
<tr>
<td>1601</td>
<td>s</td>
<td>v</td>
<td>aromatic C-C</td>
</tr>
<tr>
<td>1246</td>
<td>s</td>
<td>v$_{asym}$</td>
<td>phenyl-O-C</td>
</tr>
<tr>
<td>1049</td>
<td>m</td>
<td>v$_{sym}$</td>
<td>phenyl-O-C</td>
</tr>
<tr>
<td>766</td>
<td>m</td>
<td>δ</td>
<td>O-H (hydrogen bonded)</td>
</tr>
</tbody>
</table>
2-(2-Acetylimercaptoethoxy)benzaldehyde

The infrared spectrum of this compound shown in Figure IR-12 was obtained as a neat oil on KBr plates. The predominant feature is the carbonyl stretch at 1688 cm$^{-1}$. The other readily definable absorptions include:

<table>
<thead>
<tr>
<th>cm$^{-1}$</th>
<th>intensity</th>
<th>type</th>
<th>functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>2758</td>
<td>vw</td>
<td>v</td>
<td>aldehyde C-H</td>
</tr>
<tr>
<td>1688</td>
<td>s</td>
<td>v</td>
<td>carbonyl</td>
</tr>
<tr>
<td>1599</td>
<td>s</td>
<td>v</td>
<td>aromatic C-C</td>
</tr>
<tr>
<td>1486, 1458</td>
<td>m</td>
<td>δ</td>
<td>methylene C-H</td>
</tr>
<tr>
<td>1243</td>
<td>s</td>
<td>$\nu_{\text{asym}}$</td>
<td>phenyl-O-C</td>
</tr>
<tr>
<td>1134, 625</td>
<td>m</td>
<td>v</td>
<td>C-S-C=O</td>
</tr>
<tr>
<td>1019</td>
<td>m</td>
<td>$\nu_{\text{sym}}$</td>
<td>phenyl-O-C</td>
</tr>
</tbody>
</table>

The infrared spectra of the ethoxy series of substituted tetraphenyl porphyrins were interpreted by comparison of the members of this series with the precursor aldehyde, comparison with unsubstituted tetraphenyl porphyrins, and the literature descriptions of characteristic porphyrin vibrational frequencies.$^{52,53}$

5,10,15,20-Tetrakis[2-(2-acetylimercaptoethoxy)phenyl]porphyrin, H$_2$TAMEPP

The infrared spectrum of this compound shown in Figure IR-13 was collected as a solid in a KBr disc. The predominant feature is that of the carbonyl stretch (1688 cm$^{-1}$). It is interesting to note that in this compound the typical alkyl C-H bending modes (1490,
1445 cm⁻¹) have a more intense absorption than do the aromatic C-C stretching modes (1606, 1595, 1578 cm⁻¹) when compared with the precursor aldehydes.

<table>
<thead>
<tr>
<th>cm⁻¹</th>
<th>intensity</th>
<th>type</th>
<th>functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>3316</td>
<td>w</td>
<td>ν</td>
<td>N-H</td>
</tr>
<tr>
<td>1730, 1688</td>
<td>s</td>
<td>ν</td>
<td>carbonyl</td>
</tr>
<tr>
<td>1606-1578</td>
<td>m</td>
<td>ν</td>
<td>aromatic C-C</td>
</tr>
<tr>
<td>1490, 1445</td>
<td>s</td>
<td>δ</td>
<td>alkyl C-H</td>
</tr>
<tr>
<td>1245, 1015</td>
<td>m</td>
<td>ν</td>
<td>phenyl-O-C</td>
</tr>
<tr>
<td>1130,625</td>
<td>w,m</td>
<td>ν</td>
<td>C=S-C=O</td>
</tr>
<tr>
<td>966</td>
<td>m</td>
<td>δ</td>
<td>N-H</td>
</tr>
<tr>
<td>801</td>
<td>s</td>
<td>δ</td>
<td>pyrrole Cβ-H</td>
</tr>
</tbody>
</table>

5,10,15,20-Tetrakis[2-(2-mercaptoethoxy)phenyl]porphyrin, H₂TMEPP

The infrared spectrum of this compound shown in Figure IR-14 was collected as a solid in a KBr disc. The important feature in this spectrum is the lack of a carbonyl stretch (1688 cm⁻¹). The readily identifiable absorptions of this spectrum include:
<table>
<thead>
<tr>
<th>cm⁻¹</th>
<th>intensity</th>
<th>type</th>
<th>functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>3317</td>
<td>vw</td>
<td>ν</td>
<td>N-H</td>
</tr>
<tr>
<td>2567</td>
<td>vw</td>
<td>ν</td>
<td>S-H</td>
</tr>
<tr>
<td>1596-1560</td>
<td>m</td>
<td>ν</td>
<td>aromatic C-C</td>
</tr>
<tr>
<td>1490-1444</td>
<td>s</td>
<td>δ</td>
<td>methylene C-H</td>
</tr>
<tr>
<td>1243, 1048</td>
<td>s, m</td>
<td>ν</td>
<td>phenyl-O-C</td>
</tr>
<tr>
<td>966</td>
<td>s</td>
<td>ν</td>
<td>N-H</td>
</tr>
<tr>
<td>801</td>
<td>s</td>
<td>δ</td>
<td>pyrrole Cβ-H</td>
</tr>
</tbody>
</table>

The addition of a metal to the porphyrin ligand alters the vibrational spectrum by eliminating N-H vibrations, enhancing certain vibrational modes, while diminishing other modes. These effects are most easily discerned in the comparison of the unsubstituted tetraphenyl porphyrins, H₂TPP and [ZnII(TPP)], Figures IR-22 and IR-23. The N-H stretch (3316 cm⁻¹) and N-H bending (965 cm⁻¹) vibrational modes are gone. The N-H bending mode at 699 cm⁻¹ coincides with a porphyrin ring bending vibration, so metallation removes this N-H bending mode while leaving the less intense ring bending vibration. The pyrrole stretches νCα-Cβ and νCα-N (1002 cm⁻¹) are particularly enhanced by the addition of zinc or iron. These effects carry over into the substituted tetraphenyl porphyrins.

5,10,15,20-Tetrakis[3-(p-acetylmercaptoxyleneoxy)phenyl]porphyrinato-zinc(II), [ZnII(TAMXPP)]

The infrared spectrum of this compound shown in Figure IR-7 was collected as a solid in a KBr disc. As was the case in the free-base substituted porphyrins, the vibrational
characteristics of the substituent predominates the spectrum. The readily definable absorptions include:

<table>
<thead>
<tr>
<th>cm$^{-1}$</th>
<th>intensity</th>
<th>type</th>
<th>functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>1689</td>
<td>s</td>
<td>v</td>
<td>carbonyl</td>
</tr>
<tr>
<td>1595, 1574</td>
<td>s</td>
<td>v</td>
<td>aromatic C-C</td>
</tr>
<tr>
<td>1258, 1020</td>
<td>m</td>
<td>v</td>
<td>phenyl-O-C</td>
</tr>
<tr>
<td>1131, 625</td>
<td>m</td>
<td>v</td>
<td>C-S-C=O</td>
</tr>
<tr>
<td>1001</td>
<td>s</td>
<td>v</td>
<td>pyrrole C$<em>\alpha$-C$</em>\beta$ and C$_\alpha$-N</td>
</tr>
<tr>
<td>795</td>
<td>m</td>
<td>$\delta$</td>
<td>pyrrole C$_\beta$-H</td>
</tr>
<tr>
<td>700</td>
<td>m</td>
<td>$\delta$</td>
<td>porphyrin ring</td>
</tr>
</tbody>
</table>
5,10,15,20-Tetrakis[2-(2-acetylmercaptoethoxy)phenyl]porphyrinato-zinc(II), [Zn^{II}(TAMEPP)]

The infrared spectrum of this compound shown in Figure IR-15 was collected as a solid in a KBr disk. The predominant feature is the carbonyl stretch (1689 cm\(^{-1}\)). As was previously noted, the aromatic C-C stretch (1595, 1578 cm\(^{-1}\)) is not as prominent as the methylene C-H bending modes (1489, 1444 cm\(^{-1}\)). The readily definable absorptions include:

<table>
<thead>
<tr>
<th>cm(^{-1})</th>
<th>intensity</th>
<th>type</th>
<th>functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>1689</td>
<td>s</td>
<td>ν</td>
<td>carbonyl</td>
</tr>
<tr>
<td>1596, 1578</td>
<td>m</td>
<td>ν</td>
<td>aromatic C-C</td>
</tr>
<tr>
<td>1488, 1444</td>
<td>s</td>
<td>δ</td>
<td>methylene C-H</td>
</tr>
<tr>
<td>1130, 626</td>
<td>m</td>
<td>ν</td>
<td>C-S-C=O</td>
</tr>
<tr>
<td>997</td>
<td>s</td>
<td>ν</td>
<td>pyrrole Cα-Cβ and Cα-N</td>
</tr>
<tr>
<td>797</td>
<td>m</td>
<td>δ</td>
<td>pyrrole Cβ-H</td>
</tr>
</tbody>
</table>

The iron(III) chloro derivatives of these porphyrins are practically indistinguishable from the zinc(II) analogues in the 4000 to 500 cm\(^{-1}\) window. They do have a distinctive Fe–Cl stretching mode in the far infrared region, for [Fe^{III}(TPP)Cl] this stretch is at 380 cm\(^{-1}\) and for the iron(III) chloro derivative of octaethylporphyrin the Fe–Cl stretch is observed at 357 cm\(^{-1}\).\(^{52,54}\) The compounds, [Fe^{III}(TAMXPP)Cl] and [Fe^{III}(TAMEPP)Cl], were pelletized in a CsI matrix in order to observe these stretches (KBr IR cutoff 400 cm\(^{-1}\), CsI IR cutoff 200 cm\(^{-1}\)).
5,10,15,20-Tetrakis[3-(p-acetylmercaptoxyleneoxy)phenyl]porphyrinato-
iron(III) Chloride, [FeIII(TAMXPP)Cl]

<table>
<thead>
<tr>
<th>cm⁻¹</th>
<th>intensity</th>
<th>type</th>
<th>functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>1688</td>
<td>s</td>
<td>v</td>
<td>carbonyl</td>
</tr>
<tr>
<td>1596, 1575</td>
<td>s</td>
<td>v</td>
<td>aromatic C-C</td>
</tr>
<tr>
<td>1253, 1023</td>
<td>m</td>
<td>v</td>
<td>phenyl-O-C</td>
</tr>
<tr>
<td>1132, 626</td>
<td>m</td>
<td>v</td>
<td>C-S-C=O</td>
</tr>
<tr>
<td>1002</td>
<td>s</td>
<td>v</td>
<td>pyrrole Cα-Cβ and Cα-N</td>
</tr>
<tr>
<td>805</td>
<td>m</td>
<td>δ</td>
<td>pyrrole Cβ-H</td>
</tr>
<tr>
<td>700</td>
<td>m</td>
<td>δ</td>
<td>porphyrin ring</td>
</tr>
<tr>
<td>357</td>
<td>w</td>
<td>v</td>
<td>Fe-Cl</td>
</tr>
</tbody>
</table>

5,10,15,20-Tetrakis[2-(2-acetylmercaptoethoxy)phenyl]porphyrinato-
iron(III) Chloride, [FeIII(TAMEPP)Cl]

<table>
<thead>
<tr>
<th>cm⁻¹</th>
<th>intensity</th>
<th>type</th>
<th>functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>1688</td>
<td>s</td>
<td>v</td>
<td>carbonyl</td>
</tr>
<tr>
<td>1597, 1579</td>
<td>m</td>
<td>v</td>
<td>aromatic C-C</td>
</tr>
<tr>
<td>1486, 1445</td>
<td>s</td>
<td>δ</td>
<td>methylene C-H</td>
</tr>
<tr>
<td>1134, 625</td>
<td>m</td>
<td>v</td>
<td>C-S-C=O</td>
</tr>
<tr>
<td>998</td>
<td>s</td>
<td>v</td>
<td>pyrrole Cα-Cβ and Cα-N</td>
</tr>
<tr>
<td>803</td>
<td>m</td>
<td>δ</td>
<td>pyrrole Cβ-H</td>
</tr>
<tr>
<td>355</td>
<td>w</td>
<td>v</td>
<td>Fe-Cl</td>
</tr>
</tbody>
</table>
\(\mu\)-Oxo-bis\{5,10,15,20-tetrakis[3-(p-acetylmercaptoxyyleneoxy)phenyl]-porphyrinatoiron(III)}}, \([\text{Fe}^{\text{III}}(\text{TAMXPP})\]_2\text{O}\)

The infrared spectrum of this compound shown in Figure IR-21 was collected as a solid in a CsI disc.

<table>
<thead>
<tr>
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<th>intensity</th>
<th>type</th>
<th>functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>1691</td>
<td>s</td>
<td>ν</td>
<td>carbonyl</td>
</tr>
<tr>
<td>1597, 1576</td>
<td>s</td>
<td>ν</td>
<td>aromatic C-C</td>
</tr>
<tr>
<td>1259, 1017</td>
<td>m</td>
<td>ν</td>
<td>phenyl-O-C</td>
</tr>
<tr>
<td>1133, 626</td>
<td>m</td>
<td>ν</td>
<td>C-S-C=O</td>
</tr>
<tr>
<td>1002</td>
<td>s</td>
<td>ν</td>
<td>pyrrole C(\alpha)-C(\beta) and C(\alpha)-N</td>
</tr>
<tr>
<td>878</td>
<td>m</td>
<td>ν</td>
<td>Fe-O-Fe</td>
</tr>
<tr>
<td>802</td>
<td>m</td>
<td>δ</td>
<td>pyrrole C(\beta)-H</td>
</tr>
<tr>
<td>700</td>
<td>m</td>
<td>δ</td>
<td>porphyrin ring</td>
</tr>
</tbody>
</table>

2-(2-Hydroxyethoxy)-1-naphthaldehyde

The infrared spectrum of this compound shown in Figure IR-17 was collected as a solid in a KBr disc. The predominant features are the "free" O-H stretch (3478 cm\(^{-1}\)), the hydrogen-bonded stretch (3278 cm\(^{-1}\)), and the "free" and hydrogen-bonded carbonyl stretches (1666, 1650 cm\(^{-1}\), respectively). The comparison of this spectrum with that of 2-(2-hydroxyethoxy)benzaldehyde (Figure IR-10) illuminates the many additional bending and stretching modes of the naphthalene ring structure. The readily identifiable features include:
<table>
<thead>
<tr>
<th>cm$^{-1}$</th>
<th>intensity</th>
<th>type</th>
<th>functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>3478, 3278</td>
<td>m, w</td>
<td>v</td>
<td>O-H</td>
</tr>
<tr>
<td>2811, 2760</td>
<td>vvw</td>
<td>v</td>
<td>aldehyde C-H</td>
</tr>
<tr>
<td>1666, 1650</td>
<td>s</td>
<td>v</td>
<td>carbonyl</td>
</tr>
<tr>
<td>1618-1568</td>
<td>s-m</td>
<td>v</td>
<td>aromatic C-C</td>
</tr>
<tr>
<td>1252, 1067</td>
<td>s</td>
<td>v</td>
<td>naphthyl-O-C</td>
</tr>
<tr>
<td>765</td>
<td>m</td>
<td>δ</td>
<td>O-H (hydrogen-bonded)</td>
</tr>
</tbody>
</table>

2-(2-Methanesulfonateethoxy)-1-naphthaldehyde

The infrared spectrum of this compound shown in Figure IR-18 was collected as a solid in a KBr disc. The predominant features are those of the mesylate group and the carbonyl group. The readily definable features include:

<table>
<thead>
<tr>
<th>cm$^{-1}$</th>
<th>intensity</th>
<th>type</th>
<th>functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>1672</td>
<td>m</td>
<td>v</td>
<td>carbonyl</td>
</tr>
<tr>
<td>1356, 1180</td>
<td>s</td>
<td>v</td>
<td>O=S=O</td>
</tr>
<tr>
<td>1251, 1055</td>
<td>m</td>
<td>v</td>
<td>naphthyl-O-C</td>
</tr>
<tr>
<td>1034</td>
<td>s</td>
<td>δ</td>
<td>O=S=O</td>
</tr>
</tbody>
</table>

2-(2-Acetylmercaptoethoxy)-1-naphthaldehyde

The infrared spectrum of this compound shown in Figure IR-19 was collected as a solid in a KBr disc. An interesting feature of this spectrum, not seen in the previous thioacetate–aldehyde spectra (Figures IR-3 and IR-12) is the resolution of the two carbonyls. On the basis of the precursor naphthaldehyde, carbonyl $\nu_{C=O}$ 1673 cm$^{-1}$ is
assigned as the naphthaldehyde carbonyl and the $\nu_{C=O}$ 1693 cm$^{-1}$ is assigned as the thioacetate carbonyl. The readily definable features include:

<table>
<thead>
<tr>
<th>cm$^{-1}$</th>
<th>intensity</th>
<th>type</th>
<th>functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>3371</td>
<td>w</td>
<td></td>
<td>overtone of the carbonyl</td>
</tr>
<tr>
<td>2799</td>
<td>vw</td>
<td>v</td>
<td>aldehyde C-H</td>
</tr>
<tr>
<td>1693, 1673</td>
<td>s</td>
<td>v</td>
<td>carbonyl</td>
</tr>
<tr>
<td>1621-1566</td>
<td>s-m</td>
<td>v</td>
<td>aromatic C-C</td>
</tr>
<tr>
<td>1245, 1056</td>
<td>s</td>
<td>v</td>
<td>naphthyl-O-C</td>
</tr>
<tr>
<td>1135, 627</td>
<td>s</td>
<td>v</td>
<td>C-S-C=O</td>
</tr>
</tbody>
</table>

5,10,15,20-Tetrakis[2-(2-acetylmercaptoethoxy)naphthyl]porphyrin, H$_2$TAMENP

The infrared spectrum of this compound shown in Figure IR-20 was collected as a solid in a KBr disc. The predominant feature of this spectrum is the carbonyl stretch at 1686 cm$^{-1}$.

<table>
<thead>
<tr>
<th>cm$^{-1}$</th>
<th>intensity</th>
<th>type</th>
<th>functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>3315</td>
<td>w</td>
<td>v</td>
<td>N-H</td>
</tr>
<tr>
<td>1686</td>
<td>s</td>
<td>v</td>
<td>carbonyl</td>
</tr>
<tr>
<td>1620-1559</td>
<td>m-w</td>
<td>v</td>
<td>aromatic C-C</td>
</tr>
<tr>
<td>1240, 1050</td>
<td>s</td>
<td>v</td>
<td>naphthyl-O-C</td>
</tr>
<tr>
<td>1133, 624</td>
<td>m</td>
<td>v</td>
<td>C-S-C=O</td>
</tr>
<tr>
<td>954</td>
<td>s</td>
<td>$\delta$</td>
<td>N-H</td>
</tr>
<tr>
<td>802</td>
<td>s</td>
<td>$\delta$</td>
<td>pyrrole C$_\beta$-H</td>
</tr>
</tbody>
</table>
I.B.4 UV-visible Spectrometry

The ultraviolet-visible spectra of the unmetallated and metallated porphyrins were collected on dry, ethanol-free chloroform solutions and these spectra are shown in Appendix 1, Figures UV-1 – UV-11. For the free-base porphyrins it was imperative to use non-acidic chloroform (distilled from anhydrous potassium carbonate), otherwise, the slight acidity of the chloroform would promote the formation of the porphyrin dication, with a significantly different spectrum.

The free-base porphyrins; H₂TAMXPP, H₂TMXPP, and H₂TBrXPP provide routine etio-type spectra, that is, a spectrum with a very intense Soret band (= 420 nm) and four additional absorptions. Early protocol numbered these four additional absorptions (I, II, III, IV), with band I (≈ 645 nm) being at the longest wavelength and band IV (≈ 515 nm) being at the shorter wavelength, while more recent reports refer to these absorptions in reference to the electronic (\(\pi, \pi^*\)) transitions that produces the absorptions, i.e. Band I - \(Q_x(0-0)\), Band II - \(Q_x(0-1)\), Band III - \(Q_y(0-0)\), and Band IV - \(Q_y(0-1)\). In an etio-type spectrum these bands have the intensity ordering IV > III > II > I. The wavelength of maximum absorption and the molar extinction coefficient for those maxima for each of these free-base porphyrin are summarized in Table 8.

The ortho -substituted free-base porphyrins, H₂TAMEPP, H₂TMEPP, and H₂TAMENP provide phyllo-type spectra, which differ from the etio-type spectra with respect to the intensity ordering of the Q-bands, i.e. IV>II>III>I. A change from the etio-type spectrum to the phyllo-type spectrum has been previously reported for tetraphenylporphyrins substituted in the ortho position with electron-withdrawing substituents. The wavelength of the maximum absorptions and the molar extinction coefficient for those maxima for the ortho substituted free-base porphyrins are also summarized in Table 8.
### Table 8

<table>
<thead>
<tr>
<th>Compound</th>
<th>Soret (nm)</th>
<th>480 nm</th>
<th>IV-Q(_X)(0-0)</th>
<th>III-Q(_X)(0-1)</th>
<th>II-Q(_X)(0-0)</th>
<th>I-Q(_X)(0-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_2\text{TPP})</td>
<td>418</td>
<td>484</td>
<td>515</td>
<td>550</td>
<td>589</td>
<td>645</td>
</tr>
<tr>
<td></td>
<td>3.5 (\times) 10(^5)</td>
<td>3.7 (\times) 10(^3)</td>
<td>(1.5 \times 10^4)</td>
<td>(7.1 \times 10^3)</td>
<td>(5.6 \times 10^3)</td>
<td>(4.3 \times 10^3)</td>
</tr>
<tr>
<td>(\text{H}_2\text{TAMXPP})</td>
<td>420</td>
<td>-</td>
<td>516</td>
<td>550</td>
<td>590</td>
<td>649</td>
</tr>
<tr>
<td></td>
<td>3.2 (\times) 10(^5)</td>
<td></td>
<td>(1.7 \times 10^4)</td>
<td>(8.0 \times 10^3)</td>
<td>(6.4 \times 10^3)</td>
<td>(5.9 \times 10^3)</td>
</tr>
<tr>
<td>(\text{H}_2\text{TMXPP})</td>
<td>421</td>
<td>485</td>
<td>516</td>
<td>551</td>
<td>590</td>
<td>646</td>
</tr>
<tr>
<td></td>
<td>3.5 (\times) 10(^5)</td>
<td>4.6 (\times) 10(^3)</td>
<td>(1.7 \times 10^4)</td>
<td>(7.9 \times 10^3)</td>
<td>(6.6 \times 10^3)</td>
<td>(4.6 \times 10^3)</td>
</tr>
<tr>
<td>(\text{H}<em>2\text{TB}</em>{\text{Br}}\text{XPP})</td>
<td>421</td>
<td>462</td>
<td>516</td>
<td>551</td>
<td>589</td>
<td>645</td>
</tr>
<tr>
<td></td>
<td>4.1 (\times) 10(^5)</td>
<td>1.1 (\times) 10(^3)</td>
<td>(1.7 \times 10^4)</td>
<td>(6.7 \times 10^3)</td>
<td>(6.1 \times 10^3)</td>
<td>(3.8 \times 10^3)</td>
</tr>
<tr>
<td>(\text{H}_2\text{TAMEPP})</td>
<td>418</td>
<td>484</td>
<td>515</td>
<td>548</td>
<td>587</td>
<td>648</td>
</tr>
<tr>
<td></td>
<td>2.5 (\times) 10(^5)</td>
<td>3.1 (\times) 10(^3)</td>
<td>(1.5 \times 10^4)</td>
<td>(5.2 \times 10^3)</td>
<td>(5.5 \times 10^3)</td>
<td>(3.3 \times 10^3)</td>
</tr>
<tr>
<td>(\text{H}_2\text{TMEPP})</td>
<td>420</td>
<td>484</td>
<td>515</td>
<td>548</td>
<td>587</td>
<td>648</td>
</tr>
<tr>
<td></td>
<td>3.2 (\times) 10(^5)</td>
<td>2.9 (\times) 10(^3)</td>
<td>(1.6 \times 10^4)</td>
<td>(5.0 \times 10^3)</td>
<td>(4.8 \times 10^3)</td>
<td>(3.2 \times 10^3)</td>
</tr>
<tr>
<td>(\text{H}_2\text{TAMENP})</td>
<td>418</td>
<td>484</td>
<td>515</td>
<td>548</td>
<td>587</td>
<td>648</td>
</tr>
<tr>
<td></td>
<td>2.5 (\times) 10(^5)</td>
<td>4.5 (\times) 10(^3)</td>
<td>(1.9 \times 10^4)</td>
<td>(5.7 \times 10^3)</td>
<td>(8.1 \times 10^3)</td>
<td>(3.0 \times 10^3)</td>
</tr>
</tbody>
</table>

\(^a\) wavelength reported in nm and \(\varepsilon\) values in \(M^{-1}\text{cm}^{-1}\)
The zinc porphyrins, [ZnII(TAMXPP)] and [ZnII(TAMEPP)] (Figures UV-7 and UV-8) display an electronic absorption spectrum typical of a square-planar metalloporphyrin, i.e. a very intense Soret band and two other strong bands, Qα [Q(0-0)] at ≈585 nm and Qβ [Q(0-1)] at ≈548 nm. The band position and molar absorptivity for these new zinc porphyrin derivatives are compared with [ZnII(TPP)] in Table 9. The position of the absorption band and the molar absorptivity of these absorptions can be influenced by axial ligation by the zinc ion, with the intensity ratio of bands Qα to Qβ being especially indicative of the strength of the axial ligand; a weak axial ligand provides for a Qα/Qβ ratio of ≈0.2 to 0.3, while a strong axial ligand provides for a Qα/Qβ ratio of ≈0.5.58 The Qα/Qβ ratio for [ZnII(TAMXPP)] (0.14) and [ZnII(TAMEPP)] (0.23) give little indication for axial coordination of the thioacetate arm to the zinc metal center.

Table 9  Band Positions and Intensities (ε) for the Zinc Porphyrins in CHCl₃

<table>
<thead>
<tr>
<th>Compound</th>
<th>Soret</th>
<th>Qβ</th>
<th>Qα</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ZnII(TPP)]</td>
<td>419</td>
<td>546</td>
<td>584</td>
</tr>
<tr>
<td></td>
<td>6.2 x 10⁵</td>
<td>2.4 x 10⁴</td>
<td>3.5 x 10³</td>
</tr>
<tr>
<td>[ZnII(TAMXPP)]</td>
<td>421</td>
<td>548</td>
<td>584</td>
</tr>
<tr>
<td></td>
<td>6.1 x 10⁵</td>
<td>2.3 x 10⁴</td>
<td>3.2 x 10³</td>
</tr>
<tr>
<td>[ZnII(TAMEPP)]</td>
<td>422</td>
<td>550</td>
<td>582</td>
</tr>
<tr>
<td></td>
<td>3.9 x 10⁵</td>
<td>1.7 x 10⁴</td>
<td>3.9 x 10³</td>
</tr>
</tbody>
</table>

*a wavelength reported in nm and ε values in M⁻¹cm⁻¹
In a separate experiment, ethylthioacetate was added to \([\text{Zn}^{\text{II}}(\text{TPP})]\) at ratios varying from 0.1/1 to 1000/1 and no significant change in the \(Q_\alpha/Q_\beta\) ratio was observed, leading to the conclusion that the thioacetate carbonyl group is a poor axial ligand for the zinc(II) porphyrin. For \([\text{Zn}^{\text{II}}(\text{TAMEPP})]\), the decrease in molar absorptivity of the Soret band and the increase of the absorption band at 582 nm can be attributed to the ortho-ethoxy substitution on the phenyl rings.\(^{57}\)

The electronic absorption spectra of the iron porphyrins, \([\text{Fe}^{\text{III}}(\text{TAMXPP})\text{Cl}]\) (Figure UV-9) and \([\text{Fe}^{\text{III}}(\text{TAMEPP})\text{Cl}]\) (Figure UV-10) were acquired for comparison with the unsubstituted iron-chloro tetraphenylporphyrin, \([\text{Fe}^{\text{III}}(\text{TPP})\text{Cl}]\) and the results are tabulated in Table 10. Although the absorption spectra of the iron (III) porphyrins have been reported as insensitive to changes in the axial ligand\(^{59}\), it is apparent that the ortho phenyl substituents of \([\text{Fe}^{\text{III}}(\text{TAMEPP})\text{Cl}]\) continue to influence the electronic spectrum in a similar manner as previously seen for the zinc and free-base porphyrins.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Soret</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Fe}^{\text{III}}(\text{TPP})\text{Cl}])</td>
<td>380</td>
<td>417</td>
<td>511</td>
<td>577</td>
<td>658</td>
<td>691</td>
</tr>
<tr>
<td></td>
<td>5.9 x10^4</td>
<td>1.1 x10^5</td>
<td>1.3 x10^4</td>
<td>3.9 x10^3</td>
<td>2.8 x10^3</td>
<td>3.2 x10^3</td>
</tr>
<tr>
<td>([\text{Fe}^{\text{III}}(\text{TAMXPP})\text{Cl}])</td>
<td>381</td>
<td>420</td>
<td>511</td>
<td>578</td>
<td>658</td>
<td>688</td>
</tr>
<tr>
<td></td>
<td>6.1 x10^4</td>
<td>1.2 x10^5</td>
<td>1.4 x10^4</td>
<td>3.9 x10^3</td>
<td>2.9 x10^3</td>
<td>3.1 x10^3</td>
</tr>
<tr>
<td>([\text{Fe}^{\text{III}}(\text{TAMEPP})\text{Cl}])</td>
<td>382</td>
<td>421</td>
<td>479</td>
<td>582</td>
<td>655</td>
<td>720</td>
</tr>
<tr>
<td></td>
<td>4.5 x10^4</td>
<td>8.5 x10^4</td>
<td>3.2 x10^4</td>
<td>3.8 x10^3</td>
<td>4.8 x10^3</td>
<td>2.5 x10^3</td>
</tr>
</tbody>
</table>

\(^a\)wavelength reported in nm and \(\varepsilon\) values in M\(^{-1}\)cm\(^{-1}\)
The electronic absorption spectrum of \([\text{Fe}^{\text{III}}(\text{TAMXPP})])_2\text{O}\), Figure UV-11 is unremarkably similar to the literature spectrum of \([\text{Fe}^{\text{III}}(\text{TPP})])_2\text{O}\). The absorption maxima and their molar absorptivities in CHCl\textsubscript{3} are:

412 nm, 1.9 \times 10^5 \text{ M}^{-1}\text{cm}^{-1} (408, 2.1 \times 10^5); 569 nm, 1.5 \times 10^4 \text{ M}^{-1}\text{cm}^{-1} (575, 1.5 \times 10^4)

608 nm, 6.7 \times 10^3 \text{ M}^{-1}\text{cm}^{-1} (615, 1.0 \times 10^4), with the values for \([\text{Fe}^{\text{III}}(\text{TPP})])_2\text{O}\) in parentheses.
I.B.5  Mössbauer Spectrometry

The Mössbauer spectra of [FeIII(TAMXPP)Cl] (Figure 16) and [FeIII(TAMEPP)Cl] (Figure 17) were acquired at room temperature and 78 K, on polycrystalline solid samples. The chemical shifts are referenced to sodium nitroprusside, Na2Fe(CN)5NO•2H2O, at 297 K, δ = 0.0 mm/sec and ΔE_Q = 1.705 mm/sec. At room temperature, both compounds exhibit a broad asymmetric absorption with a minima at 0.32 mm/sec. This response is quite similar to that of the iron chloro derivative of tetraphenylporphyrin, [FeIII(TPP)Cl]. Upon cooling to 78 K, the spectrum of [FeIII(TAMEPP)Cl] hints of a broad, unresolved shoulder on the high energy side of the spectrum at approximately 1.0 to 1.5 mm/sec, again, very much like the literature spectrum of [FeIII(TPP)Cl]. On the other hand, the 78 K spectrum of [FeIII(TAMXPP)Cl] demonstrates discernable resolution of the higher energy absorption at 1.5 mm/sec. This change in the spectrum can be attributed to a shortening of the relaxation time in the ±3/2 and ±5/2 excited states, as previously described by Blume. The computer generated fit of the data for the 78 K spectrum of [FeIII(TAMXPP)Cl] provides for a δ_SNP = 0.83 mm/sec and ΔE_Q = 1.01 mm/sec ([FeIII(TPP)Cl] at 4.2K, δ_SNP = 0.68 mm/sec and ΔE_Q = 0.46 mm/sec). The shoulder on [FeIII(TAMEPP)Cl] was too weak for a reasonable computer fit.
Figure 16 The Mössbauer Spectrum of 5,10,15,20-Tetrakis-3-(p-mercaptoxylyleneoxy)phenyl]porphyrinatoiron(III) Chloride

[Fe$^{III}$(TAMXPP)Cl] (298 K)

[Fe$^{III}$(TAMXPP)Cl] (77K)
Figure 17  The Mössbauer Spectrum of 5,10,15,20-Tetrakis-[2-(2-acetylmercaptoethoxy)phenyl]porphyrinatoiron(III) Chloride
I.B.6  Electron Paramagnetic Resonance Spectroscopy

The EPR spectra of [Fe\textsuperscript{III}(TAMXPP)Cl] (Figure 18) and [Fe\textsuperscript{III}(TAMEPP)Cl] (Figure 19) were acquired as frozen, ≈0.5 mM, toluene solutions at approximately 11K. For comparison, a spectrum of [Fe\textsuperscript{III}(TPP)Cl] was collected under the same conditions. There was no discernable difference between the three spectra, $g_\perp = 6$ and $g|| = 2$, which typifies the high spin ($S = 5/2$) iron (III) ion\textsuperscript{64}. Acknowledging the potential error associated with integration of iron porphyrin EPR signals and using [Fe\textsuperscript{III}(TPP)Cl] for comparison, the integration of the EPR signal suggests five unpaired electrons for both of the new iron(III) porphyrin compounds.
Figure 18  The EPR Spectrum of 5,10,15,20-Tetrakis-[3-(p-mercaptoxylyleneoxy)phenyl]porphyrinatoiron(III) Chloride, [Fe$^{III}$(TAMXPP)Cl] in a Toluene Glass, 11K
Figure 19  The EPR Spectrum of 5,10,15,20-Tetrakis-[2-(2-acetylmercaptoethoxy)phenyl]porphyrinatoiron(III) Chloride
[Fe^{III}(TAMEPP)Cl] in a Toluene Glass, 11K
Discussion

The objective of the first phase of this project has been to synthesize a tetrathiol porphyrin ligand suitable for ligating the iron-sulfur cubane cluster. The progress towards this objective has been evolutionary, with the shortcomings of one ligand necessitating the development of an alternate ligand and subsequent insights developed with the new product then revitalizing the earlier ligands. The net result is the series of tetrathiol porphyrins described in the first portion of this report.

The direct synthesis of porphyrin from pyrrole and aldehyde was accomplished by Rothemund in 1935. The procedure involved heating a mixture of pyrrole, formaldehyde, and pyridine, with methanol as the solvent, in a sealed tube. The yield of this synthetic procedure was 0.021%. The development of the Alder-Longo porphyrin synthesis, 25 years ago, provided a titanic increase in synthetic yields of meso-tetraphenylporphyrins with yields of 20-25%. The synthetic requirements for this reaction are as simple and straightforward as the representation in Figure 20. However, the Adler-Longo procedure, with its refluxing propionic acid, limits the type of functional groups that can be present on the phenyl ring during the condensation of the pyrrole and the aldehyde.

Figure 20 The Alder-Longo Porphyrin Synthesis

\[
\begin{align*}
4 \ce{NH} + 4 \ce{C6H4} & \xrightarrow{\text{Refluxing propionic acid, adventitious O}_2} \text{Tetraphenyl porphyrin}
\end{align*}
\]
A recent advance in porphyrin synthesis developed by Lindsey and coworkers\textsuperscript{31,32,67} is outlined in Figure 21 and has mild reaction conditions that allow for the direct synthesis of functionalized porphyrins with yields approaching 40-50\%.

The synthetic conditions for the Lindsey equilibrium-condensation reaction are more exacting and time-consuming than the requirements of the earlier Adler-Longo procedure. The Lindsey procedure is not a panacea, but, the direct synthesis of the tetrathioacetate-armed porphyrins of this report would not have been possible with the Alder-Longo porphyrin synthesis procedure.

**Figure 21** The Lindsey Porphyrin Synthesis

\[\text{Pyrrole} + \text{Benzaldehyde} \xrightarrow{\text{methylene chloride or chloroform (w/ EtOH), acid catalyst, no light, no O}_2} \text{Porphyrinogen}\]

\[\text{Porphyrinogen} \xrightarrow{\text{tetrachlorodibenzoquinone (40-50\degree C) or dichlorodicyanodibenzoquinone (rt)}} \text{Tetrphenyl porphyrin}\]

The initial porphyrin ligand that was sought for this project was a "blocked" rotation ligand. However, difficulties encountered with the synthesis of sufficient quantities of the precursor aldehyde, shown in Figure 22, spawned the concept of allowing
for rotation of the "armed" phenyl groups. The ortho-thio-ethoxy-armed-phenyl porphyrins, H₂TAMEPP and H₂TMEPP, Figure 4, (acetyl protected and deprotected thiol forms, respectively) allow for a hindered rotation of the thiol arms. In a similar porphyrin, 5,10,15,20-tetrakis[2-(2-hydroxyethoxy)phenyl]porphyrin, Almog et al. noted that the atropisomer configuration appears to be maintained at < 25°C, but rapid interconversion takes place at temperatures approximating 50°C. 28

**Figure 22**

2-"R"oxy,6-Methyl Benzaldehyde

![Chemical structure](image)

R = H or methyl for subsequent conversion to EtSH

The ethoxy-armed tetrphenylporphyrin atropisomers and their rates of interconversion evidenced some confusing phenomena that were observed during the course of this work. The rate of interconversion of atropisomers offers a viable explanation for a variation observed during the silica gel chromatography of H₂TAMEPP. The chromatography of H₂TAMEPP was performed using methylene chloride as the initial eluate, then increasing the solvent strength by switching to ethanol-stabilized chloroform. On cold days, when the laboratory temperature was 20-22°C, methylene chloride would elute first a yellow impurity followed by a distinct purple band, presumably the α,α,β,β and α,β,α,β porphyrin atropisomers. 37,48 After this initial porphyrin band had eluted from the column, the methylene chloride eluate would turn colorless and a switch to a stronger eluate, ethanol-stabilized chloroform, was necessary to elute the more polar α,α,α,β and α,α,α,α atropisomers. On hot days, when the laboratory temperatures
reached 25-26°C, methylene chloride would again elute an initial purple band, however, a
distinct "end" of this band was not observed, i.e. the methylene chloride eluate would
continue to remove traces of porphyrin from the column. The switch to chloroform would,
as before, elute the more polar $\alpha,\alpha,\alpha,\beta$ and $\alpha,\alpha,\alpha,\alpha$ porphyrin atropisomers in a sharp
band. The $^1\text{H}$ NMR of the first purple band, the second purple band and the purple
"bleed" in between these two bands all revealed to be the same compound, $\text{H}_2\text{TAMEPP}$. The chromatographic behavior of the zinc derivative, ZnTAMEPP did not show the same
temperature sensitivity during the separation of the atropisomer bands, suggesting that the
variability of the free-base porphyrin is not a function of the silica gel absorptivity changing
with temperature. The chromatographic difference between the free-base and metallated
porphyrins can be attributed to a slightly higher energy barrier for phenyl rotation about the
meso-porphyrin–phenyl bond in metallated porphyrins, this higher energy barrier being a
result of the "stiffening" of the porphyrin macrocycle.$^{26,68-70}$

The process of phenyl rotation in these substituted tetraphenylporphyrins can be
observed using dynamic nuclear magnetic resonance spectroscopy, provided that several
conditions are satisfied. The first condition for observation is that the dynamic process
occurs on the NMR time scale, typically a rate constant of $10^{-1}$ to $10^5$ sec$^{-1}$. The second
condition for observation is that an observable nucleus must change its magnetic
environment as the molecule shifts between conformations. When the observed nuclei are
in "slow exchange", that is, the magnetic environments change slower than the NMR time
scale, two signals are observed. These two signals are representative of the differing
magnetic environments. However, when the observed nuclei are in "fast exchange" a
single signal is observed and the chemical shift of this signal is the average of the two slow
exchange chemical shifts. There is a condition of intermediate exchange just before the two
signals coalesce, where the line width of the two signals broadens and signal intensity
decreases. The analysis of the chemical shifts and line shapes in the three exchange conditions (slow, intermediate, fast) can provide the rate constant for the exchange process.

The early methods of line shape analysis were based on modifications to the historic Bloch equations. These line shape theories and the Bloch equations themselves are considered classical theories in that they describe the nuclear magnetic resonance phenomenon without incorporating Planck's constant, despite the fact that the spin of elementary particles and the existence of discrete spin states can only be explained by quantum theory.\textsuperscript{71,72} The use of these classical line shape theories has been discouraged due to serious systematic errors that can occur with their implementation.\textsuperscript{73} However, if one is willing to accept an estimate that can be off by several hundred percent, the relationship,

\[ k_{\text{coalescence}} = \pi \Delta \nu \sqrt{2}, \]

(where \( \Delta \nu \) is the chemical shift difference in Hz) provides an easy estimate for the rate of exchange of a nuclei between the sites A and B.\textsuperscript{71} For a dynamic system where the exchanging sites are coupled to one another, the relationship

\[ k_{\text{coalescence}} = \pi \sqrt{\left( \nuA \,- \nuB \right)^2 + 6J_{\text{AB}}^2 \sqrt{2}} \]

where \( J_{\text{AB}} \) is the spin-spin coupling constant between sites A and B provides for a quick estimate of the approximate exchange rate. The preferred method of determining exchange rates now uses molecular modelling programs based on quantum-mechanical line shape theory.\textsuperscript{71}

On the basis of the literature on phenyl rotation, it was presumed that the dynamics of the "free" rotation ligand, \( \text{H}_2\text{TAMXPP} \), occur on the NMR time scale. For the hindered rotation ligand, \( \text{H}_2\text{TAMEPP} \), a calculated rate constant of 0.8 sec\(^{-1}\) is obtained based on the
assumption that the experimental value $\Delta G_{433}^\ddagger$ (108.3± 0.8 kJ mol$^{-1}$) for phenyl rotation in 5,10,15,20-tetrakis(2-methoxy-phenyl)porphyrin$^{74}$ approximates that of H$_2$TAMEPP.

The second condition for observing the dynamics of the phenyl rotation is that there must be an observable nucleus that noticeably changes its chemical shift because of the phenyl rotation. The free rotation porphyrin, H$_2$TAMXPP, has the two ortho protons, the meta proton, and the methylene group on the ether linkage. Of these observable nuclei, the methylene group was thought to have the greatest potential because it does not have the spin-spin coupling interaction, as do the phenyl protons. H$_2$TAMXPP is in fast exchange and accordingly the ether methylene group is observed as a singlet at room temperature. The hindered rotation ligand, H$_2$TAMEPP, has the two meta protons, the one ortho proton and the ethoxy arm for potentially observable sites. Unfortunately, the $^1$H NMR spectra of H$_2$TAMEPP, Figure 1H-13 shows overlapping, unresolved atropisomer signals for each of the observable sites.

A sample of H$_2$TAMXPP was dissolved in $d_2$-methylene chloride and proton spectra were collected from 283 K to 203 K at 10°C decrements, on the 300MHz spectrometer. The resultant spectra confirm that the free rotation ligand is in fast exchange at room temperature. Figure 24 shows the coalescence temperature in the range 243 to 253 K. These spectra show that the meta proton (triplet) chemical shift is temperature invariant and that its magnetic environment does not differ significantly between atropisomers. The ortho protons (overlapping doublet and singlet at $\approx$ 7.8 ppm) are demonstrated to be temperature dependent, gradually shifting together into one unresolved signal. The xylyleneoxy arm methylene protons are temperature dependent, shifting towards higher field, and the chemical shifts of these protons do not significantly differ between the atropisomers.
Unexpectedly, the β-pyrrole protons provide the spectroscopic "handle" for observing the rotational dynamics of this freely rotating phenyl porphyrin. If the atropisomers were in slow or stopped exchange and all the β-pyrrole signals were resolved from one another, one would expect a singlet for each of the atropisomers, $(\alpha, \alpha, \alpha, \alpha)$, $(\alpha, \beta, \alpha, \beta)$, $(\alpha, \alpha, \beta, \beta)$, and two singlets (3 to 1 ratio) for the $\alpha, \alpha, \alpha, \beta$ atropisomer. It is obvious that this is not a simple A site $\rightarrow$ B site exchange system. Computerized mathematical treatments for modelling an n site exchange system exist, but were not immediately available and the definitive exchange rate of these atropisomers is not crucial to the success of this project. Ignoring the warning of Binsch and the fact that this is not a simple two site exchange, the relationship, $k_{\text{coalescence}} = \pi \Delta \nu / \sqrt{2}$, suggests a phenyl rotation rate of $1.3 \times 10^2$ sec$^{-1}$ at -30°C, which is in line with previously observed rotational rates for unhindered tetraphenylporphyrins.
Figure 23  $^1$H NMR Spectra of H$_2$TAMXPP in CD$_2$Cl$_2$, 273 K to 203 K
In view of the success with the dynamic $^1$H NMR spectroscopy of H$_2$TAMXPP, and the fact that the room temperature NMR spectrum of H$_2$TAMEPP, Figure 1H-13 shows slight multiplicity of the β-pyrrole proton signal, a dynamic NMR experiment was also attempted on H$_2$TAMEPP. Samples of H$_2$TAMEPP were dissolved in CDCl$_3$, d$_6$-benzene, d$_8$-toluene, and d$_2$-1,1,2,2-tetrachloroethane and proton spectra were collected in the ranges 300→330 K, 300→345 K, 300→380 K, 300→400 K, respectively, on the 300MHz spectrometer. Spectroscopic evidence of phenyl rotation was not observed under any of these conditions. The most plausible explanation for not seeing phenyl rotation is the lack of a suitable spectroscopic handle. In each of these NMR experiments, the β-pyrrole resonances were either observed as a broad singlet or the resolved signals shifted together as the temperature was raised, without ever going through an observable coalescence. In every case, the phenyl protons of the atropisomers were observed as groups of overlapping multiplets and the remaining spectroscopic handle, the ether methylene, suffers additional dynamic characteristics that muddle the spectral results.

**Figure 25  Representative Motions of the Phenyl Ethoxy Arm**

The additional motions depicted in Figure 25 have as great a consequence on the magnetic environment of the ether methylene group, as does the rotation of the phenyl-porphyrin bond. The rotation of the phenyl-ether bond affects the positioning of the methylene group with respect to the ring current effects of the aromatic porphyrin core, as well as, the ring
current effects of the phenyl group. The rotation of the ether-methylene bond also influences the position of the methylene in these shielding and deshielding zones. Lastly, the configuration of the entire chain influences the positioning of the carbonyl group with its own set of ring current effects.

The $^1\text{H}$ spectrum of [Zn$^{\text{II}}$(TAMXPP)], Figure 1H-7 has two signals of near equal intensity for the $\beta$-pyrrole protons at $\delta = 8.94$ and 8.93 ppm. An initial explanation for the observed multiplicity of the pyrrole protons was a symmetry related consequence due to the zinc atom not fitting completely into the porphyrin core, thereby reducing the symmetry from $C_{4v}$ to $C_4$. Some of the early literature suggested that zinc(II) forms a "sitting on top complex", however, Scheidt established that the zinc atom does indeed fit into the center of the porphyrin molecule. Having ruled out symmetry effects, the more likely explanation for this multiplicity is that the pyrrole proton resonances of two groups of the [Zn$^{\text{II}}$(TAMXPP)] atropisomers have been resolved. With that explanation in mind, experimental NMR attempts to observe the phenyl rotation dynamics were instituted, but the success of these attempts was thwarted by the temperature dependency of the chemical shifts of the resolved atropisomers. In all the solvents tried, CDCl$_3$, d$_6$-benzene, d$_8$-toluene, and d$_2$-1,1,2,2-tetrachloroethane, the atropisomer chemical shifts merged into a single signal before the transition from slow exchange to fast exchange was observed.

During one of the evolutionary periods of this research project, H$_2$TAMENP, a blocked-rotation porphyrin was envisioned (Figure 7), a derivative of the commercially available material, 2-hydroxy-1-naphthaldehyde. This porphyrin utilized the ethoxy-arm chemistry that was developed with H$_2$TAMEPP and allowed the proton in the peri position (proton H$_8$) to block the rotation of the naphthyl ring about the meso carbon bond. The synthetic details of adding the ethoxy-arm to the hydroxynaphthaldehyde and the
subsequent conversion of the initial hydroxy terminus to the thioacetate terminus by way of a mesylate have previously been presented, *a priori*. The initial synthetic attempts towards H$_2$TAMENP were by way of the 1987 Lindsey method$^{67}$ and the yields were disappointingly low, $\approx$1 to 2%. A subsequent report by Lindsey et al. revealed that trace amounts of ethanol act as a co-catalyst in the condensation reaction of pyrrole and ortho-substituted benzaldehydes leading to increased yields of ortho-substituted porphyrins$^{32}$. This method was tried and the yield of H$_2$TAMENP was improved to a level of approximately 15 to 20%. Assuming that the ratio of synthesized atropisomers approximates the statistical ratio, the yield of the desired atropisomer would equate to 2% of the final yield.

In reality, the yield of the all-cis atropisomer is lower than 2% owing to losses during chromatographic isolation, because, the $\alpha,\alpha,\alpha,\alpha$-atropisomer is the most polar of the four atropisomers$^{37,48}$ and unfortunately, this feature results in chromatographic properties similar to the many polypyrrolic by-products of the condensation reaction. It should be noted that literature preparative methods for H$_2$TPP and other simple derivatives of H$_2$TPP use crystallization as the preliminary step in purification of the porphyrin reaction mixture. However, all of the armed porphyrins of this report refused to crystallize, which necessitated the use of column chromatography to separate the porphyrin product from the other reaction by-products. Of all of these armed porphyrins, H$_2$TAMENP is by far the most difficult to purify. During the final stages of this work, a diethyl ether/toluene solvent system exhibited good results towards resolving the difficulty of separating the H$_2$TAMENP all-cis atropisomer from the polypyrrolic by-products. This solvent system (5-10% diethyl ether in toluene) was cursorily tested on the other free-base porphyrins with similar good resolution between the porphyrin product and the tar-like by-products.
In considering blocked rotation porphyrins, the statistical ratio of the different atropisomers is noteworthy: one part \( \alpha,\alpha,\alpha,\alpha \)-atropisomer to seven parts of the other atropisomers. In view of this low yield of the desired atropisomer, a method of pre-configuring the "arms" into an all \( \text{cis} \) position is desirable. This effect can be achieved by using a synthesis analogous to that used in the preparation of Baldwin's capped porphyrin, as shown in Figure 26.\(^{28,77}\) After purifying the capped porphyrin, the ester cap can, in principle, be cleaved to generate the \( \alpha,\alpha,\alpha,\alpha \)-atropisomer and the alcohol termini can then be converted to thiols to generate the desired ligand.

**Figure 26**  
The "\( \text{C}_2 \)-Capped Porphyrin"

In pursuit of the capped naphthyl porphyrin, the precursor tetranaphthaldehyde, 1,2,4,5-tetrakis[2-(1-formyl-2-naphthalenylxyloxy)ethyl]benzenetetracarboxylate was synthesized using the procedure described in Appendix 1 (additional syntheses). This tetraaldehyde
was then used unsuccessfully in the condensation reaction with pyrrole using the 1989 Lindsey method and variations thereof. The exact reason for the failure of this tetraaldehyde to form porphyrin is unknown, but two plausible explanations stand out. The first explanation is the limited solubility of the tetrarnaphthaldehyde in chloroform. For the porphyrin condensation reaction, the solvent had to be heated to near refluxing temperatures in order to dissolve the tetrarnaphthaldehyde (to create a 2.5 x 10^{-4} \text{ M} solution). This limited solubility allows for the possibility of the tetraaldehyde precipitating out of solution during the time period allowed for condensation of the aldehyde and pyrrole (the light sensitive nature of the porphyrinogen intermediate prevents direct observation). Another and perhaps better explanation comes from making a stick model of the capped tetrarnaphthaldehyde porphyrinogen intermediate. Using the porphyrin atropisomer nomenclature, there are six theoretical isomers of this porphyrinogen \( \alpha\alpha\alpha\alpha, \alpha\alpha\alpha\beta, \alpha\alpha\beta\beta, \alpha\beta\alpha\beta, \alpha\beta\beta\beta, \text{ and } \beta\beta\beta \), as depicted in Figure 27. Of these six confirmations, only the \( \alpha\alpha\alpha\alpha \) and \( \alpha\alpha\alpha\beta \) atropisomers are sterically acceptable, the \( \alpha\alpha\beta\beta \) atropisomer is strained, and the remaining three configurations are sterically impossible.
Figure 27  The Capped Porphyrinogen Isomers

\[ \alpha,\alpha,\alpha,\alpha \ - \text{Isomer} \]

\[ \alpha,\alpha,\alpha,\beta \ - \text{Isomer} \]

\[ \alpha,\beta,\alpha,\beta \ - \text{Isomer} \]

\[ \alpha,\alpha,\beta,\beta \ - \text{Isomer} \]

\[ \alpha,\beta,\beta,\beta \ - \text{Isomer} \]

\[ \beta,\beta,\beta,\beta \ - \text{Isomer} \]
An alternative blocked rotation porphyrin is 5,10,15,20-tetrakis[2-(2-acetylmercaptoethoxy),6-methyl phenyl]porphyrin, depicted earlier in Figure 7. Indeed, this was the porphyrin initially sought for ligating the iron-sulfur cluster. The precursor aldehyde, 2-hydroxy,6-methyl benzaldehyde, was the major stumbling block to achieving the synthesis of this porphyrin. This aldehyde can be synthesized via the Riemer-Tiemann reaction with m-cresol (see supplemental syntheses, Appendix 1), however, this particular synthetic procedure is not selective and places the formyl moiety in the para and both ortho positions, thereby producing the three isomeric compounds;

2-Hydroxy,6-methyl benzaldehyde  2-Methyl,4-hydroxy benzaldehyde

2-Hydroxy,4-methyl benzaldehyde

The desired isomer and the 2-hydroxy,4-methyl benzaldehyde isomer are capable of intramolecular hydrogen bonding and by virtue of that property can be steam distilled away from the 2-methyl,4-hydroxy benzaldehyde isomer, which forms intermolecular hydrogen bonds. This initial separation is easily achieved. The separation of the two remaining isomers is time consuming and difficult to reproduce with consistently acceptable yields. For this reason, this blocked-rotation porphyrin ligand was abandoned in favor of the naphthaldehyde porphyrin.

A recent insight has provided a convenient solution to the aldehyde isomer separation problem. If 3,5-dimethyl phenol, a commercially available reagent, is selected as the starting material, formylation at either ortho position results in the formation of
2-hydroxy,4,6-dimethyl benzaldehyde.\textsuperscript{78} Of course, formylation of the \textit{para} position also occurs, but again, the \textit{para} isomer is incapable of intramolecular hydrogen bonding, allowing for a simple separation of these two isomers using steam distillation.

One would think that blocking the \textit{para} position with an additional methyl group would eliminate the isomerization problem altogether, and it does. However, the Reimer-Tiemann reaction product of the substrate, 3,4,5-trimethyl phenol is the "abnormal" reaction product, 3,4,5-trimethyl,4-dichloromethyl,2,5-cyclohexadienone\textsuperscript{78}.

![Chemical Reaction Diagram]

The base promoted reaction of 4,6-dimethyl,2-hydroxybenzaldehyde with 2-chloroethanol (or 2-bromoethanol) and the subsequent conversion of this intermediate to the tetraaldehyde, 1,2,4,5-tetakis[2-(2-formyl,3,5-dimethylphenoxy)ethyl]benzene tetracarboxylate should be uneventful. This tetraaldehyde should have better solubility characteristics than does the tetrانaphthaldehyde. This improved solubility increases the likelihood of successfully utilizing this tetraaldehyde in the higher yielding Lindsey porphyrin preparation. If the Lindsey method fails on this aldehyde, the Almog adaptation of the Adler porphyrin procedure should succeed.\textsuperscript{*} The ester cap can then be cleaved and the alcohol termini sequentially converted to thiols to yield the blocked rotation, all \textit{cis} isomer of 5,10,15,20-tetakis[2-(2-mercaptoethoxy),4,6-dimethyl phenyl]porphyrin.

\textsuperscript{*}

An important synthetic note: During the course of this research, there were attempts to reproduce the synthesis of the "capped" porphyrins reported by Almog et. al. The synthesis of the "C\textsubscript{2}-capped porphyrin" was achieved, although, the
best experimental yield, 8%, did not replicate the literature yield of 28%. The yield of the C₂-naphthyl capped porphyrin was less than 1%, compared with the literature yield of 14%. The literature syntheses were performed at a fairly large scale (10 liters), while the attempts to reproduce these syntheses were done on a smaller scale (1 to 2 liters), but, this alteration doesn't offer much explanation for the large variance in synthetic yield. A hidden factor that can be postulated is exposure to light. (Mechanistic studies on the synthesis of meso-tetraarylporphyrins indicate that the propionic acid catalyzed condensation of aldehyde and pyrrole proceeds through a porphyrinogen intermediate⁵⁶ and in the report on the equilibrium-condensation of aldehyde and pyrrole, Lindsey emphasizes the light-sensitive nature of the porphyrinogen intermediate.³²,⁵⁶,⁶⁷) In the attempts to reproduce the "capped" porphyrin synthesis, no efforts to prevent exposure to light were made and while, Almog doesn't specifically describe the exclusion of light during the synthesis of the capped porphyrins, it isn't hard to envision the light excluding effects of the insulation used to retain the heat that would otherwise be lost from a 12-liter flask. Although light-sensitivity of the Adler procedure has not been noted in the literature, it is strongly recommended that light exposure be minimized, if in the future it becomes necessary to synthesize capped porphyrins via the high-dilution propionic acid condensation reaction as outlined by Almog.

In continuation, the stepwise conversion of the hydroxyl moiety to thiol proceeds through the methanesulfonate and thioacetate intermediates, as described in the procedures of the synthesis section of this report. The overall experimental yield for this series of conversions from hydroxyl to thiol is approximately 78%. The purity of the different
intermediates, as ascertained by NMR spectroscopy, suggests that the reduction in yield is due more to manipulative losses than to incomplete reactions.

Of these "routine" conversion procedures, the deprotection of the thiol group provided one of the unexpected difficulties during the course of this project. A common procedure for cleavage of ester type protecting groups proceeds by base-catalyzed hydrolysis producing a thiolate salt, which is then acidified to create the thiol group.\textsuperscript{79,80} The advantage of proceeding via the thiolate is that this mechanism drives the thioacetate-thiol hydrolysis equilibrium towards complete hydrolysis by removal of the hydrolysis products.

\[
\begin{align*}
R-S-(C=O)-CH_3 + H_2O & \quad \xrightarrow{(OH^-)} \quad R-S-H \\
& \quad \xrightarrow{2NaOH} \quad \text{H-O-(C=O)-CH}_3 + \text{Na-O-(C=O)-CH}_3 + 2H_2O
\end{align*}
\]

Base-promoted hydrolysis procedures were used independently on \textit{H}_2\text{TAMEPP} and \textit{[Zn\textsuperscript{II}(TAMEPP)]}, the deprotected thiolate porphyrins were then neutralized, recovered, and characterized. Proton NMR and infrared spectroscopy confirmed the removal of the acetate protecting group, but the NMR spectrum exhibited broadened resonances (0.5 to 1 ppm full-width at half-height), poorer than expected signal to noise ratio (typically S/N of 5:1 to 10:1), and the operational performance of the NMR instrument indicated the presence of a paramagnetic substance. Considerable experimental effort was expended in efforts to obtain the tetrathioc by porphyrin without this paramagnetic character. Acid-promoted hydrolysis was investigated despite reports of low yields (5%).\textsuperscript{79} Reductive cleavage\textsuperscript{80} of the acetate protecting group using LiAlH\textsubscript{4} was not considered because of problems with concurrent metallation of the porphyrin with aluminum\textsuperscript{81}, and investigations with the milder agent, NaBH\textsubscript{4}, failed to produce substantial deprotection. Persistence in the laboratory and library eventually delivered an acid-catalyzed hydrolysis procedure\textsuperscript{21} that
succeeded in producing the diamagnetic deprotected tetrathiol porphyrin. This method uses an esterification reaction to drive the thioester hydrolysis towards completion, as shown;

\[
\begin{align*}
R-S-(C=O)-CH_3 & \xrightleftharpoons{(H^+)} H_2O & R-S-H & \ \xrightarrow{(H^+)} & \text{CH}_3OH & \text{(excess)} \\
 & + & & \text{H-O-(C=O)-CH}_3 & \ \xrightarrow{(H^+)} & R-S-H \ \text{+ CH}_3O-(C=O)-CH_3 \ \text{+ H}_2O
\end{align*}
\]

During the early work on purifying H$_2$TAMXPP, there were difficulties in chromatographically isolating the purified porphyrin with all of the acetate protecting groups intact. The NMR spectrum of this porphyrin isolate varied from batch to batch, but, was consistent in that the deprotected thiol group was observed as a clean triplet at $\delta = 1.74$ ppm and the associated thiol methylene group was seen as a doublet at $\delta = 3.74$ ppm. This result was exciting because it was the first demonstration that these desired tetrathiol porphyrins need not be paramagnetic and thereby provoked the renewed efforts that resulted in the emergence of the acid-catalyzed hydrolysis procedure.

The failure to obtain samples of fully-protected H$_2$TAMXPP prompted the synthesis of 5,10,15,20-tetraakis[3-(p-bromoxylloxy)phenyl]porphyrin, H$_2$TBrXPP, as an alternate pathway for the production of the tetrathioacetate, H$_2$TAMXPP. Following the synthesis of H$_2$TBrXPP, efforts were expended towards optimizing the chromatographic conditions for purifying this tetrabromoporphyrin and through these experiments a startling discovery was made: these porphyrins are extremely sensitive to light. For H$_2$TBrXPP, with chromatography under minimal light exposure conditions, a yield of $\approx 48\%$ was attained, while, in the case of only modest exposure to light the yield was reduced to $\approx 20\%$. Implementation of this procedure of minimizing exposure of the porphyrin to light resulted in the isolation of pure, fully-protected H$_2$TAMXPP.
I.D

Conclusions

1) $H_2$TAMXPP is a light-sensitive porphyrin that can be synthesized and purified in reasonable yields. The purified free-base porphyrin exhibits rapid interconversion of the atropisomers even at -30°C. The acetate protecting group can be quantitatively cleaved to obtain the tetrathiol derivative. $H_2$TAMXPP can be metallated (Zn, Fe) without disturbing the acetate groups that protect the thiol moieties.

2) $H_2$TAMEPP can be synthesized and purified in reasonable yields. The purified free-base porphyrin is a mixture of atropisomers that slowly interconvert in solution at room temperature. The acetate protecting group can be quantitatively cleaved to obtain the tetrathiol derivative which is light-sensitive. $H_2$TAMEPP can be metallated (Zn, Fe) without disturbing the acetate groups that protect the thiol moieties.

3) $H_2$TAMENP as a mixture of atropisomers can be synthesized in lower, yet, reasonable yields. Purification of the $\alpha,\alpha,\alpha,\alpha$-atropisomer is exceedingly difficult and extremely consumptive in terms of chromatographic media and solvents. Finally, the ultimate yield of the all-cis atropisomer is very low (< 1%).

Future Work

1) Provided that $H_2$TMXPP proves to be a viable ligand for reacting with an iron-sulfur cluster, the next milestone will be to develop methodology for deprotection of the thiol substituents on the metallated forms of $H_2$TMXPP.

2) If $H_2$TMEPP proves to be an equal or better ligand for the iron-sulfur cluster than $H_2$TMXPP, a second milestone would be to develop methodology for deprotection of the thiol substituents on the metallated forms of $H_2$TAMEPP.
3a) Thus far, conventional column chromatography has demonstrated insufficient resolving power to fully purify and separate the H2TAMENP atropisomers. High performance liquid chromatographic separation of the atropisomer mixture may be a more effective method for isolating the desired $\alpha,\alpha,\alpha,\alpha$-atropisomer in greater quantity.

3b) The use of the pyromellitic acid-based tetranaphthaldehyde and appropriate modifications of the Lindsey method may allow for the formation of the naphthyl "capped" porphyrin in higher yield. Alternately, one could revert to the high dilution Adler procedure\textsuperscript{28} to synthesize the capped naphthyl porphyrin, then cleave the carboxylic ester cap to obtain the desired $\alpha,\alpha,\alpha,\alpha$-atropisomer.

3c) The use of 1,4,5,8-naphthalene tetracarboxylate in place of pyromellitic acid would allow for the synthesis a slightly larger tetranaphthaldehyde. The increased size of the "cap" would reduce the steric strain of the porphyrinogen intermediate and should lead to higher yields, provided that solubility problems are not encountered. Again, cleavage of the carboxylic ester cap will result in the desired $\alpha,\alpha,\alpha,\alpha$-atropisomer.

4) The "locked" rotation version of H2TAMEPP can be pursued synthetically using the 2-hydroxy,4,6-dimethyl benzaldehyde precursor, as outlined \textit{a priori}.

5) Crystals of these new porphyrins and metalloporphyrins, suitable for single-crystal x-ray structure determination, are desirable as confirmation of structure. These structural details could prove useful for computer modelling of the proposed porphyrin/iron-sulfur cluster molecule.
Part II

Reaction of Tetrathiol-Armed
Porphyrin Ligands

with Iron-Sulfur Cubane Cluster
II

Introduction

The anaerobic ligand exchange reaction of the iron-sulfur cubane cluster with a tetrathiol porphyrin ligand is conceptually a simple reaction. Finding the appropriate conditions for combining the tetrathiol porphyrin and the iron-sulfur cluster that allows for isolation of the desired, unimolecular, 1:1 porphyrin/cluster product has been the challenge of the second phase of this project.

The synthesis of \((\text{Et}_4\text{N})_2[\text{Fe}_4\text{S}_4(\text{SCH}_2\text{Ph})_4]\) was reported in 1972 by Herskovitz et al.\(^{17}\) A subsequent report provided the details allowing for generic synthesis of \((\text{cation}^+)_2[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}\), where \(\text{R} = \text{methyl, ethyl, t-butyl, phenyl, and others.}\)\(^{82}\) Ibers has described the iron-sulfur cubane cluster formation as being a process of "spontaneous self-assembly" where the cubane cluster is the most thermodynamically-stable soluble reaction product.\(^{83}\) In the cluster synthesis reaction, ferric chloride combines with the thiolate anions to produce a polymeric iron(III) thiolate intermediate, as follows:\(^{84}\)

\[
4 \text{FeCl}_3 + 12 \text{NaSR} \rightarrow (4/n) [\text{Fe(SR)}_3]_n + 12 \text{NaCl}
\]

The polymeric iron(III) thiolate intermediate is then reacted with sodium hydrogen sulfide and sodium methoxide to generate the iron-sulfur cluster anion, as shown:

\[
(4/n) [\text{Fe(SR)}_3]_n + 4 \text{NaSH} + 4 \text{NaOMe} \rightarrow [\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-} + 2 \text{Na}^+ + \text{RSSR} + 6 \text{NaSR} + 4 \text{MeOH}
\]

The net stoichiometry of this reaction being:

\[
4 \text{FeCl}_3 + 12 \text{NaSR} + 4 \text{NaSH} + 4 \text{MeONa} \rightarrow

[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-} + 2\text{Na}^+ + \text{RSSR} + 12 \text{NaCl} + 6\text{NaSR} + 4 \text{MeOH}
\]

An alternate synthetic method with less demanding anhydrous procedural constraints was published in 1979 by Christou and Garner.\(^{85}\) These reactions use ferric or
ferrous chloride, elemental sulfur, and a lithium thiolate as the starting reagents and have
the overall stoichiometry shown:


\[
4 \text{FeCl}_3 + 4 \text{S} + 14 \text{Li(SR)} \rightarrow \text{Li}_2[\text{Fe}_4\text{S}_4(\text{SR})_4] + 12 \text{LiCl} + 5 \text{RSSR}
\]

or


\[
4 \text{FeCl}_2 + 4 \text{S} + 10 \text{Li(SR)} \rightarrow \text{Li}_2[\text{Fe}_4\text{S}_4(\text{SR})_4] + 8 \text{LiCl} + 3 \text{RSSR}
\]

These reactions proceed through an identified intermediate, [Fe\text{4(SR)}_\text{10}]^{2-} as follows:

\[
4 \text{FeCl}_3 + 14 \text{RS}^- \rightarrow [\text{Fe}_4\text{S}_4(\text{SR})_\text{10}]^{2-} + 2 \text{RSSR} + 12 \text{Cl}^- 
\]

or


\[
4 \text{FeCl}_2 + 10 \text{RS}^- \rightarrow [\text{Fe}_4\text{S}_4(\text{SR})_\text{10}]^{2-} + 8 \text{Cl}^- 
\]

and

\[
[\text{Fe}_4\text{S}_4(\text{SR})_\text{10}]^{2-} + 4 \text{S} \rightarrow [\text{Fe}_4\text{S}_4(\text{SR})_\text{d4}]^{2-} + 3 \text{RSSR}
\]

An interesting feature of these reactions is that when the reaction mixture is deficient in
sulfur, a mixture of the iron-sulfur cubane cluster and the decathiolate cluster are produced
with the following stoichiometry:

\[
[\text{Fe}_4\text{S}_4(\text{SR})_\text{10}]^{2-} + n \text{S} \rightarrow n/4 [\text{Fe}_4\text{S}_4(\text{SR})_\text{d4}]^{2-} + (4-n)/4 [\text{Fe}_4\text{S}_4(\text{SR})_\text{10}]^{2-} + 3n/4 \text{RSSR}
\]

Que et al. established a ligand substitution series, wherein, the ligating ability of
various thiols followed the trend of their aqueous acidity. Representative of the ligand
strengths are thiol acetic acid = thiophenol > benzyl mercaptan > β-mercaptoethanol >
ethanethiol. The ligand substitution was demonstrated to be an equilibrium reaction that
proceeds through mixed-ligand intermediates [Fe\text{4S}_4\text{S}(\text{SR})_\text{4-n}(\text{SR'})_\text{n}]^{2-} , however, the
individual equilibrium constants, \( K_n \), were not determined due to experimental difficulties
for monitoring thiol concentrations.

\[
K_n = \frac{[\text{Fe}_4\text{S}_4(\text{SR})_4(\text{SR'})_n]^{2-}[\text{RSH}]}{[\text{Fe}_4\text{S}_4(\text{SR})_4(\text{SR'})_{n-1}]^{2-}[\text{R'SH}]} 
\]
The ligand exchange reaction, $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-} + \text{R'SH}$, where $\text{R} = \text{alkyl}$ and $\text{R'} = \text{aryl}$ can be monitored by observing electronic absorption spectra, but the exchange reactions, alkyl $\rightarrow$ alkyl' and aryl $\rightarrow$ aryl' do not provide significant spectral changes.\textsuperscript{86} The NMR spectrum provides a better means for evaluating the products of the exchange reaction in that the iron nuclei cause a large isotropic shift (9 to 10 ppm) in the chemical shift of the protons nearest the coordinated thiolate.

In a series of $^1\text{H}$ NMR experiments, Que et al. determined the relative tendency for substitution by monitoring the amount of $t$-butyl mercaptan released upon the addition of four equivalents of R'SH. Those experiments yielded the following data:\textsuperscript{23}

<table>
<thead>
<tr>
<th>R'SH</th>
<th>% $t$-BuSH released</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_3\text{COSH}$</td>
<td>98</td>
</tr>
<tr>
<td>$\text{C}_6\text{H}_5\text{SH}$</td>
<td>96</td>
</tr>
<tr>
<td>$\text{PhCH}_2\text{SH}$</td>
<td>85</td>
</tr>
<tr>
<td>$\text{HOCH}_2\text{CH}_2\text{SH}$</td>
<td>78</td>
</tr>
<tr>
<td>$\text{CH}_3\text{CH}_2\text{SH}$</td>
<td>59</td>
</tr>
</tbody>
</table>

The electronic spectra further revealed that the more acidic aryl mercaptans require 4.5 to 4.9 equivalents of R'SH to completely displace the $t$-butyl mercaptan in this equilibrium substitution reaction. The extent of alkyl thiol substitution could not be monitored, because of insufficient difference between the electronic spectra.

The low affinity of the ethanethiol and its volatile nature (bp 35°C) suggest that this mercaptan would be a good ligand for a precursor cluster. The equilibrium of the exchange
reaction can be driven towards the desired porphyrin-cluster compound by removal of the exchanged ethanethiol in vacuo.

There is little doubt that the porphyrin thiol arms will substitute for ethanethiol in the exchange reaction of $[\text{Fe}_4\text{S}_4(\text{SEt})_4]^{2-}$. The primary concern is the configuration of the thiol arms on the porphyrin. As previously discussed, the original intent of phase one of this project was to develop a "blocked" rotation, all cis-armed tetrathiol porphyrin. Subsequent syntheses lead to the development of "hindered" and "free" rotation tetrathiol porphyrins with the intent of developing appropriate conditions whereby the ligand exchange would lead to the desired porphyrin-cluster compound.

Concurrent with the development of the tetrathiol porphyrin ligands in this report, Stack et al. developed a tridentate thiol ligand.\textsuperscript{18} This particular ligand has sterically interacting substituents that direct the three thiols inward to form a pocket, a "cavitation" in their nomenclature. Further characterization of this ligand and a related trithiol that lacks the steric directionality was reported in 1990.\textsuperscript{19} This later report states that the "ligand which lacks any orienting substituents, forms a mixture of products that are predominantly oligomeric in nature." Strictly on the basis of this statement, the prospect for successful isolation of the desired porphyrin/iron-sulfur cluster complex using the rotating arm porphyrins seems poor.

Closer inspection of the synthetic details of the ligand exchange reaction, used by Stack for generating the trithiol cluster derivatives\textsuperscript{19}, reveal the possibility for conditions under which the non-oriented trithiol could have succeeded. First, the concentration of the reactants in the published reaction, $\approx 15$ millimolar, could be diluted to reduce the likelihood of the ligand simultaneously encountering multiple clusters. Secondly, Stack was exchanging the fourth iron site on the cluster with a chloride ion by adding pivaloyl chloride (trimethyl acetyl chloride) to the reaction mixture. The halide ligands on the iron-
sulfur cluster have been demonstrated to be more labile than thiolate ligands and may perhaps be promoting further ligand exchange between the cluster ligands, thereby leading to oligomerization.87,88

In the present work, the tetrathiol-armed porphyrin, H2TMXPP, was reacted with (cation)2[Fe4S4(SEt)4] under various dilute conditions, as an effort towards the synthesis and isolation of the product shown in Figure 28. The isolated products have been characterized spectroscopically and crystal growth studies attempted.

Figure 28  {5,10,15,20-Tetrakis[3-(p-thiolatoxylyleneoxy)phenyl]porphyrin}-tetra(μ3-sulfido-iron)dianion

M = 2H+, Zn2+, Fe3+,2+
II.A  Experimental Section

II.A.1  Materials

Solvents for synthesis were reagent grade (Burdick & Jackson, EM Science, Mallinckrodt), unless noted otherwise. When specified as dry, the solvents were dried by standard laboratory methods [Perrin, 1988 #94; Gordon, 1972 #114]. In general, solvents were dried by refluxing with, then distilling from an appropriate drying agent, as follows: diethyl ether (LiAlH₄), methanol (Na metal or NaOMe), methylene chloride (CaH₂), tetrahydrofuran (LiAlH₄), ethanol (Na metal and ethyl formate), dimethyl formamide (CaO).

Chloroform (EM Science, reagent grade) was obtained with 0.75% ethanol as the stabilizing agent. Ethanol-free chloroform was obtained by washing the chloroform with water, pre-drying the organic layer with anhydrous CaCl₂, and distilling from CaH₂.

Deoxygenated solvents and solutions were prepared by purging the solvent with dioxygen-free nitrogen or argon, unless noted otherwise.

Commercial reagents, inorganic and organic, were reagent grade and were used without further purification unless noted otherwise; anhydrous ferric chloride (Aldrich), sodium methoxide (Aldrich), ethanethiol (Aldrich), ethanol (Aaper Alcohol & Chemical), anhydrous calcium chloride (EM Science), ethyl formate (Aldrich), phosphorus pentoxide (EM Science), calcium hydride (Aldrich), calcium chloride (Baker), lithium aluminum hydride (Aldrich).

Anhydrous sodium hydrogen sulfide was prepared according to the method of Eibekc.⁸⁹
Argon and nitrogen gases were dried through a column of Drierite and then passed through a column of R3-11 catalyst (Chemical Dynamics, Inc.) to remove traces of dioxygen. Hydrogen sulfide (Matheson) was dried by passing the gas through a tube filled with phosphorus pentaoxide.

II.A.2 Physical and Spectroscopic Measurements

Proton NMR and $^{13}$Carbon NMR were obtained on an IBM/Brüker AF-300 NMR spectrometer or an IBM/Brüker AF-250 NMR spectrometer. Infrared spectra were collected on a Perkin-Elmer 1600 Series FT-IR spectrometer. Fast-atom bombardment mass spectra were obtained on a Kratos MS50TC mass spectrometer, calibrated with cesium iodide. UV-visible spectra were collected on a Hewlitt Packard Model 8452A Diode Array Spectrometer interfaced with a Hewlitt Packard series 9000 computer system. Mössbauer spectra were acquired on a Ranger Scientific MS-900 spectrometer with a Cryo Industries Model 8CC variable-temperature Mössbauer cryostat and a TRI Research Model T-200 cryogenic controller; manipulation of the resultant spectral data was performed on an IBM clone computer using the Ranger Scientific Mössbauer curve fitting program Mossfit version 1.0. X-band Electron Paramagnetic Resonance spectra were recorded as frozen solutions at ~11K on a Varian E-Line EPR spectrometer (Varian E-101 microwave bridge). Elemental analyses were done on a Carlo Erba Instruments NA 1500 series 2 Analyzer (C, H, N, S), Perkin-Elmer Plasma 400 Emission Spectrometer (Fe), or were performed by Galbraith Laboratories.
II.A.3 Syntheses

II.A.3.a Bis(cation)-tetra(ethylthiolato)-tetra(μ₃-sulfido-iron)dianion, (cation)₂[Fe₄S₄(SEt)₄]²⁻

The ethyl mercaptan derivative of the iron-sulfur cluster was prepared following the generic procedure of Averill et al. Strict anaerobic and (initially) anhydrous conditions are required for successful synthesis of these clusters. Changes in the type of cation used to crystallize the cluster, dramatically alter the solubility characteristics of the final product.

Ethyl mercaptan was distilled under reduced pressure, into a chilled Schlenk flask (partial immersion in liquid nitrogen). The vacuum was replaced with argon, the distillation apparatus was removed from the receiving flask, and the flask was stoppered. The ethanethiol was then degassed using the freeze-thaw technique. Three, Schlenk flasks were set up with a Y adapter and filter tube as shown in Figure 29: Flask 1 (1000 ml) contained sodium methoxide (4.86 g, 90 mmole) and a stir bar; Flask 2 (500 ml) contained sodium hydrogen sulfide (1.68 g, 30 mmole), sodium methoxide (1.62 g, 30 mmole), and a stir bar; Flask 3 contained a stir bar; The filter tube (medium porosity glass frit) held a layer of celite filter aid (= 2 cm) using a wad of glass wool to hold it in place. The entire assembly was evacuated and refilled with argon (3x) to displace dioxygen. In a separate Schlenk flask/filter tube assembly, anhydrous ferric chloride (4.87 g, 30 mmole) was subjected to an equivalent evacuate and fill procedure.

Dry, deoxygenated methanol was then added to the following flasks, using a cannula transfer technique; Flask 1- 200 ml, Flask 2- 100 ml, Ferric chloride flask- 100 ml. The solutions were stirred until the solids were dissolved. The degassed ethanethiol (6.5 ml, 90 mmole) was transferred to Flask 1 with a gas tight syringe. The Schlenk flask
assembly containing the ferric chloride solution was inverted and the yellow solution was filtered. The ferric chloride solution was transferred with a cannula into Flask 1, containing the sodium ethylthiolate, which created a very dark green (nearly black) slurry. Upon completion of the transfer, the three flask assembly was tipped so as to pour the sodium hydrogen sulfide solution (Flask 2) into Flask 1. The dark green precipitate redissolved and the resultant reddish black solution was stirred overnight. An oil bubbler was fitted to the side arm of Flask 3 and a slight flow of argon was maintained over the reaction mixture during the overnight period.

Figure 29  A Schematic of the Cluster Synthesis Assembly

Fifteen hours later, the three flask assembly was cautiously rotated in a manner that prevented the reaction mixture from immediately running down into the filter tube. The reaction mixture was allowed to settle for 30-40 minutes and then the supernatant was
cautiously decanted into the filter tube. When the filtration step was performed in the manner, it was feasible to wash the precipitate with deoxygenated methanol and filter the resultant solution to improve the final yield. On other occasions, the filtration became exceedingly slow due to the fine sediments of the reaction mixture. In those cases argon pressure was used to backflush the filter and mix the celite in with the reaction fines and then the filtration was reinitiated.

A solution of quaternary cation (25 mmole) in deoxygenated methanol (50 ml) was added to the filtrate using a cannula transfer technique and the procedural manipulations vary from this juncture depending upon the cation used. For the quaternary cation, tetraphenylarsonium chloride, the volume of the reaction mixture was reduced to approximately 250 ml in vacuo, during which time, black crystals of the product were formed. The product was collected by filtration, washed successively with a small portions of cold methanol, water, and cold methanol. The washed crystals were transferred to a clean Schlenk flask and any residual solvent was removed in vacuo.

For the quaternary cations, tetramethylammonium chloride or tetraethylammonium chloride, the combined filtrate and cation solution was reduced to a volume of approximately 200 ml, filtered to removed sodium chloride, and the reddish black filtrate was layered with dry deoxygenated diethyl ether. The flask was placed in the freezer and crystallization occurred overnight. The black crystalline product was isolated from the brownish-grey supernatant by filtration. The crystalline material was transferred to a clean Schlenk flask and residual solvent was removed in vacuo.

For the quaternary cation tetraphenylphosphonium bromide, the product began to crystallize from the mixed solutions, within 15 to 20 minutes of the addition of the quaternary cation. The black crystalline product was collected by filtration and the isolated crystals were dried in vacuo. A second growth of crystals (≈20% of first growth) was
obtained from the black filtrate by reducing the volume of the solvent by approximately 20%, using vacuum. This second batch of product was contaminated with a visible amount of NaBr.

For the salt, PPN chloride, [(Ph₃P)₂N]Cl, the methanol volume was reduced to approximately 300 ml, filtered to remove sodium chloride, layered with dry deoxygenated diethyl ether (500 ml) and placed in the freezer for two days. The methanol-diethyl ether solution was decanted from the resultant black oil, which was redissolved in methylene chloride (30 ml), layered with dry deoxygenated diethyl ether, and replaced in the freezer overnight. The resultant crystalline product was collected by filtration and dried in vacuo.

(Ph₄P)₂[Fe₄S₄(Se₄)₄]

FABMS (3-nitrobenzyl alcohol), m/z 1273.8 (M⁺); Figure 34;

¹H NMR (DMSO-d₆, 298 K, 300 MHz, reference DMSO δ = 2.48, Figure 33):

δ = 2.28 (s, 4 CH₃), 7.7-7.8 (m, 32 CH), 8.0 (m, 8 CH), 12.45 (s, 4 CH₂);

Anal. Calculated for C₅₆H₆₀Fe₄S₈P₂: C, 52.76; H, 4.74; Fe, 17.52; S, 20.12;

Found: C, 52.38; H, 4.96; Fe, 16.97; S, 19.77.

II.A.3.b Bis(tetraphenylphosphine){5,10,15,20-Tetrakis-[3-(p-thiolatoxylyleneoxy)phenyl]porphyrin}-tetra(μ₃-sulfido-iron)dianion,

(Ph₄P)₂[Fe₄S₄(tetrathiolato-armed porphyrin)]

The target compound, (Ph₄P)₂[Fe₄S₄(tetrathiolato-armed porphyrin)] was prepared from (Ph₄P)₂[Fe₄S₄(Se₄)₄] and H₂TMXPP using a ligand exchange reaction under dilute conditions (10⁻⁴ M). Strict anaerobic conditions were maintained to prevent oxidative
decomposition of the iron-sulfur cluster and precautions to minimize light exposure were undertaken to avoid the possibility of porphyrin-promoted photochemistry.

The ethylmercaptan derivative of the iron-sulfur cluster, \((\text{Ph}_4\text{P})_2[\text{Fe}_4\text{S}_4(\text{SEt})_4]\) (100 mg, 7.8 x10^{-5} mol) was dissolved in 250 ml of dry, deoxygenated dimethyl formamide (DMF). The tetraethiol porphyrin, \(\text{H}_2\text{TMXPP}\) (96 mg, 7.8 x10^{-5} mol) was transferred to an aluminum foil-wrapped 1-liter Schlenk flask and dissolved in 250 ml of dry tetrahydrofuran (THF). The resultant solution was deoxygenated by bubbling a stream of dinitrogen through the solution for 20 minutes and then the solution was further diluted by adding 250 ml of dry deoxygenated DMF, using a cannula technique. Using a cannula, the ethylmercapto-iron-sulfur cluster solution was added to the magnetically stirred tetrathiyl porphyrin solution over a ten minute period. When the addition of the cluster solution was complete, a stream of dinitrogen was bubbled through the combined solution for a period of 15 to 18 hours. The solvent was then removed in vacuo, using a water bath (30 °C) to assist in solvent removal. The resultant purple film was redissolved in DMF (10-20 ml) and filtered to remove an insoluble purple component and the filtrate was either subjected to crystal growth studies or once more evacuated to dryness. A variable yield of 50 to 80% was estimated by visual comparison of the quantities of insoluble purple residue with the isolated porphyrin-cluster compound.

\((\text{Ph}_4\text{P})_2[\text{Fe}_4\text{S}_4(\text{H}_2\text{TMXPP})]\);

\(^1\text{H NMR}\) (DMSO-\(d_6\), 298 K, 300 MHz, reference DMSO \(\delta=\) 2.48, Figure 41): \(\delta=\) ;

\textit{Anal. Calculated} for \(\text{C}_{124}\text{H}_{98}\text{Fe}_4\text{N}_4\text{O}_4\text{P}_2\text{S}_8\cdot3\text{DMF}\): C, 64.69; H, 4.86; Fe, 9.05; N, 3.97; S, 10.39; \textit{Found}: C, 62.75; H, 5.01; Fe, 9.02; N, 4.08; S, 9.86.
II.B. Spectroscopic Results

II.B.1. $^1$H NMR Spectroscopy

The $^1$H NMR spectra of the various cationic [Fe$_4$S$_4$(SEt)$_4$]$^{2-}$ compounds, Figures 30-33, demonstrate chemical shifts that approximate the literature values$^{91}$, with the downfield shift of the thiolate methylene group resulting from the isotropic shift caused by the [Fe$_4$S$_4$]$^{2+}$ core. The chemical shifts of the ethyl thiolate protons are summarized in Table 8.

Table 8 The $^1$H Chemical Shifts of (Cation)$^+$$_2$[Fe$_4$S$_4$(SEt)$_4$]$^{2-}$

<table>
<thead>
<tr>
<th>Cation</th>
<th>Solvent</th>
<th>Thiolate CH$_2$</th>
<th>Thiolate CH$_3$</th>
<th>Cation Protons</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Me$_4$N)$^+$</td>
<td>CD$_3$CN</td>
<td>12.69</td>
<td>2.34</td>
<td>3.13</td>
</tr>
<tr>
<td>(Et$_4$N)$^+$</td>
<td>DMSO</td>
<td>12.47</td>
<td>2.29</td>
<td>3.09 (CH$_3$), 3.34 (CH$_2$)</td>
</tr>
<tr>
<td>(PPN)$^+$</td>
<td>CDCl$_3$</td>
<td>11.94</td>
<td>2.39</td>
<td>7.45 ($o,m$), 7.65 ($p$)</td>
</tr>
<tr>
<td>(Ph$_4$P)$^+$</td>
<td>DMSO</td>
<td>12.45</td>
<td>2.28</td>
<td>7.7-7.8 ($o,m$), 8.0 ($p$)</td>
</tr>
</tbody>
</table>

The $^1$H NMR spectra of the (Ph$_4$P)$^+$ and (Me$_4$N)$^+$ derivatives of [Fe$_4$S$_4$(H$_2$TMXPP)]$^{2-}$, Figures 41 and 42, exhibit changes in the porphyrin spectrum due to the isotropic shift of the thiolate methylene group promoted by the [Fe$_4$S$_4$]$^{2+}$ core. The diminished solubility of these compounds and slight paramagnetism of the iron-sulfur cluster lowers the achievable signal/noise ratio of the spectra. For (Ph$_4$P)$^+$ and (Me$_4$N)$^+$ derivatives respectively, the inner pyrrole proton resonance is found upfield at -2.97 and -2.85 ppm and the outer,$\beta$, pyrrole proton resonance is found downfield at 8.88 and 8.86
ppm. For both derivatives, the phenyl and xylyl protons provide for a broad signal from 7 to 8 ppm. In the (Ph₄P)⁺ derivative, the xylyl ether methylene proton resonance is found at 5.18 ppm, while the thiolate methylene provides two signals at 11.75 and 13.50 ppm. In the (Me₄N)⁺ derivative, the xylyl ether methylene proton resonance is found at 5.47 ppm, while the thiolate methylene provides one signal, perhaps two unresolved resonances, at 13.2 ppm.

II.B.2. FAB Mass Spectroscopy

The fast atom bombardment mass spectrum of (Ph₄P)₂[Fe₄S₄(SEt)₄], Figure 34, shows the molecular ion at m/z 1273.7. The experimental isotopic distribution pattern closely resembles the calculated distribution (reminding the mirror image presentation). The ion cluster at m/z 1296.6 is most likely Na(Ph₄P)₂[Fe₄S₄(SEt)₄], a result of oxidation within the ion source and the sodium coming from a trace of NaCl impurity within the sample. The cluster at m/z 1212.6 results from the loss of one ethanethiol group, while the clusters at the higher masses are the result of molecular reactions within the ion source.

Fast atom bombardment mass spectrometry was attempted unsuccessfully, with the iron-sulfur/porphyrin compound, (Ph₄P)₂[Fe₄S₄(H₂TMXPP)], using a nitrobenzyl alcohol matrix.

II.B.3. Mössbauer Spectroscopy

The Mössbauer spectrum of (Ph₄P)₂[Fe₄S₄(SEt)₄] was acquired on a polycrystalline sample at both room (297 K) and liquid nitrogen (77 K) temperatures, using sodium nitroprusside as a reference standard (at 297 K, δ = 0.0 mm/sec and ΔE₀ = 1.705
mm/sec). The raw and computer fit data are shown in Figure 35 and provide the following parameters: $\delta_{297} = 0.62$ mm/sec, $\Delta E_{Q297} = 0.51$ mm/sec, $\Gamma_{297} = 0.15$ mm/sec; $\delta_{77} = 0.75$ mm/sec, $\Delta E_{Q77} = 0.90$ mm/sec, $\Gamma_{77} = 0.19$ mm/sec. These values parallel the literature values of (Et$_4$N)$_2$[Fe$_4$S$_4$(SCH$_2$Ph)$_4$]$\delta_{297} = 0.60$ mm/sec, $\Delta E_{Q297} = 1.10$ mm/sec, $\Gamma_{77} = 0.23$ mm/sec; $\delta_{77} = 0.62$ mm/sec, $\Delta E_{Q77} = 1.26$ mm/sec, $\Gamma_{77} = 0.28$ mm/sec. Here $\delta$, $\Delta E$, and $\Gamma$ represent the chemical shift, quadrupole splitting, and peak half width at half maximum, respectively.

The Mössbauer spectrum of (Ph$_4$P)$_2$[Fe$_4$S$_4$(H$_2$TMXPP)] was acquired on a polycrystalline sample under the same conditions as the preceding precursor cluster compound, although the sample size was smaller. The smaller sample size is the most probable cause for the lower signal to noise ratio which is observed in Figure 36. The computer fit parameters for the porphyrin cluster compound are as follows: $\delta_{297} = 0.65$ mm/sec, $\Delta E_{Q297} = 0.81$ mm/sec, $\Gamma_{297} = 0.32$ mm/sec; $\delta_{77} = 0.76$ mm/sec, $\Delta E_{Q77} = 0.93$ mm/sec, $\Gamma_{77} = 0.36$ mm/sec. The peak half width at half maximum values for the porphyrin/iron-sulfur cluster compound are larger than the values reported in the literature for [Fe$_4$S$_4$(SR)$_4$]$^{2-}$ compounds. Mössbauer spectroscopic studies of iron-sulfur cluster proteins have shown that the iron atoms can form two inequivalent pairs, and in the case of a reduced ferredoxin isolated from *B. stearothermophilus* the two pairs are resolved into two doublets. The spectra for (Ph$_4$P)$_2$[Fe$_4$S$_4$(H$_2$TMXPP)], with one absorption more intense than the other, resemble the spectra published by Dickson et al. for reduced ferredoxin. A better signal to noise ratio might allow for the resolution of the two doublets that appear to be present.
II.B.4.  UV-visible Spectroscopy

The UV-visible spectrum of (Ph₄P)₂[Fe₄S₄(SEt)₄] was acquired on a deoxygenated DMF solution, Figure 37. The bands at 277 nm (ε = 3.0 x 10⁴), 433 nm (ε = 8.0 x 10³), and the shoulder at 324 nm (ε = 1.6 x 10⁴) differ slightly from the literature values determined for (n-Pr₄N)₂[Fe₄S₄(SEt)₄] ; 298 nm (ε = 2.3 x 10⁴), 355 nm (ε = 1.5 x 10⁴), and 420 nm (ε = 1.7 x 10⁴).⁸⁶

The UV-visible spectrum of (Ph₄P)₂[Fe₄S₄(H₂TXPP)] was acquired as a DMF solution, Figure 38. For comparison, the electronic absorption spectrum of H₂TXPP was also acquired in DMF and is shown in Figure 39. The electronic absorption features of the porphyrin functionality dominate the spectrum of the porphyrin/cluster compound, with the Soret band intensity being a factor of 10 greater that the iron-sulfur cluster intensity. At the longer wavelengths, the intensity of the porphyrin Q-bands are a factor of 4 greater than the broad, rather featureless absorption of the iron-sulfur cluster. The small absorption seen at 277 nm (ε = 3.9 x 10⁴) provides further confidence that the iron-sulfur cluster is indeed present along with the porphyrin. Additionally, a comparison of the spectrum of H₂TXPP, Figure 39, with that of the porphyrin/cluster compound, Figure 38, reveals a gradually decreasing background absorption (from 460 nm → 680 nm) that closely resembles the absorption curve of the precursor cluster compound, Figure 37.

II.B.5.  Electron Paramagnetic Resonance Spectroscopy

A sample of (Ph₄P)₂[Fe₄S₄(SEt)₄], 0.102 millimolar in 1:1 DMF-toluene, was tested for EPR activity as a frozen glass at =11K. As expected⁹⁴ for a sample of
[Fe₄S₄(SR)₄]²⁻, there was no detectable EPR signal (even at high sensitivity settings), a result of the strong exchange coupling within the tetranuclear metal center.

The EPR spectrum of (Ph₄P)₂[Fe₄S₄(H₂TMXPP)] was acquired at ~11K on a 1:1 DMF-toluene glass with a concentration of 0.109 millimolar. At nominal gain and amplitude no EPR signal was detected, however at much higher sensitivity, Figure 40, there were EPR signals at g⊥ = 6 and g∥ = 2, signals that like those previously seen for high-spin (S=5/2) [FeIII(TAMXPP)Cl], Figure 18. Using [FeIII(TPP)Cl] as a reference compound, the normalized-integration of the EPR signal indicates that 6% of the porphyrin/cluster compound is in a porphyrin-metallated form, possibly in the form, (Ph₄P)+[Fe₄S₄(FeIII(TMXPP))]⁻, although [FeIII(TMXPP)Z] can not be ruled out (where Z is some anion or other axial ligand).
Figure 30 The 300MHz $^1$H NMR Spectrum of $(Me_4N)_2[Fe_4S_4(SEt)_4]$ in CD$_3$CN at 298K
Figure 31 The 300MHz $^1$H NMR Spectrum of $(\text{Et}_4\text{N})_2[\text{Fe}_4\text{S}_4(\text{SEt})_4]$ in DMSO at 298K
Figure 32 The 300MHz $^1$H NMR Spectrum of (PPN)$_2$[Fe$_4$S$_4$(SEt)$_4$] in CDCl$_3$ at 298K
Figure 33 The 300MHz $^1$H NMR Spectrum of (Ph$_4$P)$_2$[Fe$_4$S$_4$(SEt)$_4$] in DMSO at 298K
Figure 34 The FAB Mass Spectrum of \((\text{Ph}_4\text{P})_2\text{[Fe}_4\text{S}_4(\text{SEt})_4]\)

![Mass Spectrum Diagram]

- **Calculated Isotopic Distribution** for \(\text{C}_{56}\text{H}_{60}\text{Fe}_4\text{P}_2\text{S}_8\)
- **Experimental Isotopic Distribution** for \((\text{Ph}_4\text{P})^+\_2\text{[Fe}_4\text{S}_4(\text{SEt})_4]^{2-}\)

The diagram shows a detailed mass spectrum with notable peaks at masses 1273.9 and 1273.7, indicating the presence of the compounds specified.
Figure 35 The Mössbauer Spectrum of \((\text{Ph}_4\text{P})_2[\text{Fe}_4\text{S}_4(\text{SEt})_4]\)
Figure 36  The Mössbauer Spectrum of \((\text{Ph}_4\text{P})_2[\text{Fe}_4\text{S}_4(\text{H}_2\text{TMXPP})]\)
Figure 37  The UV-visible Spectrum of (Ph₄P)₂[Fe₄S₄(SEt)₄] in DMF
Figure 38  The UV-visible Spectrum of \((\text{Ph}_4\text{P})_2[\text{Fe}_4\text{S}_4(\text{H}_2\text{TMXP})_4]\) in DMF
Figure 39  The UV-visible Spectrum of \( \text{H}_2\text{TMXPP} \) in DMF
Figure 40  The EPR Spectrum of $\text{(Ph}_4\text{P)}_2[\text{Fe}_4\text{S}_4(\text{H}_2\text{TMXPP})]$ in a 1:1 DMF-Toluene Glass, 11K
Figure 41  The 300 MHz $^1$H NMR Spectrum of 

$(\text{Ph}_4\text{P})_2[\text{Fe}_4\text{S}_4(\text{H}_2\text{TMXPP})]$ in DMSO-$d_6$ at 298K
Figure 42  The 300 MHz $^1$H NMR Spectrum of

$\text{(Me}_4\text{N})_2\text{[Fe}_4\text{S}_4\text{(H}_2\text{TMXPP)}\text{]}$ in DMSO-$d_6$ at 298K
II.C  Discussion

The initial attempts to produce a molecular porphyrin/cluster compound were performed with the hindered-rotation porphyrin, H$_2$TMEPP, that had been prepared by base-catalyzed hydrolysis of the thiolacetate ester compound, H$_2$TAMEPP. These early trials were plagued with the paramagnetic character of the deprotected porphyrin, previously described in Part I of this report, which limited the utility of $^1$H NMR spectroscopy in characterizing the final compounds. However, several observations from these early trials helped focus the efforts that were later applied in the experiments with the free-rotation porphyrin, H$_2$TMXPP.

One of the encouraging observations was the strong olfactory evidence for off-gassing of ethanethiol during the addition of a (cation)$_2$[Fe$_4$S$_4$(SEt)$_4$] solution to the tetrathiol porphyrin solution. These early experiments utilized chloroform or methylene chloride for dissolution of the porphyrin compound and methanol or acetonitrile for the precursor iron-sulfur cluster compound. In one particular set of experiments, the mixed solvent system was refluxed in an effort to increase the rate of rotation of the thiol-armed-phenyl groups on the hindered-rotation porphyrin molecule. The porphyrin compound that was recovered from these experiments was no longer in the free-base form, but instead was isolated as a high-spin (S = 5/2) iron(III) porphyrin. The quantity of sample recovered from these experiments was insufficient for Mössbauer spectroscopy, so, whether there was undegraded iron-sulfur cluster coordinated with the porphyrin is uncertain. The most likely cause for the degradation of the iron-sulfur cluster is the residual acidity of the chloroform solvent, in as much as, the literature describes acid-catalyzed solvolysis of [Fe$_4$S$_4$(SR)$_4$]$^{2-}$ compounds. The lack of success in isolating a fully verifiable
porphyrin/cluster compound from these experiments with H₂TMEPP led to renewed efforts towards alternative tetrathiophorphyrins.

After the successful preparation of the free-rotation tetrathiophorphyrin, H₂TMXPP, attempts to produce (Me₄N)₂[Fe₄S₄(H₂TMXPP)] were initiated. In these experiments, tetrahydrofuran (THF) was substituted for chloroform to circumvent the possibility of acid-catalyzed degradation of the cluster, and precautions were taken to minimize exposure of the porphyrin solution to light. The cluster compound, (Me₄N)₂[Fe₄S₄(SEt)₄], was dissolved in methanol, and these THF and methanol solutions were combined and manipulated in a manner similar to that described in the experimental section (Part II). The ¹H NMR spectral results of these experiments were encouraging but a crystalline product was not achieved, leading to the preparation of the tetraphenylphosphonium derivative of [Fe₄S₄(SEt)₄]²⁻ in anticipation that this cation might promote crystallinity in the porphyrin/cluster product, [Fe₄S₄(H₂TMXPP)]²⁻.

The initial attempt to perform the ligand substitution reaction of (Ph₄P)₂[Fe₄S₄(SEt)₄] dissolved in methanol and the porphyrin dissolved in THF produced an immediate precipitation of the iron-sulfur cluster compound during the combination of the two solutions. This problem was solved by using N,N-dimethyl formamide (DMF) as is described in the experimental section.

The porphyrin/cluster residue left after reduced-pressure evaporation of the reaction solvent displays solubility properties, that in general, differ from the solubility properties of the initial components. The solubility of the reaction residue is in part determined by the cation used. The tetramethylammonium and tetraethylammonium derivatives display poor solubility in chloroform, methanol, or THF, moderate solubility in acetonitrile, and good solubility in DMF or DMSO. The PPN derivative was used only in the early experiments
with H₂TMEPP and demonstrated solubility in chloroform. The tetraphenylphosphonium derivative displays poor solubility in any solvent other than DMF or DMSO.

In each of the various substitution reactions, after the "product" was recovered by dissolution in an appropriate solvent, there remained an insoluble purple solid that was thought to be a porphyrin/cluster oligomer. This hypothesis was derived from the observation that, when this insoluble material was exposed to dioxygen for a few days, allowing the iron-sulfur cluster to oxidatively decompose, the porphyrin portion became soluble once again (leaving behind a brown insoluble material, presumably an iron oxide/iron sulfide composite). Alternately, if the insoluble material was treated with a small amount of hydrochloric acid, the iron-sulfur cluster was immediately hydrolyzed releasing the porphyrin in the dication form, H₄TMXPP²⁺, as evidenced by the dication's brilliant blue-green color.

The previous hypothesis may require re-evaluation based upon an observation made late in the course of this research. During efforts to purify the soluble porphyrin/cluster product, the soluble fraction of the reaction mixture was rendered insoluble, on more than one occasion. A description of the "purification" procedure that was altering the solubility character of the porphyrin/cluster product is as follows;

1) The porphyrin/cluster reaction product was dissolved in a small amount of either DMSO or DMF.

2) Several volumes of either THF or diethyl ether was "layered" on top of the porphyrin/cluster solution, with the intent of precipitating (or crystallizing) the porphyrin/cluster compound while maintaining any excess cation or excess porphyrin in solution.

3) After allowing a day or two for solvent diffusion, the solvent mixture was decanted and the isolated solid was dried in vacuo.
4) At this juncture, the porphyrin/cluster material was "insoluble". The cause for the insolubility of the "purified" material was initially ascribed to either polymerization or inadvertent exposure to dioxygen. Later it was discovered, that, when the "polymer" was left exposed over a period of days to DMF (or DMSO to a lesser extent), the compound would redissolve. This suggests that the initial "dry" film of porphyrin/cluster is partially solvated ($^1$H NMR confirms the presence of residual solvent) and that removal of this residual solvent with THF or diethyl ether dramatically alters the solubility of the final isolate. To test this hypothesis, a sample of "insoluble" porphyrin/cluster was redissolved in DMF, the resultant solution was redried to a film in vacuo, and this film once again demonstrated quick solubility in DMF.

Previous studies with alkyl and aryl derivatives of the iron-sulfur cubane cluster have established that the [Fe₄S₄]$^{2+}$ core promotes an isotropic shift of the NMR resonances of the thiolate ligands (RS⁻)₄ and that the magnitude of these contact-derived isotropic shifts is temperature dependent. To confirm this feature in this new porphyrin/cluster compound, variable-temperature $^1$H NMR studies were performed on both the tetraphenylphosphonium and tetramethylammonium derivatives of [Fe₄S₄(H₂TMXPP)]$^{2-}$. These experiments were performed with DMSO-d₆ solutions which prohibited accessibility of data below room temperature (DMSO mp = 18°C). The upper temperature limit for these studies was determined by the broadening and weakening of the resonances being monitored. The isotropic shift is derived from the relationship;

$$(\Delta H/H_0)^{isotropic} = (\Delta H/H_0)^{observed} - (\Delta H/H_0)^{diamagnetic}$$

where $\Delta H/H_0$ is the chemical shift in ppm.

The compound (Ph₄P)$_2$[Fe₄S₄(H₂TMXPP)] displays two broad resonances for the methylene group nearest the coordinated thiolate, with chemical shifts of 11.9 ppm and 13.5 ppm (room temperature spectrum shown in Figure 41). Being that the diamagnetic
chemical shift for this methylene group is 3.74 ppm, this translates to an isotropic shift of 8.2 ppm and 9.8 ppm at \( \approx 297K \). Examination of a ball and stick model of \([\text{Fe}_4\text{S}_4(\text{H}_2\text{TMXPP})]^2-\), pictorially represented in Figure 28, shows that two of the thiolate arms are extended high above the plane of the porphyrin, while the other two arms are folded in closer to the plane of the porphyrin, providing a reasonable account for two inequivalent chemical shifts. The temperature dependency of the isotropic shifts is presented graphically in Figure 43. The disparity between between the two ranges of isotropic shifts in \((\text{Ph}_4\text{P})_2[\text{Fe}_4\text{S}_4(\text{H}_2\text{TMXPP})]\) maybe the result of ion-pairing between the cluster molecule and the tetraphenylphosphonium cation. This supposition is based upon the results of the variable-temperature \(^1\text{H} \) NMR study with \((\text{Me}_4\text{N})_2[\text{Fe}_4\text{S}_4(\text{H}_2\text{TMXPP})]\), which presents only one signal for the thiolate methylene protons and an intermediate range for the isotropic shift (room temperature spectrum shown in Figure 42). Figure 44 presents the isotropic shift observed for the tetramethylammonium derivative, while Figure 45 provides a "same scale" comparison of the isotropic shifts demonstrated by the two different cation derivatives of \([\text{Fe}_4\text{S}_4(\text{H}_2\text{TMXPP})]^2-\).
The difference between these two thiolate methylene groups is described in the preceding text.
Figure 44  The Isotropic Shift of (Me₄N)₂[Fe₄S₄(H₂TMXPP)]

The thiolate methylene groups provide only one broad resonance in this derivative.
The isotropic shifts observed for (Me₄N)₂[Fe₄S₄(H₂TMXPP)], 10.0 ppm to 11.2 ppm over the temperature range 300 K to 350 K, closely approximates the reported literature values⁹¹, 10.2 ppm to 11.1 ppm for the same temperature range. The isotropic shifts of the more strongly influenced resonance (8–20 ppm, 24 to 67°C) in (Ph₄P)₂[Fe₄S₄(H₂TMXPP)] resembles the isotropic shifts (11–18 ppm, 0 to 80°C) reported for the iron-sulfur cluster within the "high-potential" protein isolated from Chromatium.⁹¹ The demonstrated isotropic shift of the thiolate methylene groups in H₂TMXPP provides further confidence that the intact iron-sulfur cluster is indeed coordinated by this tetra-thiol-armed porphyrin.
II.D Conclusions

The ligand substitution reaction of \((\text{cation})_2[\text{Fe}_4\text{S}_4(\text{SEt})_4]\) with \(\text{H}_2\text{TMXPP}\) has shown that the tetrathiolo-armed porphyrin is capable of fully displacing the ethylthiolate ligand, when vacuum is used to drive the equilibrium reaction. The DMF-soluble portion of the reaction mixture contains both the iron-sulfur cluster and the porphyrin functionalities, with \(^1\text{H}\) NMR confirming coordination between the thiolate arms of the porphyrin and the iron-sulfur cluster. In at least one case, the isolated porphyrin/cluster compound contains a small amount of high-spin \((S = 5/2)\) iron(III) porphyrin impurity. Residual solvent (or lack of residual solvent) has a profound effect on the solubility of the isolated porphyrin/cluster compound. The general approach, employed for the first time in this work, of reacting tetrathiolo-armed porphyrins with an \([\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}\) cluster appears to be a fruitful avenue of pursuit for the synthesis of a host of new porphyrin/iron-sulfur cluster compounds for use as probes for better understanding the active site of sulfite reductase.

Future Work

1) Using \(^1\text{H}\) NMR spectroscopy, it should be possible to observe the ligand exchange reaction between \([\text{Fe}_4\text{S}_4(\text{SEt})_4]^{2-}\) and \(\text{H}_2\text{TMXPP}\) to create an intermediate species, \([\text{Fe}_4\text{S}_4(\text{SEt})_{4-x}(\text{H}_2\text{TMXPP})_x-\text{arms}]^{2-}\). With a molar ratio of one cluster to four porphyrin, there may be an opportunity to observe an entropy driven chelate effect.

2) The quality of \(^1\text{H}\) NMR spectra of these porphyrin/cluster compounds might be improved using DMF-\(d_7\), in that \((\text{Ph}_4\text{P})_2[\text{Fe}_4\text{S}_4(\text{H}_2\text{TMXPP})]\) appears to be more soluble in DMF than it is in DMSO.
3) The compound, \((\text{cation})_2[\text{Fe}_4\text{S}_4(\text{SCH}_2\text{Ph})_4]\), may prove to be a better spectroscopic reference for comparison with the \(\text{H}_2\text{TMXPP}\) ligand-cluster complex, as opposed to the \((\text{cation})_2[\text{Fe}_4\text{S}_4(\text{SEt})_4]\) that is used for the ligand exchange reaction.

4) Crystals of porphyrin/iron-sulfur cluster and metalloporphyrin/iron-sulfur cluster products, suitable for single-crystal x-ray structure determination, are desirable for confirmation of structure and the resultant structural details will enhance the interpretive value of the magnetic and spectroscopic properties of these first-generation model compounds.
Appendix

\(^1\text{H}\) Nuclear Magnetic Resonance Spectra
\(^13\text{C}\) Nuclear Magnetic Resonance Spectra
Mass Spectra
Fourier Transform Infrared Spectra
Ultraviolet-Visible Spectra
Additional Syntheses
Figure $^1$H-1 300 MHz $^1$H Spectrum of α-Bromo,α$'$-(3-formylphenoxy)-
p-xylene in CDCl$_3$ at 298 K
Figure $^1$H-2  300 MHz $^1$H Spectrum of $\alpha,\alpha'$-Bis(3-formylphenoxy)-
p-xylene in CDCl$_3$ at 298 K
Figure $^1$H-3 300 MHz $^1$H Spectrum of $\alpha$-Acetylmercapto,$\alpha'$-(3-formylphenoxy)-$p$-xylene in CDCl$_3$ at 298 K
Figure $^1$H-4  300 MHz $^1$H Spectrum of $\alpha,\alpha'$-Bis(acetylmercapto)-$p$-xylene in CDCl₃ at 298 K
Figure 1H-5 300 MHz $^1$H Spectrum of 5,10,15,20-Tetrakis[3-(p-acetylmercaptoxylyleneoxy)phenyl]porphyrin, H$_2$TAMXPP, in CDCl$_3$ at 298 K
Figure $^1$H-6  250 MHz $^1$H Spectrum of 5,10,15,20-Tetrakis[3-(p-mercaptoxylyleneoxy)phenyl]porphyrin, H$_2$TMXPP, in CDCl$_3$ at 298 K
Figure 1H-7 300 MHz $^1$H Spectrum of 5,10,15,20-Tetrakis[3-($p$-acetylmercaptoxylyleneoxy)phenyl]porphyrinatozinc(II), $[\text{Zn}^{II}(\text{TAMXPP})]$, in CDCl$_3$ at 298 K
Figure $^1$H-8 300 MHz $^1$H Spectrum of 5,10,15,20-Tetrakis
[3-(p-acetylmercaptoxylyleneoxy)phenyl]porphyrinato-
iron(III) Chloride, [Fe$^{III}$ (TAMXPP)Cl], in CDCl$_3$ at 298 K
Figure 1H-9 250 MHz $^1$H Spectrum of 5,10,15,20-Tetrakis[3-(p-bromoxyleneoxy)phenyl]porphyrin, H$_2$TBrXPP, in CDCl$_3$ at 298 K
Figure $^1$H-10  300 MHz $^1$H Spectrum of 2-(2-Hydroxyethoxy)benzaldehyde in CDCl$_3$ at 298 K
Figure \textsuperscript{1}H-11 300 MHz \textsuperscript{1}H Spectrum of 2-((2-Methanesulfonateethoxy)benzaldehyde in CDCl\textsubscript{3} at 298 K
Figure $^1$H-12 250 MHz $^1$H Spectrum of 2-(2-

Acetylmercaptoethoxy)benzaldehyde in CDCl$_3$ at 298 K
Figure 1H-13  300 MHz $^1$H Spectrum of 5,10,15,20-Tetrakis
[2-(2-acetylmercaptoethoxy)phenyl]porphyrin, H$_2$TAMEPP,
in CDCl$_3$ at 298 K
Figure 1H-14 300 MHz $^1$H Spectrum of 5,10,15,20-Tetrakis [2-(2-mercaptoethoxy)phenyl]porphyrin, H$_2$TMEPP, in CDCl$_3$ at 298 K
Figure $^1$H-15 300 MHz $^1$H Spectrum of 5,10,15,20-Tetrakis [2-(2-acetylimercaptoethoxy)phenyl]porphyrinatozinc(II), [Zn$^{II}$ (TAMEPP)], in CDCl$_3$ at 298 K
Figure 1H-16 300 MHz $^1$H Spectrum of 5,10,15,20-Tetrakis[2-(2-acetylmercaptoethoxy)phenyl]porphyrinatoiron(III) Chloride, [Fe$^{III}$(TAMEPP)Cl], in CDCl$_3$ at 298 K
Figure 1H-17  300 MHz $^1$H Spectrum of 2-(2-Hydroxyethoxy)-1-naphthaldehyde in CDCl₃ at 298 K
Figure 1H-18  300 MHz 1H Spectrum of 2-(2-Methanesulfonateethoxy)-1-naphthaldehyde in CDCl₃ at 298 K
Figure 1H-19  300 MHz $^1$H Spectrum of 2-(2-Acetylmercaptoethoxy)-1-naphthaldehyde in CDCl$_3$ at 298 K
Figure 1H-20 300 MHz $^1$H Spectrum of 5,10,15,20-Tetrakis [2-(2-acetylmercaptoethoxy)naphthyl]porphyrin, H$_2$TAMENP, in CDCl$_3$ at 298 K
Figure 1H-21 300 MHz $^1$H Spectrum of μ-Oxo-bis{5,10,15,20-tetrakis[3-(p-acetylmercaptoxylyleneoxy)phenyl]porphyrinato-iron(III)}, [Fe$^{III}$(TAMXPP)]$_2$O, in CDCl$_3$ at 298 K
Figure $^{13}$C-1  300 MHz $^{13}$C Spectrum of $\alpha$-Bromo,$\alpha'$-(3-formylphenoxy)-
p-$\text{xyylene}$ in CDCl$_3$ at 298 K
Figure 13C-2  300 MHz $^{13}\text{C}$ Spectrum of $\alpha,\alpha'$-Bis(3-formylphenoxy)-
p-xylene in CDCl$_3$ at 298 K
Figure $^{13}$C-3 300 MHz $^{13}$C Spectrum of $\alpha$-Acetylmercapto,

$\alpha'(3$-formylphenoxy)-$p$-xylene in CDCl$_3$ at 298 K
Figure $^{13}$C-4  300 MHz $^{13}$C Spectrum of $\alpha,\alpha'$-Bis(acetylimercapto)-
p-xylene in CDCl$_3$ at 298 K

![Chemical structure diagram]
Figure ¹³C-5 300 MHz ¹³C Spectrum of 5,10,15,20-Tetrakis [3-(p-acetylmercaptoxylyleneoxy)phenyl]porphyrin, H₂TAMXPP, in CDCl₃ at 298 K
Figure $^{13}\text{C}-6$ 250 MHz $^{13}\text{C}$ Spectrum of 5,10,15,20-Tetrakis [3-(p-mercaptoxylyleneoxy)phenyl]porphyrin, H$_2$TMXPP in CDCl$_3$ at 298 K
Figure $^{13}$C-7 300 MHz $^{13}$C Spectrum of 5,10,15,20-Tetrakis [3-(p-acetylmercaptoxylyleneoxy)phenyl]porphyrinatozinc(II), [Zn$^{II}$(TAMXPP)], in CDCl$_3$ at 298 K
Figure $^{13}$C-8 250 MHz $^{13}$C Spectrum of 5,10,15,20-Tetrakis [3-(p-bromoxylyleneoxy)phenyl]porphyrin, $\text{H}_2\text{TBrXPP}$, in CDCl$_3$ at 298 K
Figure $^{13}$C-9 300 MHz $^{13}$C Spectrum of 2-(2-Hydroxyethoxy)benzaldehyde

in CDCl$_3$ at 298 K
Figure $^{13}$C-10  300 MHz $^{13}$C Spectrum of 2-(2-Methanesulfonateethoxy)benzaldehyde in CDCl$_3$ at 298 K
Figure $^{13}$C-11 300 MHz $^{13}$C Spectrum of 2-

(2-Acetylmercaptoethoxy)benzaldehyde in CDCl$_3$ at 298 K
Figure $^{13}$C-12 300 MHz $^{13}$C Spectrum of 5,10,15,20-Tetrakis[2-(2-acetylmercaptoethoxy)phenyl]porphyrin, H$_2$TAMEPP, in CDCl$_3$ at 298 K
Figure 13C-13 300 MHz $^{13}$C Spectrum of 5,10,15,20-Tetrakis[2-(2-mercaptoethoxy)phenyl]porphyrin, H$_2$TMEPP, in CDCl$_3$ at 298 K
Figure 13C-14 300 MHz 13C Spectrum of 5,10,15,20-Tetrakis
[2-(2-acetylmercaptoethoxy)phenyl]porphyrinatozinc(II),
[Zn\textsuperscript{II} (TAMEPP)], in CDCl\textsubscript{3} at 298 K
Figure 13C-15  300 MHz $^{13}$C Spectrum of 2-(2-Hydroxyethoxy)-1-naphthaldehyde in CDCl$_3$ at 298 K
Figure 13C-16  300 MHz $^{13}$C Spectrum of 2-(2-Methanesulfonateethoxy)-1-naphthaldehyde in CDCl$_3$ at 298 K
Figure $^{13}\text{C}$-17  300 MHz $^{13}\text{C}$ Spectrum of 2-(2-Acetylmercaptoethoxy)-1-naphthaldehyde in CDCl$_3$ at 298 K
Figure $^{13}$C-18 300 MHz $^{13}$C Spectrum of 5,10,15,20-Tetrakis[2-(2-acetylmercaptoethoxy)naphthyl]porphyrin, 

$\text{H}_2\text{TAMENP}$, in CDCl$_3$ at 298 K
Figure MS-1  Mass Spectrum of α-Bromo,α'-[(3-formylphenoxy)-p-xylene
Figure MS-2  Mass Spectrum of α,α'-Bis(3-formylphenoxy)-p-xylene
Figure MS-3  Mass Spectrum of $\alpha$-Acetylmercapto,$\alpha'$-(3-formylphenoxy)-$p$-xylene
Figure MS-4  Mass Spectrum of α,α'-Bis(acetylmercapto)-p-xylene
Figure MS-5  FAB Mass Spectrum of 5,10,15,20-Tetrakis [3-(p-acetylmercaptoxyleneoxy)phenyl]porphyrin, H₂TAMXPP
Figure MS-6  FAB Mass Spectrum of 5,10,15,20-Tetrakis
[3-(p-mercaptoxylyleneoxy)phenyl]porphyrin,
H₂T MXPP
Figure MS-7 FAB Mass Spectrum of 5,10,15,20-Tetrakis
[3-(p-acetylmercaptoxylylenoxy)phenyl]porphyrinatozinc(II),
[Zn\textsuperscript{II}(TAMXPP)]
Figure MS-8  FAB Mass Spectrum of 5,10,15,20-Tetrakis
[3-(p-acetylmercaptoxylyleneoxy)phenyl]porphyrinato
iron(III) Chloride, [Fe^{III}(TAMXPP)Cl]

Calculated Isotopic Distribution
for C_{84}H_{68}N_{4}O_{8}S_{4}FeCl

Experimental Isotopic Distribution
for [Fe^{III}(TAMXPP)Cl]
Figure MS-9  FAB Mass Spectrum of 5,10,15,20-Tetrakis [3-(p-bromoxyleneoxy)phenyl]porphyrin, $\text{H}_2\text{TBrXPP}$

Calculated Isotopic Distribution
for $\text{C}_{76}\text{H}_{59}\text{N}_4\text{O}_4\text{Br}_4$

Experimental Isotopic Distribution
For $\text{H}_2\text{TBrXPP}$
Figure MS-10 Mass Spectrum of 2-(2-Hydroxyethoxy)benzaldehyde
Figure MS-11 Mass Spectrum of 2-(2-Methanesulfonateethoxy)-benzaldehyde
Figure MS-12 Mass Spectrum of 2-(2-Acetylmercaptoethoxy)benzaldehyde
Figure MS-13 FAB Mass Spectrum of 5,10,15,20-Tetrakis [2-(2-acetylmercaptoethoxy)phenyl]porphyrin, H₂TAMEPP

Calculated Isotopic Distribution for C₆₀H₅₅N₄O₈S₄

Experimental Isotopic Distribution For H₂TAMEPP
Figure MS-14 FAB Mass Spectrum of 5,10,15,20-Tetrakis [2-(2-mercaptoethoxy)phenyl]porphyrin, H₂TMEPP
Figure MS-15 FAB Mass Spectrum of 5,10,15,20-Tetrakis
[2-(2-acetylmercaptoethoxy)phenyl]porphyrinatozinc(II),
[Zn^II(TAMEPP)]
Figure MS-16  FAB Mass Spectrum of 5,10,15,20-Tetrakis [2-(2-acetylmercaptoethoxy)phenyl]porphyrinato iron(III) Chloride, [Fe$^{III}$ (TAMEPP)Cl]

Calculated Isotopic Distribution for C$_{60}$H$_{52}$N$_4$O$_8$S$_4$FeCl
Mirror Image
Experimental Isotopic Distribution for [Fe$^{III}$ (TAMEPP)Cl]
Figure MS-17  Mass Spectrum of 2-(2-Hydroxyethoxy)-1-naphthaldehyde
Figure MS-18  Mass Spectrum of 2-(2-Methanesulfonateethoxy)-1-naphthaldehyde
Figure MS-19  Mass Spectrum of 2-(2-Acetylmercaptoethoxy)-1-naphthaldehyde
Figure MS-20  FAB Mass Spectrum of 5,10,15,20-Tetrakis [2-(2-acetylmercaptoethoxy)naphthyl]porphyrin, H$_2$TAMENP
Figure MS-21  FAB Mass Spectrum of μ-Oxo-bis[5,10,15,20-tetrakis[3-(p-acetylmercaptoxylyleenoxy)phenyl]porphyrinato-iron(III)], \([\text{Fe}^{\text{III}}(\text{TAMXPP})]_2\text{O}\)

![Graph showing mass spectrum with peaks at 2906.8 and 2906.9.]

Calculated Isotopic Distribution for \(\text{C}_{168}\text{H}_{137}\text{Fe}_2\text{N}_8\text{O}_{17}\text{S}_8\)

Experimental Isotopic Distribution for \([\text{Fe}^{\text{III}}(\text{TAMXPP})]_2\text{O}\)
Figure IR-1 FTIR Spectrum of α-Bromo,α'-(3-formylphenoxy)-p-xylene (neat, KBr plates)
Figure IR-2 FTIR Spectrum of α,α'-Bis(3-formylphenoxy)-p-xylene
(KBr disc)
Figure IR-3 FTIR Spectrum of $\alpha$-Acetylmercaptoo,$\alpha'$-(3-formylphenoxy)-$p$-xylene (neat, KBr plates)
Figure IR-4 FTIR Spectrum of α,α'-Bis(acetylmercapto)-p-xylene

(KBr disc)
Figure IR-5  FTIR Spectrum of 5,10,15,20-Tetrakis
[3-(p-acetylmercaptoxylyleneoxy)phenyl]porphyrin,
H$_2$TAMXPP, (KBr pellet)
Figure IR-6 FTIR Spectrum of 5,10,15,20-Tetrakis [3-(p-mercaptoxylyleneoxy)phenyl]porphyrin, H$_2$TMXPP, (KBr pellet)
Figure IR-7 FTIR Spectrum of 5,10,15,20-Tetrakis

[3-(p-acetylmercaptoxylyleneoxy)phenyl]porphyrinatozinc(II),
[Zn$^\text{II}$(TAMXPP)], (KBr pellet)
Figure IR-8  FTIR Spectrum of 5,10,15,20-Tetrakis
[3-\((p\text{-acetylmercaptocarboxylato})\text{phenyl}\)]porphinatoiron(III)
Chloride, [Fe\text{III}\text{(TAMXPP)Cl}] (KBr pellet)
Figure IR-9  FTIR Spectrum of 5,10,15,20-Tetrakis
[3-(p-bromoxyleneoxy)phenyl]porphyrin, H₂TBrXPP,
(KBr pellet)
Figure IR-10 FTIR Spectrum of 2-(2-Hydroxyethoxy)benzaldehyde

(KBr disc)
Figure IR-11 FTIR Spectrum of 2-(2-Methanesulfonateethoxy) benzaldehyde (KBr disc)
Figure IR-12 FTIR Spectrum of 2-(2-Acetylmercaptoethoxy)benzaldehyde
(neat, KBr plates)
Figure IR-13 FTIR Spectrum of 5,10,15,20-Tetrakis [2-(2-acetylmercaptoethoxy)phenyl]porphyrin, H₂TAMEPP, (KBr pellet)
Figure IR-14 FTIR Spectrum of 5,10,15,20-Tetrakis[2-(2-mercaptoethoxy)phenyl]porphyrin, H$_2$TMEPP, (KBr pellet)
Figure IR-15 FTIR Spectrum of 5,10,15,20-Tetrakis

[2-(2-acetylimercaptoethoxy)phenyl]porphyrinatozinc(II), [Zn$^{II}$ (TAMEPP)], (KBr pellet)
Figure IR-16 FTIR Spectrum of 5,10,15,20-Tetrakis [2-(2-acetylmercaptoethoxy)phenyl]porphyrinatoiron(III)

Chloride, [Fe\textsuperscript{III}(TAMEPP)Cl], (KBr pellet)
Figure IR-17 FTIR Spectrum of 2-(2-Hydroxyethoxy)-1-naphthaldehyde
(KBr disc)
Figure IR-18 FTIR Spectrum of 2-(2-Methanesulfonateethoxy)-1-naphthaldehyde (KBr disc)
Figure IR-19 FTIR Spectrum of 2-(2-Acetylmercaptoethoxy)-1-naphthaldehyde (KBr disc)
Figure IR-20 FTIR Spectrum of 5,10,15,20-Tetrakis [2-(2-acetylmercaptoethoxy)naphthyl]porphyrin, $\text{H}_2\text{TAMENP}$, (KBr pellet)
Figure IR-21 FTIR Spectrum of μ-Oxo-bis{5,10,15,20-Tetrakis [3-(p-acetylmercaptoxyleneoxy)phenyl]porphyrinato-iron(III)}, [Fe$^{III}$ (TAMXPP)]$_2$O, (CsI pellet)
Figure IR-22 FTIR Spectrum of 5,10,15,20-Tetraphenylporphyrin, H₂TPP, (KBr pellet)
Figure IR-23 FTIR Spectrum of 5,10,15,20-Tetraphenylporphyrinato-
zinc(II), [Zn$^{II}$ (TPP)], (KBr pellet)
Figure UV-vis-1  The UV-visible spectrum of 5,10,15,20-Tetrakis[3-(p-acetylmercaptoxylyleneoxy)phenyl]porphyrin, $\text{H}_2\text{TAMXPP}$, in CHCl$_3$
Figure UV-vis-2 The UV-visible spectrum of 5,10,15,20-Tetrakis [3-(p-mercaptopxyleneoxy)phenyl]porphyrin, H₂TMXPP, in CHCl₃
Figure UV-vis-3  The UV-visible spectrum of 5,10,15,20-Tetrakis [3-(p-bromoxyllyleneoxy)phenyl]porphyrin, H$_2$TBrXPP, in CHCl$_3$
Figure UV-vis-4  The UV-visible spectrum of 5,10,15,20-Tetrakis[2-(2-acetylmercaptoethoxy)phenyl]porphyrin, H$_2$TAMEPP, in CHCl$_3$
Figure UV-vis-5  The UV-visible spectrum of 5,10,15,20-Tetrakis[2-(2-mercaptoethoxy)phenyl]porphyrin, H$_2$TMEPP, in CHCl$_3$
Figure UV-vis-6 The UV-visible spectrum of 5,10,15,20-Tetrakis[2-(2-acetylmercaptoethoxy)naphthal]porphyrin, H$_2$TAMENP, in CHCl$_3$
Figure UV-vis-7  The UV-visible spectrum of 5,10,15,20-Tetrakis [3-(p-acetylmercaptoxylyleneoxy)phenyl]porphyrinatozinc(II), [Zn^{II}(TAMXPP)], in CHCl₃
Figure UV-vis-8  The UV-visible spectrum of 5,10,15,20-Tetrakis[2-(2-acetylmercaptoethoxy)phenyl]porphyrinatozinc(II), [Zn^{II}(TAMEPP)], in CHCl₃
Figure UV-vis-9  The UV-visible spectrum of 5,10,15,20-Tetrakis [3-(p-acetylmercaptoxylyleneoxy)phenyl]porphyrinatoiron(III) Chloride, [Fe\textsuperscript{III}(TAMXPP)Cl], in CHCl\textsubscript{3}
Figure UV-vis-10  The UV-visible spectrum of 5,10,15,20-Tetrakis [2-(2-acetylmercaptoethoxy)phenyl]porphyrinatoiron(III) Chloride, [FeIII(TAMEPP)Cl], in CHCl₃
Figure UV-vis-11 The UV-visible spectrum of μ-Oxo-bis{5,10,15,20-Tetrakis[3-(p-acetylmercaptoxylyleneoxy)phenyl]porphyrinatoiron(III)}, [FeIII(TAMXPP)]2O, in CHCl₃
6-Methylsalicylaldehyde

6-Methylsalicylaldehyde was synthesised using the Reimer-Tieman reaction as outlined in a procedure published by Bruce et al. A three neck flask fitted with a condenser, mechanical stirrer, and addition funnel, m-cresol (108 g, 1 mol) was added to a solution of NaOH (80 g, 2 mol) in 400 ml of water. A slight excess of chloroform, (ethanol-free, but not dried; 164 ml, 2.04 mol) was added dropwise over a two hour period. After the addition was complete, the reaction mixture was heated on a steam bath for one hour. The reaction mixture was cooled to room temperature and neutralized with 10% sulfuric acid. This mixture was then steam distilled to isolate the 6-methylsalicylaldehyde, 4-methylsalicylaldehyde, and residual m-cresol from the 2-methyl-4-hydroxybenzaldehyde isomer. The steam distillate was then extracted with diethyl ether. The 4-methylsalicylaldehyde and 6-methylsalicylaldehyde isomers were separated on the basis of pKa by repeatedly extracting the diethyl ether solution with aqueous 5% (w/v) Na₂CO₃, pH 11.7. The resultant oil was chromatographed in 5 g batches on 60 g of silica gel using 1% ethyl acetate in hexanes as the eluant, with 6-methylsalicylaldehyde eluting first and m-cresol being more strongly retained. The isolated yield was 8%, 10.6 g.

¹H NMR (CDCl₃, 298 K, 300 MHz, reference TMS δ=0.0): δ=2.60 (s, methyl), δ=6.70 (d, H), δ=6.80 (d, H), δ=7.36 (m, H), δ=9.81 (s, OH), δ=11.90 (s, CHO)

2-(3-Hydroxypropoxy)-6-methylbenzaldehyde

2-(3-Hydroxypropoxy)-6-methylbenzaldehyde was synthesised by alkoxyalkylation of 6-methylsalicylaldehyde with bromopropanol as outlined in the procedure of Almog et al. 6-methylsalicylaldehyde (10.1 g, 75 mmol) was added to an
aqueous solution (150 ml) of NaOH (3.2 g, 80 mmol) in a three necked flask fitted with a reflux condensor and a mechanical stirrer. 3-Bromo-1-propanol (10.4 g, 75 mmol) was added dropwise over a 10 minute period. After the addition was complete, the reaction mixture was heated on a steambath for 24 hours. The resultant mixture was cooled and extracted with chloroform. The recovered red oil was chromatographed on silica gel using 1:1 ethyl acetate/hexanes as the eluate, with the product eluting after the starting material (6-methylsalicylaldehyde). Removal of the eluting solvent under reduced pressure yielded a red oil (5.5 g, 28 mmol) for a yield of 37%.

$^1$H NMR (CDCl$_3$, 293 K, 300 MHz, reference CHCl$_3$ $\delta$=7.26): 1.60 (br s, OH), 2.55 (s, CH$_3$), 2.07 (m, CH$_2$), 3.83 (br m, CH$_2$), 4.18 (m, CH$_2$), 6.7-6.8 (m, 2 CH), 7.33 (t, CH), 10.52 (s, CHO).

1,2,4,5-Tetrakis-[3-(2-formyl-3-methylphenoxy)propyl]benzenetetraacetate

1,2,4,5-Tetrakis-[3-(2-formyl-3-methylphenoxy)propyl]benzenetetraacetate was synthesised by alcoholysis of an acyl halide as outlined in the procedure of Almog. 28

2-(2-Hydroxyethoxy)-6-methylbenzaldehyde (5.5 g, 28 mmol) was dissolved in dry THF, dry triethylamine (3.0 g, 30 mmol) was added, and the flask was placed in a dry ice bath. Pyromellitic acid chloride (3.35 g, 7 mmol) in dry THF was added dropwise over a 5 minute period, using a cannula to prevent the introduction of moisture. After the addition was complete the reaction mixture was allowed to come to room temperature overnight. Triethylamine hydrochloride was filtered off and the THF was removed by rotary evaporation. The resultant oil was dissolved in chloroform washed with 5% aqueous sodium bicarbonate, dried over magnesium sulfate and the chloroform solvent removed under vacuum. The orange-brown oil was chromatographed on silica gel using 10%
diethyl ether in methylene chloride. The yield of the recovered yellow oil was 40% (2.83 g, 3 mmol).

$^1$H NMR (CDCl$_3$, 298 K, 90 MHz, reference CHCl$_3$ δ=7.26): 2.35 (m, 4CH$_2$), 2.85 (s, 4CH$_3$), 4.25 (m, 4CH$_2$), 4.72 (m, 4CH$_2$), 6.7-7.1 (m, 8CH), 7.2-7.3 (m, 4CH), 8.0 (s, 2 CH), 10.87 (s, 4CHO).

5,10,15,20-[Pyromellitoyl(tetrakis-2-oxypropoxy-6-methylphenyl)]porphyrin

The synthesis of a C3-capped porphyrin with a locking methyl group in the distal ortho position was attempted using the previously described tetraaldehyde in a reaction procedure akin to that used to produce H$_2$TAMXPP. The reaction yielded a small amount of porphyrin ≈2% that was not effectively separated from the polypyrrolic by-products.
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(39) Occasionally during the synthesis of 2-(2-acetylmercaptoethoxy)benzaldehyde, an unusually large amount of the thionoacetate was produced (20% by NMR integration). The thionoacetate and thioloacetate isomers can be separated chromatographically on silica gel. However, the more favorable action is to convert the less stable thionoacetate compound into the more stable thioloacetate by refluxing the mixture of isomers in absolute ethanol for 30 minutes.


(43) PANIC: Parameter Adjustment in NMR by Iteration Calculation, is a minicomputer version of the LAOCOON type programs used in large computer systems, and is available in the ASPECT 3000 Computer Program Library.


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