U.S.N.A. --- Trident Scholar project report; no. 297 (2002)

TOWARDS IMPROVED OPTICAL LIMITERS

by

Midshipman Peter D. Huffman, Class of 2002
United States Naval Academy
Annapolis, Maryland

(signature)

Certification of Adviser Approval

Professor Jeffrey P. Fitzgerald
Department of Chemistry

(signature)

(date)

Acceptance for the Trident Scholar Committee

Professor Joyce E. Shade
Deputy Director of Research & Scholarship

(signature)

(date)

REPORT DOCUMENTATION PAGE	Form Approved OMB No. 0704-0188

1. REPORT DATE (DD-MM-YYYY) 03-05-2002	2. REPORT TYPE	3. DATES COVERED (FROM - TO) xx-xx-2002 to xx-xx-2002

4. TITLE AND SUBTITLE Towards Improved Optical Limiters Unclassified	5a. CONTRACT NUMBER 5b. GRANT NUMBER 5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) Huffman, Peter D. ;	5d. PROJECT NUMBER 5e. TASK NUMBER 5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME AND ADDRESS US Naval Academy Annapolis, MD21402	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME AND ADDRESS ,	10. SPONSOR/MONITOR'S ACRONYM(S) 11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
APUBLIC RELEASE
,

13. SUPPLEMENTARY NOTES

14. ABSTRACT
See report

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Public Release	18. NUMBER OF PAGES 73	19. NAME OF RESPONSIBLE PERSON email from USNA, Annapolis, MD, (blank) lfenster@dtic.mil
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER International Area Code Area Code Telephone Number 703767-9007 DSN 427-9007

	Standard Form 298 (Rev. 8-98) Prescribed by ANSI Std Z39.18

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 074-0188

1. AGENCY USE ONLY (Leave blank)	**2. REPORT DATE** 3 May 2002	**3. REPORT TYPE AND DATE COVERED**

4. TITLE AND SUBTITLE
Towards improved optical limiters

5. FUNDING NUMBERS

6. AUTHOR(S)
Huffman, Peter D. (Peter Daniel), 1980-

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
US Naval Academy
Annapolis, MD 21402

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
Trident Scholar project report no. 297 (2002)

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
This document has been approved for public release; its distribution is UNLIMITED.

12b. DISTRIBUTION CODE

13. ABSTRACT: Optical limiters are materials that are transparent to low-intensity, ambient light but become opaque to high-intensity light. Such materials are of particular interest to the Navy for protecting optical sensors and human eyes from battlefield lasers. The most successful optical limiters known are soluble phthalocyanines, in particular those metallated with lead and indium. Yet further improvements are needed. This research project used a two-pronged approach to create improved optical limiters. The first approach was to synthesize and study soluble thallium phthalocyanines. Thallium, due to its proximity to lead and indium on the periodic table, should exhibit favorable optical limiting properties. Yet soluble thallium phthalocyanines had never been synthesized. A substituted thallium(III) phthalocyanine complex which is readily soluble in organic solvents has been prepared. The second approach to improved optical limiters was to prepare covalently-linked phthalocyanine complexes which allow control of aggregation, an important parameter affecting optical limiting properties. Towards this end, a “clamshell” phthalocyanine dimer has been prepared and metallated with lead. Both of these new materials, the soluble thallium phthalocyanine and the lead phthalocyanine dimer, have been characterized using UV-vis and NMR spectroscopy and mass spectrometry. Their optical properties have been examined using Z-scan and degenerate four wave mixing (DFWM) techniques.

14. SUBJECT TERMS
Optical limiter, Phthalocyanine, Thallium, Lead, Nonlinear

15. NUMBER OF PAGES
73

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	**18. SECURITY CLASSIFICATION OF THIS PAGE**	**19. SECURITY CLASSIFICATION OF ABSTRACT**	**20. LIMITATION OF ABSTRACT**

NSN 7540-01-280-5500 **Standard Form 298**

Abstract

Optical limiters are materials that are transparent to low-intensity, ambient light but become opaque to high-intensity light. Such materials are of particular interest to the Navy for protecting optical sensors and human eyes from battlefield lasers. The most successful optical limiters known are soluble phthalocyanines, in particular those metallated with lead and indium. Yet further improvements are needed. This research project used a two-pronged approach to create improved optical limiters. The first approach was to synthesize and study soluble thallium phthalocyanines. Thallium, due to its proximity to lead and indium on the periodic table, should exhibit favorable optical limiting properties. Yet soluble thallium phthalocyanines had never been synthesized. A substituted thallium(III) phthalocyanine complex which is readily soluble in organic solvents has been prepared. The second approach to improved optical limiters was to prepare covalently-linked phthalocyanine complexes which allow control of aggregation, an important parameter affecting optical limiting properties. Towards this end, a "clamshell" phthalocyanine dimer has been prepared and metallated with lead. Both of these new materials, the soluble thallium phthalocyanine and the lead phthalocyanine dimer, have been characterized using UV-vis and NMR spectroscopy and mass spectrometry. Their optical properties have been examined using Z-scan and degenerate four wave mixing (DFWM) techniques.

Keywords: Optical limiter, Phthalocyanine, Thallium, Lead, Nonlinear

Acknowledgements

Acknowledgements go to James Shirk, Steve Flom, and Richard Pong in the Optical Sciences Division and Arthur Snow in the Chemistry Division at the Naval Research Laboratory for conducting the optical limiting studies and for their thoughtful discussion of the project, to John H. Callahan for conducting the mass spectrometry analysis at the Naval Research Laboratory, and to the United States Naval Academy Trident Scholar Committee for their support of the project.

TABLE OF CONTENTS

Introduction

Lasers have become increasingly more prominent on the modern battlefield. They are used in a variety of applications including directed attack, targeting, and ranging. Modern militaries are searching for methods to protect their personnel and equipment from laser damage, particularly optical elements such as human eyes or optical sensors. While fixed wavelength filters may be effective against a particular type of laser, in order to protect an optical element against the spectrum of possible threats, multiple filters would be required. However, stacking of filters would render the optical element useless. Also, multiple filters would be ineffective against any sort of agile or variable wavelength laser threat. A general, broad spectrum protection method is needed.

Optical limiters are devices designed to allow normal transmission of light at low intensities and limited transmission of light of higher intensities. Keeping transmitted light intensity below a certain maximum value is useful in protecting such light sensitive detectors as optical sensors and human eyes from high intensity light. Of particular interest to the Navy are applications of optical limiters for protection against laser dazzling. Lasers directed at aircraft pilots, optical sensors, or through the sights of a tank gunner can do serious damage to the operator or the equipment. Optical limiting devices would allow the pilot, for example, to see through his face shield under normal conditions. When a laser or other high intensity light shines through the face shield protected by an optical limiting substance, the substance turns opaque at the point of contact, thus protecting the pilot from damage while allowing him to see out the rest of the face shield. When the high intensity light is removed, the opaque material reverts back to transparent. Materials that possess useful optical limiting characteristics may also be used in other applications such as optical modulation and switching.

A primitive example of optical limiting is a pair of photo-gray sunglasses. Imbedded in the lenses of the sunglasses is an ionic compound comprised of positive silver cations and negative chloride anions. As strong sunlight hits the lenses, electrons are transferred from the chloride ions to the silver ions, turning the silver cations into neutral metallic silver atoms. These neutral silver atoms are now gray colored and the sunglass lenses darken. Although the mechanism by which advanced optical limiters dissipate light is more complicated, the general idea is the same.

There are several important considerations when designing an optical limiting device. Because of the speed at which light travels, and the fact that damage can be caused by nanosecond scale pulses, the device must be able to react almost instantaneously to the changing light intensity. This fast response time favors a materials-based device over a mechanical one. The material must be able to bear the brunt of prolonged exposure to high intensity light, as well as allow for continuous transparency in regions outside the path of the high intensity light. All these factors favor a device incorporating a solution or film of molecules, which act as stand-alone optical limiters.

The behavior of an ideal optical limiter is shown below in Figure 1.

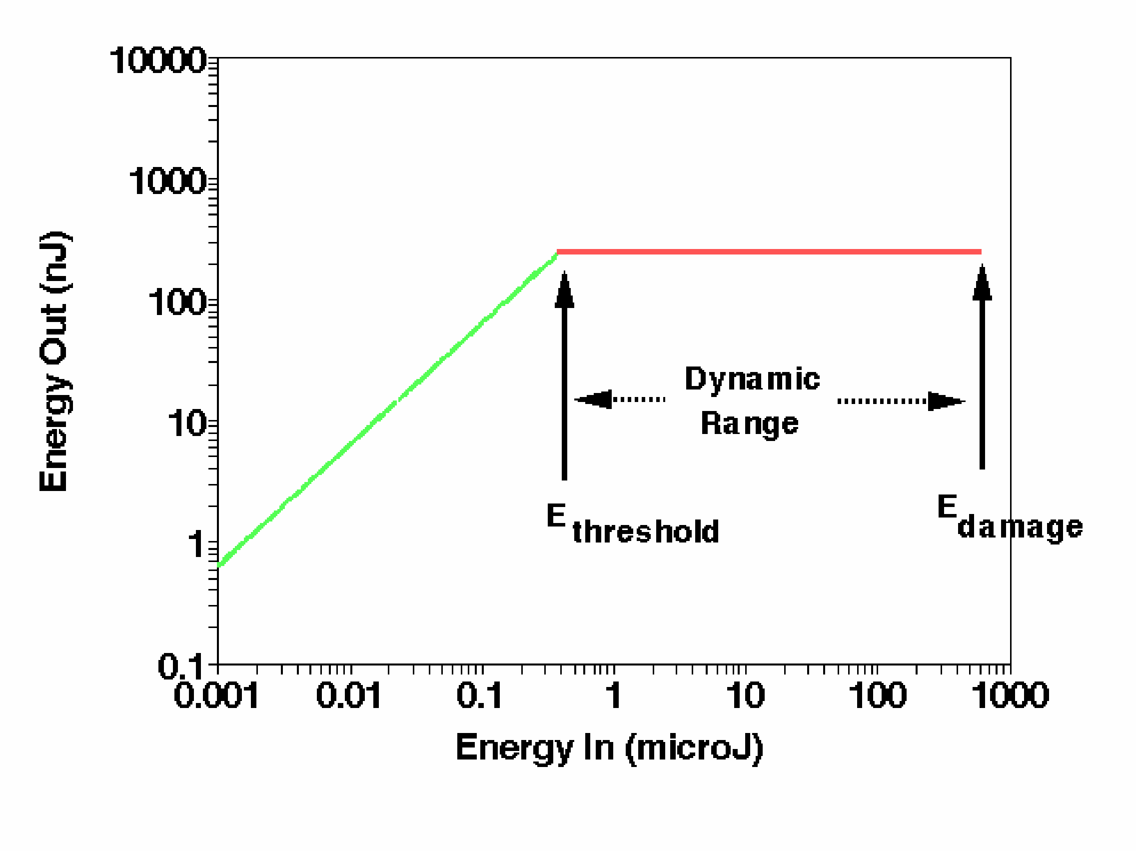


Figure 1 - Ideal Optical Limiting Response

At low input energies, the transmitted energy increases linearly with increasing input. However, at some input energy $E_{threshold}$, the optical limiter turns on. Past this threshold energy, further input energy is not transmitted through the limiter. The device has effectively capped the amount of energy transmitted regardless of the amount of energy entering into the limiter. At a certain input energy, E_{damage}, the device breaks down. The range of input energies from when the device switches on until the device fails is called the dynamic range.

Several materials have been found that possess properties useful for optical limiting applications. Large conjugated electron systems such as phthalocyanines and porphyrins as well as carbon graphite suspensions, etc[a] have been studied as optical limiters. Phthalocyanines are particularly attractive because of the ability to tailor the central ion and peripheral substituent groups to adjust the properties of the material. These will be discussed in detail later.

Background

A. Absorbance

White light is composed of all the colors of the visible spectrum. Materials appear to be colored because they absorb certain wavelengths of visible light. The color of a material that we perceive with our eyes in fact absorbs the complementary color of light. A red object appears so because it absorbs green light.

The wavelengths of light that a molecule absorbs depend on the electronic structure of the molecule. In general, electrons in a molecule begin in their lowest energy configuration, or ground state. When a molecule absorbs light, energy is transferred to an electron and it becomes excited and transitions to a higher energy configuration. Each molecule has specific, discrete possible transitions that depend on characteristics of the material. When a molecule is exposed to light possessing the exact amount of energy necessary for a transition, the molecule may absorb it and promote one of its electrons to an excited state.

Figure 2 shows a plot of absorbance versus incident wavelength for a particular molecule:

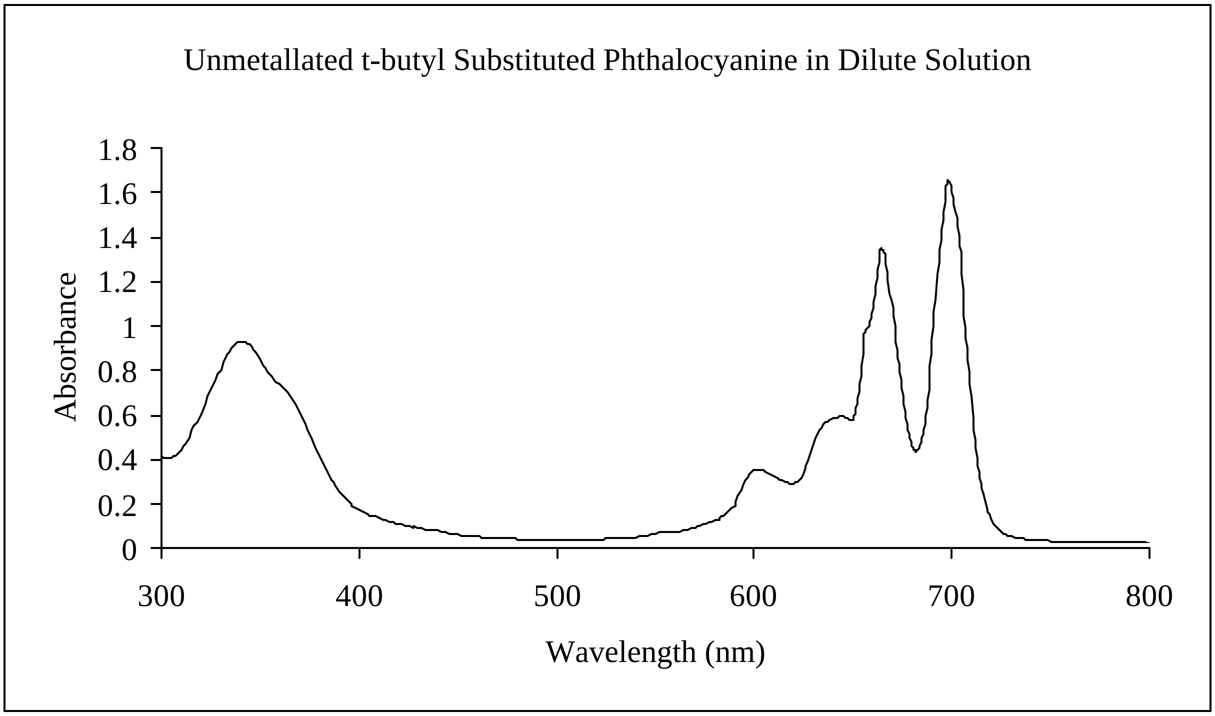


Figure 2 – UV-Visible Absorbance Spectrum for Unmetallated Phthalocyanine

Absorbance is related to the percentage of incident light intensity transmitted through the sample by the equation

$$A = - \log (\%T/100)$$

where A is the absorbance, and %T is the percentage of transmitted light intensity at a particular wavelength. A molecule that absorbs ninety percent of the incident light intensity (i.e. it transmits ten percent) would have an absorbance of one at that particular wavelength. Rewriting the equation above in terms of the % transmittance

$$\%T = 100 * 10^{-A}$$

it is apparent that a change in absorbance produces an exponential change in percent transmittance.

Each possible transition has a certain probability that it will absorb light. This absorption probability is referred to as an absorption cross section (σ). A high absorption cross section at a particular wavelength means that there is a high probability that the molecule will absorb light. At this wavelength the percentage of transmitted light intensity will be low and the absorbance of the molecule will be high.

The peaks in the example spectrum above are spread over a wavelength range, rather than appearing as spikes at specific wavelengths. In fact the molecular electronic transitions exist as clusters of very similar energy transitions that give rise to broad peaks. Other chemical and instrumental considerations also affect the breadth of the absorption peaks.

Absorption measurements are usually done on a dilute solution of the sample of interest. Thus the spectrum produced would in fact be the combination of the absorbances of the sample molecules and the solvent molecules. To get an accurate picture of the absorbance spectrum of the sample molecules alone the spectrum of pure solvent is recorded first and then subtracted from the experimental solution spectrum. This procedure is referred to as running a blank or a background spectrum.

Absorbance spectra are useful for several reasons. One important use is for identification of unknown samples through comparison to known molecular spectra. Another important use is for determining the concentration of a known molecule in solution. The absorbance of a solution is related to the concentration of analyte by a relation known as Beer’s law:

$$A = \varepsilon\ c\ l$$

where A is the absorbance at a particular wavelength, c is the concentration of analyte in solution, l is the length of sample through which light passes on the way to the detector, and ε is the molar absorptivity coefficient of the molecule. This coefficient is specific to each molecule at a specific wavelength and can be determined by measuring a solution of known concentration in a known path length of light. For most molecules, at any given wavelength there is a linear relationship between absorbance and concentration. The absorbances of a series of solutions of varying concentration will plot as a straight line with slope (ε l) as illustrated in Figure 3. Such molecules are called linear absorbers.

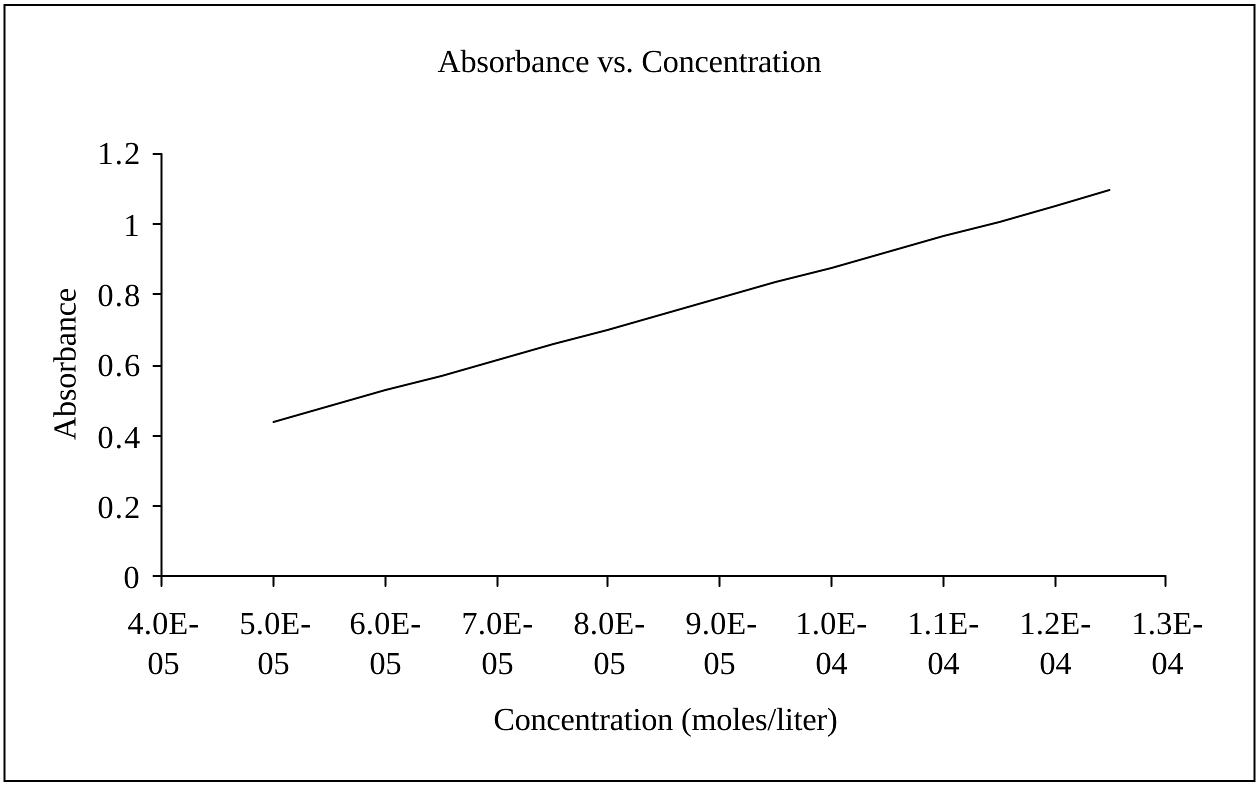


Figure 3 – Linear Relationship Between Absorbance and Concentration

However, sometimes a plot of absorbance versus concentration does not return a straight line. There are a number of different factors that might cause a solution to deviate from linear behavior. At higher concentrations, molecules may be in close enough proximity to one another that they clump together, or aggregate. Two or more molecules in close proximity may interact with one another electronically, altering the electronic energy levels of the molecules which in turn affects the possible transitions which an electron may undergo. Thus a molecule may absorb light more or less strongly depending on the concentration of the solution it is in.

Other molecules deviate from linear behavior due to varying response to the intensity of the incident light. Ordinarily, a molecule will absorb the same percentage of incident light (based on its absorption cross section) regardless of the intensity of the light. However, certain molecules exhibit non-linear optical properties. The absorbance of these molecules depends upon the intensity of the incident light. At low light intensities the material may be transparent, allowing virtually all of the incident light to pass through. At a certain threshold intensity, these molecules undergo some sort of electronic change and begin to absorb more of the incident light. Such molecular properties would be useful in designing an optical limiter.

B. Optical Limiting Mechanisms

There are several mechanisms by which a material may act as an optical limiter. A relatively simple mechanism involves the material changing its refractive index when exposed to high intensity light. A solution of molecules which have a large change in refractive index at high intensities would scatter the incident light to such a degree as to render it harmless. A similar mechanism relies on a change in refractive index, but that of the solvent molecules rather than the optical limiting molecules. Light energy absorbed by the molecules is released into the solvent as thermal or heat energy. This thermal energy could cause a change in refractive index for the solvent, with the similar result of scattering the incident light intensity.

A more complicated but potentially more effective mechanism for optical limiting involves the absorption of multiple photons of light energy by a molecule. In the simplest case, this mechanism is called sequential two photon absorption and is depicted below Figure 4.

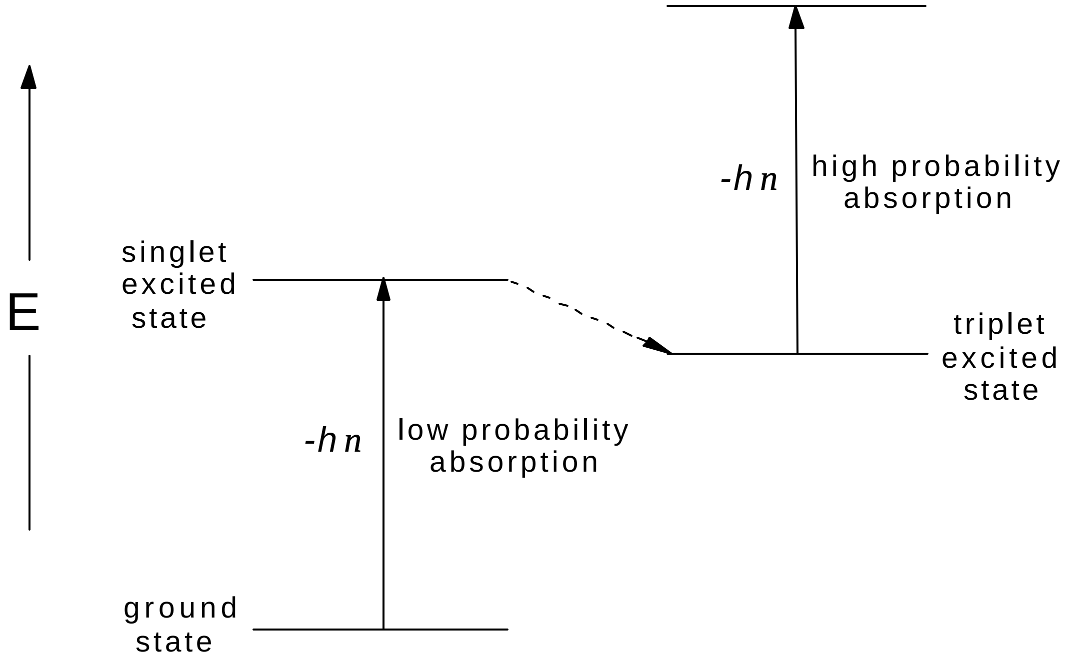


Figure 4 – Sequential Two-Photon Absorption Process

At room temperature, a molecule has its electrons in its ground state energy configuration. If the incident light energy, *hn*, corresponds to the energy of an allowed transition in the molecule, an electron may be promoted to an excited state. Initially this electron retains its spin, opposite that of its previous partner. This initial excited state is called a singlet state. The electron may then flip its spin and fall to a slightly lower energy excited state called a triplet state. This excited state may also be able to absorb an addition photon of light and promote this triplet electron to an even higher energy state.

For the two-photon mechanism to enable a molecule to function as an effective optical limiter, several important characteristics must be present. The initial transition to the first excited state must have a low probability of occurrence. Such a molecule is said to have a small absorption cross section for that transition. This low cross section is necessary for the material to be transparent at low intensities. If the probability for this absorption was high, the material would be opaque at operating intensities. A second parameter is that the transition from the singlet to the triplet excited state should be very fast. This transition, or intersystem crossing, needs to be rapid so that once excited by high intensity light, the molecule will quickly be in a position to absorb a second photon. The molecule must also have a long triplet excited state lifetime, so that it can absorb the second photon of light before it decays back to the ground state. Just as a low absorption cross section was necessary for the ground state to be transparent at low intensities, the excited state needs to have a high probability of absorption, or a large cross section, in order to effectively absorb high intensity light. The absorption probability change effectively changes the molar absorptivity coefficient of the molecule. This causes a deviation from the linear absorption behavior predicted by Beer’s law and such materials are known as non-linear absorbers. Rewriting the equation for percent transmittance with (ε c l) substituted in for absorbance from Beer's law, the equation becomes

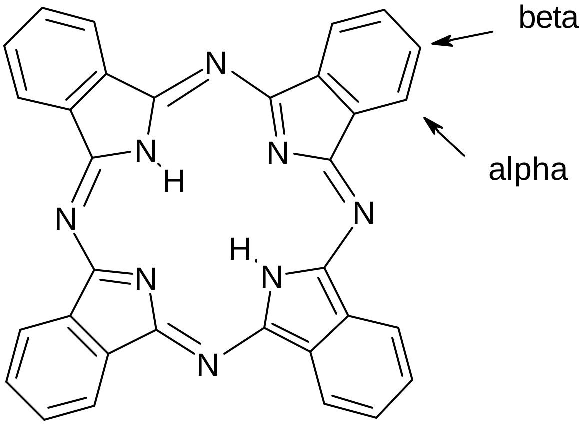
$$\%T = 100 * 10^{-(\varepsilon c l)}$$

and demonstrates that a change in the molar absorptivity coefficient will have an exponential effect on the percent transmittance. Once the intense light is removed, the molecules should relax back to their ground states and allow the transmittance of low intensity light.

Other parameters are important to consider when studying potential optical limiting materials. The intensity at which a material begins to absorb nonlinearly, the threshold intensity, needs to be considered. The stability of the molecule and its behavior at damage intensities is also important. A molecule which decays to a transparent species is ineffective above its damage threshold. Once destroyed by incoming light, it is no longer effective at limiting. A molecule which decays to an opaque species is desirable because although irreversibly damaged, it will at least keep the remaining light energy from passing through the device.

C. Phthalocyanines

Figure 5 depicts a molecule called phthalocyanine (abbreviated Pc):



Phthalocyanine (Pc)

Figure 5 – Phthalocyanine

In this diagram the N's represent nitrogen atoms and the H's represent hydrogen atoms. The vertices in the diagram represent carbon atoms. Lines connecting any two vertices to one another, an N, or an H, represent a chemical bond between those two atoms. Where two lines connect atoms, there is additional electron density creating a double bond which holds the two atoms more tightly together. In reality, the picture depicting discrete double bonds is not accurate. In fact the electron density is distributed, or delocalized, around the entire ring system. Also, the two hydrogens in the center of the ring are not discretely bound to any particular nitrogen atom, but are rather held in the center of the ring by the delocalized electron density. Without the two hydrogens, the ring itself would carry a –2 charge.

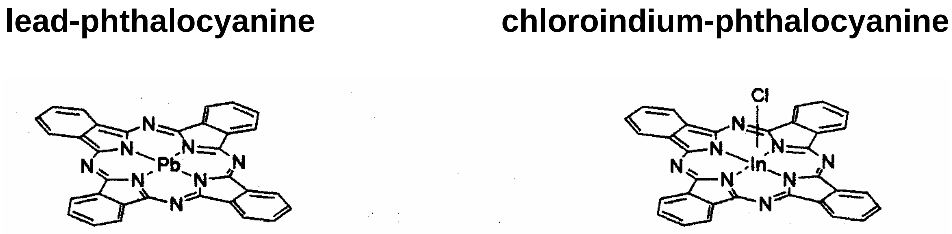
The six sided rings on the periphery of the molecule are referred to as benzo groups. The alpha and beta labels refer to specific positions on the benzo ring, and are useful descriptors when discussing the addition of other chemical groups to the outside of the phthalocyanine ring. The beta position refers to either of the two outermost vertices of any benzo ring, as they are identical. Likewise, a group added in the alpha position might be attached at either of the middle vertices on a benzo group. The basic phthalocyanine ring is also referred to as the macrocycle. Various chemical groups can be substituted onto the periphery of the molecule in the alpha (α) or beta (β) positions. Phthalocyanines with additional groups attached around the periphery of the macrocycle are said to be substituted.

Phthalocyanines tend to be highly colored molecules, both in their solid state and when dissolved in solution. Generally they absorb visible light of longer wavelengths and therefore appear various shades of blue and green. Several factors influence the exact absorption profile and chemical properties of a particular phthalocyanine. The internal hydrogens may be replaced by a wide variety of metals which usually bond evenly to the four nitrogens in the center of the ring. Phthalocyanine macrocycles which complex a metal ion at their center are said to be metallated, while molecules which have hydrogens in the center are referred to as unmetallated.

Figure 5 is a top down view of a phthalocyanine molecule. In three-dimensional space the molecule is flat. This shape allows the phthalocyanine molecules in solution to clump together or aggregate, by stacking one on top of the other like poker chips. This aggregation affects the absorption profile of the molecules as well as their solubility. Large stacks of phthalocyanines become insoluble and precipitate out of the solution as solids. The concentration of phthalocyanines in a given solution affects their tendency to aggregate. At higher concentrations, phthalocyanines will aggregate more readily than at dilute concentrations.

Important to this project are phthalocyanine aggregates that consist of only two molecules stacked together. Such a pair of molecules is referred to as a dimer, while single molecules may be referred to as monomers.

Several different phthalocyanine derivatives have been examined as possible optical limiting materials. Among these, the most promising to date have been various substituted lead and indium phthalocyanines. Basic forms of these two derivatives are shown in Figure 6.


lead-phthalocyanine

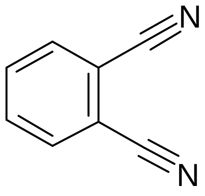
chloroindium-phthalocyanine

Figure 6 – Promising Metallophthalocyanines for Optical Limiting

As mentioned above the phthalocyanine macrocycle caries a –2 charge and so the central metal ion must counteract this charge in order to make a neutral molecule. In the case of the lead phthalocyanine, the lead cation carries a +2 charge and the resultant molecule is neutral. The indium cation carries a +3 charge and so requires the chloride ion (which has a –1 charge) to render the entire molecule neutral. The chloride ion is bonded to the central indium cation, and sticks up perpendicular to the plane of the phthalocyanine macrocycle. The chloride ion (or other similarly situated group) is referred to as an axial ligand or substituent.

Phthalocyanines are generally synthesized in one of two general ways. The first involves the synthesis of the phthalocyanine macrocycle backbone followed by the introduction of the metal cation into the preformed ring. Such a reaction is called an insertion metallation synthesis.

The starting material for the synthesis is a molecule called phthalonitrile or 1,2-dicyanobenzene shown in Figure 7.



Phthalonitrile

Figure 7 - Phthalonitrile

Under certain conditions, four of these phthalonitrile units will bind together or cyclize and form the phthalocyanine macrocycle as shown in Figure 8. One of the phthalonitrile units that comprise the phthalocyanine ring is shown in bold print for illustrative purposes.

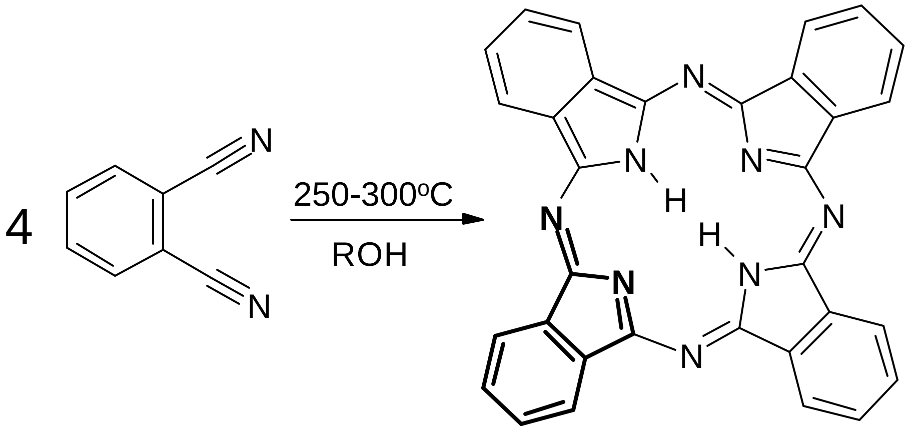


Figure 8 – Cyclization of Phthalonitriles to form Phthalocyanine

The central hydrogens will either come from the solvent or through the addition of an acid to the reaction mixture. Once the macrocycle is purified from any reaction byproducts or unreacted starting materials, a metal cation can be inserted into the center of the ring. This is generally achieved by adding a base to pull the hydrogens out of the center of the ring to allow the phthalocyanine macrocycle to complex a dissolved metal ion as shown in Figure 9.

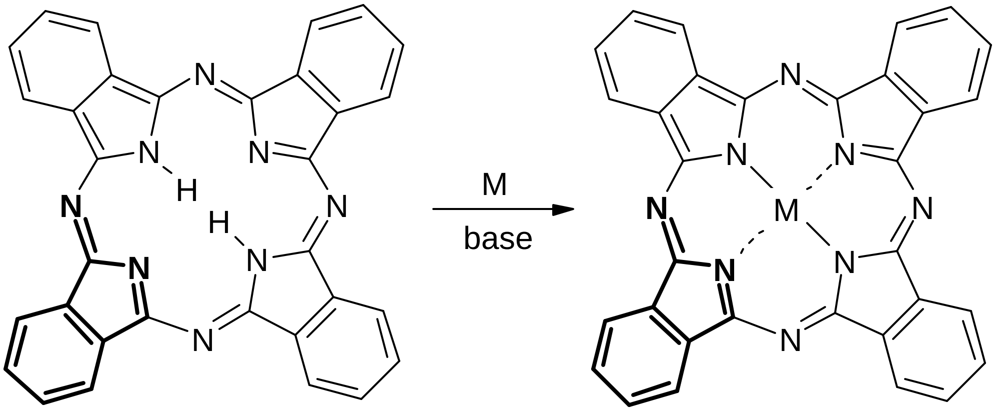


Figure 9 – Metallation of Phthalocyanine Ring

The second general synthetic pathway involves a concerted one-step reaction in which a metal atom or ion serves as a template around which the phthalonitrile units cyclize. This method is called a template metallation synthesis and is depicted in Figure 10.

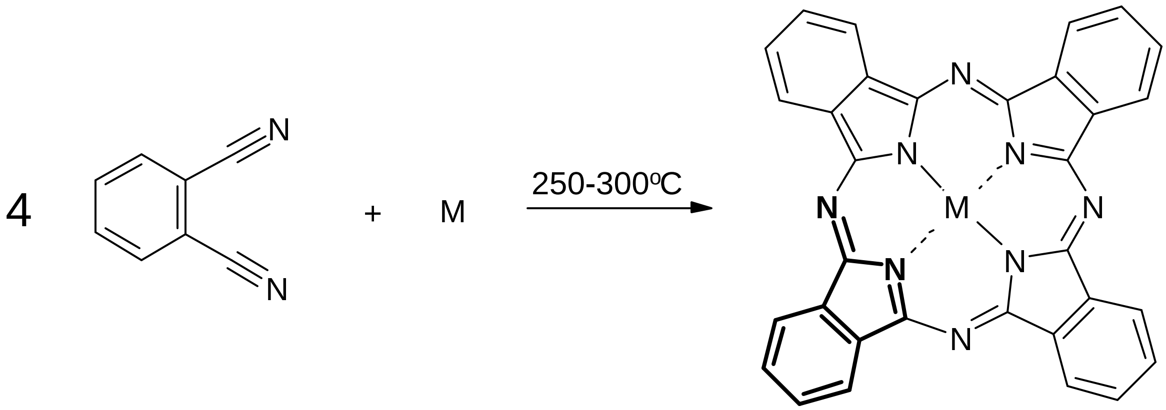
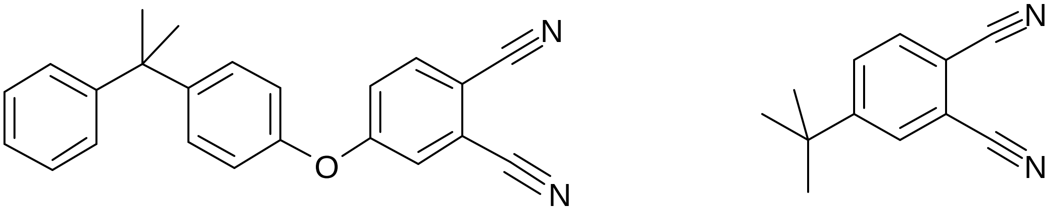


Figure 10 – Template Phthalocyanine Synthesis

To prepare peripherally substituted phthalocyanines, it is necessary only to tailor the phthalonitrile starting units. Substituted phthalonitriles will cyclize to form substituted phthalocyanines. Two substituted phthalonitriles important to this project are shown in Figure 11.



cumylphenoxyphthalonitrile tertbutylphthalonitrile

Figure 11 – Substituted Phthalonitriles

The starting units shown are substituted at the β positions. It is important to note that during the reaction these starting units may approach one another in multiple orientations such that the substituent position in the final molecule may be on either β position at each of the four benzo sites around the phthalocyanine macrocycle. This means that in fact a synthesis will produce several varieties of phthalocyanine macrocycles, called isomers, varying only slightly in the relative positions of the β substituents. However, these slight structural differences do not cause significant differences in optical or chemical properties between isomers. Isomerism is also present when using α substituted starting units or a combination of the two.

While the type of substituent may affect the electronic environment of a phthalocyanine and thereby affect its optical properties, peripheral substitution is primarily used in this project to help limit aggregation. Limiting aggregation is important in promoting both solubility and the desired optical properties. Large bulky substituent groups tend to hinder two phthalocyanine molecules from approaching close together and aggregating. The size of the substituent group, chemical makeup, and its ability to rotate in space affect the extent to which they hinder aggregation and enhance solubility or optical properties.

D. Research Goals

The coordinated central metal has a significant effect on the optical properties of the phthalocyanine complex. The most successful phthalocyanine limiters have been lead and indium substituted. The lead complexes have produced the fastest experimental response times (<10 ps)[b], while the indium complexes allow for coordination of an axial ligand which helps limit aggregation[cd]. The axial ligand also provides another molecular parameter which can be used to affect the optical properties of the molecule. Due to its proximity to lead and indium on the periodic table, thallium could be expected to produce favorable optical limiting characteristics when complexed in a phthalocyanine macrocycle. Ideally it would exhibit the fast response times seen in lead phthalocyanines while also allowing the coordination of an axial substituent similar to indium phthalocyanines. However, soluble thallium phthalocyanines have not been previously synthesized. The synthesis and characterization of a soluble thallium phthalocyanine was the first goal of this project.

The flat structure and delocalized electron density of the phthalocyanine macrocycle cause the molecules to stack together or aggregate in solution. The extent of aggregation depends on the concentration of the molecules in solution, with the molecule existing primarily as a monomer in dilute solutions and as aggregates (dimer, trimer, or higher) in more concentrated solutions. Solutions in which the molecules primarily exist as dimers have been observed to possess enhanced optical limiting properties[e]. Aggregation beyond dimers, however, tends to have a deleterious effect on optical limiting properties. A practical optical limiter needs to be concentrated enough to absorb a sufficient amount of light energy, but below a concentration at which either the ground state absorbs too much light to be useful or the molecules aggregate beyond dimers.

There are several possible ways to limit the formation of higher order aggregates beyond dimers. Capped phthalocyanines[f] and phthalocyanines which can coordinate an axial ligand such as indium and thallium phthalocyanines effectively block one side of the ring from being accessible to aggregation. This will limit the formation of higher order aggregates in concentrated solution. However, the formation of dimers and the resulting enhancement of optical limiting properties often occurs at an impractical concentration, one at which the material is semi-opaque at low light intensities. While limiting aggregation to dimers, the hindered phthalocyanines have no additional driving force to aggregate at low concentrations.

The synthesis of binuclear, or two-centered, phthalocyanines has been reported in the literature[gh]. These compounds are two phthalocyanine macrocycles linked by a bridge of atoms shown in Figure 12.

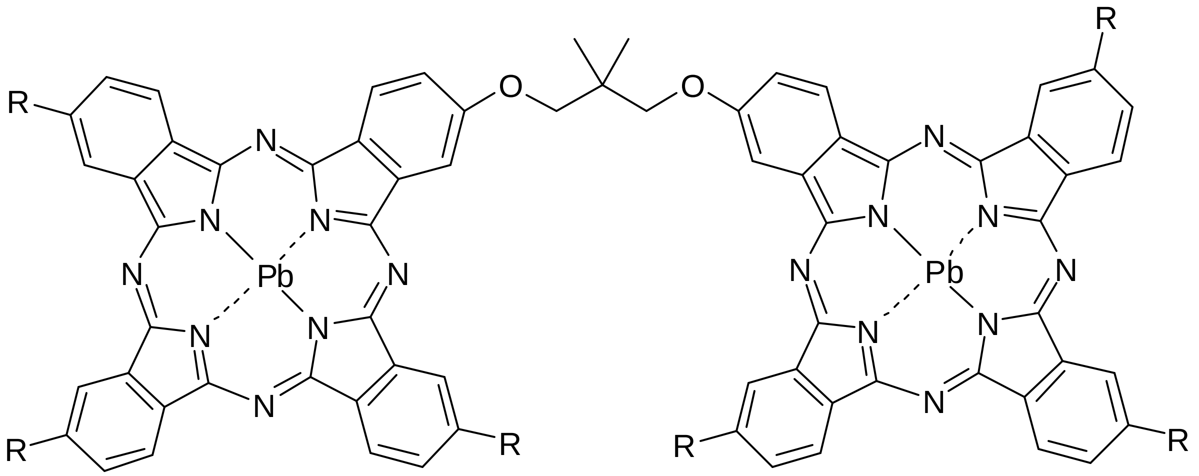


Figure 12 – Metallated "Clamshell" Phthalocyanine

Such molecules should exhibit enhanced optical limiting due to intramolecular aggregation, and the synthesis and characterization of soluble, metallated binuclear phthalocyanines was the second goal of this research. The two phthalocyanine rings are kept in close proximity by the bridge, and although free to rotate in solution should be encouraged to adopt a cofacial orientation through the same forces which encourage dimerization at higher concentrations[i]. Although aggregation is technically an intermolecular phenomenon, the intramolecular orientation of the two rings on top of one another within the molecule effectively mimics a true dimer. The advantage imparted by this molecule is the formation of dimer structures at low concentrations, so that the aggregation enhancement can be attained without breaching the concentration limit for a practical device.

Results and Discussion

A. Thallium Phthalocyanines

a. Synthesis

Initial attempts to synthesize thallium phthalocyanines followed an analogous procedure to the synthesis of monomeric lead phthalocyanines by an insertion of the metal into a preformed macrocycle. However after several weeks of refluxing in o-dichlorobenzene (b.p. 180° C) and 1,2,4-trichlorobenzene (b.p. 214° C) no change appeared in the visible spectrum. Portions removed from the reaction mixtures produced spectra nominally identical to the spectrum of the unmetallated phthalocyanine starting material. Thallium was added as equal portions of thallium triflate and thallium iodide salts. Iodine crystals were added to the reactions but produced no noticeable change in the absorption spectra.

The second approach to synthesizing thallium phthalocyanines involved reacting thallium metal with the precursor phthalonitrile units in a concerted template metallation as shown in Figure 13. The procedure was a modification of a synthesis developed by Suga et. al.[j] Thallium metal flakes and tert-butyl substituted phthalonitrile crystals were packed in the bottom of a Pyrex tube which was then evacuated and sealed. The tube was placed at a slight angle from the horizontal in a tube furnace and heated to 260 C. A green color developed within five minutes, a qualitative indicator of phthalocyanine formation. Several reactions were performed following this procedure and allowed to run for lengths of time ranging from three to seven days. However low yields, apparent decomposition of the product during purification, and presence of organic byproducts complicated the synthesis. Several procedural changes were found to reduce or eliminate these problems. The thallium metal was shaved to increasingly finer flakes and mixed with the phthalonitrile prior to being sealed in the tube. The tube was also placed horizontally in the furnace with the contents distributed roughly evenly along the bottom. These measures presumably increased the surface area of the thallium metal which was available to react. Keeping the tube flat also prevented the solid metal from sinking to the bottom of the tube during the reaction. There was some indication that temperature differences along the length of the tube (a hot end near the center of the furnace versus a cooler end near the edge) resulted in varying levels of reaction completion, and that inverting the tube throughout the week might produce higher yields. Shaking the tube throughout the reaction should also serve to open up thallium metal sites for reaction. The reaction also worked better when the mixture was allowed to run for at least seven days, although beyond that period of time no significant benefit was observed.

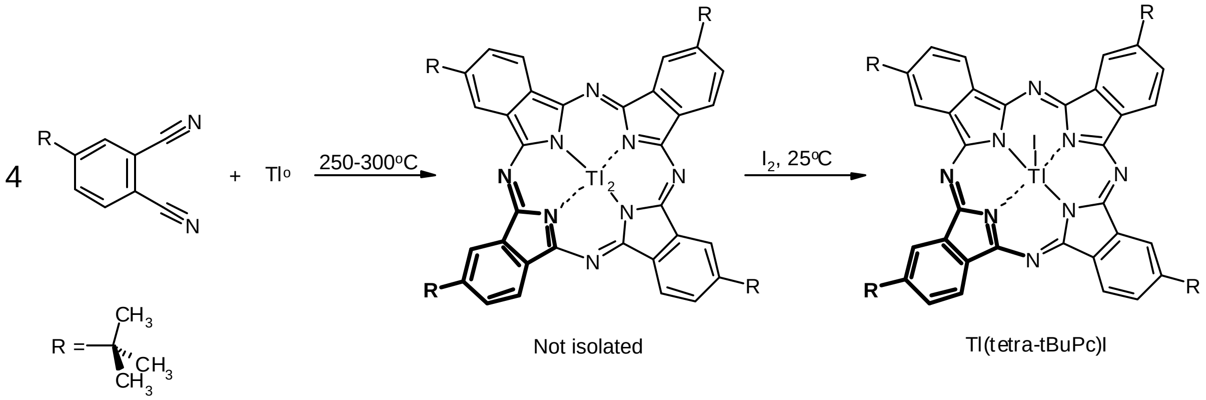


Figure 13 – Synthesis of Substituted Thallium Phthalocyanine Complex

Upon removal from the furnace, the tubes were cooled to room temperature and then in liquid nitrogen. The tubes were cracked open and the contents dissolved in dichloromethane. Slight differences in color were observed when dissolving products from different ends of the reaction tube. These qualitative differences gave rise to the hypothesis that intratube temperature differences were affecting the reaction. The result of such temperature differences might be variance in the relative concentration of unmetallated phthalocyanine to thallium phthalocyanine.

The solution was decanted or filtered to remove any thallium metal solids or other insoluble byproducts. The thallium phthalocyanine formed from the furnace melt reaction is believed to be a dithallium species, with +1 thallium cations held on either side of the macrocycle plane. This species showed a strong absorption in the visible at 728 nm. This dithallium species is extremely acid sensitive. The visible spectrum of the mixture after addition of a few drop of concentrated acetic acid appeared identical to the spectrum of unmetallated phthalocyanine. The dithallium species also degraded in solution over time, either through acid reactivity or another mechanism.

To produce a stable thallium phthalocyanine, the dithallium species was reacted with iodine crystals in solution to produce a +3 oxidation state thallium phthalocyanine complex with an iodide axial ligand following a procedure outlined by Schweiger et. al.[k] Iodine crystals were stirred into the solution at room temperature. Very fine yellow particulates settled out slowly, likely a thallium iodide salt. The visible spectrum of the oxidized solution showed a shift in the maximum absorbance from 728 nm for the dithallium species to 704 nm for the thallium iodide phthalocyanine complex. The thallium (III) species was stable in solution in the presence of acid, tested through the addition of excess concentrated acetic acid, over both the long and short time frame.

A quantitative study of the dithallium oxidation reaction was conducted by adding aliquots of a 6.304 x 10^{-4} M iodine solution to crude dithallium phthalocyanine dissolved in 4.5 mL of dichloromethane. The reaction progress was monitored by observing the change in the absorbance spectrum with the addition of successive aliquots of iodine as illustrated in Figure 14.

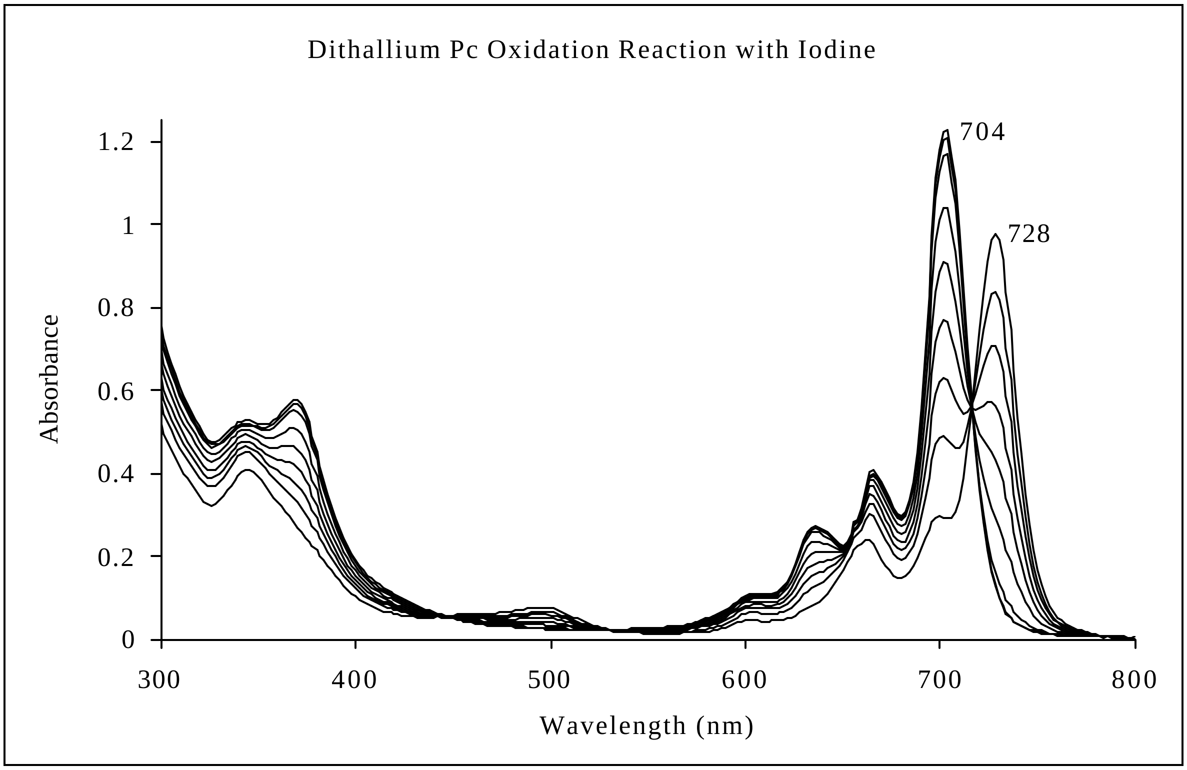


Figure 14 – Tracking Dithallium Oxidation Reaction by UV-Visible Absorbance Spectra

The figure above shows a composite overlay of UV-visible spectra taken at 5 microliter increments of iodine solution addition. The green line with maximum absorbance at 728 nm shows the spectrum of the crude dithallium phthalocyanine before the addition of any iodine solution. The red line with maximum absorbance at 704 nm shows the spectrum of the thallium(III) phthalocyanine complex when enough iodine has been added to completely oxidize all of the dithallium species, at which point the spectrum stopped changing with the addition of iodine. This technique is known as spectral titration. The general trend observed throughout the intermediate spectra is the gradual reduction of the 728 nm absorbance as the 704 nm absorbance grows in. There is also a gradual increase in the absorbance of the solution from approximately 300 to 400 nm as the reaction goes to completion.

The reaction depicted above required approximately eight 5 microliter aliquots of iodine solution to go to completion. In all, approximately 2.52 x 10^{-8} moles of I_2 were added. The known molar absorptivity calculated for a known concentration thallium(III) phthalocyanine solution at 704 nm is 1.52 x 10^{5} $M^{-1}cm^{-1}$. Using this value, and the experimental absorbance of 1.225 of the final oxidation reaction at 704 nm, the original concentration of thallium phthalocyanine in the cuvette was 8.06 x 10^{-6} M. Assuming approximately 4 milliliters of solution in the cuvette, there would have been 3.83 x 10^{-8} moles of thallium phthalocyanine present. The mole ratio indicates that it requires two iodine molecules to oxidize three dithallium phthalocyanines to the monothallium iodide species. One potential reaction that fits the experimental data is shown below.

$$2\ I_2 + 3\ Tl_2Pc \rightarrow 3\ TlPc\text{-}I + 2\ Tl + Tl\text{-}I$$

The solution was filtered to removed the precipitated salts and the solvent evaporated in preparation to purify the product through column chromatography. Column chromatography was used extensively in this research to separate the desired product from other reaction byproducts. The technique involves packing very fine silica particulates into a glass tube. A solvent is flushed repeatedly through the silica packed tube to ensure that there are no residual air pockets or cracks within the silica column. The crude reaction mixture is mixed with a small amount of silica and the mixture packed on top of the column in a very thin layer. Then solvent is added to the top of the column and flushed through under pressure. The molecules in the sample band are carried down the column by the eluting solvent, but are constantly coming out of solution and attaching to silica particles in the column. The more soluble a substance is in the eluting solvent, the less time it will spend out of solution and attached to the silica column and the faster it will travel down the column. In this way materials are separated based on their relative solubilities and affinity for the silica in the column. The solvent is collected in portions, and the product portion is evaporated to leave the desired isolated product. The metallated thallium(III) complex eluted quickly off the ligroine packed silica gel column as a blue/green band with a 2:1 ratio solution of ligroine and dichloromethane. Unmetallated phthalocyanine eluted more slowly off the column. In the initial syntheses, the product was found to have an unusually high yield. However this was subsequently determined to be the result of organic byproducts coming off the column with the product and inflating the weight of the collected material. The organic material may have been unreacted phthalonitrile or some other product such as a triazine derivative. Leaving the reaction to run longer in the furnace and increasing the surface area of the thallium metal able to react help limit the formation of competing products and react all of the starting material. It is possible as well to remove organic byproducts during the column elution. Thin layer chromatography (TLC) tests suggested that even at a 2:1 ligroine to dichloromethane ratio the product should elute significantly earlier than the starting material or other crude organic byproducts, and later purifications bear this out.

TLC is a technique analogous to column chromatography but on a much smaller scale. Very small amounts of material are spotted onto the bottom of a small glass slide coated with silica. The slide is then placed in a covered glass container called a developing chamber. The end of the slide with the sample spots sits in a small amount of solvent. The solvent is carried up the slide through capillary action, and the sample spots are carried along, falling in and out of solution as in the column chromatography and thus separating based upon relative solubilities and affinity for the silica. Often this technique is used to determine an effective solvent for a column chromatography by running several TLC plates in different solvents to find one which gives good separation of the reactions products.

While the phthalocyanine reaction products are highly colored and their progress on the column can be easily observed, the organic contaminants do not absorb in the visible spectrum and therefore appear colorless in solution. Using a quartz column for the purification allowed the position of the organic band to be monitored using an ultraviolet lamp as the organic products appear bright green under the lamp. A glass column would absorb the ultraviolet light. It is likely that the presence of organic byproducts contaminating the thallium phthalocyanine product after a few of the early purifications was due to a very large amount of organic material saturating the column and eluting in a very broad band. Running the reaction for a longer time, and taking steps to increase reactive thallium metal surface area, would minimize the amount of organic byproduct contaminants and allow them to be removed easily through column chromatography.

b. Characterization

A critical part of any chemical synthesis is the identification and characterization of the product. To identify and characterize molecules, several indirect spectroscopic methods are used to piece together the structure of a synthetic product. By combining information about the relative atomic compositions, molecular vibrations, rotations, absorptions and a host of other behaviors the identity of a molecule can be reasonably deduced.

UV-Visible Spectroscopy

Figure 15 shows the absorbance spectrum for a solution of purified thallium(tetra-t-butylphthalocyanine)iodide in chloroform. This compound’s characteristic absorbance is the strong 704-708 nm absorbance. The precise position of this peak may vary slightly due to precision of the spectrometer, the solvent, and a variety of other factors. The single peak, rather than the double peak seen in this region for unmetallated phthalocyanines (in Figure 2 above), is indicative of the additional symmetry of the metallated product over the unmetallated starting material.

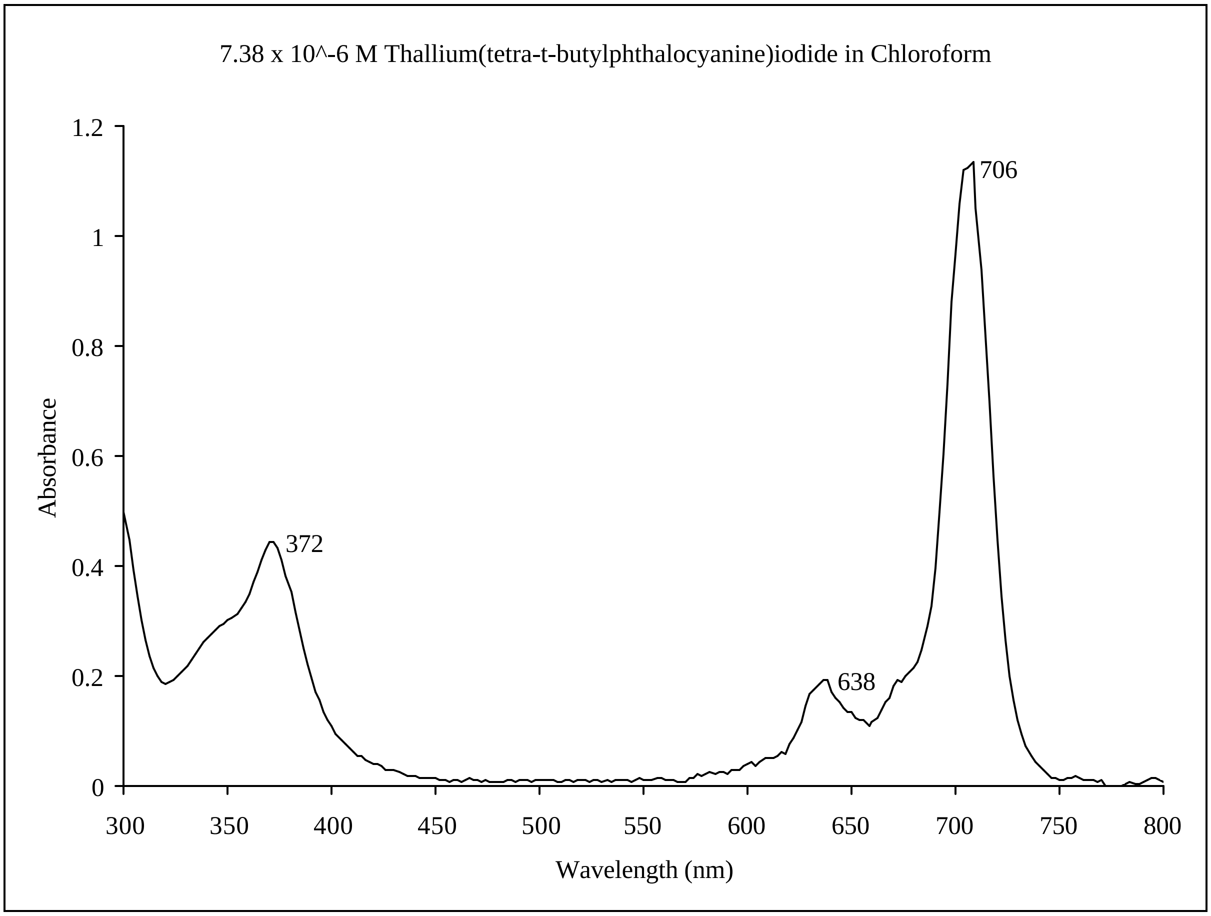


Figure 15 – UV-Visible Absorbance Spectrum of Thallium Phthalocyanine Iodide

Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance spectroscopy is a powerful analytical technique that uses radio waves to study the nuclear moments of certain atoms in a molecule. The nucleus of an atom spins, and the movement of the charged protons creates a small magnetic field around the atom. The nucleus can be thought of as a small bar magnet, with north and south poles. Under normal conditions, these nuclear magnets in a molecule are randomly oriented. However, if a strong external magnetic field is applied to a sample of molecules, the nuclear magnets will be forced to align in the field. The magnets can align in one of two orientations. The low energy orientation puts the north pole of the nuclear magnet towards the south pole of the external magnetic field. The nuclei can also be oriented in a higher energy state, with the north pole of the nucleus towards the north pole of the external magnetic field.

The energy difference between the two orientations depends upon the strength of the external magnetic field. A strong field will lower the energy level of the aligned orientation and increase the energy of the opposed orientation, effectively increasing the energy difference between the two nuclear orientations. The electrons surrounding a nucleus mediate the effect of the external magnetic field upon the nucleus inside. When electron density is pulled away or donated to an atom, the effective magnetic field felt by the nucleus changes. The nucleus of an atom which donates a large amount of its electron density into a bond will “see” a stronger magnetic field because it is not as strongly shielded by its electrons. An atom which receives electron density through a bond will be more strongly shielded from the external magnetic field and it will appear to be in a weaker field.

When an aligned nucleus is imparted with the precise amount of energy that separates the aligned and opposed orientations for that particular nucleus in a particular magnetic field strength, it can flip its orientation to the high energy opposed orientation. The nucleus will eventually relax, releasing the energy corresponding to the difference in orientation, and this energy release can be detected. Only one type of nucleus can be considered at a time, and not all nuclei have a nuclear moment necessary for NMR. One nucleus that does and is frequently studied is hydrogen. Different amounts of released energy indicate that some hydrogen nuclei are more shielded from the external magnetic field than others. This shielding difference is the result of hydrogen atoms “seeing” different amounts of electron density based upon their electronic environment in a molecule.

This nuclear behavior in an applied magnetic field is the principle behind nuclear magnetic resonance spectroscopy. A sample is introduced into a magnetic field to align the individual nuclei. While there are a number of ways to detect the electronic environments of the nuclei, the most straightforward involves varying the external magnetic field while irradiating the sample with a constant energy. As the external magnetic field changes, the energy difference between the aligned and opposed orientations of the nucleus changes. When the energy difference is equal to the irradiating energy, the nucleus can absorb the energy and flip orientations. The energy released when the nuclei relax can be plotted against applied magnetic field strength to generate a spectrum.

In the spectrum, hydrogen nuclei that are less shielded, that is they have more of their electron density pulled into the bond, give rise to peaks shifted farther to the left or downfield from the sample reference point. Hydrogens bonded to less electron withdrawing parts of the molecule are more strongly shielded and their peaks are not shifted as far down the spectrum.

An extremely important characteristic of nuclear magnetic resonance (NMR) spectra is that the relative areas underneath peaks in the spectrum correspond to the number of nuclei that caused the peak. Thus the relative numbers of nuclei in different environments in a molecule can be calculated. Based upon the proposed target molecular structure, the numbers of hydrogen nuclei which should “see” the same external magnetic field can be counted. The experimental peak area ratios should then correspond to this theoretical ratio.

Another characteristic of NMR spectra is splitting of peaks. Peaks in the spectrum will sometimes appear not as single peaks but as doublets, triplets, or higher multiplets. Splitting is caused by the nuclei of other nearby hydrogens. The magnetic field of these nearby hydrogen nuclei affect the overall magnetic field seen by a particular nuclei. If these neighboring nuclei are aligned with the external magnetic field, the overall field “seen” by the examined nuclei is effectively stronger. If neighboring nuclei are opposed to the external magnetic field, the overall field “seen” is weaker. If a nucleus has multiple nearby neighbors, the possible overall field strength seen by the nucleus can vary depending on the number of neighbors aligned or opposed to the external magnetic field. The numbers of neighbors in aligned or opposed orientations will vary between molecules in a sample, and so a particular hydrogen nucleus location in a molecule will see slightly different magnetic fields and give rise to split peaks in the spectrum.

The knowledge of relative electronic environments, relative ratios of nuclei, and splitting caused by neighboring hydrogens can give invaluable information for determining or confirming the structure of a sample molecule. However, as with any analytical technique, there are several potential difficulties with NMR spectroscopy. Impurities in the sample will cause the experimental peak ratios to be different than the theoretical predictions. Also, the solvent used in preparing the sample should not have the same nuclei as those being examined. In the case of hydrogen NMR the solvent used contains isotopes of hydrogen, deuterium, so that solvent nuclei do not interfere with the sample spectrum. However these “deuterated” solvents are more expensive to make and must be kept extremely pure to prevent contamination of the sample. The NMR spectrometer itself is an extremely expensive instrument, and while extremely useful for characterization, the technique carries a high cost.

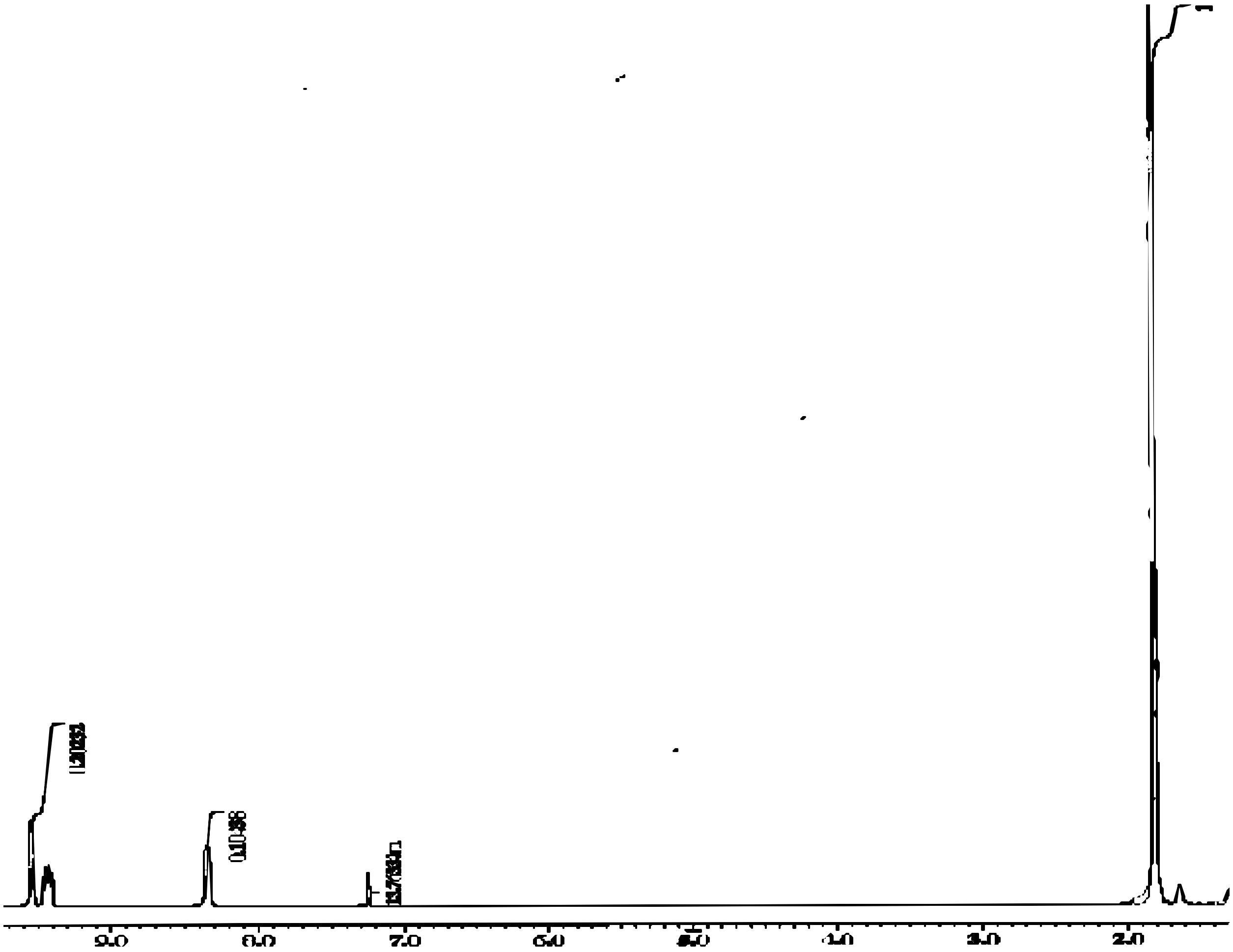


Figure 16 – NMR Spectrum of Thallium Phthalocyanine Iodide

Figure 16 shows the ^1H nuclear magnetic resonance spectrum of a thallium(tetra-t-butylphthalocyanine)iodide in d-chloroform solution. There are nine identical alkyl hydrogens on each t-butyl substituent group around the periphery of the thallium phthalocyanine ring, and a total of thirty-six alkyl hydrogens in all four substituent groups. There are three aromatic hydrogens on each benzo ring and a total of 12 for the entire compound. In the spectrum we observe three groupings of aromatic peaks at 9.55, 9.43, and 8.35 and four very tightly spaced alkyl peaks around 1.81. The small peak at 7.26 is due to hydrogen impurities in the chloroform solvent, and the other alkyl region peaks are due to water and residual solvent impurities from the column chromatography separation. Theoretically we would expect a 3:1 ratio of alkyl to aromatic hydrogens and the peak integrals experimentally provide a 3:0.97 ratio. As the nature of the synthesis does not control the position of the substituent groups to either of the β positions, there are several different isomers which are present in the solution and these are responsible for the four different alkyl peaks. However, each of these isomers has a very similar electronic environment which is seen by the alkyl hydrogens, and as a result the alkyl peaks fall so close together. The three aromatic peaks are due to the three basic types of aromatic hydrogens present in all of the isomers. The first is the β hydrogen, responsible for the peak at 8.35. The other two hydrogens are the α hydrogens, different in their location on the same or opposite side of the benzo from the t-butyl substituent. The peak integrals (assuming the 0.20232 integral in Figure 16 to be the result of equal contributions from the 9.55 and the 9.43 groups) fall very close to the expected 1:1:1 ratio.

Elemental Analysis

Another piece of valuable information for confirming the identity of the reaction product is to determine the relative weight ratios of atoms in the molecule. The myriad elements on the periodic table are defined by the number of protons in an atom of the element. Each element also has a characteristic atomic mass, roughly equivalent to the number of the protons and neutrons in the nucleus of the atom, each defined to have a mass of one atomic mass unit (amu). The weight of the electrons is negligible in comparison. An examination of atomic masses on a periodic table will show that the listed masses are not whole numbers. This is due to the existence of isotopes. Isotopes are atoms of the same element, that is with the same number of protons, but with differing numbers of neutrons. The listed masses are weighted averages based on the natural abundances of isotopes for that element. While is it possible and sometimes useful to isolate particular isotopes, in general when using a particular element it is safe to assume that it is present as a mixture of isotopes in a ratio such as they are found in nature.

Using these characteristic masses it becomes possible to determine relative amounts of different elements present in a molecule. A theoretical percentage of an element by weight in a compound can be calculated based upon the predicted molecular structure. The actual weight percentage can be found experimentally through a technique known as elemental analysis. A sample of the product is placed in a sealed glass apparatus and heated until it combusts. All of the carbon present in a sample reacts with the oxygen stream to form carbon dioxide, the hydrogen reacts to form water, and the nitrogen is converted into dinitrogen gas. Each of these gases is preferentially trapped in a different absorbant in the apparatus. Once the sample has been completely combusted, the absorbants can be separated and weighed. The increased weight of the absorbant is due to the trapped carbon dioxide, water vapor, or nitrogen. From these weights the weight of the carbon, hydrogen, and nitrogen in the original sample can be determined and their percent weights in the compound calculated. If experimentally determined percent compositions match those based on the proposed structure, that structure may be correct. The experimental percent compositions determined for thallium(tetra-t-butylphthalocyanine) iodide using elemental analysis were 60.56% carbon, 6.29% hydrogen, and 8.05% nitrogen. The theoretical percent compositions for thallium(tetra-t-butylphthalocyanine) iodide (along with two moles of hexane and one mole of heptane residual from the ligroine chromatography solvent) are 60.38% carbon, 6.35% hydrogen, and 8.41% nitrogen.

Mass Spectrometry

Every molecule has a given molecular weight based upon its constituent atoms. Determining the molecular weight of a sample is a useful means to help confirm the identity of a molecule. Such a technique is called mass spectrometry. There are several different mass spectrometry techniques, but the governing principles remain essentially the same. A sample of molecules is converted into the gas phase and then bombarded by electrons. These electrons will knock out an outer electron from the molecule, giving the molecule an overall positive charge. The molecule has been said to be ionized. These molecular ions are then attracted by a negatively charged element and accelerated into a flight chamber. The time it takes for a molecule to reach the end of the flight chamber corresponds is related to its molecular weight. Heavier molecules will travel more slowly down the flight chamber than lighter ones. Knowing the molecular weight of a sample molecule is a very useful piece of information for confirming the identity of a reaction product.

There are several difficulties with mass spectrometry techniques, particularly when trying to examine large molecules. These large molecules are difficult to get into the gas phase for ionization without the molecule falling apart. A technique called matrix assisted laser DI? mass spectrometry is a recent technique which allows mass determinations for large molecules. The sample molecules are mixed with a substance which strongly absorbs laser light energy. This mixture, the matrix, is spread onto a flat surface with tiny wells imbedded in it, so that the mixture settles into the wells. A laser is then directed onto the sample wells, causing the matrix material to quickly absorb a large amount of energy and promote the sample molecules almost instantly into the gas phase. From here the molecules can be ionized and passed into a flight chamber. The mass spectrometry results for the thallium phthalocyanine molecule were inconclusive, not producing results which could be reconciled with either the proposed molecular structure or with any fragments of the molecule which may have broken off during the analysis.

c. Aggregation

One of the predicted advantages of a thallium phthalocyanine in optical limiting applications was its ability to coordinate an axial ligand. The iodide ligand in this case greatly affects the ability of the phthalocyanine to aggregate in solution. High levels of aggregation have deleterious effects on both the solubility and optical limiting ability of phthalocyanine complexes in solution. The large iodide ligands oriented perpendicular to the phthalocyanine ring certainly prevent aggregation beyond dimer formation. Theoretically, two thallium(tetra-t-butylphthalocyanine)iodide molecules could dimerize with their two “ligand-free” faces oriented towards one another.

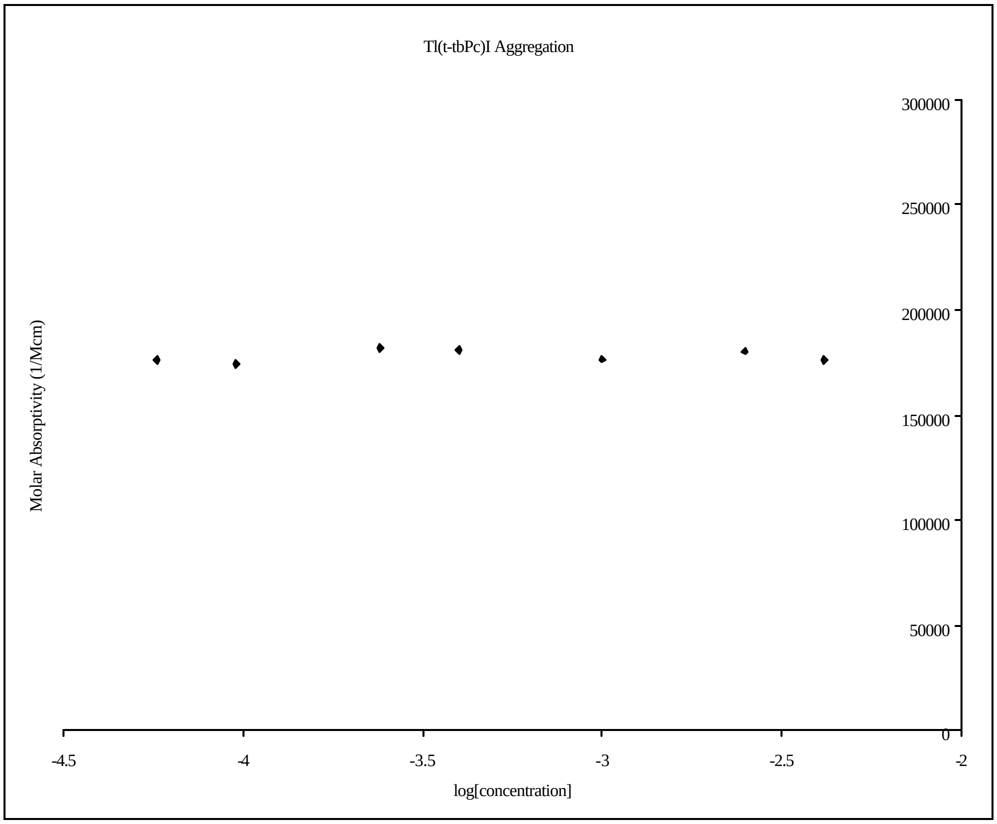


Figure 17 – Thallium Phthalocyanine Aggregation

Figure 17 shows that in fact at concentrations up to approximately 10^{-2} M, the thallium phthalocyanine exists entirely in the monomeric form. The chart shows the relationship between the molar absorptivity coefficient at the wavelength of maximum absorbance (704-708 nm) versus the log of the concentration of phthalocyanine in solution. If the thallium(III) complex were dimerizing the molar absorptivity coefficient would change with increasing concentration, leveling out at the coefficient value corresponding to a solution of only dimerized molecules. It is possible that the iodide ligand exerts enough push downwards on the t-butyl substituent groups as to provide a significant steric barrier to aggregation. Also, the larger positive charge imparted to the thallium by the iodide withdrawing group causes the phthalocyanines to experience significant repulsive forces to a symmetric cofacial aggregate and the bulky t-butyl groups prevent a slipped aggregate from forming. It is possible that at higher concentrations the thallium(III) complex would show the formation of dimers.

d. Optical Limiting Studies

In order to determine the suitability of the thallium(tetra-t-butylphthalocyanine) iodide molecule for optical limiting applications, several optical tests were performed upon the molecule. The most straightforward optical study is called a z-scan depicted in Figure 18.

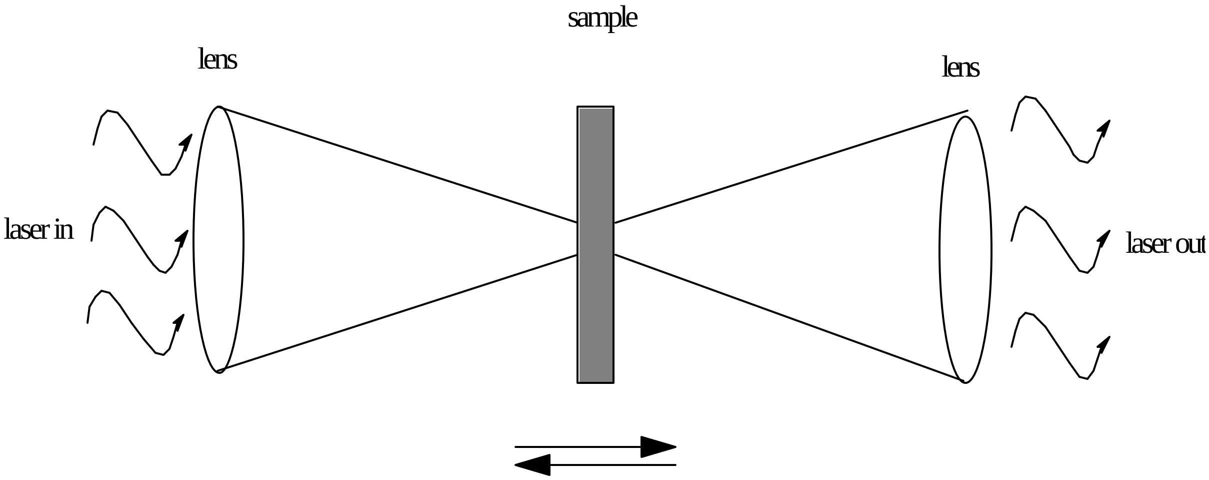


Figure 18 – Z-Scan Study Diagram

A laser is passed through a lens causing the beam to focus to a point before widening and passing through another lens. A concentrated solution of the molecule is placed in a very thin cell between the two lenses. The sample is moved slowly along the path of the laser. The laser is most intense at the focal point and less intense as the distance away from the focal point increases in either direction. Thus, as the sample is translated along the beam, the energy incident upon it changes. Monitoring the intensity of the transmitted beam as a function of distance from the focal point produces the graph shown in Figure 19.

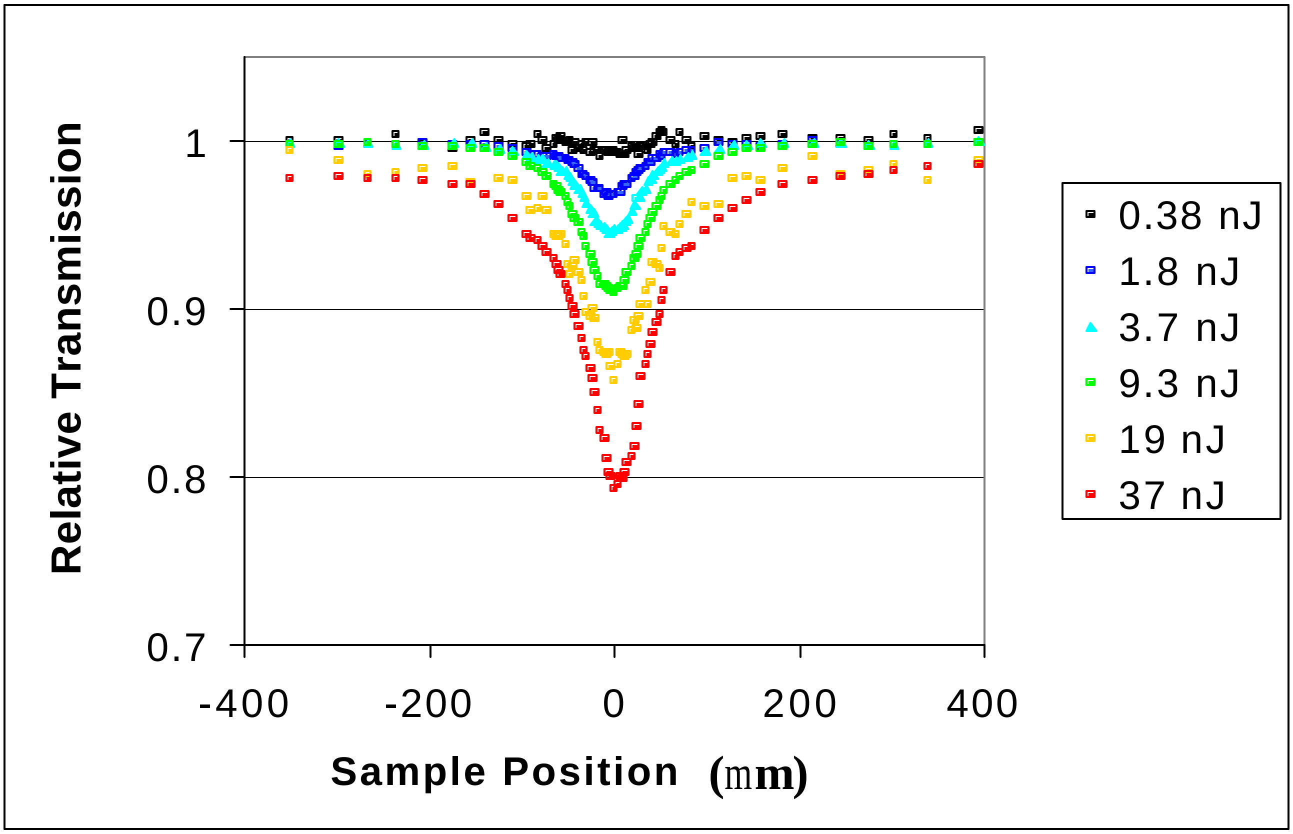


Figure 19 – Z-Scan Output for Thallium Phthalocyanine

Each different series of points corresponds to a different incident laser energy. The x-axis of the graph charts the sample's translational position in the beam, with the center of the graph corresponding to the focal point of the laser and the point of maximum intensity. Each energy line shows a dip in percent transmission as the sample approaches the focal point indicating that the sample transmits less energy in the higher intensity regions of the beam. Also the dip is more pronounced for the higher energy beams, indicating again that the sample has a lower transmission at higher energies. As the sample leaves the focal point, the relative transmission increases indicating that the process is reversible. It is also important to note an inflection point, where the slope of the dip increases noticeably, in the higher energy scans. This suggests an additional limiting mechanism such as the presence of additional excited states with large absorption cross sections that become active at these higher intensities. Although these analytical tests are carried out at relatively low beam intensities, the molecule exhibits nonlinear optical behavior over the range of the test.

The z-scan output graphs include all the contributions to limiting, the excited state refractive and the thermal refractive components as well as nonlinear absorption. A second z-scan test is performed but with a reduced aperture before the detector. This aperture prevents highly refracted laser light from reaching the detector. By comparing the reduced aperture output scans to the initial scans, it is possible to separate out the refractive and absorptive components of the overall limiting. The deduced refractive limiting contributions are shown in Figure 20.

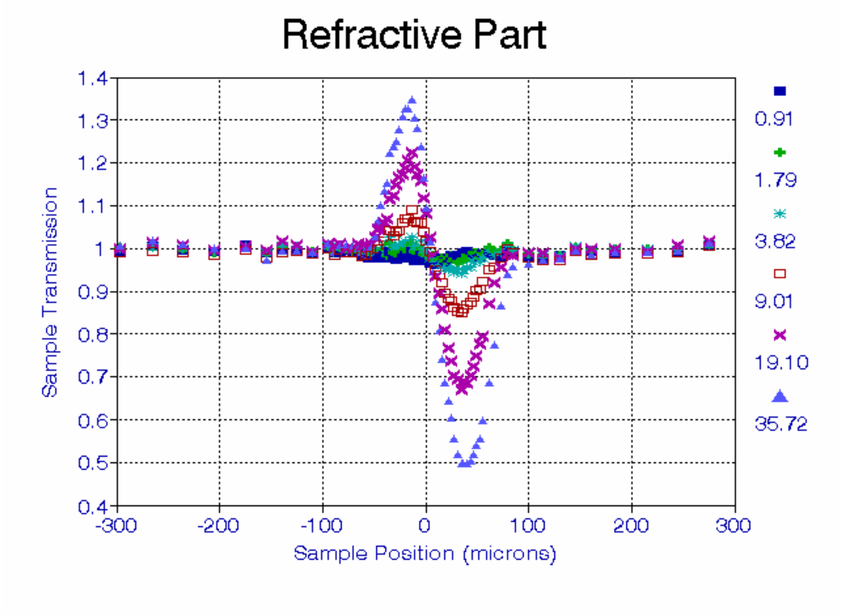


Figure 20 – Z-scan Refractive Component for Thallium Phthalocyanine

The change in sign observed on either side of the focal point is due to the fact that before the focal point the refraction is focusing the laser while after the focal point refraction is scattering the light. The two refractive components cannot be separated from this information.

This indicates that either both the change in the solvent's refractive index due to produced thermal energy and the change in the molecule's refractive index due to its excitation have the same sign, that is they bend the light the same way, or one of them is small compared to the other.

A characteristic of a good optical limiter mentioned above was a large excited state cross section and a relatively low ground state cross section. The ground state cross section (at 532 nanometers, the wavelength of the test) calculated from the visible absorption spectrum is 1.6×10^{-18} cm^2. The excited state cross section can be estimated from the z-scan data and is calculated to be 6.1×10^{-17} cm^2. Thus the excited state absorption probability is more than 35 times that of the ground state.

Figure 21 shows the transmission of a sample of the thallium phthalocyanine over a much broader range of input energies. The sample transmits almost all of the input energy out to around 10 nJ of input at which point the transmission begins to decrease with increasing input energy. This behavior continues until the sample saturates around 1000 nJ of input energy.

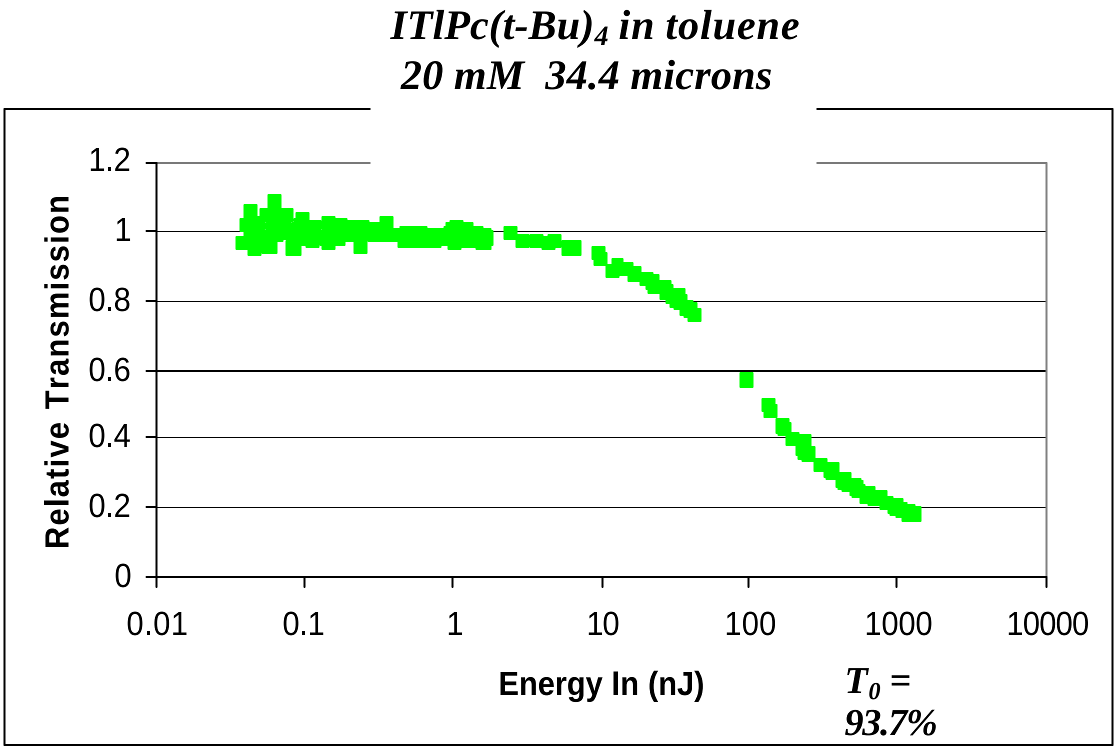


Figure 21 – Relative Transmission Curve for Thallium Phthalocyanine

B. Binuclear Phthalocyanines

a. Synthesis

The synthesis of a binuclear phthalocyanine "clamshell" molecule, a modification of the procedure outlined by Leznoff et. al.[1], begins with the formation of the bridge from the molecule neopentylglycol shown in Figure 22.

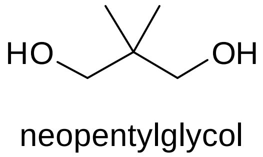


Figure 22 - Neopentylglycol

The first step is to attach two phthalonitrile units, the starting unit from which the phthalocyanine ring is formed, to each end of the neopentylglycol molecule. In a basic solution, the hydrogens are pulled from the glycol oxygens which in turn replace the nitro groups of the phthalonitrile and form a bond. This substitution reaction produces the bridge unit as shown in Figure 23.

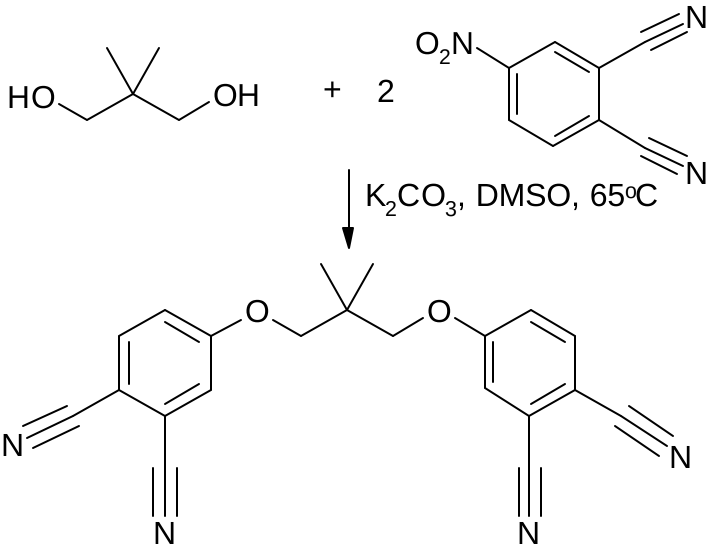


Figure 23 – Synthesis of "Clamshell" Bridge Unit

After purification of the bridging unit, the synthesis proceeds in an analogous manner to the cyclization of a phthalocyanine monomer. Single units of phthalonitrile, these already possessing the desired peripheral substituents to enhance solubility, are reacted with the bridging units. The phthalonitrile units cyclize with the starting units on either end of the bridge, resulting in a linked pair of phthalocyanine rings as shown in Figure 24. Again shading is used to illustrate the origin of the units in the final product.

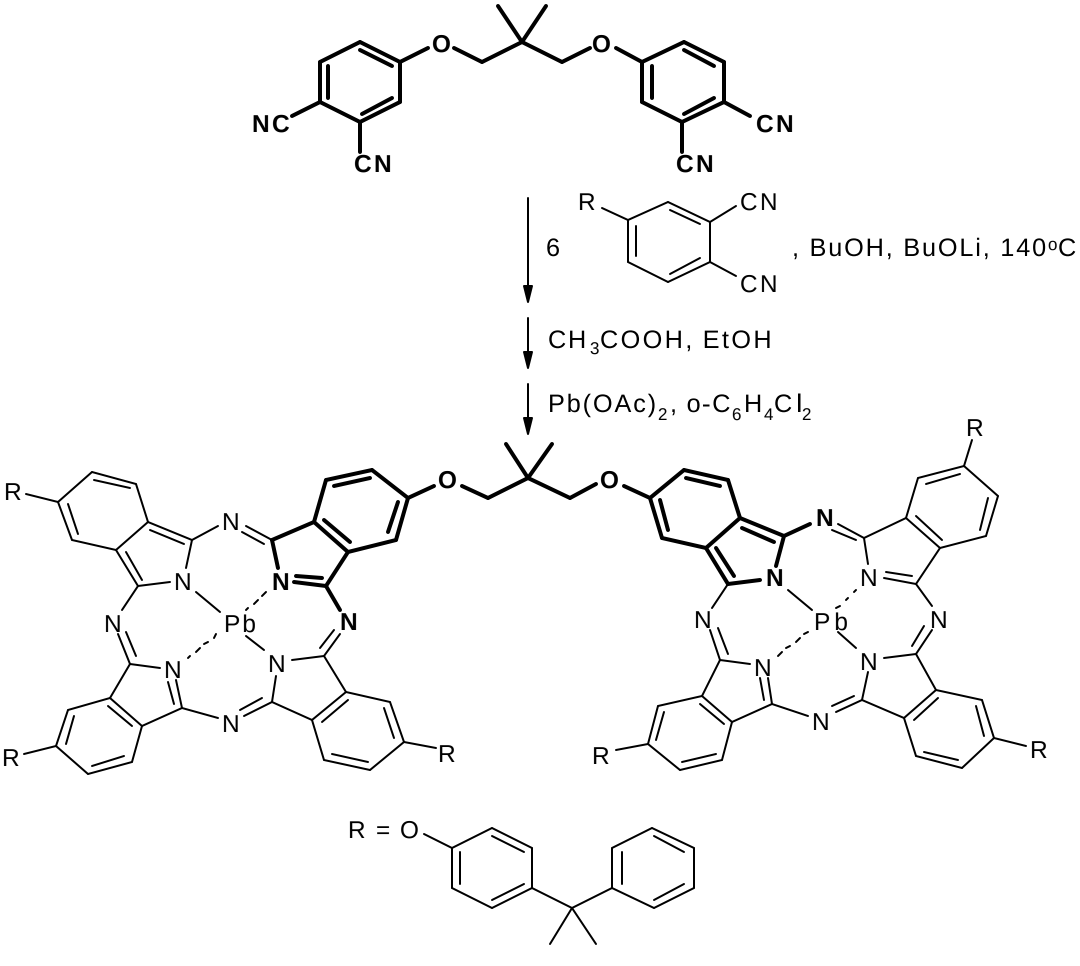


Figure 24 – Synthesis of Metallated "Clamshell" Phthalocyanine

One difficulty with this reaction is the formation of a multitude of byproducts. The phthalonitrile units cyclize with themselves to form monomeric phthalocyanine rings. Multiple bridging units could react together in a host of arrangements, forming products that range from two rigidly linked phthalocyanine rings formed from four bridging units polymeric phthalocyanine chains. The products are separated by column chromatography to isolate the single-linkage structure. Metallation can then be accomplished through an insertion reaction, using a base to pull the central hydrogens away from the ring and allowing a metal ion, in this case lead, to take their place.

b. Characterization

UV-Visible Spectroscopy

While UV-Visible absorbance spectra do not reveal much structural information about the “clamshell” molecule, it is useful for tracking the reaction progress of the metallation. Shown below are the spectra of the unmetallated “clamshell” (Figure 25) and the spectrum of the “clamshell” after the metallation reaction (Figure 26). There is an obvious change in the absorption spectrum that is very similar to the changes observed during the metallation of phthalocyanine monomers.[m]

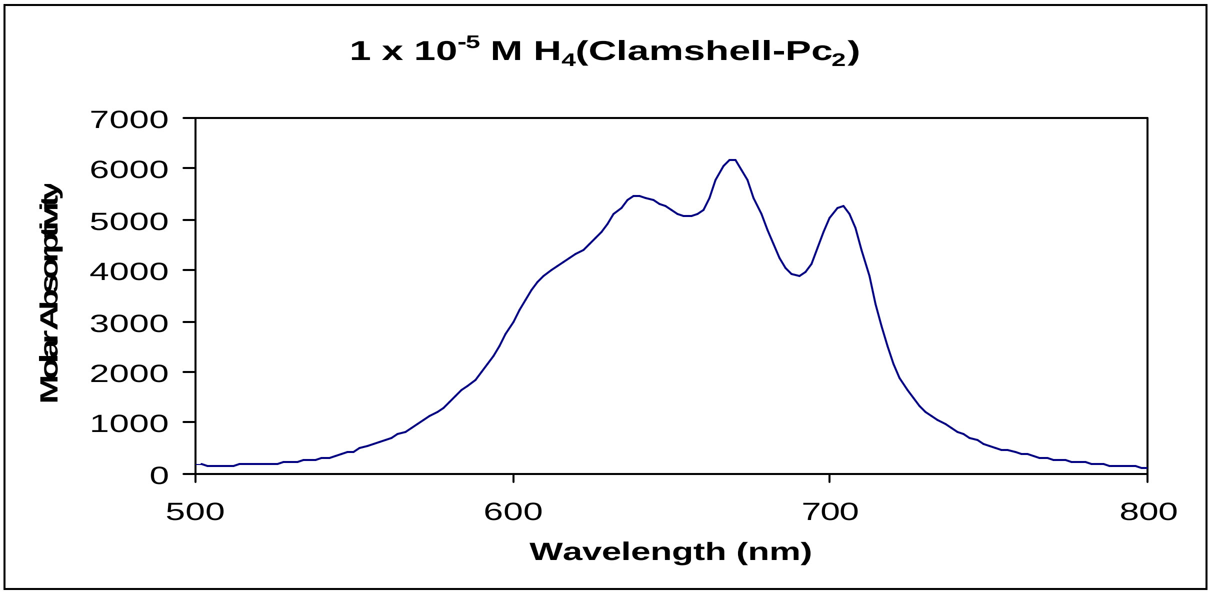


Figure 25 – Absorbance Spectrum of Dilute "Clamshell" Solution

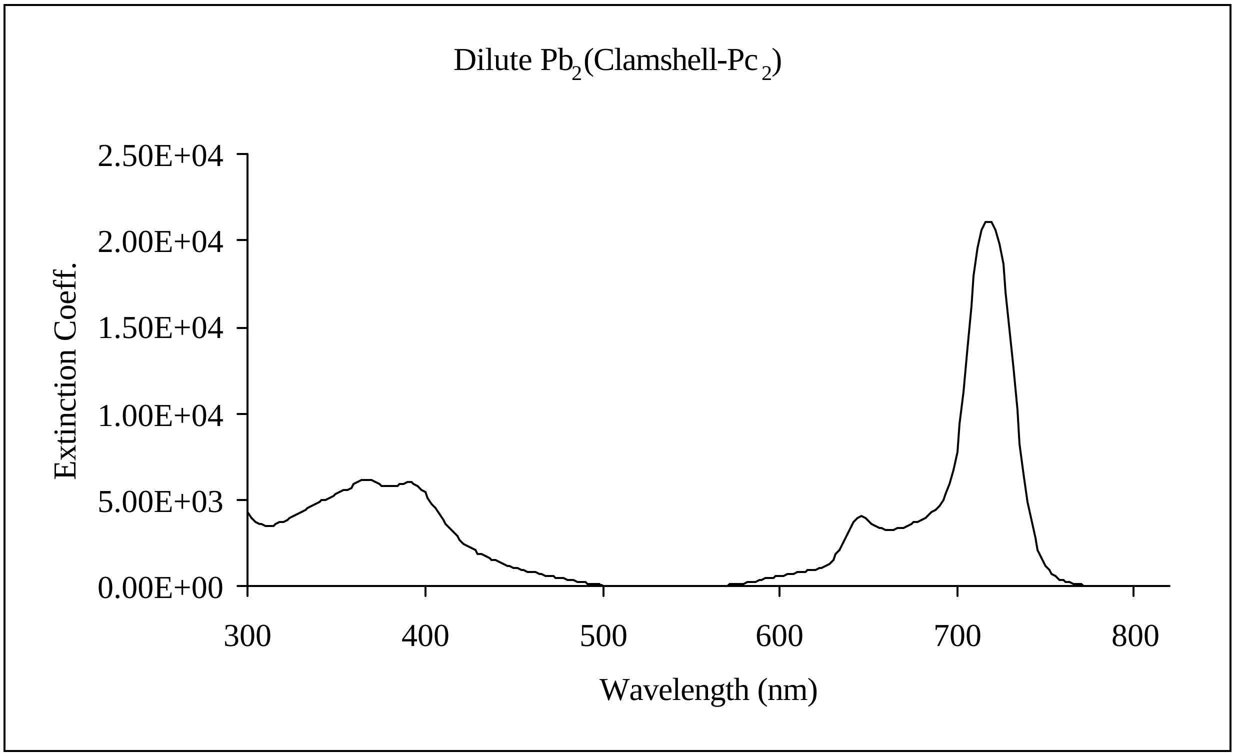


Figure 26 – Absorbance Spectrum of Dilute Lead "Clamshell" Solution

Nuclear Magnetic Resonance Spectroscopy

The NMR spectrum of the clamshell molecule was not nearly as clean as that of the thallium phthalocyanine and the direct analysis done above was complicated for this molecule. However, the spectrum did shown peaks in the expected regions. The cumylphenoxy substituted "clamshell" was the primary molecule synthesized and studied. The spectrum shows the large aromatic peaks of the cumylphenoxy and the phthalocyanine ring benzo groups and the lesser alkyl peaks of the cumylphenoxy methyl methyl and the bridge hydrogens in the ratio predicted by the proposed structure.

Elemental Analysis

The calculated weight percentages for the lead cumylphenoxy substituted "clamshell" were 68.2% carbon, 4.5% hydrogen, and 8.0% nitrogen. Elemental analysis produced weight percentages of 59.51% carbon, 4.21% hydrogen, and 5.55% nitrogen. The calculated weight percentages for the metal free cumylphenoxy substituted "clamshell" were 79.877% carbon, 5.396% hydrogen, and 9.374% nitrogen while elemental analysis returned 78.25% carbon, 6.14% hydrogen, and 6.80% nitrogen. The discrepancies are likely the result of trapped solvent molecules from purification or incomplete metallation of the "clamshell".

Mass Spectrometry

The experimental molecular weight of the unmetallated "clamshell" molecule was 2391.63 grams per mole, which corresponds very closely to the theoretical molecular weight of 2390.864 grams per mole calculated from the proposed molecular structure. The mass spectrometry results for the lead metallated "clamshell" molecule were inconclusive, not producing results which could be reconciled with either the proposed molecular structure or with any fragments of the molecule which may have broken off during the analysis.

c. Aggregation

The aggregation of phthalocyanines has been studied[no] primarily through the observation of changes in the visible spectrum with a change in concentration. When two phthalocyanine molecules aggregate, the absorption spectrum of the solution changes, due to interaction between the rings. The delocalized electron systems interact to create new absorption transition possibilities. The absorption spectra[p] of a phthalocyanine solution at various concentrations is shown in Figure 27.

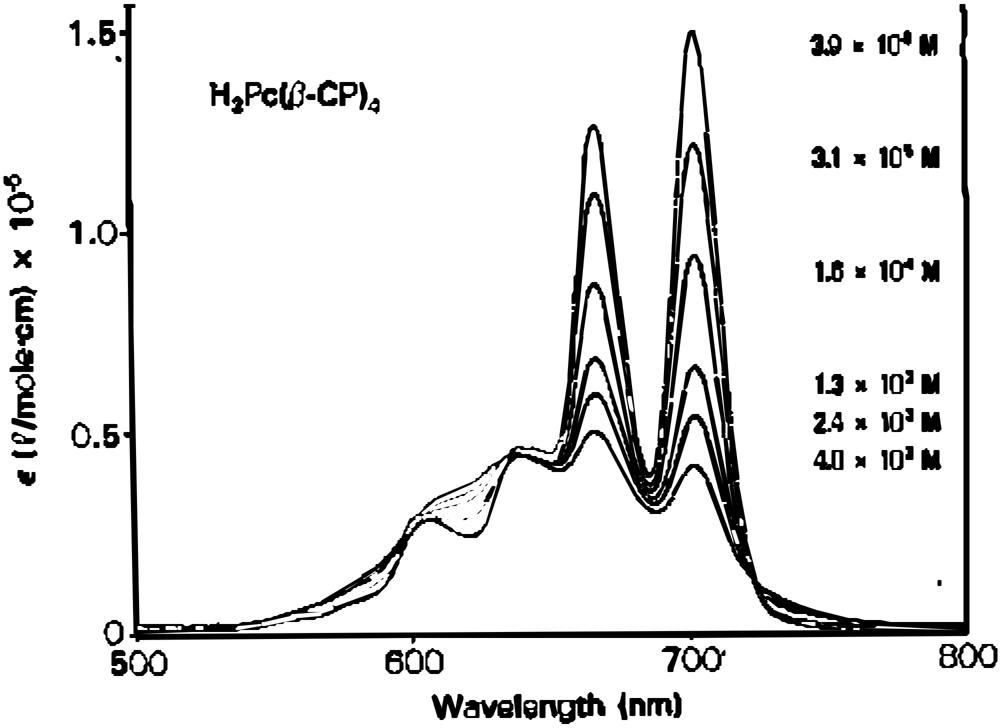


Figure 27 – Tracking Aggregation as a Function of Concentration

The two characteristic peaks of the monomer lower in intensity and the maximum absorbance is shifted as the concentration increases. The spectrum at the highest concentration suggests what a solution of dimers would look like. Figure 28 illustrates the equilibrium between two free floating monomers and two monomers aggregating to form a dimer. The relative amounts of each depend upon the concentration, with a high concentration solution being shifted to the right of the equation.

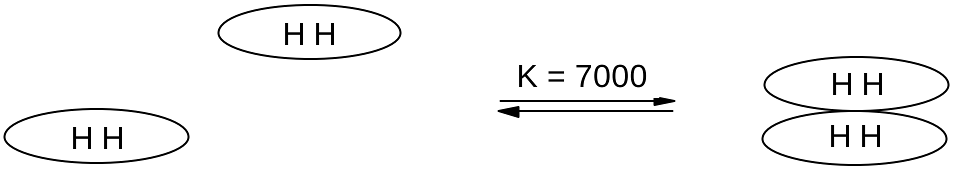


Figure 28 – Aggregation of Monomeric Phthalocyanines

Shown below are spectra of an unmetallated phthalocyanine monomer (Figure 29), and the corresponding linked "clamshell" analogue (Figure 30).

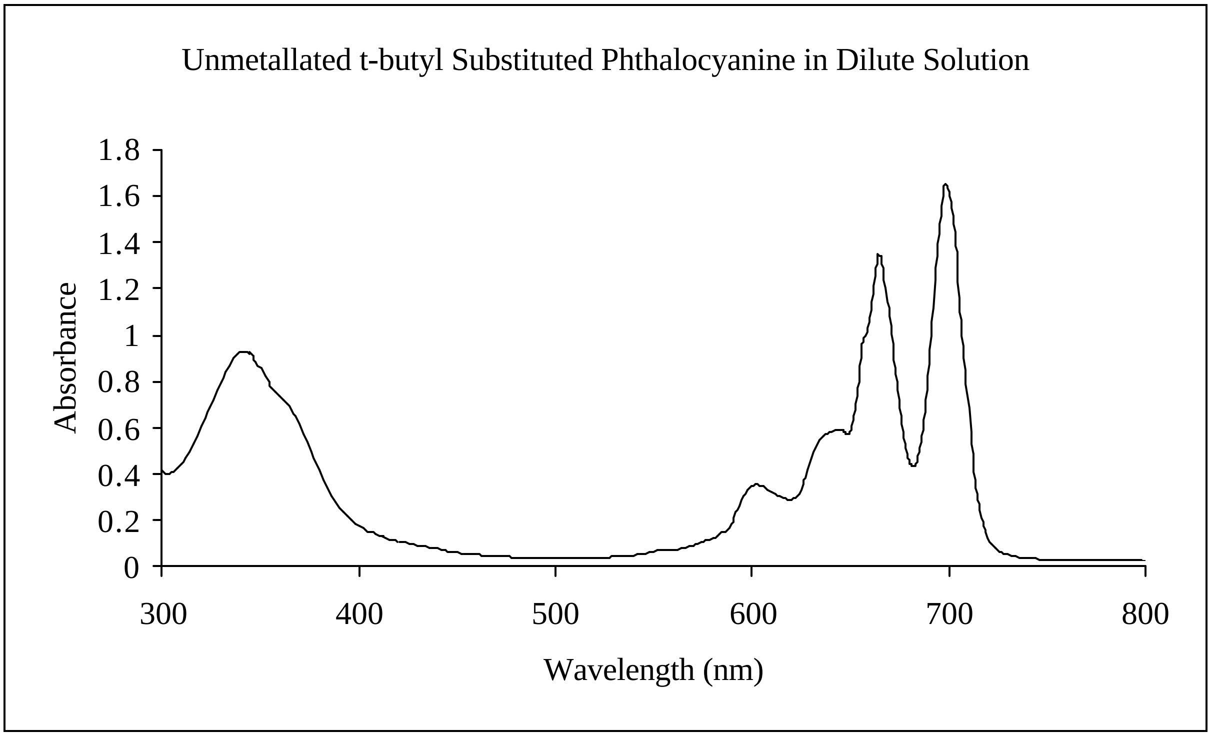


Figure 29 - UV-Visible Absorbance Spectrum for Unmetallated Phthalocyanine

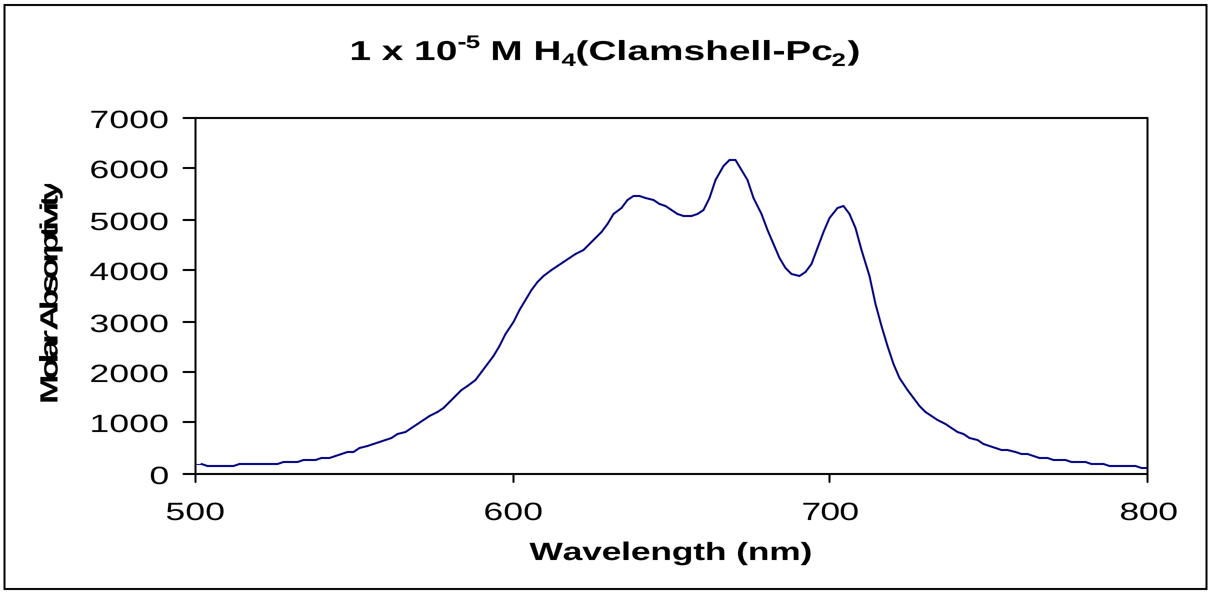


Figure 30 - Absorbance Spectrum of Dilute “Clamshell” Solution

The spectrum of the “clamshell” phthalocyanine at dilute concentration looks like the spectrum of the monomer at high concentration where it is aggregating as dimers. This spectrum suggests that the two linked rings of the “clamshell” molecule exist primarily oriented one on top of the other in solution. Because absorbance is an additive property, that is a solution of multiple substances will have an absorbance at a given wavelength that is the sum of the absorbances of all the components of the solution at that wavelength, the spectrum of the “clamshell” compound is a blend of the absorbance due to the molecule existing in a skewed or “open” and in a stacked or “closed” conformation. By comparing the absorbance of the characteristic monomer peak in the “clamshell” spectrum to the absorbance of the same peak in a dilute solution of the monomer, one in which it is not aggregating, the percentage of the “clamshell” in each conformation can be determined with the results shown in the Figure 31. These values are the result of comparing the intensity of the dominant monomer absorbance peak (approximately 703 nm) in both the monomer and “clamshell” spectra. A dilute solution of “clamshell” molecules at half the concentration (as there are two rings per molecule) should be identical to a dilute solution of monomers if the "clamshell" existed only in an "open" conformation. The reduction in the 703 nm peak intensity is a result of the reduction of the effective concentration of "open" clamshell molecules in solution.

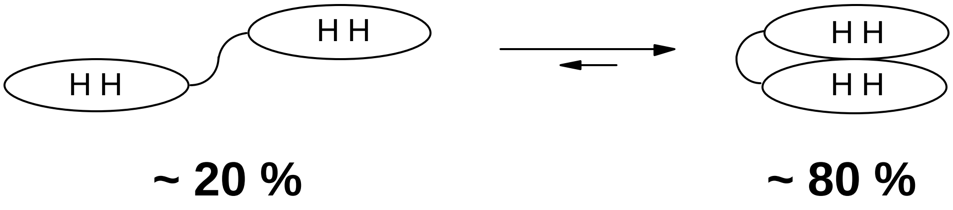


Figure 31 – Intramolecular Orientations of "Clamshell" Phthalocyanine

Another consideration for the "clamshell" molecule is the aggregation of multiple "clamshells" at higher concentrations. Several potential aggregation possibilities exist, representatives of which are shown in Figure 32.

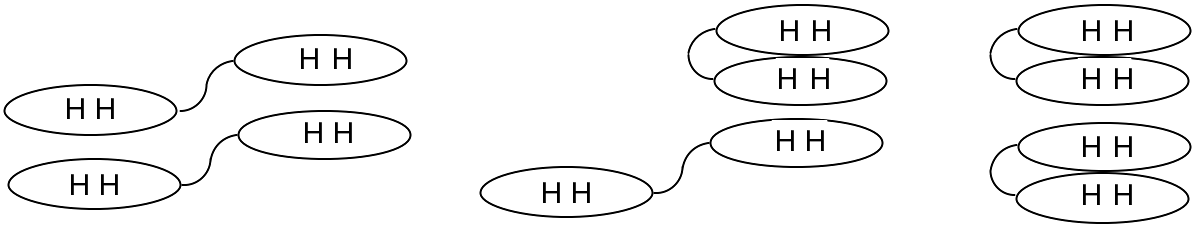


Figure 32 – Possible Intermolecular Aggregation Structures of "Clamshell" Phthalocynines

While clearly the "clamshell" is orienting as an intramolecular dimer even at low concentrations, its behavior at high concentrations is more similar to the monomer analog. The conformational orientations, the relative positions of the two linked rings within the molecule, do not depend on concentration. Thus any change observed in the absorption spectrum of the "clamshell" at higher concentrations would be the result of intermolecular aggregation, rather than intramolecular conformation.

The following figures show the change in the molar absorptivity coefficient, also called the extinction coefficient, of the characteristic monomer peak for both the monomer^{q}” (Figure 33) and the “clamshell (Figure 34) molecules as a function of concentration. The two lines in the monomer graph are for alpha and beta substituted variants. The beta monomer line is most useful for comparison as the “clamshell” molecule is substituted at the beta positions.

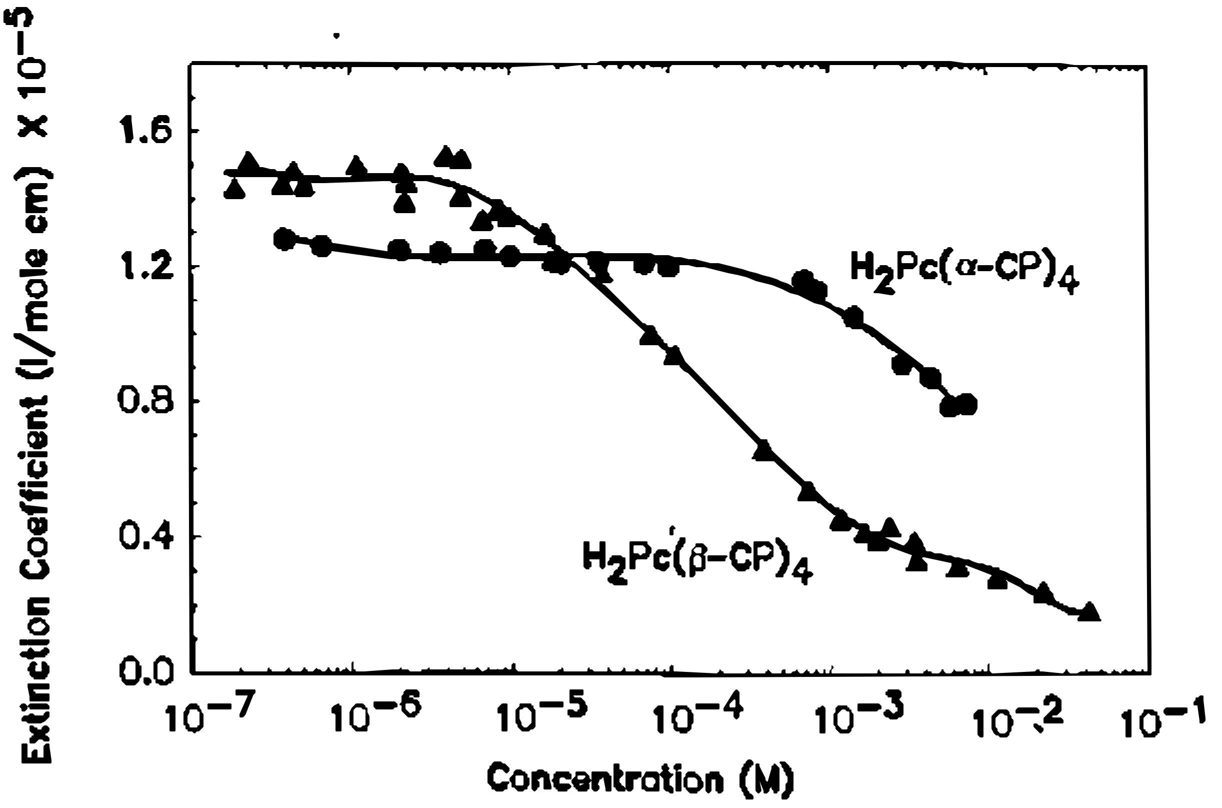


Figure 33 – Aggregation of Alpha and Beta Substituted Phthalocyanines

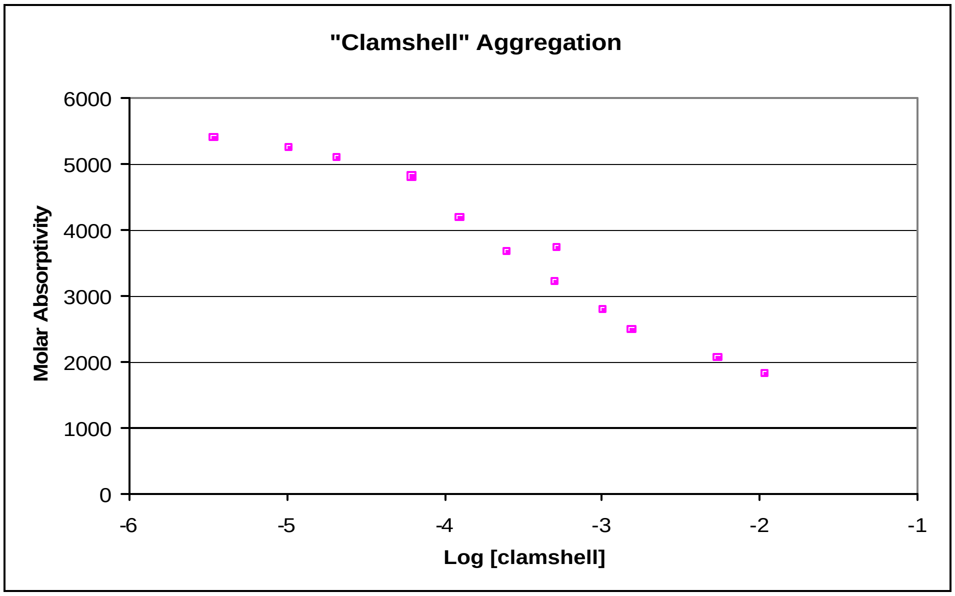


Figure 34 – Intermolecular Aggregation of "Clamshell" Phthalocyanines

The two curves appear very similar. Both curves are level, indicating the dominance of molecular monomers, in dilute solutions. The curves begin to slope downwards around concentrations of 10^{-5} M indicating the formation of intermolecular aggregates. Finally both curves begin to level out, indicating the dominance of intermolecular dimers in solution, between concentrations of 10^{-3} and 10^{-2} M. This mimicry indicates that the binuclear "clamshell" aggregates with other "clamshells" in the same concentration ranges as the monomeric phthalocyanine.

The linked binuclear structure appears not to affect intermolecular aggregation. It does however significantly promote the formation of intramolecular dimers by the stacked orientation of the two linked phthalocyanine rings. The stacked conformation should confer the enhanced optical limiting properties seen for dimer pairs even at low concentrations. However, it is the lead metallated “clamshell” which is of particular interest for optical limiting because of the success of lead metallated monomers in such applications.

Unlike the obvious difference between the monomer and “clamshell” spectra for the unmetallated variant at dilute solutions, a comparison of lead monomer and “clamshell” does not show a dramatic difference in the wavelength of maximum absorbance. However, the relative absorbances at dilute solution are different, indicating a difference in the molar absorptivity coefficient in the “clamshell”. The implication is that the lead “clamshell” exists in some amount as an intermolecular dimer, adopting a cofacial or closed conformation even in dilute solutions.

Figure 35 shows overlaid spectra of the lead metallated “clamshell” at dilute (tallest peak), intermediate, and high concentration solutions. There is clearly a change in the spectra with the dilute solution dominated by the large absorbance at 720 nm and the concentrated solution with a broad absorbance from 600-800+ nm. This data clearly indicates that the lead clamshell does aggregate intermolecularly at higher concentrations.

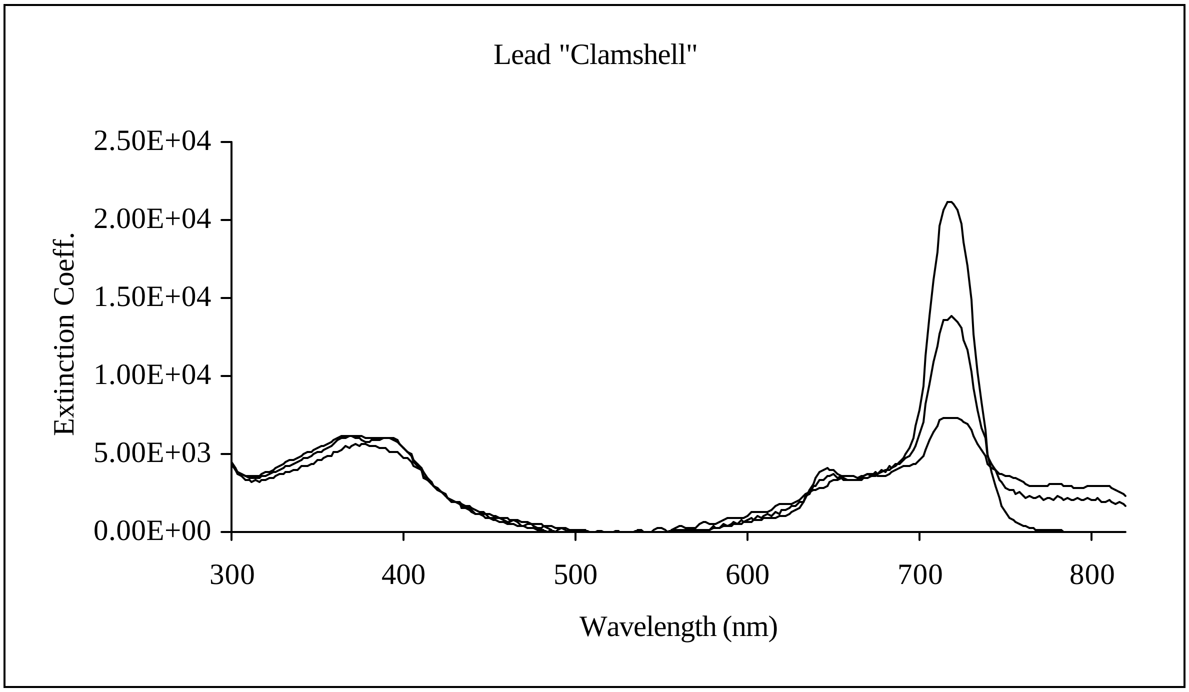


Figure 35 – Tracking Aggregation of "Clamshell" Phthalocyanines by UV-VIS Spectra

Figure 36 shows the molar absorptivity coefficient versus concentration comparison used above for the unmetallated phthalocyanines. Although the line exhibits the same behavior, notably the downward slope indicating the onset of aggregation, it does not change at corresponding concentrations. The lead "clamshell" does not begin to aggregate until closer to 10^{-4} M concentrations. Also, although the slope begins to decrease, the line has not leveled out by a 10^{-2} M concentration, indicating that there is still a portion of the lead "clamshell" that has not aggregated even at this high concentration.

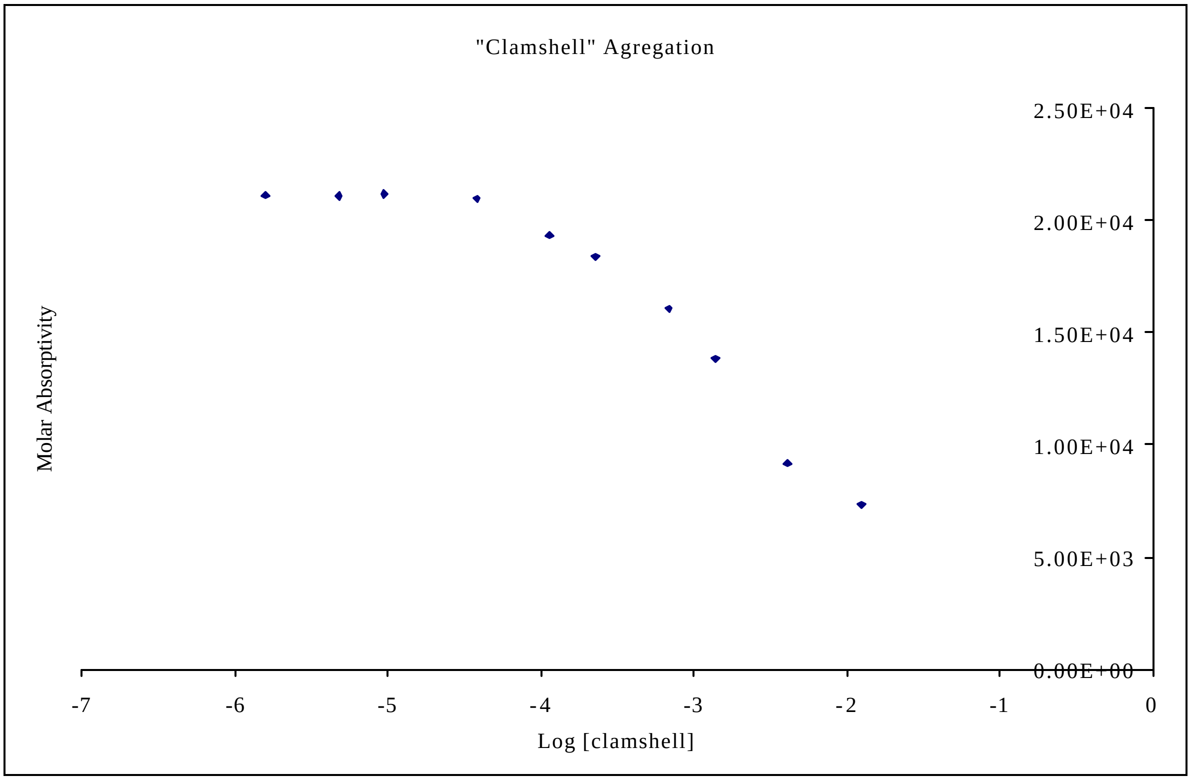


Figure 36 – Aggregation of Lead “Clamshell” Phthalocyanines

d. Optical Limiting Studies

Figure 37 is the z-scan output graph for a cumylphenoxy substituted lead "clamshell" phthalocyanine.

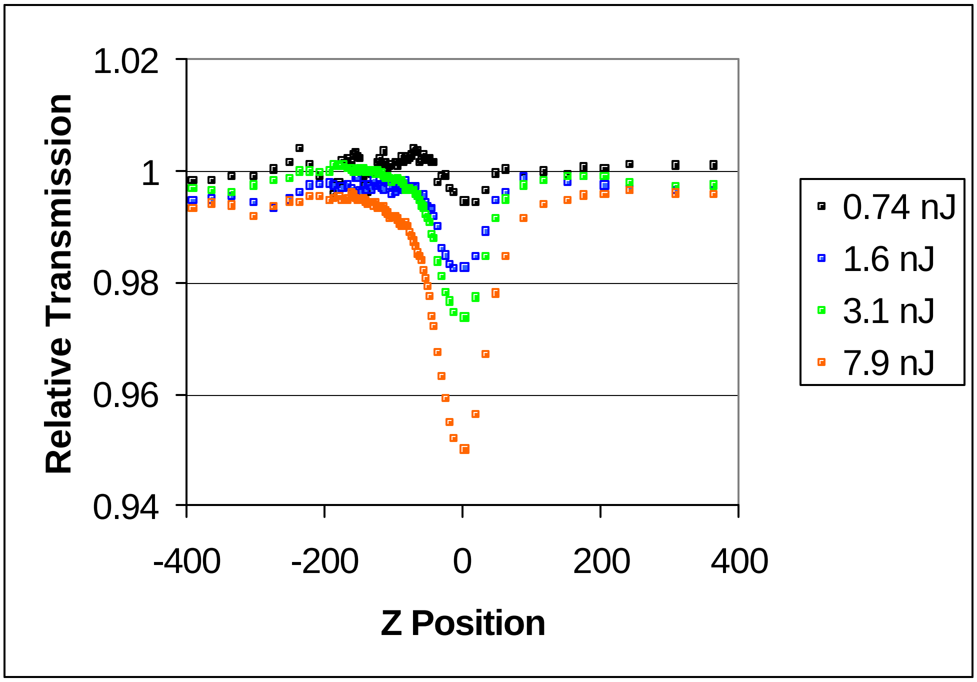


Figure 37- Z-Scan Output for Lead "Clamshell" Phthalocyanine

The graph is similar to that of the thallium phthalocyanine and the lead clamshell shows evidence for non-linear absorption even at these low input energies. Figure 38 shows the transmission of a sample of the lead "clamshell" over a much broader range of input energies. The transmission decreases with increasing intensity to a few hundred nanojoules where the transmission suddenly begins an even steeper decrease. This sharp change is evidence for the onset of another limiting mechanism which becomes active at a few hundred nanojoules of input energy. A likely mechanism is the presence of a second excited state with an even higher absorption cross section which is the result of aggregation of the "clamshell" molecule to dimers and the resulting creation of the potential excited state.

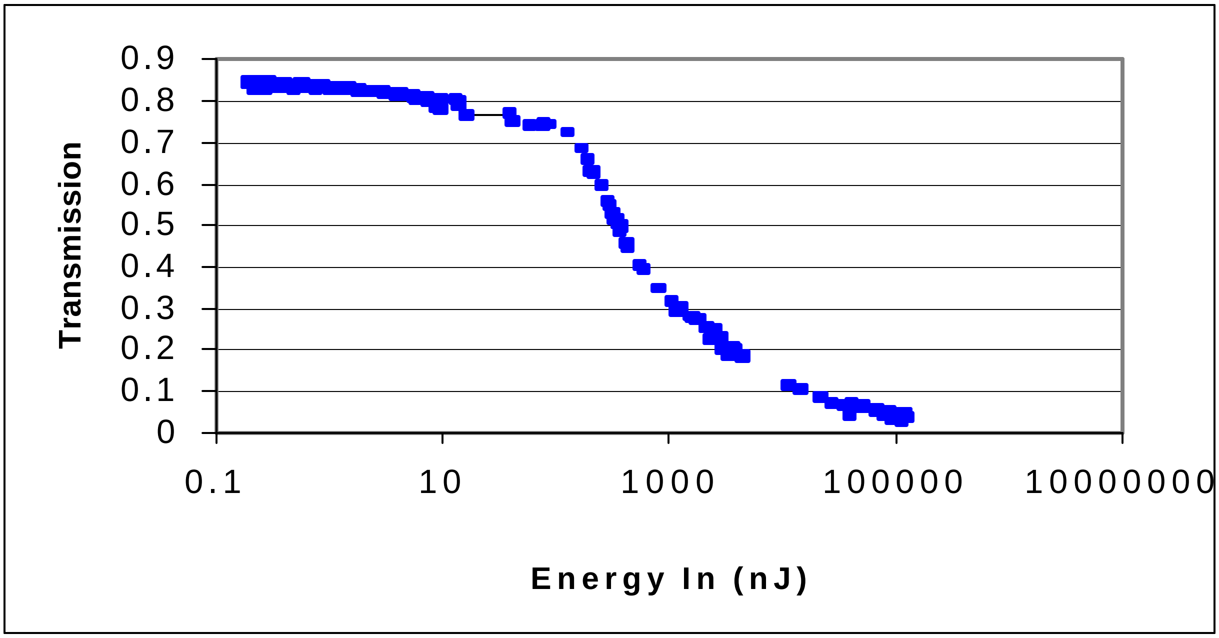


Figure 38 - Relative Transmission Curve for Lead “Clamshell” Phthalocyanine

Conclusions

Both target molecules, the soluble thallium phthalocyanine and the soluble binuclear lead phthalocyanine, were successfully synthesized. Although the yields for the reactions were relatively low and both molecules required isolation from a number of similar byproducts, both the syntheses were simple and straightforward and the reagents are all commercially available. Even with the focus of this research on synthesizing the molecules for study, several methods were found to increase the reaction yields and a more directed research into synthetic optimization should develop more efficient syntheses.

The thallium-(tetra-t-butylphthalocyanine) iodide was fully characterized. The UV-Visible spectra were consistent with previously synthesized metallophthalocyanines. The NMR spectrum was very clean, producing peaks at the expected locations and at the expected ratios. The elemental analysis corresponded very closely with predicted atomic percentages, particularly with the inclusion of some residual solvent expected from the purification process. The aggregation studies showed that the thallium complex did not begin to aggregate even at the high concentration end of the study, probably the result of the large iodide axial ligand and the large t-butyl substituent groups. The initial optical limiting studies on the thallium phthalocyanine molecule were very promising, with the molecule possessing a large excited state cross section compared to that of the ground state. The molecule also showed evidence for an additional mechanism such as another excited state at higher intensities.

The lead "clamshell" phthalocyanine was not characterized to the extent as was done for the thallium phthalocyanine, but all the characterization results could be explained by the proposed product structure. The UV-Visible spectrum was consistent with previous binuclear metallophthalocyanines, and the unmetallated precursor exhibited similar consistency with previous syntheses. NMR spectra, although complicated by the absence of symmetry resulting in multiple overlapping peaks, showed peaks in the proper regions with expected ratios. The unmetallated "clamshell" was found to exist primarily as an intramolecular dimer in solution, with the linked rings situated on top of one another. The lead variant did not show evidence for this cofacial conformation, although it is possible that the spectra of the lead monomer and dimer were much more similar than the pronounced differences seen for the unmetallated form. As with the thallium complex, the lead "clamshell" exhibited nonlinear optical response even at low input energies. At higher energies above a few hundred nanojoules, the "clamshell" showed an even stronger response attributed to additional excited states due to the formation of dimers in solution. This transmission drop continued to much higher input energies.

It is difficult to compare the performance of two optical limiters directly as there are a host of parameters which could be used to determine performance. The threshold energy at which limiting begins, the damage energy, the response time, the relative absorption of the ground and excited states, the presence of multiple complementary mechanisms, and the behavior of the limiter at its damage threshold could all be compared. Both the molecules synthesized exhibit strong non-linear behavior and show evidence for the existence of additional complementary limiting mechanisms. The thallium complex possesses a high excited state cross section relative the ground state. Its axial ligand provides aggregation control and the potential to tailor the optical properties through ligand substitution. The lead "clamshell" complex also showed evidence for intramolecular dimerization, and it is certainly reasonable to surmise that the "clamshell" should show enhanced limiting due to aggregation at a lower concentration than the monomer analog due to a combination of intra and inter molecular effects.

There are several further avenues of research to be pursued. A study of different axial ligands on the thallium phthalocyanine should be conducted. Metallation of the clamshell with other metals, particularly thallium, should be studied. Varying the length and nature of the bridge linkage in the clamshell should be studied to find an optimal structure to encourage pseudo aggregation. The synthesis and study of a tetranuclear phthalocyanine[r] which might exist as dimer pairs and which could be used to enhance limiting at even lower concentrations should be pursued. The potential for a substituent group to enhance solubility which also enhancing limiting through a refractive index change should be investigated. The potential for these molecules to be used as practical optical limiters is strong, and further investigation should find ways to tailor the basic molecules to produce effective limiters.

Appendix A: Experimental

Instrumentation

A JEOL 400 MHz spectrometer was used for the collection of all nuclear magnetic resonance spectra. UV-Visible spectra for characterization and reaction monitoring were collected on a Hewlett-Packard diode array instrument. Elemental analysis of products was performed at Galbraith Laboratories in Knoxville, Tennessee. Mass spectrometry was performed at the Naval Research Laboratory using a MALDI-TOF apparatus. Optical studies were performed by researchers in the Optical Sciences Division at the Naval Research Laboratory.

Materials

Reagent grade solvents were used in all synthetic and analytical steps. 1-Butanol was distilled from magnesium prior to use. Deuterated solvents were obtained from Aldrich. Lithium amide was weighed in an inert atmosphere glove box. All other reagents were purchased at the highest level of purity available.

Aggregation Studies

Thallium-(tetra-t-butylphthalocyanine) iodide

The aggregation study was performed on seven different solutions with concentrations ranging from 5.75 x 10^{-5} M to 4.16 x 10^{-3} M in chloroform. The solutions were prepared through a serial dilution scheme. The absorbance spectra were measured in path lengths from 1.43 x 10^{-3} cm to 0.10 cm. The path length values up to 5.00 x 10^{-3} cm were calculated using interference patterns. For longer path lengths the manufacturer's nominal value was used. Where practical multiple measurements of same concentration solutions were made in different path length cells and averaged calculated molar absorptivities were used in producing the aggregation plot.

Unmetallated Cumylphenoxy Substituted "Clamshell" Phthalocyanine

The aggregation study was performed on twelve different solutions with concentrations ranging from 3.41 x 10^{-6} M to 1.06 x 10^{-2} M chloroform. The solutions were prepared through a serial dilution scheme. The absorbance spectra were measured in path lengths from 1.17 x 10^{-3} cm to 1.00 cm. The path length values up to 2.50 x 10^{-3} cm were calculated using interference patterns. For longer path lengths the manufacturer's nominal value was used. Where practical multiple measurements of same concentration solutions were made in different path length cells and averaged calculated molar absorptivities were used in producing the aggregation plot.

Lead Metallated Cumylphenoxy Substituted "Clamshell" Phthalocyanine

The aggregation study was performed on ten different solutions with concentrations ranging from 1.59 x 10^{-6} M to 1.23 x 10^{-2} M in chloroform. The solutions were prepared through a serial dilution scheme. The absorbance spectra were measured in path lengths from 1.21 x 10^{-3} cm to 1.00 cm. The path length values up to 5.00 x 10^{-3} cm were calculated using interference patterns. For longer path lengths the manufacturer's nominal value was used. Where practical multiple measurements of same concentration solutions were made in different path length cells and averaged calculated molar absorptivities were used in producing the aggregation plot.

Syntheses

1,3-bis-(3',4'-dicyanophenoxy)-2,2-dimethyl propane. 1.92 g of 4-nitrophthalonitrile, 3.37 g of potassium carbonate, and 0.54 g of neopentyl glycol were added to 10 mL of dry DMSO in a round bottom flask. The reaction mixture was heated in 65 C oil bath under argon until TLC plate in dichloromethane showed all 4-nitrophthalonitrile had reacted (further addition of potassium carbonate helped reaction to completion). Filtered solution with ethyl acetate to remove solids and then extracted filtrate with water to remove DMSO. The ethyl acetate solution was dried over magnesium sulfate, filtered, and the solvent was evaporated off. The product was isolated on a silica gel column using dichloromethane as the eluting solvent and then recrystallized from boiling acetonitrile/water.

2,9,16,23-tetracumylphenoxyphthalocyaninatolithium. 0.1 g of $LiNH_2$ was dissolved in 5 mL of Butanol and heated to boiling. Addition of 1 g of 4-(4-cumylphenoxy)-phthalonitrile rapidly turned the solution dark emerald green. After heating at reflux for 1 hour, rxn mixture was transferred into 100 mL ethanol and 200 mL of water. The resulting precipitate was filtered and placed in a vacuum desicator to dry.

1,3-Bis-2’-(9’,16’,23’-tricumylphenoxyphthalocyaninoxylithium)-2,2-dimethylpropane. Dissolved .053 g of lithium amide in 5 mL of butanol in a 25 mL round bottom flask. Heated mixture to boiling under argon. Added ground mixture of 0.50 g 4-(4-cumylphenoxy)-phthalonitrile and 0.0354 g 1,3-bis-(3’,4’-dicyanophenoxy)-2,2-dimethyl propane to boiling solution. Mixture developed green color in approximately five minutes and was kept under reflux conditions for six hours. Added green solution to a 100 mL ethanol and 200 mL water mixture in a 500 mL flask. Addition of saturated sodium chloride solution increased the size of precipitate particles and allowed for suction filtration to collect solid and dried under vacuum. Product was isolated on a silica gel/ligroin column initially using 2:1 ligroine/chloroform as the eluting solvent, gradually adding chloroform and dichloromethane to solvent.

1,3-Bis-2’-(9’,16’,23’-tritertbutylphthalocyaninoxylithium)-2,2-dimethylpropane. Followed similar procedure as for the cumylphenoxy substituted compound described above, adding ground mixture of 0.3615 g 4-tertbutylphthalonitrile and 0.0698 g 1,3-bis-(3’,4’-dicyanophenoxy)-2,2-dimethyl propane to 0.0965 g lithium amide dissolved in 10 mL of boiling butanol. Product was purified by procedure analogous to cumylphenoxy substituted compound above.

2,9,16,23-tetracumylphenoxyphthalocyaninatolead. Combined 0.2278 g of 2,9,16,23-tetracumylphenoxyphthalocyanine and 0.20 g of lead acetate in 10 mL of o-dichlorobenzene. Heated under nitrogen at reflux conditions for five hours until UV-Visible spectrum indicated shift from metal free peaks at 668 nm and 702 nm to single peak at 720 nm. After removal of solvent by heating under vacuum, remaining solid was dissolved in dichloromethane and filtered to remove undissolved white solids. The dichloromethane was evaporated and the product dried under vacuum. ^{1}H NMR ($CDCl_3$, ppm): 7.20 (1), 1.75 (.59336). UV-VIS (CH_2Cl_2, nm): 720 (1.15), 364 (0.40), 670 (0.36), 656 (0.29).

1,3-Bis-2’-(9’,16’,23’-tricumylphenoxyphthalocyaninoxy)-2,2-dimethylpropane. Compound was prepared using procedure for 1,3-Bis-2’-(9’,16’,23’-tricumylphenoxyphthalocyaninoxylithium)-2,2-dimethylpropane. Crude reaction was stirred with 3 mL of acetic acid to remove the lithium metal from the macrocycle and extracted in 1 M NaOH. Purification proceeded as above for metallated form. ^{1}H NMR ($CDCl_3$, ppm): 7.25 (.49962), 1.55 (1). UV-VIS (CH_2Cl_2, nm): 336, 668, 638, 702.

1,3-Bis-2’-(9’,16’,23’-tricumylphenoxyphthalocyaninoxylead)-2,2-dimethylpropane. 0.14 g of lead acetate and 0.150 g of 1,3-Bis-2’-(9’,16’,23’-tricumylphenoxyphthalocyaninoxy)-2,2-dimethylpropane were combined in 15 mL of 0-dichlorobenzene and heated at reflux under argon for four hours. The solvent was removed under vacuum, and the resulting solid was dissolved in dichloromethane and filtered to remove undissolved white solids. The dichloromethane was evaporated and the solid was dried under vacuum. UV-VIS (CH_2Cl_2, nm): 720, 368, 656.

2,9,16,23-tetracumylphenoxyphthalocyaninatolithium. Mononuclear compound was prepared by an analogous procedure for the binuclear compound, heating 0.55 g of 2,9,16,23-tetracumylphenoxyphthalocyanine and 0.42 g lead acetate in 20 mL of o-dichlorobenzene. ^1H NMR ($CDCl_3$, ppm): 7.25 (1), 1.70 (.58621).

2,9,16,23-tetratertbutylphthalocyaninatoiodothallium. In glass tube combined 0.50 g 4-tertbutylphthalonitrile and 0.52 g of Tl metal flakes. Tube was evacuated and sealed and placed in tube furnace at 260 C. After five days, tube was removed and opened, dissolving green solid in dichloromethane. Stirred solution with iodine crystals with mild heat. Compound was purified on silica gel/ligroine column using ligroine/dichloromethane as the eluting solvent. Solvent was evaporated and product was dried under vacuum. UV-VIS (CH_2Cl_2, nm): 708, 372, 638.

Bibliography

Brach, P., Grammatica, S., Ossanna, O., Weinberger, L. *Notes* **7**, 1403-1405 (1970).

Dodsworth, E., Lever, A., Seymour, P. Leznoff, C. *J. Phys. Chem.* **89**, 5698-5705 (1985).

Dominguez, D., Snow, A., Shirk, J., Pong, R. *J. Porphyrins Phthalocyanines* **5**, 582-592 (2001).

Farina, R., Halko, D., Swinehart, J. *J. Phys. Chem* **76**, 2343-2348 (1972).

George, R., Snow, A., Shirk, J., Barger, W. *J. Porphyrins Phthalocyanines* **2**, 1-7 (1998).

Hanack, M., Schneider, T., Barthel, M., Shirk, J., Flom, S., Pong, R. "Indium Phthalocyanines and Naphthalocyanines for Optical Limiting," manuscript for submission.

Janczak, J., Kubiak, R. *Acta Chemica Scandinavica* **49**, 871-877 (1995).

Leznoff, C., Greenberg, S., Marcuccio, S., Minor, P., Seymor, P., Lever, A. *Inorganica Chemica Acta* **89**, L35-L38 (1984).

Leznoff, C., Marcuccio, S. Greenberg, S., Lever, A., Tomer, K. *Can. J. Chem.* **63**, 623-631 (1985).

Maya, E., Shirk, J., Snow, A., Roberts, G. "Peripherally-substituted polydimethylsiloxane phthalocyanines: a novel class of liquid materials" manuscript for submission.

Monahan, A., Brado, J., DeLuca, A. *J. Phys. Chem* **76** 1994-1996 (1972).

Monahan, A., Brado, J., DeLuca, A. *J. Phys. Chem.* **76** 446-449 (1972).

Nalwa, H., Shirk, J. "Nonlinear optical properties of metallophthalocyanines," in *Phthalocyanines: Properties and Application, C.C. Leznoff and A.B.P. Lever,* eds., **4**, 79-181 (VCH Publishers, New York, 1996).

Nevin, W., Liu, W., Greenberg, S., Hempstead, M., Marcuccio, S., Melnik, M., Leznoff, C., Lever, A. *Inorg. Chem.* **26**, 891-899 (1987).

Nevin, W., Liu, W., Lever, A. *Can. J. Chem.* **65**, 855-858 (1987).

Schelly, Z., Farina, R., Eyring, E. *J. Phys. Chem* **74**, 617-620 (1970).

Schelly, Z., Harward, D., Hemmes, P., Eyring, E. *J. Phys. Chem* **74**, 3040-3042 (1970).

Schweiger, Hückstädt, H., Homborg, H. *Zeitschrift für anorganische und allgemeine Chemie* **624**, 167-168 (1998).

Shirk, J. *Optics & Photonics News* 19-23 (April 2000).

Shirk, J., Lindle, J., Bartoli, F., Hoffman, C., Kafafi, Z., Snow, A. *Appl. Phys. Lett.* **55**, 1287-1288 (1989).

Shirk, J., Pong, R., Bartoli, F., Snow, A. *Appl. Phys. Lett.* **63**, 1880-1882 (1993).

Shirk, J., Pong, R., Flom, S., Heckmann, H., Hanack, M. *J. Phys. Chem. A.* **104**, 1438-1449 (2000).

Snow, A., Griffith, J., Marullo, N. *Macromolecules* **17**, 1614-1624 (1984).

Snow, A., Shirk, J., Pong, R. *J. Porphyrins Phthalocyanines* **4**, 518-524 (2000).

Suga, T., Isoda, S., Kobayashi, T. *J. Porphyrins Phthalocyanines* **3**, 397-405 (1999).

---

[a] Shirk, J. *Optics & Photonics News* 19-23 (April 2000).

[b] Dominguez, D., Snow, A., Shirk, J., Pong, R. *J. Porphyrins Phthalocyanines* **5**, 582-592 (2001).

[c] Hanack, M., Schneider, T., Barthel, M., Shirk, J., Flom, S., Pong, R. "Indium Phthalocyanines and Naphthalocyanines for Optical Limiting," manuscript for submission.

[d] Shirk, J., Pong, R., Flom, S., Heckmann, H., Hanack, M. *J. Phys. Chem. A.* **104**, 1438-1449 (2000).

[e] Dominguez, D., Snow, A., Shirk, J., Pong, R. *J. Porphyrins Phthalocyanines* **5**, 582-592 (2001).

[f] Dominguez, D., Snow, A., Shirk, J., Pong, R. *J. Porphyrins Phthalocyanines* **5**, 582-592 (2001).

[g] Leznoff, C., Marcuccio, M., Greenberg, S., Lever, A., Tomer, K., *Can. J. Chem.* **63**, 623-631 (1985).

[h] Leznoff, C., Greenberg, S., Marcuccio, S., Minor, P., Seymor, P., Lever, A. *Inorganica Chemica Acta* **89**, L35-L38 (1984).

[i] Dodsworth, E., Lever, A., Seymour, P. Leznoff, C. *J. Phys. Chem.* **89**, 5698-5705 (1985).

[j] Suga, T., Isoda, S., Kobayashi, T. *J. Porphyrins Phthalocyanines* **3**, 397-405 (1999).

[k] Schweiger, Hückstädt, H., Homborg, H. *Zeitschrift für anorganische und allgemeine Chemie* **624**, 167-168 (1998).

[l] Leznoff, C., Marcuccio, M., Greenberg, S., Lever, A., Tomer, K., *Can. J. Chem.* **63**, 623-631 (1985).

[m] Leznoff, C., Marcuccio, M., Greenberg, S., Lever, A., Tomer, K., *Can. J. Chem.* **63**, 623-631 (1985).

[n] George, R., Snow, A., Shirk, J., Barger, W. *J. Porphyrins Phthalocyanines* **2**, 1-7 (1998).

[o] Nevin, W., Liu, W., Lever, A. *Can. J. Chem.* **65**, 855-858 (1987).

[p] George, R., Snow, A., Shirk, J., Barger, W. *J. Porphyrins Phthalocyanines* **2**, 1-7 (1998).

[q] George, R., Snow, A., Shirk, J., Barger, W. *J. Porphyrins Phthalocyanines* **2**, 1-7 (1998).

[r] Nevin, W., Liu, W., Greenberg, S., Hempstead, M., Marcuccio, S., Melnik, M., Leznoff, C., Lever, A. *Inorg. Chem.* **26**, 891-899 (1987).