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Eugene G. Mueller

ENTITLED

Linkage of Bisporphyrin Complexes to Generate a Chiral Molecule

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE Bachelor of Science in Chemistry DEGREE OF

Instructor in Charge

APPROVED:

HEAD OF DEPARTMENT OF Chemistry
LINKAGE OF BISPORPHYRIN COMPLEXES TO GENERATE AN EIGHT COORDINATE, CHIRAL MOLECULE

By Eugene G. Mueller

Thesis for the Degree of Bachelor of Science in Chemistry

College of Liberal Arts and Sciences University of Illinois Urbana, Illinois

1987
DEDICATION

To my beloved parents, Eugene J. and Marjorie B. Mueller, in thanks for both their nature and nurture; they have instilled a desire and sense of duty to achieve all that I can with the talents which have been bestowed upon me. Their encouragement and patience have been matched only by their love. Thank you for being such superlative parents.

To Mrs. Elizabeth Halloran whose class so favorably introduced chemistry to me; to Dr. Steven S. Zumdahl whose contagious enthusiasm for the science and excellent teaching of it convinced me that chemistry was, indeed, my field of choice; and to Dr. Kenneth S. Suslick whose generous employment of me these past three years has allowed me to discover that I wish to make a career in research science. Thank you for your time, effort and help.
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I. Introduction

Synthesis of an eight coordinate, chiral complex has a Hillarian* appeal, for no such molecule has been reported in the literature. A compound in which two tetraphenylporphyrin (TPP) rings, Figure 1a, sandwich a single metal would be eight coordinate, and well-chosen interporphyrin linkages would render the molecule chiral.

In space-filling models, the pyrrolic β-hydrogens restrict the angle between the plane of the porphyrin ring and the plane of the phenyl rings to a range of 60° to 120°: the phenyl groups markedly protrude above and below the porphyrin plane. Rotation of one TPP ring of a sandwich complex relative to the other TPP ring would, therefore, be restrained by the steric interactions of the protruding phenyl groups. In solution, the two rings constantly move between the extreme conformations mutually imposed by the phenyl groups; at one extreme, the phenyl rings of one TPP ring abut those of the other to form a right-handed helix while a left-handed helix arises from the other extreme, as is shown schematically in Figure 2. If a population of sandwich complexes were randomly frozen in an extreme conformation, a racemic mixture would result, and the enantiomers could be separated and isolated. A linkage agent which just spanned the distance between the para-positions of abutting phenyl groups would freeze the sandwich complex in

*Hillarian is an adjective coined to express the desire to do something simply "... because it's there" and can be done.
Figure 1: Drawing of Tetraphenylporphyrins

a: $\text{H}_2\text{TPP}$   \hspace{1cm} R = H
b: $\text{H}_2\text{TCP}$   \hspace{1cm} R = $\text{CO}_2\text{H}$
c: $\text{H}_2\text{TMFP}$  \hspace{1cm} R = $\text{CO}_2\text{CH}_3$
**Figure 2: Schematic Drawing of a Linked Species**

The corners of the squares represent the porphyrin phenyl groups.
either extreme conformation at random and generate the first chiral, eight coordinate complex.

The synthesis of TPP derivatives in which the para-position of the phenyl groups is occupied by an acyl moiety is facile, and reactions which interconvert acyl groups are well-known. Therefore, linkage through amidation of para-acyl moieties by a diamine was thus planned. Using space-filling models, 1,3-diaminopropane (DAP) was chosen to be of appropriate length to span the dimer. Uranium(IV) was chosen as a suitable metal ion, for its valence and large size will allow the coordination of two dianionic porphyrinate rings to form a complex whose symmetry will not be complicated by the presence of counter ions.

The $\mu$-oxo-[porphyrinate iron(III)] derivative of TPP, Figure 3a, is well characterized and would serve as an excellent model for eventual linkage of a uranium(IV) bisporphyrinate complex. In addition, facile acid cleavage and demetallation/remetallation of a linked $\mu$-oxo dimer would yield a face-to-face porphyrin. Several such molecules have been synthesized and found to model natural systems and have interesting chemical properties.

Iron porphyrins in which a copper(II) ion is held near the iron(III) have been prepared and used as models for the cytochrome-C-oxidase active site, and direct reduction of molecular oxygen to water has been reported using a face-to-face cobalt porphyrin dimer. Myoglobin and hemoglobin have
Figure 3: Drawing of \( \mu \)-oxo Dimers

a: \([\text{Fe(PP)}]_2O\) \(R = H\)
b: \([\text{Fe(TCPP)}]_2O\) \(R = \text{CO}_2\text{H}\)
c: \([\text{Fe(TMPP)}]_2O\) \(R = \text{CO}_2\text{CH}_3\)
also been modeled by compounds in which two porphyrin rings are held in close contact. In addition, linkage groups of varying length could be employed to generate a series of dimers in which the distance between the porphyrin rings differs; such a series would reveal useful information regarding orbital interaction. Attempting to link the porphyrin rings of a μ-oxo dimer, then, would be doubly productive, allowing development of an efficient linkage system using an easily prepared species and generating a product which is itself chemically interesting.

II. Discussion

A. Choice of the Porphyrin System

Tetra(paracarboxyphenyl)porphyrin (TCPP), Figure 1b, was the derivative selected as the first choice for linkage, for several convenient synthetic routes from carboxylic acids to amides which do not require acid catalysis exist. A nonacidic synthesis is necessary due to the susceptibility of μ-oxo dimers to acid cleavage. The routes from carboxylic acids to amides require anhydrous conditions, however, and the TCPP μ-oxo dimer ([Fe(TCPP)]2O), Figure 3b, was water soluble due to deprotonation of the carboxyl groups. Acidification of the aqueous solution led to the cleavage of the μ-oxo dimer before the carboxylate groups were reprotonated. Inability to generate (FeTCPP)2O in an organic solvent necessitated the substitution of the methyl ester derivative of TCPP, tetra-
(paracarbomethoxyphenyl)porphyrin (TMPP), Figure 1c. Generation of [Fe(TMPP)]_2O, Figure 3c, in organic solvent proved to be facile.

B. Initial Linkage Attempts

The aminolysis of esters to form amides is a thermodynamically favored process. Therefore, the first set of attempts to link the porphyrin rings of the methyl ester $\mu$-oxo dimer were simple additions of DAP to refluxing solutions of (FeTMPP)$_2$O. Slow addition of the DAP and high dilution were employed in these reactions in order to avoid inter-dimer linkages leading to $\mu$-oxo polymers, Table 1.

Linkage was first attempted using toluene as the solvent. The visible spectrum and FAB mass spectrogram gave no evidence of reaction. The next linkage reactions were carried out in refluxing o-dichlorobenzene. (FeTMPP)$_2$O was more soluble in this polar solvent than it had been in toluene, and this solvent's higher boiling point (178°C versus 111°C for toluene) should have also enhanced the chances of amidation by faster and more complete removal of the methanol produced by the reaction.

Eight hours after complete addition of the DAP to a refluxing o-dichlorobenzene solution of [Fe(TMPP)]$_2$O, a precipitate was noticed. This solid was insoluble in dichloromethane, tetrahydrofuran (THF), and acetonitrile; methanol affected some solution, but the visible spectrum showed only tailing and gave no indication of porphyrin. An off-white,
Table 1: Initial Linkage Attempts

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( [\text{Fe(TMPP)}]_2O )</th>
<th>( \text{DAP} )</th>
<th>time of addition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \mu\text{mol} )</td>
<td>( V_0 )</td>
<td>( \text{conc} )</td>
</tr>
<tr>
<td>toluene</td>
<td>2.9</td>
<td>200</td>
<td>14.6</td>
</tr>
<tr>
<td>o-dichlorobenzene</td>
<td>2.9</td>
<td>200</td>
<td>14.6</td>
</tr>
<tr>
<td></td>
<td>3.1</td>
<td>200</td>
<td>15.7</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>200</td>
<td>14.9</td>
</tr>
</tbody>
</table>
water-soluble, nonporphyrinic solid remained on the frit following the methanol rinse. Refluxing o-dichlorobenzene was too harsh an environment for [Fe(TMPP)]_{2}O. Two other linkage attempts were also performed, but visible spectra of both reaction products indicated demetallation of the (FeTMPP)_{2}O to H_{2}TMPP. Table 1 summarizes the initial linkage attempts.

C. Modelling Systems

Due to the difficulties encountered in generating a linked μ-oxo dimer species and the delay inherent in characterizing products by mass spectrometry, a model system whose products would be detectable by gas chromatography was sought. DAP was therefore added to methyl benzoate in refluxing o-dichlorobenzene. No reaction was detectable even when the solvent and reagents were purified, the solutions refluxed under nitrogen, and acid catalysis employed.

The desired diamide was obtained by refluxing methyl benzoate and DAP together in the absence of solvent; however, the gas chromatographic analysis of this compound, a solid at room temperature, was difficult due to the extremely high injection port and column temperatures required (350°C and 250°C, respectively). Substituting methyl propanoate for methyl benzoate alleviated the problem, but the products were still very difficult to analyse by gas chromatography.

D. n-Butyllithium Mediated Linkage Attempts

Based upon the method of Yang, Cannon, and Rose, n-Butyl-
lithium (BuLi) was mixed with DAP to generate the dilithiated DAP dianion (Li₂DAP), a much more active nucleophile. The first two reactions, labeled D and E, using Li₂DAP were run at concentrations high relative to those of the earlier linkage attempts, approximately 1 mM. The quantities of reactants were on the order of µmoles, and the total volume of the reaction solutions were around 2.5 ml, Table 2.

Chromatography of the Reaction D THF solution over silica gel using dichloromethane as eluent separated the a new species. The visible spectrum showed primarily μ-oxo dimer peaks, but a new peak at 505.2 nm fell in the vicinity of a Fe(TMPP)(Cl) peak. A shoulder on the Soret fell on the peak's red side; the Soret of Fe(TMPP)(Cl) is red shifted from the Soret of [Fe(TMPP)]₂O while linkage was expected to induce a blue shift.⁵

The fraction was concentrated and submitted for FAB mass spectrometry. A visible spectrum of this sample showed essentially complete conversion of the μ-oxo dimer species to an iron(III) porphyrinato chloride moiety, Figure 4. The FAB mass spectrogram confirmed this conversion and revealed the nature of the reaction which had occurred at the methyl ester groups: amidation by Li₂DAP without linkage. Such an amidation would result in the displacement of an -OCH₃ group by an -NH(CH₂)₃NH₂ group for a net mass gain of 41 amu. Reaction D product's mass spectrogram, Figure 5, displayed a very intense peak at 1,069.6, corresponding to a iron(III) porphyrinato moiety where
Table 2: Formulations of Reactions D and E

<table>
<thead>
<tr>
<th>Reaction</th>
<th>[Fe(TMPP)]_2O</th>
<th>Li_2DAP</th>
<th>time of addition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>µmol V₀ (THF)</td>
<td>conc -M</td>
<td>µmol V_added</td>
</tr>
<tr>
<td>D</td>
<td>2.8 1.4</td>
<td>1.4m</td>
<td>14.3 1.4</td>
</tr>
<tr>
<td>E</td>
<td>1.6 2.0</td>
<td>0.8m</td>
<td>6.5 0.65</td>
</tr>
</tbody>
</table>
Figure 4: Visible Spectrum of Reaction D Product

peak locations: 376.4, 418.0, 507.6 nm
Figure 5: FAB Mass Spectrogram of Reaction D Product

1,069.6 tetra-(DAP amidated) Fe(TMPP)(Cl), Figure 6
1,027.6 loss of a 56 amu fragment
968.6 loss of CONH(CH₂)₃NH₂
1,013.6 tri-(DAP amidated) Fe(TMPP)(Cl)
four amidations by Li₂DAP had occurred, Figure 6. The cluster at 1,028 was due to a species with only three amidations while the peak at 968.6 was accounted for by a loss of -CONH(CH₂)₃-NH₂; the peak at 1,013.6 might have been due to a loss of a 56 amu fragment from the peak at 1,069.6 or to a species with three amidations and one hydrolysis of the ester groups (each hydrolysis results in a mass loss of 14). The peaks at 1,083.6 and 1,102.6 were analogous to Fe(TMPP)(Cl) peaks at 914 and 935.

Reaction D, then, yielded starting material and amidation at all of the ester groups of a TMPP ring with no linkage between the rings; exposure of the product to dichloromethane with its trace hydrochloric acid formation resulted in μ-oxo dimer cleavage over time.

The procedure followed for Reaction E was identical to that of Reaction D without long exposure of the product to dichloromethane. The reaction was quenched with five drops of water. The visible spectrum of the Reaction E solution was a characteristic μ-oxo dimer spectrum with a shoulder on the Soret and a small peak just to the red side of the peak at 609.2 nm suggestive of multiple species in solution.

The complicated mass spectrogram of the product, Figure 7, indicated that amidation of the esters but not linkage of the porphyrin rings had occurred. Random numbers of amidations and hydrolyses accounted for the peak locations though not the peak pattern observed in the spectrogram, and common amine and amide
Figure 6: Drawing of Reaction D Product

\[ R = \text{CONH(CH}_2\text{)}_3\text{NH}_2 \]
Primary pattern: successive loss of 28 amu fragments from octa-(DAP amidated) [Fe(TMPP)]_2O

Secondary pattern: successive loss of 28 from another species or a minor elimination of 14 amu fragments
rearrangements also failed to adequately explain the spectrogram.

A species with eight amidations of the methyl ester groups by DAP, Figure 8a, would have a mass of 2,146; a peak corresponding to this moiety would be expected if the spectrogram resulted from random amidation and hydrolysis, for random amidation should produce an octa-amidated species as well as species with lower numbers of amidations. The pattern of the spectrogram and the absence of the octa-amidated \( \mu \)-oxo dimer peak would both be explained if this species were the major component of the sample and underwent a highly probable fragmentation. Successive loss of 28 amu fragments would produce the pattern observed if the initial molecule had one lithium ion coordinated to it to give a total mass of 2,153; such coordination was clearly seen in later spectrograms. The minor peaks which fell exactly between and mirrored the major peaks were consistent with either the same fragmentation from a species whose mass was 14 amu less than that of the octa-amidated \( \mu \)-oxo dimer or from a minor fragmentation which resulted in the loss of 14 amu fragments.

The fragmentation interpretation of the Reaction E spectrogram was enhanced by the large amount of \([Fe(TMPP)]_2O\) which remained unreacted and by the fact that the Reaction D product had been amidated in all of its positions. The appearance of two weak peaks at 14 and 28 amu less than the Reaction D molecular ion and the coincidence of peaks expected by this pattern
Figure 8: Drawing of Substituted $\mu$-oxo Dimers

a: Reaction E product 
R = CONH(CH$_2$)$_3$NH$_2$

b: Reaction J product 
x R = CONH(CH$_2$)$_3$NH$_2$
(8-x)R = CO$_2$CH$_3$

The most common x is three or four.
with the peaks assigned as three amidations and as three amidations/one hydrolysis or loss of a 56 amu fragment also greatly enhanced the scheme. Reaction E product, then, was most probably the species resulting from amidation of all of the methyl ester groups of \([\text{Fe(TMPP)}]_2\text{O}\).

Two reactions, labeled F and G, were run under high dilution in an attempt to increase the time that elapsed between the first amidation on a porphyrin ring and the next encounter with a free molecule of \(\text{Li}_2\text{DAP}\); such an increase would have enhanced the probability of linkage by reducing the chances of attack on the ester by a free \(\text{Li}_2\text{DAP}\) while not affecting the probability of an intramolecular reaction. These reactions were performed in the same manner as Reactions D and E, Table 3.

Reaction F generated no porphyrinic product; visible spectra showed only tailing, and its mass spectrogram showed no peaks above 535 amu. Silica gel TLC of the Reaction G solution gave ambiguous results; only the faintest of bands other than \([\text{Fe(TMPP)}]_2\text{O}\) appeared, and they were very near to the starting material. The visible spectrum and the mass spectrogram of the product showed the primary component of the Reaction G solution to be \([\text{Fe(TMPP)}]_2\text{O}\).

Reactions H and I sought to ensure reaction while solving the problem of aminolysis without linkage. Highly dilute solutions of \(\text{Li}_2\text{DAP}\) were added to solutions of \((\text{FeTMPP})_2\text{O}\) of similar concentration to those used in Reactions D and E,
<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\mu$mol</th>
<th>$V_0$ (THF)</th>
<th>conc</th>
<th>$\mu$mol</th>
<th>$V_{added}$</th>
<th>time of addition</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe(TMPP)]$_2$O</td>
<td></td>
<td></td>
<td></td>
<td>Li$_2$DAP</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>2.8</td>
<td>200.0</td>
<td>14.0$\mu$</td>
<td>12.2</td>
<td>200.0</td>
<td>6h</td>
</tr>
<tr>
<td>G</td>
<td>11.2</td>
<td>200.0</td>
<td>56.0$\mu$</td>
<td>49.0</td>
<td>140.0</td>
<td>4h</td>
</tr>
</tbody>
</table>
Table 4. Visible spectroscopy and FAB mass spectrometry again failed to detect any moieties but (FeTMPP)$_2$O. The DAP, however, had been stored under the same rubber septum for some time, and its dryness was suspect; it was purified.

Reaction J employed $\mu$-oxo dimer concentrations similar to and Li$_2$DAP concentrations half of those used in Reactions D and E, Table 4. The visible spectrum showed the product to be a $\mu$-oxo dimer species. The FAB mass spectrogram, Figure 9, was consistent with amidation without linkage; based upon the peak intensities, the most common number of amidations per (FeTMPP)$_2$O was three or four and the most frequent number per porphyrin ring was two, Figure 8b. The clusters at 1,860, 1,902, 1,944, 1,987, 2,029, and 2,071 corresponded to one, two, three, four, five, and six amidations, respectively; coordination of one lithium atom to these species accounted for the small peaks of seven amu greater mass. Similarly, the peaks at 901, 944, 985, 1,028, and 1,069 were consistent with zero, one, two, three, and four amidations of single porphyrin rings.

The Reaction J product was treated with sixteen equivalents of n-BuLi; some precipitation occurred. $\mu$-oxo dimer features dominated the visible spectrum was of the solution. The solution was taken to dryness, but the resultant solid was not soluble enough in methanol, THF, or dichloromethane for FAB mass spectrometry.

Reaction K employed the same concentrations of (FeTMPP)$_2$O
Table 4: Formulations of Reactions H – K

<table>
<thead>
<tr>
<th>Reaction</th>
<th>[\text{Fe(TMPP)}]_2\text{O}</th>
<th>Li\text{2PAP}</th>
<th>time of addition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\mu\text{mol})</td>
<td>(V_0) (THF)</td>
<td>conc</td>
</tr>
<tr>
<td>H</td>
<td>2.5</td>
<td>10.0</td>
<td>0.25m</td>
</tr>
<tr>
<td>I</td>
<td>2.9</td>
<td>10.0</td>
<td>0.29m</td>
</tr>
<tr>
<td>J</td>
<td>1.3</td>
<td>2.0</td>
<td>0.65m</td>
</tr>
<tr>
<td>K</td>
<td>1.6</td>
<td>2.0</td>
<td>0.80m</td>
</tr>
</tbody>
</table>
The peaks at 1860, 1902, 1944, 1987, 2029, and 2071 are the mono- to hexa- (DAP amidated) \([\text{Fe(TMPP)}]_2\text{O}\), Figure 8b; the peaks from 901 to 944 represent the same series of amidation on \([\text{Fe(TMPP)}]\).
and Li$_2$DAP, but a 14.5-fold excess of n-BuLi was added to DAP to generate the Li$_2$DAP, Table 4. The visible spectrum of the product possessed the features characteristic of $\mu$-oxo dimer, and the FAB mass spectrogram was again consistent with (FeTMP)$_2$O undergoing an average of three or four amidations without linkage per $\mu$-oxo dimer and principally two amidations per porphyrin ring.

A vast excess of n-BuLi was added to a THF solution of the Reaction K product, and this solution was brought to reflux. Considerable tailing in the visible spectrum of the resultant solution revealed that decomposition had occurred; the FAB mass spectrogram had no peaks corresponding to any porphyrin peaks, amidated or otherwise.

E. Other Routes to be Pursued

The failure to effect linkage does not lie with the method of aminolysis, for amidation through n-butyllithium mediation is evident. Furthermore, even if Li$_2$DAP is not generated in the first instance, the amine groups on the amidated $\mu$-oxo dimer's from Reactions J and K certainly were deprotonated by n-BuLi treatment so that an activated amine was in a position to make the linkage.

Either the free amine group of a DAP amide experiences a steric hindrance not evident from the space-filling models or entropic factors prevent the linkage. Hypothesizing the latter alternative to be the more likely, a linkage attempt utilizing 2,2-dimethyl-1,3-diaminopropane (Me$_2$DAP) will be run. The
methyl groups should kink the amino group of a $\text{Me}_2\text{DAP}$ amide into the vicinity of a methyl ester group on the other porphyrin ring.

F. Synthesis of $\text{U(TMPP)}_2$
performed with Stanley Milam

The synthesis of bis[tetra(paracarbomethoxyphenyl)porphyrinato] uranium(IV) ($\text{U(TMPP)}_2$) based upon the synthesis of $\text{U(TPP)}_2$ was attempted. A solution of uranium(IV) tetra(diethylamide) ($\text{U(NEt}_2)_4$) was added to a solution of $\text{H}_2\text{TMPP}$. Chromatography of the reaction solution separated four fractions other than $\text{H}_2\text{TMPP}$ and immobile residue; the visible spectra of the reaction mix and the three fractions which were collected all display the characteristics of free base porphyrin. Since the reaction between porphyrin and $\text{U(NEt}_2)_4$ is necessarily dissociative and therefore generates diethylamide, these fractions were suspected to be mono-, di-, tri-, and tetra-diethylamidated free base species. FAB mass spectrometry of the first two fractions confirmed the hypothesized identities of the species. Another method will be required to synthesize $\text{U(TMPP)}_2\text{O}$.

III. Experimental

A. Synthesis of Starting Materials

1. Synthesis of Free Base Porphyrins

Free base tetraphenylporphyrin derivatives were synthesized using the method of Adler.$^6$ Equimolar amounts of
pyrrole and the appropriately para-substituted benzaldehyde were added to refluxing propanoic acid; the solutions were approximately 0.24 M in the two reagents. The reflux was maintained for thirty minutes, and the solution was then allowed to cool to room temperature overnight with constant stirring. The crystalline, purple precipitate was filtered from the black solution, rinsed with methanol, and dried. Several different methods to retrieve a second crop of porphyrin from the propanoic acid solution were not expedient.

The crude free base porphyrin was refluxed in ethanol-free chloroform with excess 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to oxidize the analogous chlorin which was present as an impurity. After four hours, the reflux was stopped, and the solution was filtered through alumina; the purified porphyrin passed through the column while the reflux byproducts and unreacted DDQ remained on the alumina. The porphyrin was recrystallized from chloroform/hexanes and dried.

2. Synthesis of Metalloporphyrins

Metallation to the iron(III) chloride species was accomplished by refluxing overnight a N,N'-dimethylformamide (DMF) solution of free base porphyrin with excess iron(II) chloride. The DMF was removed by heating under an air stream, and the residue was dissolved in dichloromethane. After filtration through Celite, the solution was washed with a small amount of concentrated hydrochloric acid. The solution of iron(III)porphyrinatochloride was rotary evaporated with concomitant
hexanes addition to effect recrystallization. μ-oxo dimers were prepared from the iron(III)porphyrinatochlorides by stirring an organic phase containing the porphyrin species over an aqueous base solution.

3. Synthesis of Specific Porphyrins

The synthesis of H₂TCPP proceeded according to the general outline, with the exception that the porphyrin was soluble in methanol. The methanol rinse therefore dissolved the product which was then recrystallized from methanol/chloroform; the yield was 15.4%. The DDQ reaction was not performed, since the visible spectrum, Figure 10, gave no indication of chlorin, which exaggerates the highest energy peak. The spectrum displays the Soret (420 nm) and four smaller, higher energy peaks (514, 549, 590, 645 nm) characteristic of free base spectra and compares well to that published by Longo, et al.7 The elemental composition was determined: calc. C 72.9%, N 7.08%, H 3.82%; found C 62.39%, N 5.79%, H 3.60%.

The H₂TCPP was mixed with FeCl₂ in refluxing DMF to afford Fe(TCPP)(Cl); however, the filtrate from the Celite filtration showed no porphyrin. Acidified tetrahydrofuran, THF, was used to dissolve the layer on top of the Celite plug, and recrystallization with chloroform afforded Fe(TCPP)(Cl) which was purified by further recrystallization from THF and from methanol; the yield was 64.72%. The visible spectrum, Figure 11, is characteristic of iron(III) porphyrinato chloride species: a Soret with two broad, small peaks at higher energy
Figure 10: Visible Spectrum of H$_2$TCPP

Peak locations: 420, 514, 549, 590, 645 nm
Figure 11: Visible Spectrum of Fe(TCPP)(Cl)
and a charge transfer band at lower energy. FAB mass spectrometry yielded a spectrogram, Figure 12, which showed FeTCPP$^+$ as the molecular ion; dissociation of the counter ion from iron(III) porphyrins is a very common phenomenon. Loss of $-\text{CO}_2\text{H}$ and $-\text{PhCO}_2\text{H}$ are seen at 800.1 and 724.1. The elemental composition of Fe(TCPP)(Cl) was determined: calculated C 65.51%, N 6.37%, H 3.21%, Fe 6.35%, Cl 4.03%; found C 60.81%, N 5.83%, H 3.30%, Fe 6.50%, Cl 4.12%.

The TCPP $\mu$-oxo dimer was generated by stirring a toluene solution of Fe(TCPP)(Cl) over a 6 M aqueous solution of sodium hydroxide; the aqueous phase turned a brilliant emerald green. The visible spectrum of the aqueous phase, Figure 13, confirmed that [Fe(TCPP)]$_2$O was formed and water soluble, for the broadened Soret (411.2 nm) and two small, higher energy peaks (568.0 and 612.0 nm) characteristic of $\mu$-oxo dimer spectra are evident. The peaks between 680 nm and 695 nm are an instrumental artifact, not a part of the species' spectra. Acidification of the solution resulted in $\mu$-oxo dimer cleavage before reprotonation of the carboxylate groups led to the precipitation of [Fe(TCPP)]$_2$O.

Treatment of a THF solution of Fe(TCPP)(Cl) with sodium hydroxide pellets succeeded in generating $\mu$-oxo dimer, but the [Fe(TMPP)]$_2$O adsorbed to the pellet. Water was necessary to dissolve the $\mu$-oxo dimer; all linkage methods being considered required anhydrous conditions, so this method was abandoned. Treatment of Fe(TCPP)Cl in THF with alumina induced some $\mu$-oxo
Figure 12: FAB Mass Spectrogram of Fe(TCPP)(Cl)

845.1  Fe(TCPP)
800.1  loss of -CO₂H
724.1  loss of -PhCO₂H
Figure 13: Visible Spectrum of [Fe(TCPP)]$_2$O

Peak locations: 411.2, 568.0, 612.0 nm
dimer formation, but chromatography of the tightly-bound species with non-acidic organic solvents did not prove expedient.

H$_2$TMPF was prepared from pyrrole and methyl 4-formyl-benzoate and purified with DDQ exactly as described in the general synthesis section; the average yield was 16.4%. The visible spectrum, Figure 14, displayed the characteristic free base features (418.0, 514.8, 550.0, 590.0, 646.8 nm). FAB mass spectrometry showed a molecular ion peak at 847, loss of -CH$_3$ at 833, loss of -CO$_2$CH$_3$ at 788, and loss of all four carbomethoxy groups at 613, Figure 15. The elemental composition was determined: calculated C 72.16%, N 6.62%, H 4.52%; found C 72.91%, N 6.37%, H 4.51%. NMR of the sample, Figure 16, was consistent with H$_2$TMPF: the porphyrin ring current shifted the pyrrole N-hydrogens to a far higher field (δ=-2.8 ppm) and the pyrrole β-hydrogens to a lower field (δ=8.8 ppm); the expected doublet of doublets from the phenyl hydrogens was found (δ=8.29-8.44 ppm); and the methyl proton singlet was apparent (δ=4.1 ppm). The integration is consistent with these assignments, and the other two small peaks (δ=1.5, 5.3 ppm) are due to the solvent, deuterio-dichloromethane.

Fe(TMPP)(Cl) was also prepared as stated in the general synthesis section with a yield of 75.6%. The visible spectrum, Figure 17, displayed features similar to those seen for other iron(III) porphyrinato chlorides (377.2, 417.6, 510.4, 575.6 nm); the elemental composition was determined: calculated
Figure 14: Visible Spectrum of H₂TPMP

Peak locations: 414.0, 514.8, 550.0, 590.0, 646.8 nm
Figure 15: FAB Mass Spectrogram of H$_2$TMPP

847  H$_2$TMPP
833  loss of $-\text{CH}_3$
788  loss of $-\text{CO}_2\text{CH}_3$
613  loss of 4 $-\text{CO}_2\text{CH}_3$
Figure 16: NMR Spectrum of $H_2$TMPP
Figure 17: Visible Spectrum of Fe(TMPP)(Cl)

Peak locations: 377.2, 417.6, 510.4, 575.6 nm
C 66.7%, N 5.98%, H 3.38%, Fe 5.97%, Cl 3.79%; found C 64.10%, N 5.82%, H 3.91%, Fe 6.42%, Cl 4.54%. The mass spectrogram showed a small molecular ion cluster at 935, a large Fe(TMPP)\(^+\) cluster at 900, and losses of \(-\text{CH}_3\), \(-\text{OCH}_3\), and \(-\text{CO}_2\text{CH}_3\) from Fe(TMPP)\(^+\), Figure 18. The NMR spectrum, Figure 19, possessed the expected features: the pyrrolic protons shifted far upfield by the spin 5/2 iron(III) (δ=82 ppm); the methyl proton singlet shifted upfield from its location in H\(_2\)TMPP by the iron(III) (δ=4.9); the two broadened, upfield-shifted peaks of the no longer degenerate (due to the chloride ion) phenyl protons meta to the porphyrin (δ=13.0, 14.3 ppm); and two very broad peaks due to the two phenyl protons ortho to the porphyrin (beginning at δ=9.2 and 6.0).

Fe(TMPP)(Cl) was dissolved in dichloromethane and stirred with aqueous 1 M sodium carbonate to effect the formation of [Fe(TMPP)]\(_2\)O. An initial synthesis of the µ-oxo dimer using 6 M sodium hydroxide resulted in greater hydrolysis of the ester groups and subsequent loss of µ-oxo dimer to the aqueous phase. Characterization by visible spectroscopy (408.8, 570.4, 609.2 nm) and mass spectrometry were consistent with [Fe(TMPP)]\(_2\)O, Figures 20-21. The spectrogram of [Fe(TMPP)]\(_2\)O revealed the following fragmentation pattern: the molecular ion at 1,817 and Fe(TMPP)\(^+\) at 900 with the corresponding methyl- and methoxy-group losses, and two unidentified clusters at 914 and 932. The peaks around 1,052 resulted from the coordination of dithiothreitol (the FAB matrix) to Fe(TMPP)\(^+\).
Figure 18: FAB Mass Spectrogram of Fe(TMPP)(Cl)

935  Fe(TMPP)(Cl)
900  Fe(TMPP)
886  loss of -CH₃
842  loss of -CO₂CH₃
Figure 19: NMR Spectrum of Fe(TMPP)(Cl)

$R = \text{CO}_2\text{CH}_3$
Figure 20: Visible Spectrum of [Fe(TMPP)]_2O

Peak locations: 408.8, 570.4, 609.2 nm
Figure 21: FAB Mass Spectrogram of $[\text{Fe(TMPP)}]_2\text{O}$

1817 \hspace{1cm} [\text{Fe(TMPP)}]_2\text{O}

990 \hspace{1cm} \text{Fe(TMPP)}
The elemental composition was determined: calculated C 68.73%, N 6.17%, H 3.99%, Fe 6.15%; found C 68.21%, N 6.16%, H 3.81%, Fe 6.25%.

B. Initial Linkage Attempts

These reactions were carried out in reagent grade solvents with reagent grade reagents; the refluxing solutions were open to the air. Table 1 summarizes the exact formulations.

1. Reaction in Refluxing Toluene

\([\text{Fe(TMPP)}]_2\text{O}\), 5.3 mg, was dissolved in toluene, and 100 ml of 1.15 mM DAP in toluene was added by slow addition funnel over approximately 48 hours; after an additional 24 hours at reflux, the reaction solution was allowed to cool. After rotary evaporation to dryness, the solid was recrystallized from dichloromethane/hexanes. The visible spectrum, Figure 22, clearly revealed the product to be a \(\mu\)-oxo dimer species (417.2, 572.4, 684.0 nm). The shifts from \([\text{Fe(TMPP)}]_2\text{O}\) peak locations may have been caused by the difference in solvents or a substitution at the para-positions of the phenyl rings; no change in gross spectral features from the aminolysis of the ester groups was expected. The FAB mass spectrogram, Figure 23, conclusively showed that no reaction occurred: the "product" of the toluene reflux was the starting material.

2. Reaction in Refluxing o-Dichlorobenzene

\((\text{FeTMPP})_2\text{O}\), 5.4 mg, was dissolved in 200 ml o-dichlorobenzene, and this solution was brought to reflux. 100 ml of
Figure 22: Visible Spectrum of Toluene Reflux Product

Peak locations: 417.2, 572.4, 684.0 nm
Figure 23: FAB Mass Spectrogram of Toluene Reflux Product

Identical to the spectrogram of [Fe(TMPP)]$_2$O
0.4 mM DAP in o-dichlorobenzene was added over 24 hours by slow addition funnel. Approximately eight hours after the completion of the addition of the DAP, a precipitate was noticed; after another 14 hours had elapsed, the solution was allowed to cool to room temperature. The solvent was filtered away from the tan, fibrous precipitate which was then washed with o-dichlorobenzene and dichloromethane and thoroughly dried. Solubility tests revealed a partial solubility in methanol, so the precipitate was rinsed with that solvent. A visible spectrum of the resultant yellow-orange solution revealed no porphyrinic characteristics, Figure 24. The residue from the methanol wash was white, water-soluble, and intuitively nonporphyrinic.

Two other linkage attempts were performed in the same manner, but a calculation error led to the addition of a limiting amount of DAP. Visible spectra of both reaction products indicated demetallation of the \([\text{Fe(TMPP)}]_2\) to \(\text{H}_2\text{TMPP}\). Figure 25 shows the visible spectrum of the product of one of the reactions (418.8, 512.0, 551.2, 592.8 nm), and Table 1 summarizes the initial linkage attempts.

C. n-Butyllithium Mediated Linkage Attempts

1. General Procedure

These reactions were all carried out at room temperature, under nitrogen, with purified reagents and dried glassware. The solvent, THF, was freshly distilled over potassium and under nitrogen. The DAP was purified following Perrin's method
Figure 24: Visible Spectrum of First Dichlorobenzene Reflux Product

Peak locations: only tailing
Figure 25: Visible Spectrum of Second Dichlorobenzene Reflux Product

Peak locations: 418.8, 512.0, 551.2, 592.8 nm
for ethylenediamine purification: three hours' stirring over sodium hydroxide at room temperature followed by distillation over sodium metal under nitrogen. The purified DAP was stored under nitrogen in a freezer. The n-BuLi was titrated using the method of Lipton, Sorensen, and Sadler. All glassware was dried at 110°C overnight, fitted with a rubber septum, and evacuated and back-filled with nitrogen three times before use.

Freshly prepared THF solutions of DAP were treated with two equivalents of n-BuLi to generate Li$_2$DAP; this solution was added to a THF solution of (FeTMPP)$_2$O. Addition was via syringe over several minutes in Reactions D, E, J, and K, via slow addition funnel in Reactions F and G, and via cannulation in Reactions H and I. Table 5 gives the addition times and exact formulations of all of the reaction solutions. Reactions D and E were worked-up ten minutes after complete Li$_2$DAP addition; the other reactions were worked-up after being left stirring overnight.

2. Specific Reactions
a. Reaction D

A dark precipitate developed within minutes of complete Li$_2$DAP addition. A visible spectrum of a homogenate of the precipitate and solution in dichloromethane, Figure 26, was virtually identical to that of starting material (410.0, 570.4, 610.0 nm). Silica gel thin layer chromatography (TLC) of a dichloromethane solution of the precipitate showed only [Fe(TMPP)]$_2$O and origin residue, and nothing further was done
Table 5: n-Butyllithium Reaction Formulations

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( [\text{Fe(TMPP)}]_2\text{O} )</th>
<th>( \text{Li}_2\text{DAP} )</th>
<th>time of addition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \mu\text{mol} )</td>
<td>( V_0 \text{ (THF)} )</td>
<td>conc</td>
</tr>
<tr>
<td>D</td>
<td>2.8</td>
<td>1.4</td>
<td>1.4M</td>
</tr>
<tr>
<td>E</td>
<td>1.6</td>
<td>2.0</td>
<td>0.8M</td>
</tr>
<tr>
<td>F</td>
<td>2.8</td>
<td>200.0</td>
<td>14.0( \mu )</td>
</tr>
<tr>
<td>G</td>
<td>11.2</td>
<td>200.0</td>
<td>56.0( \mu )</td>
</tr>
<tr>
<td>H</td>
<td>2.5</td>
<td>10.0</td>
<td>0.25M</td>
</tr>
<tr>
<td>I</td>
<td>2.9</td>
<td>10.0</td>
<td>0.29M</td>
</tr>
<tr>
<td>J</td>
<td>1.3</td>
<td>2.0</td>
<td>0.65M</td>
</tr>
<tr>
<td>K</td>
<td>1.6</td>
<td>2.0</td>
<td>0.80M</td>
</tr>
</tbody>
</table>

A 14.5-fold excess of n-BuLi was used to prepare the Li₂DAP in Reaction K.
Figure 26: Visible Spectrum of Reaction D Homogenate

Peak locations: 410.0, 570.4, 610.0 nm
with the precipitate. Silica gel TLC of the Reaction D THF solution using dichloromethane showed a species other than the starting material. A micro-preparatory TLC of the THF solution was performed; the band of the new species was removed, and a visible spectrum of this moiety was taken in dichloromethane, Figure 27 (410.8, 505.2, 572.8, 607.2, 628.4 nm); conversion to Fe(TMPP)(Cl) was evident. A TLC, using dichloromethane, of the precipitate revealed only starting material and origin residue. Chromatography of the Reaction D solution over silica gel and eluting with 1:1 :: dichloromethane:chloroform separated the new species, which was concentrated and submitted for FAB mass spectrometry, Figures 4-5.

b. Reaction E

The addition of Li₂DAP caused no precipitate; the reaction was quenched with five drops of water. A visible spectrum of the reaction solution was taken, Figure 28 (409.2, 569.2, 609.2 nm), and silica gel TLC indicated the presence of a moiety similar to the Reaction D product. One half of the solution was rotary evaporated to dryness, dried overnight at 120° C, and submitted for FAB mass spectrometry. The remaining half was chromatographed over silica gel eluting with 1:1 :: chloroform : dichloromethane with a few drops of triethylamine to eliminate hydrochloric acid. The fraction, shown to contain both product and [Fe(TMPP)]₂O by TLC, was condensed and submitted for FAB mass spectrometry, Figure 6; an interpretation of the spectrogram is included in Section II D.
Figure 27: Visible Spectrum of Reaction D TLC Band

Peak locations: 410.8, 505.2, 572.8, 607.2, 628.4 nm
Figure 28: Visible Spectrum of Reaction B Solution

Peak locations: 409.2, 569.2, 609.2 nm
c. Reactions F and G

Reaction F was quenched with water, and a visible spectrum was run of an aliquot of the solution, Figure 29 (only tailing). TLC showed a very faint spot which corresponded neither to [Fe(TMPP)]\textsubscript{2}O nor origin residue and an even fainter spot corresponding to the starting material; the product was stored as a chloroform solution, and the spots disappeared over time. A sample of the chloroform solution was submitted for FAB mass spectrometry, Figure 30; no TMPP peaks were seen.

After air quenching, a visible spectrum was taken of an aliquot of the Reaction G solution; it showed the three characteristic \(\mu\)-oxo dimer peaks (408.8, 569.6, 610.0 nm) and an additional peak at 640.8 nm, Figure 31. The Reaction G solution was rotary evaporated to dryness, vacuum oven-dried, and submitted for FAB mass spectrometry, Figure 32; [Fe(TMPP)]\textsubscript{2}O was the primary component. The minor peak at 1,887 was accounted for by coordination of DAP to the molecular ion; coordination of a DAP molecule to Fe(TMPP)+ explained the peak at 970, while water coordination to the species at 970 explained the peak at 988. Coordination could also explain the additional peak in the visible spectrum. Dithiothreitol coordination accounted for the peaks at 1,041 and 1,058. TLC of the sample revealed only [Fe(TMPP)]\textsubscript{2}O.

d. Reactions H and I

These linkage attempts were quenched with three drops of water after an overnight reaction time. Visible spectra, TLC,
Figure 29: Visible Spectrum of Reaction F Solution

Peak locations: only tailing
Figure 30: FAB Mass Spectrogram of Reaction F Product

No peaks correspond to a porphyrinic species.
Figure 31: Visible Spectrum of Reaction G Solution

Peak locations: 408.8, 569.6, 610.0 nm
Figure 32: FAB Mass Spectrogram of Reaction G Product

Identical to [Fe(TMPP)]_3O with peaks due to coordination of DAP, water, and dithiothreitol appearing at 970, 988, 1041, and 1058.
and FAB mass spectrometry of the products of these reactions were performed, but no porphyrinic material was detected in the Reaction H product, Figures 33-34, and only [Fe(TMPP)]$_2$O was detected in the Reaction I product, Figures 35-36.

e. Reaction J

The reaction was quenched by addition of one milliliter of reagent grade THF which had been opened and stored in air for some time. An aliquot was withdrawn, and a visible spectrum, Figure 37, was run (412.0, 572.0, 614.8 nm). The remainder of the solution was rotary evaporated to dryness and submitted for FAB mass spectrometry, Figure 8. A THF solution of the Reaction J product was treated with a 16-fold excess of n-BuLi (based upon the molar quantity of [Fe(TMPP)]$_2$O used in Reaction J), and this solution was taken to dryness after stirring overnight. The sample was soluble in methanol and THF, and the visible spectrum, Figure 38, indicated the presence of some μ-oxo dimer (411.2, 572.0, 611.6 nm), but neither solvent would effect solutions of sufficient concentration for mass spectrometry.

f. Reaction K

The Li$_2$DAP solution in this linkage trial was prepared by adding a 14.5-fold excess of n-BuLi to a THF solution of DAP. After addition of this Li$_2$DAP solution to the [Fe(TMPP)]$_2$O, the mixture was left stirring overnight. The solution was rotary evaporated to dryness and submitted for FAB mass spectrometry,
Figure 33: Visible Spectrum of Reaction H Product
Figure 34: FAB Mass Spectrogram of Reaction H Product

Identical to the spectrogram of [Fe(TMPP)]₂O
Figure 35: Visible Spectrum of Reaction I Product

Peak locations: 410.4, 446.8, 504.8, 569.6, 609.2, 629.6 nm
Figure 36: FAB Mass Spectrogram of Reaction I Product

Identical to the spectrogram of [Fe(TMPP)]$_2^0$
Figure 37: Visible Spectrum of Reaction J Solution

Peak locations: 412.0, 572.0, 614.8 nm
Figure 38: Visible Spectrum of Reaction J Product after Treatment with n-Butyllithium

Peak locations: 411.2, 572.0, 611.6 nm
Figure 39. The returned sample was dissolved in dichloromethane which had been passed through a sodium bicarbonate plug, and this solution was rinsed with a dilute, aqueous solution of sodium bicarbonate and then water to remove any lithium salts; a visible spectrum, Figure 40, gave no indication of iron(III)porphyrinato chloride formation (409.2, 569.2, 610.8 nm).

A 14.5-fold excess of n-BuLi was added to a THF solution of the rinsed sample, and the solution was refluxed for 60 hours. After washing to remove any lithium salts and unreacted n-BuLi, the sample was concentrated and submitted for FAB mass spectrometry, Figures 41-42. Silica gel chromatography of the sample resulted in the separation of an iron(III) porphyrinato species and a \( \mu \)-oxo dimer species. However, the exposure of iron(III) porphrinato species to silica gel often results in the formation of \( \mu \)-oxo dimer, and the uncertainty as to the origin of the \( \mu \)-oxo dimer fraction introduced by this phenomenon rendered further separation pointless.

3. Isolation of Solid Li\(_2\)DAP with Stanley Milam

All steps were performed in dried Schlenkware under Argon. 5.0 ml of DAP, freshly distilled from sodium metal, was dissolved in 150 ml of diethylether (Et\(_2\)O), and 85 ml of 1.6 M n-BuLi was added in an ice bath to the magnetically stirred DAP solution; a white precipitate immediately formed. After stirring overnight, the solution was cannula-filtered, and the
Figure 39: FAB Mass Spectrogram of Reaction K Product

Identical to the spectrogram of Reaction J product (Figure 8)
Figure 40: Visible Spectrum of Reaction K Product

Peak locations: 409.2, 569.2, 610.8 nm
Figure 41: Visible Spectrum of Reaction K Product after Treatment with n-Butyllithium

Peak location: 419.6 nm
Figure 42: FAB Mass Spectrogram of Reaction K Product after Treatment with n-Butyllithium

No peaks corresponded to a porphyrinic species.
precipitate was rinsed with two 40 ml portions of Et₂O then vacuum dried. The pale yellow product had a mass of 5.16 g or 0.06 mole for a yield of 100%.

20 ml of THF was added to 280 mg of the product; complete solution was not effected. Approximately 2 ml of reagent grade methyl iodide was added to this solution; the generation of the tetramethyl species, characterized by electron impact mass spectrometry, Figure 43, implies that methyl iodide will methylate even unactivated amines, for the generation of Li₄DAP when only two equivalents of n-BuLi have been added is unlikely. The experiment neither confirmed nor precluded the presence of Li₂DAP. The THF solution was cannula-filtered away from the white solid which remained, and the THF was removed from the filtrate by vacuum.

200 ml of boiling THF failed to dissolve the remainder of the solid product from the reaction of n-BuLi and DAP. 61 ml of tetramethylethylenediamine (TMEDA), freshly distilled from sodium metal, was added but failed to solubilize the solid. The THF supernatant was filtered away, and a gross excess of methyl propanoate was added, and the solution was left stirring overnight. The presence of Li₂DAP would be confirmed by the generation of N,N'-dipropyl-1,3-diaminopropane; this diamide had been prepared as part of the linkage model reactions (see above) and was readily available as a standard. The NMR spectrum of the yellow, gelatinous solid which remained after the THF had been removed by vacuum was not that of the stan-
Figure 43: Mass Spectrogram of Me₂N(CH₂)₃NMe₂

128       Me₂N(CH₂)₃NMe₂
114       Me₂N(CH₂)₃NHMe
85        Me₂N(CH₂)₃
71        Me₂N(CH₂)₂
57        Me₂NCH₂
44        Me₂N
D. Synthesis of U(TMPP)_2O

with Stanley Milan

All steps were performed in dried Schlenkware under Argon. 246 mg uranium(IV) chloride and 214 mg lithium diethylamide, both rigorously purified and dried, were mixed, and 45 ml of freshly distilled Et_2O was condensed onto them in an ethanol/dry ice bath. After stirring overnight, the Et_2O was pumped off, and U(NEt_2)_4 was extracted with toluene. This solution was added to 1.19 g of H_2TMPP in toluene; the total volume was approximately 100 ml, and the solution was left stirring overnight. The solution was then heated to 55°C and left stirring for another night.

The purple toluene solution was filtered away, leaving a purple residue which was dissolved in chloroform. Visible spectroscopy (422.0, 514.0, 550.0, 590.0, 628.0, 646.0 nm) and TLC of both solutions were performed, Figure 45. TLC of the toluene solution showed four spots other than origin residue and H_2TMPP; chromatography over a silica gel column separated three fractions. The first fraction contained both H_2TMPP and one of the new species, so preparatory TLC of this fraction was performed; it succeeded in isolating the species responsible for the fastest moving new TLC spot. The second column chromatography fraction consisted almost entirely of the species accounting for the second and third fastest moving of the new TLC spots. This fraction and a solution of the
Figure 44: NMR Spectrum of Propanoylating Reaction Product

The spectra of the product clearly differs from that of the standard.
Figure 48: Visible Spectrum of U(TMPF)$_2$ Synthesis

Reaction Solution

Peak locations: 422.0, 514.0, 559.0, 586.0, 638.0, 646.0 nm
preparatory TLC band containing the fastest moving new species were submitted for FAB mass spectrometry, Figures 46-49. The peak at 888 in Figure 47 corresponded to one amidation of H₂TMPP by Et₂N⁻ while the peak at 1042 were due to the coordination of dithiothreitol. The peaks at 929 and 1081 in Figure 49 were similarly assigned as arising from the di-amidated H₂TMPP.
Figure 46: Visible Spectrum of the Fastest-moving New Species in U(TMPP)_2 Synthesis Solution

Peak locations: 420.4, 514.3, 552.0, 587.2, 646.2 nm
Figure 47: FAB Mass Spectrogram of the Fastest-moving New Species in U(TMPP)₂ Synthesis Solution

698 mono-(Et₂N⁻)amidated H₂TMPP

1042 coordination of dithiothreitol
Figure 48: Visible Spectrum of the Second New Species in U(TMPP)$_2$ Synthesis Solution

Peak locations: 420.4, 515.6, 551.2, 589.2, 645.2 nm
Figure 49: FAB Mass Spectrogram of the Second New Species in U(TMPP)$_2$ Synthesis Solution

929 di-(EtN$^-$)amidated H$_2$TMPP

1081 coordination of dithiothreitol
ENDNOTES


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