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## **Modeling the Particle-On-A-Ring Theory in an Undergraduate Laboratory**

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MODELING THE PARTICLE-ON-A-RING THEORY IN AN UNDERGRADUATE  
LABORATORY

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## **I. Abstract**

In early chemistry education, students are often taught to think about electrons as small, negatively charged particles existing in planetary orbits around the nucleus of an atom, rather than creating an electron cloud. In reality, electrons exhibit wave-particle duality, and are best described as wave functions. This idea that the electrons travel as waves and are moving around the nucleus so quickly that it is not possible to know the speed or location of an electron at any given moment is extremely abstract and difficult to visualize. This concept is essential to the theory of quantum mechanics, and therefore is fundamental to undergraduate physical chemistry courses. To assist students in gaining a better understanding of these concepts, this thesis project proposes an undergraduate laboratory experiment, focusing on applying the particle-on-a-ring theory to porphyrins. Several porphyrin molecules with different *meso*-substitutions were synthesized and analyzed using UV/Vis spectroscopy and the particle-on-a-ring model to calculate experimental carbon-carbon bond lengths. All the calculated bond lengths differed from the literature value by varying degrees. It appears that the difference in values is due primarily to the presence of additional orbitals of appropriate orientation allowing the porphyrin  $\pi$  system to delocalize into them and thus expand the ring. These additional orbitals are likely affected by the presence of an additional  $\pi$  system, the electronegativity of the atoms in the substituent groups, and/or the possibility of hyperconjugation of the substituent molecular orbitals. Synthesizing their own porphyrin molecules for analysis gives students a sense of ownership over their experiment and writing a report on that analysis gives students the opportunity to explore the particle-on-a-ring model on a deeper level. By asking students to explain how the model works and at what point it breaks allows them to gain a better understanding of the particle-on-a-ring system, and therefore, basic quantum mechanics.

## **II. Introduction**

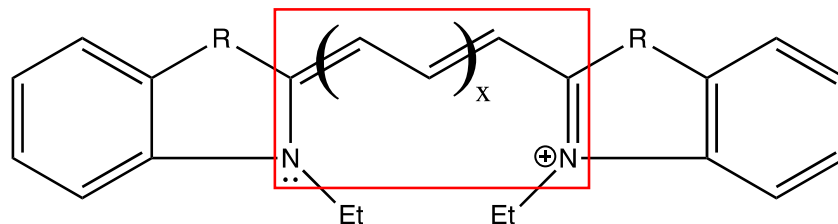
In early undergraduate chemistry education, students are taught to think about chemical interactions in a very rudimentary manner. This is effective for introductory chemistry classes, in which students are simply learning more about the results of certain interactions of molecules rather than what happens within those interactions. However, as those students begin to reach higher level chemistry courses, the concepts begin to become much more abstract, and are more difficult for students to ascribe to a physical picture. A common chemical discipline that brings this issue to light is physical chemistry, particularly material regarding quantum mechanics. Quantum mechanics is the branch of chemistry and physics that describes the properties of atoms and molecules through the interaction of light and matter on the subatomic level. Typically, students have not learned about the topic of quantum mechanics before, meaning they have no background in the concepts being presented to them. Physical chemistry also teaches students to think about the seemingly simple concepts they learned in early chemistry courses in a much deeper and often completely different manner.

For example, general chemistry courses often teach students that the electrons in an atom exist in simple orbits around the nucleus similar to planets in a solar system. However, this is not an accurate picture, since the electrons in an atom exhibit wave-particle duality, and therefore travel more as a wave than as a particle. As a result, these electrons are constantly in motion and moving around atoms and through molecules faster than we can measure or visualize them. It is therefore impossible to know where any single electron is at any given time. To address this, quantum mechanics introduces wave functions to describe the probability of an electron being at a given location at a certain time. Since neither electrons nor wave functions can be directly observed by humans easily and are often quite complex to visualize or even describe for many undergraduate chemistry students, instructors frequently look to model systems as a tool to help their students understand the material.

## Particle-in-a-Box Theory

The particle-in-a-box theory describes the free translational motion of an electron confined in a finite box.<sup>1</sup> This can be referred to generally as the free electron model. Since electrons exhibit wave-particle duality, and their motion can be described as waves, the particle-in-a-box model describes the motion of the electron as a wave through the system. The system is defined as a one-dimensional box of finite length, within which the particle can move freely (zero potential energy). However, the walls of the box have infinite potential energy resulting in the particle being trapped in the box, essentially bouncing back and forth. A common molecular model for this system is a molecule that has a linear conjugated pi ( $\pi$ ) system, with two atoms on either end that break the conjugation. At all points within the box, or between those atoms breaking the conjugation, the potential energy is assumed to be zero, while at all points outside the box, or outside of those atoms, the potential energy is assumed to be very high. The electron, or the wave, can travel back and forth freely between those two atoms breaking the conjugation. Because this motion can be described by a wave function, that wave function can be used to mathematically predict the probability of the electron being at a certain point in the conjugated  $\pi$  system at a certain time.

This theory is often demonstrated in a physical chemistry laboratory, in which it is commonly applied to cyanine dyes. For a  $\pi$  electron in a conjugated  $\pi$  system, the particle-in-a-box theory draws a theoretical box around a planar polymethine chain with its ends at the nitrogen atoms on either end of the chain. A depiction of this metaphorical box is shown in Figure 1. Within this box, the potential energy is assumed to be approximately zero, as the electrons are allowed to move freely without any restrictions and rises sharply to infinity at the ends with the nitrogen atoms, where the conjugation is broken.<sup>1</sup>



**Figure 1.** An image of the basic structures of cyanine dyes (3, 3'-diethylthiacyanine iodides) used in the typical experiment. The section in parentheses may be repeated any number of times. The box indicates the area analyzed by the particle-in-a-box theory. The potential energy at any point within the box is assumed to be approximately zero.

The probability of a particle being in a given location within the box at a certain time is given by a wave function governed by the one-dimensional Schrödinger equation. The energy levels for the  $\pi$  system within the box can be determined from the eigenvalues of the Schrödinger equation for a particle in a one-dimensional box:

$$E_n = \frac{h^2 n^2}{8mL^2}, n = 1, 2, 3 \dots \quad (1)$$

where  $h$  is Planck's constant ( $6.626 \times 10^{-34}$  J·s),  $n$  is the energy level of the electron,  $m$  is the mass of an electron ( $9.109 \times 10^{-31}$  kg), and  $L$  is the length of the polymethine chain between the N atoms.<sup>1</sup>

This equation can then be used to write a new equation for the energy change resulting from the promotion of an electron from one energy level ( $n$ ) to an adjacent energy level ( $n + 1$ ). The change in energy can be determined from the following equation:

$$E_{n+1} - E_n = \Delta E = \frac{hc}{\lambda} = (N + 1) \frac{h^2}{8mL^2} \quad (2)$$

where  $c$  is the speed of light in a vacuum ( $2.998 \times 10^8$  m/s),  $\lambda$  is the wavelength of the dye, and  $N$  is the total number of  $\pi$  bonds in the conjugated chain.<sup>1</sup> This equation can then be used to solve for the length of the chain ( $L$ ), from which the carbon-carbon conjugated bond lengths can be calculated by dividing the length of the box by the total number of bonds in the chain. The particle-in-a-box theory is commonly taught in undergraduate chemistry education, and is

successful and widely accepted, as it is simple and can connect theoretical and experimental exercises without too much complexity to confuse students.<sup>2</sup> However, the model is far from perfect. For example, the potential energy of the system is not exactly zero within the box, or inside the conjugated  $\pi$  system, and infinity outside of the box, or outside of the atoms breaking the conjugation. Therefore, it is possible that the electron could potentially be found outside of the box. As a result, the particle-in-a-box model consistently overestimates the length of the box and the length of carbon-carbon conjugated bond lengths.

### **Particle-on-a-Ring Theory**

A similar theory can be applied to cyclic structures with a “two-dimensional box.”<sup>2</sup> Cyclic molecules are often overlooked with teaching the free-electron model, as the particle-in-a-box theory is simpler and introduced first. However, in the particle-on-a-ring theory, the “box,” now a “ring,” is drawn around the entire cyclic structure containing the conjugated  $\pi$  system. In all other aspects, the theory works the same way as the particle-in-a-box theory such that there are quantized equations for the energy levels and transition energies.

The equations used for the particle-in-a-box are not the same as those for the particle-on-a-ring, however they are similar as they are both based on a sine wave. The major difference in the allowed wave functions arises from the boundary conditions. For particle-in-a-box, both half and whole sine waves within the box are allowed, while the boundary conditions for the particle-on-a-ring require only whole sine waves. This is because for the particle-on-a-ring model, the wave function must arrive at the same point of the sine wave for every revolution around the ring of  $2\pi$ . The wave function for the particle-on-a-ring system is given as:

$$\psi = e^{-im_l\varphi} \quad (3)$$

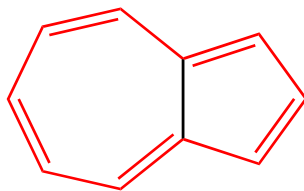
where  $m_l$  is the angular momentum quantum number (0, positive and negative integers),  $i$  is the imaginary number  $i^2 = -1$ , and  $\varphi$  describes the position of the particle via equatorial angle.<sup>3</sup> The solution to the corresponding two-dimensional Schrödinger equation gives the following energy result:

$$E = \frac{m_l^2 \hbar^2}{2mr^2} \quad (4)$$

where  $\hbar$  is Planck's constant divided by  $2\pi$ ,  $r$  is the radius of the ring, and  $m$  is the mass of an electron.<sup>3</sup> The value of  $m_l$  may be positive or negative, depending on the direction of the motion of the particle around the ring: either clockwise or counterclockwise. This equation is analogous to equation (1) for the particle-in-a-box theory, as they both define discrete energy levels. They differ only in that the energy equation for the particle-in-a-box model takes into account the length of the box, while the equation for particle-on-a-ring takes into account the radius of the ring. This is because the shape of the metaphorical "box" is different in each case.

The classic model of the particle-on-a-ring theory is benzene ( $C_6H_6$ ). However, it is not particularly safe for undergraduate laboratory experimentation and its HOMO-LUMO transition is in the short UV range making it difficult to measure spectroscopically. Benzene is therefore not a good candidate molecule to create an experiment around to better the understanding of the particle-on-a-ring model for undergraduates.<sup>2</sup> Additionally, the use of azulene has been proposed as a useful model of the particle-on-a-ring model. Azulene is a molecule containing a seven-membered ring connected to a five-membered ring, with a peripheral conjugated  $\pi$  system. This peripheral conjugated  $\pi$  system can be treated as one large cyclic structure in which the electrons are free to move.<sup>2</sup> The structure of azulene is shown below in Figure 2. The proposed experiment using azulene as a model used purchased rather than synthesized azulene.<sup>2</sup> There is currently no simple synthesis procedure for azulene that is feasible for undergraduate students with laboratory experience likely from only general chemistry and organic chemistry courses.





**Figure 2.** An image of the structure of azulene.

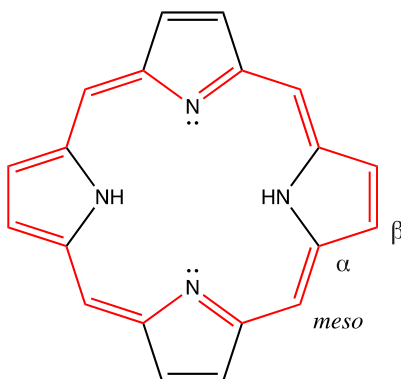
Cyclic polyynes have also been proposed as a successful model of the particle-on-a-ring system.<sup>3</sup> However, cyclic polyynes are not currently commercially available nor easily synthesized.<sup>3</sup> Therefore, an undergraduate laboratory experiment would not be able to use real molecules to collect and analyze their own data. The laboratory experiment proposed using cyclic polyynes suggests having students build their own cyclic polyynes in a quantum chemistry modeling software, such as Spartan, and using UV/Vis spectra generated by the software as experimental data rather than actual UV/Vis spectra collected for comparison to theoretical calculations.<sup>3</sup> The use of data generated by a software rather than data collected by the students themselves may result in a greener experiment, but ultimately serves a different purpose, as the use of modeling software turns the experiment into more of a computational exercise more so than a quantum mechanics chemistry experiment. Performing a laboratory experiment in which students can use skills they already possess to synthesize their own products from which they can collect data for quantum mechanical analysis to determine the effectiveness of a fundamental theory holds extraordinary educational value for the undergraduate chemistry student.

### **Porphyrins as a Potential Model for Particle-On-A-Ring**

Porphins are molecules containing four pyrrole rings linked by methine bridges and may have a metal atom complexed into the center or a variety of substitutions around the outside of the molecule.<sup>4</sup> The basic structure of a porphin is shown below in Figure 3. Porphyrins are substituted porphin molecules.<sup>5</sup> Porphyrins are an essential structural component of biological molecules that

bind the necessary metal ion in hemoglobin (iron) and chlorophyll (magnesium) so that they can achieve their function of transporting O<sub>2</sub> and CO<sub>2</sub> around biological systems. If the particle-on-a-ring theory is applicable to simple and slightly functionalized porphyrins, they could potentially be an excellent model of the theory for undergraduate physical chemistry laboratories.

Porphyrins have the potential to be better models of the particle-on-a-ring theory due to the conjugated  $\pi$  system along the outside of the two protonated pyrrole rings and the inside of the two deprotonated pyrrole rings. This allows for the inclusion of the lone pairs of electrons on the nitrogen atoms of the deprotonated pyrrole rings into the conjugated  $\pi$  system. The ability of the porphyrin to be substituted both inside and outside the ring also significantly increases the number of possible molecules that can be modeled by the particle-on-a-ring theory. Since porphyrins are very common in nature, such as in hemoglobin or chlorophyll, they are a much more stable compound for use in an undergraduate laboratory than other previously proposed molecules, such as azulene or cyclic polyynes, if synthesis is not possible. Additionally, porphyrins are much more stable molecules than either azulene or cyclic ring-strained molecules, like polyynes.



**Figure 3.** An image of the basic structure of a porphin. A metal ion can be substituted into the center of the molecule, and additional substitutions can be made on the outside of the ring structures, making the molecule a porphyrin. The conjugated  $\pi$  system that makes the particle-on-a-ring theory applicable is highlighted in red.

Ideally, porphyrins can be obtained for an undergraduate laboratory by having the students synthesize the molecules themselves, as the synthesis should connect to students' prior knowledge from their organic chemistry courses. A desirable synthesis procedure for this experiment would be one that is very feasible for undergraduates to perform, and one that can produce a variety of different molecules to which the particle-on-a-ring model can be applied under different conditions. There are a variety of successful synthesis procedures for porphyrins with different substituents. The most conventional of these procedures is the Adler-Longo method (1967), traditionally used to produce 5,10,15,20-tetraphenylporphyrin (TPP), but also adapted to produce other *meso*-substituted porphyrins. The adaptation is most successful for aromatic substituents, since the aldehydes used to produce the porphyrins with non-aromatic substituents result in increased solubility in the reaction solvent due to the formation of porphyrin acid salts.<sup>6</sup> The Adler-Longo method consists of distilling pyrrole and adding it along with benzaldehyde to refluxing propionic acid.<sup>6</sup> The solution is then refluxed for 30 minutes before it is cooled, filtered, and washed with methanol and then hot water.<sup>6</sup> The resulting purple crystals can then be air-dried or dried in a vacuum to remove any excess acid adsorbed to the flask.<sup>6</sup> This product is then purified. The Adler-Longo method uses a batchwise purification technique in which TPP and Fuller's earth (a clay) are mixed with trichloroethane, which is then passed through a 0.25-inch bed of Fuller's earth washed with solvent on a vacuum funnel.<sup>6</sup> The filtrate is then passed through a fresh bed of Florex several times.<sup>6</sup> However, this method results in only about a  $20\pm 3\%$  yield of crystalline TPP of high purity.<sup>6</sup>

The Adler-Longo method was revisited about 20 years later in an attempt to increase the percent yield and expand the number of potential uses for which this synthetic method can be used. This new procedure, hereafter referred to as the Lindsey synthesis, identified several issues with the Adler-Longo method. First, the reaction conditions prevent any benzaldehydes with acid-

sensitive functional groups from being used.<sup>7</sup> This significantly limits the number of porphyrins that can be synthesized using this procedure, as any benzaldehydes with functional groups that will fall apart cannot be used in the synthesis, and therefore no porphyrins with those functional groups can be produced. Lindsey and his colleagues also point out that the Adler-Longo synthesis only works particularly well with porphyrins that crystallize or precipitate at the end of the reaction, since the synthesis produces tar as a byproduct.<sup>7</sup> Any porphyrin that remains in solution cannot be synthesized using this method. Finally, the Adler-Longo method has poor reproducibility from one batch to another, as there are large differences in percent yield each time the procedure is performed.<sup>7</sup> The Lindsey synthesis aimed to specifically correct the third of these problems, to improve the percent yield without overly complicating the purification process.

Lindsey and his colleagues concluded that the highest yield of TPP was obtained when a solution of methylene chloride under N<sub>2</sub> is mixed with benzaldehyde, pyrrole, and triethylorthoacetate at equimolar concentrations.<sup>7</sup> An aliquot of boron trifluoride etherate is then added, and the reaction is allowed to proceed to completion.<sup>7</sup> After an hour, 2, 3, 4, 5, 6-tetrachlorobenzoquinone (*p*-chloranil) is added and the reaction mixture is refluxed for an hour.<sup>7</sup> Analysis suggested that the yield of TPP was about 50% for the overall synthesis.<sup>7</sup> This procedure can be used to synthesize over 30 substituted porphyrins in yields of about 30-40% for *meso*-phenyl substituents and was also extended to synthesize porphyrins with *meso*-alkyl substituents.<sup>7</sup> This process is reversible, and hybrid porphyrins, or those with more than one but less than four of the *meso*-substituents, can be produced.<sup>7</sup> While this synthetic method results in a much higher yield than the Adler-Longo method, the procedure is more complex than the Adler-Longo method, so the conventional method often remains as the default for the synthesis of *meso*-substituted porphyrins.

For an undergraduate physical chemistry student, it is expected that the student will have already taken organic chemistry and therefore possess basic organic laboratory skills. The Adler-Longo method can be simplified such that a student can perform the synthesis independently with the skills they already know. For a physical chemistry laboratory experiment, students can be expected to perform the following one-pot synthesis based on the general Adler-Longo procedure: adding a substituted aldehyde and pyrrole to boiling propionic acid, heating under reflux for 30 minutes, washing with solvent to eliminate impurities, and purifying by vacuum filtration. Heating under reflux, carefully washing a product with solvent, and vacuum filtration are all skills that the students would have already learned and can therefore be reinforced by a physical chemistry laboratory experiment in the later years of their chemistry education. The Lindsey synthesis relies on several laboratory skills that students would not possess after an undergraduate organic chemistry course, such as carrying out a reaction under N<sub>2</sub> or working with boron trifluoride etherate, which is both air and water sensitive, and could result in serious burns if not handled carefully. While these skills could be taught through the use of this synthetic method, this is beyond the scope of the desired physical chemistry experiment.

Porphyrins are also commonly found in nature as metalloporphyrins, or porphyrins with a metal ion complexed into the center of the ring structure (see Figure 3).<sup>8</sup> A successful synthetic method has been proposed to produce metalloporphyrins with various substituents. The substituents in the *meso* positions can be added to the porphyrin base by using aldehydes with the desired functional groups attached.<sup>8</sup> The procedure used to substitute the metal ion into the center of the porphyrin base begins with the dissolution of distilled benzaldehyde in argon-purged dimethylformamide (DMF).<sup>8</sup> Concentrated hydrochloric acid is added before distilled pyrrole, and the mixture is then stirred under argon gas for one hour.<sup>8</sup> A metal chloride or metal sulfate solution is added, and the final mixture is refluxed for 8 hours in air.<sup>8</sup> The solvent is removed by vacuum

filtration and the crude product is washed with acidic water and dried.<sup>8</sup> The product is dissolved in chloroform and purified with flash chromatography using chloroform as an eluent.<sup>8</sup> This procedure was shown to produce significantly higher yields than either the Adler-Longo or Lindsey methods.<sup>8</sup> This procedure is advantageous in that it is also valid for any type of substituted aldehyde, as opposed to only aromatic substituted aldehydes, and that it produces a higher yield in a shorter amount of time.<sup>8</sup> This procedure can be used for metal chloride or metal sulfate solutions containing  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{VO}^{2+}$ ,  $\text{Co}^{2+}$ , or  $\text{Fe}^{2+}$ , but was shown to produce the largest yields using cupric sulfate and vanadyl sulfate.<sup>8</sup>

Models are often used in undergraduate chemistry classes to demonstrate particularly difficult concepts for students to grasp. Instructors often turn to models to illustrate new and abstract concepts that students have difficulty visualizing without a frame of reference. One of the models often used for this purpose is that of the particle-in-a-box theory, used to demonstrate the free motion of electrons in one direction. A similar theory is demonstrated in cyclic structures using the particle-on-a-ring model. This model follows the same idea as the particle-in-a-box theory but applies to cyclic molecules with a conjugated  $\pi$  system rather than planar linear ones. That is, the free motion around the cyclic conjugated  $\pi$  system is described by the theory. Azulene and cyclic polyynes have previously been proposed as models for the particle-on-a-ring theory, but neither molecule is ideal for undergraduate synthesis. Porphyrins, which have a conjugated  $\pi$  system and a variety of possible substitutions, hold the potential to be an excellent model of the particle-on-a-ring theory that can be implemented into an undergraduate physical chemistry laboratory. There are several successful porphyrin synthesis methods that could be performed by undergraduate chemistry students to produce their own models, however, some of these are more useful than others. Synthetic methods utilizing materials that are easily obtainable and minimally hazardous and laboratory techniques that are familiar to students are better suited for the

development of this project for students. This thesis project aimed to answer the question of whether the particle-on-a-ring theory can be applied to the  $\pi$  system on porphyrins, and to design an undergraduate laboratory experiment for students to perform to explore the application of the model.

### III. Experimental

To test the effectiveness of porphyrins as a model for the particle-on-a-ring theory, a variety of *meso*-substituted porphyrin molecules were synthesized. The conventional Adler-Longo procedure for the synthesis of TPP was used as a general procedure for the synthesis of various substituted porphyrins.<sup>9</sup> The Adler-Longo method consists of bringing a portion of propionic acid (40 mL) to a boil, and adding 15.75 mmol of benzaldehyde and 14.4 mmol pyrrole to the boiling acid.<sup>9</sup> This reaction mixture is then heated under reflux, in which the reaction mixture is heated in a round bottom flask by a heating mantle, with a reflux condenser fitted into it, through which cold water runs into the bottom and out through the top of the condenser. After 30 minutes of reflux, the porphyrin typically precipitates out as dark purple crystals, allowing the porphyrin product to be filtered out by vacuum filtration.<sup>9</sup> The porphyrin product is then washed with methanol to rinse out any remaining unreacted reagents from the reaction mixture.<sup>9</sup> The Adler-Longo procedure was adapted to synthesize other *meso*-substituted porphyrins by using an appropriately substituted aldehyde in place of unsubstituted benzaldehyde for TPP and using a solvent that would not dissolve the crystal products for washing. The substituted benzaldehydes and solvents for washing for each substituted porphyrin are listed in Table 1 at the end of this section.

This general procedure worked for most of the substituted porphyrins for which the synthesis was attempted, however, it did not work on every porphyrin. For most of the porphyrins for which this method did not work, the issue was often the solubility of the porphyrin product in

the acid. For each porphyrin for which this procedure did not immediately work, there was a set of steps taken to attempt to reduce the solubility of the product and precipitate the porphyrin. The first of these steps was to place the reaction mixture in an ice bath to decrease the temperature of the mixture, since solubility generally decreases with temperature. The second of these steps was to add a portion of water, typically equivalent to approximately half of the volume of the reaction mixture. The reaction mixture was split in half so that there was a portion of original reaction mixture left over for use in additional attempts at precipitating the porphyrin crystals if necessary. The addition of water to one half of the reaction mixture alters the solubility of the porphyrin based on intermolecular forces, as it will make the reaction mixture more polar. Since the nonpolar porphyrin ring will not mix well with the now polar reaction mixture, it will be more likely to precipitate out. If, after vacuum filtering this reaction mixture, there were still no crystals present, then the final step taken to try to precipitate crystals was to neutralize the acid in the reaction mixture with sodium bicarbonate. In this case, the reaction mixture was typically again split in half, and sodium bicarbonate in the form of baking soda or a saturated sodium bicarbonate solution was added to one half of the reaction mixture in small portions in a large beaker. This would again make the reaction mixture more polar and cause the nonpolar porphyrin to be more likely to precipitate. Often, some sort of precipitate would form and be immediately visible upon the addition of only the first portion of sodium bicarbonate. Depending on the desired amount of product, the reaction mixture did not need to be fully neutralized. The mixture only needed to be neutralized to produce enough product such that each student or group of students can perform their own spectroscopic analyses. Minimal neutralization of the reaction mixture not only saves time during the lab period, but significantly reduces the amount of waste produced from the synthesis.



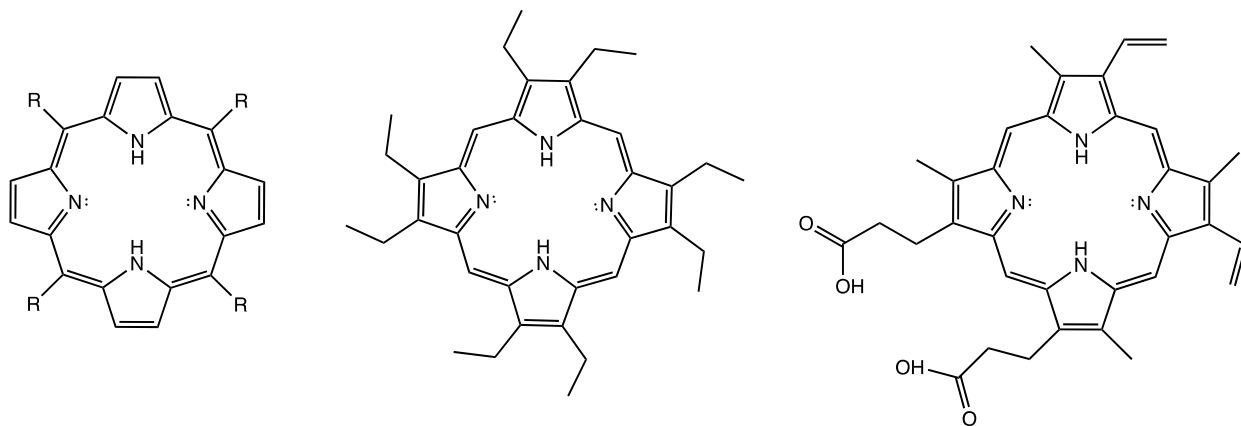
It was also found that due to the solubility properties of certain porphyrins, propionic acid was a poor solvent for some syntheses. These were porphyrins for which the completion of any of the steps described above did not result in any precipitated product. In those cases, an organic acid with a longer carbon tail was used as the solvent with the goal of reducing the solubility of the porphyrins so that they would precipitate more easily. In this experiment, isobutyric acid was used as an alternative to propionic acid, but it is likely that other organic acids would be successful solvents as well, with varying results from those reported in this thesis.

To confirm the identity of the synthesized porphyrins, each product was analyzed with UV/Vis, IR, and  $^1\text{H}$  NMR spectroscopy. UV/Vis spectroscopy (Agilent Technologies, Cary 8454) was performed immediately following the synthesis of each product. Porphyrins have a very distinct spectrum, so it was typically very clear if the desired porphyrin was present in the product by UV/Vis alone. However, IR spectroscopy was also used following each synthesis to ensure that the proper functional groups of the desired substituent were present in the porphyrin product. The NMR spectra were collected later to confirm with confidence that the reaction completed and the porphyrin is fully substituted, and that the substitution occurred as expected.

UV/Vis spectroscopy was used as the primary method of analysis for the synthesized porphyrins. To prepare solutions for analysis, a few crystals (approximately the tip of a small spatula) were placed in a cuvette and dissolved in dichloromethane.<sup>9</sup> Two of the synthesized porphyrins, tetramethylporphyrin and tetrakis(4-hydroxyphenyl)porphyrin, did not dissolve in dichloromethane and were instead analyzed in methanol solutions. The solutions were then diluted in the cuvette until the maximum absorbance of the Q band (up to four peaks in the visible wavelength region, around 500 - 700 nm) was below a measured value of 2. IR spectra were collected by placing a small amount of the porphyrin sample onto the diamond platform of the IR spectrometer (Bruker, Alpha II) and acquiring the spectra. NMR spectra were collected by

dissolving a small amount of the porphyrin crystals (5-10 mg) in either deuterated chloroform or deuterated acetone, depending on which solvent would dissolve the crystals, and ensuring that the NMR instrument was set to the correct solvent.

Additionally, in order to confirm the success of the synthetic method, several porphyrins were purchased from commercial sources and analyzed using UV/Vis for comparison to the synthesized porphyrins. This was not done for each of the synthesized porphyrins, but rather for a sample with a variety of substituents. The following porphyrins were purchased commercially: protoporphyrin IX, tetrakis(pentafluorophenyl)porphyrin, tetrakis(4-hydroxyphenyl)porphyrin, tetra(4-pyridyl)porphyrin, and octaethylporphyrin. Two of the purchased porphyrins were not able to be synthesized using the standard Adler-Longo procedure: octaethylporphyrin and protoporphyrin IX. These porphyrins differ from the others that were synthesized in that they are not *meso*-substituted but rather  $\beta$ -substituted (see Figure 4). As a result, the synthetic procedures required are significantly more complex than the Adler-Longo procedure. Literature confirmed that the synthetic methods required to synthesize these two porphyrins were well beyond the undergraduate level, and therefore beyond the scope of this experiment. However, the structure and substituents present in these two porphyrins are interesting in the context of applying particle-on-a-ring theory to different types of porphyrins.



**Figure 4.** Structures of a *meso*-R-substituted porphyrin, 2,3,7,8,12,13,17,18-octaethylporphyrin, and protoporphyrin IX.

**Table 1.** The table contains information needed to synthesize a variety of *meso*-substituted porphyrins. Information provided includes the name of the necessary starting substituted aldehyde, the solvent needed for synthesis, and the solvent needed to collect UV/Vis spectra. Additionally, aldehydes marked by \* at the end of the name are likely to be more soluble in the solvent used for the synthesis and are therefore likely to require the neutralization step of the procedure. It should also be noted that tetraethylporphyrin was synthesized under mildly heating propionic acid rather than boiling.

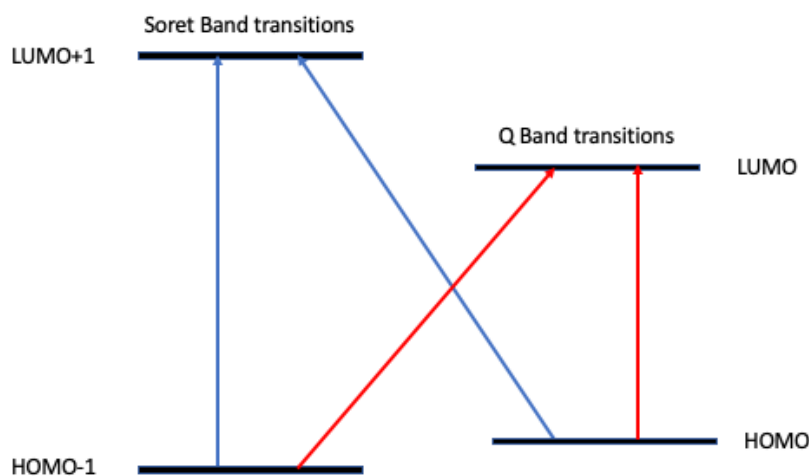
*IsoB*: Isobutyric acid; *Prop* = Propionic acid; *Meth.* = Methanol;  
*DCM* = Dichloromethane; *PE* = Petroleum ether

Substituted Aldehyde (R-Group in Figure 4)	Acidic Solvent	Solvent for Washing	Solvent for UV/Vis Analysis	Synthesized Porphyrin
Acetaldehyde	IsoB	N/A	Meth.	Tetramethylporphyrin
Propionaldehyde*	Prop	N/A	DCM	Tetraethylporphyrin
Benzaldehyde	Prop	Meth.	DCM	Tetraphenylporphyrin
Pentafluorobenzaldehyde*	IsoB	Dilute HCl	DCM	Tetrakis(pentafluorophenyl)porphyrin
4-pyridinecarboxaldehyde*	IsoB	N/A	DCM	Tetra(4-pyridyl)porphyrin
4-(methylthio)benzaldehyde	Prop	PE	DCM	Tetrakis(4-methylthiophenyl)porphyrin
4-(methoxy)benzaldehyde	Prop	PE	DCM	Tetrakis(4-methoxyphenyl)porphyrin
Vanillin	IsoB	N/A	DCM	Tetrakis(4-hydroxy-3-methoxyphenyl)porphyrin
4-chlorobenzaldehyde	IsoB	N/A	DCM	Tetrakis(4-chlorophenyl)porphyrin
4-hydroxybenzaldehyde	IsoB	PE	Meth.	Tetrakis(4-hydroxyphenyl)porphyrin
Salicylaldehyde	IsoB	PE	DCM	Tetrakis(2-hydroxyphenyl)porphyrin
2-fluorobenzaldehyde	Prop	PE	DCM	Tetrakis(2-fluorophenyl)porphyrin
4-fluorobenzaldehyde	Prop	PE	DCM	Tetrakis(4-fluorophenyl)porphyrin
4-(dimethylamino)benzaldehyde	IsoB	PE	DCM	Tetra(4-dimethylaminophenyl)porphyrin
p-tolualdehyde	Prop	Meth.	DCM	Tetra-p-tolylporphyrin

4-(trifluoromethyl)benzaldehyde*	IsoB	N/A	DCM	Tetrakis(4-(trifluoromethyl)phenyl)porphyrin
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#### IV. Results and Discussion

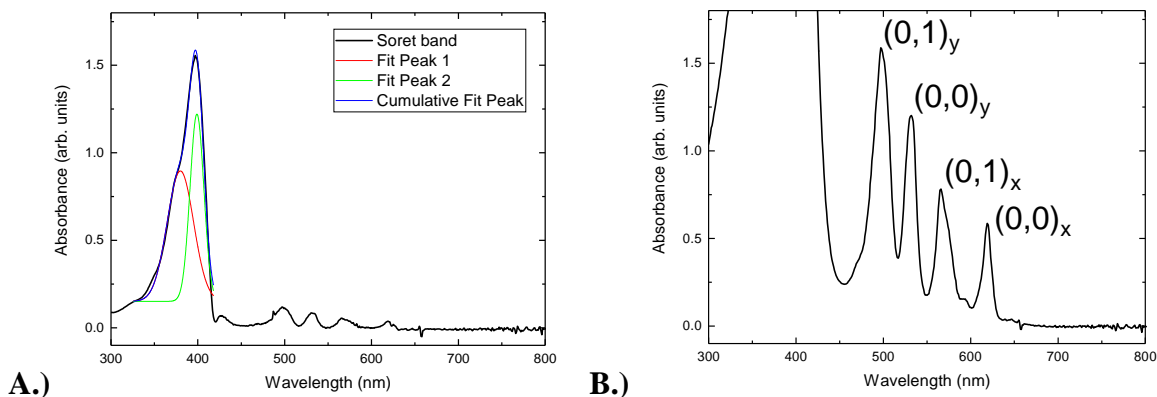
The UV/Vis spectra obtained from the synthesized porphyrins were analyzed to observe the effect of various *meso*-substitutions on the validity of the particle-on-a-ring model. Porphyrins have a distinct general spectral pattern. Each spectrum contains a high-energy Soret band and a Q band.<sup>10</sup> The Soret band represents the transition from the highest two occupied molecular orbitals, HOMO and HOMO-1, to the LUMO+1, the second lowest unoccupied molecular orbital. The Q band can contain up to four peaks, and represents the transition from the highest two occupied molecular orbitals to the LUMO, the lowest unoccupied orbital. The additional peaks present in the Q band are a result of a vibrational transition within the electronic HOMO/LUMO transition. The transitions represented by each band of the porphyrin UV/Vis spectrum are illustrated in Figure 5.



**Figure 5.** An image illustrating the electronic transitions that result in the two major bands composing the general spectral pattern of a porphyrin spectrum.

Figure 6 contains the UV/Vis spectrum collected for octaethylporphyrin, which was purchased for comparison to the synthesized porphyrins. While the appearance of the Soret band

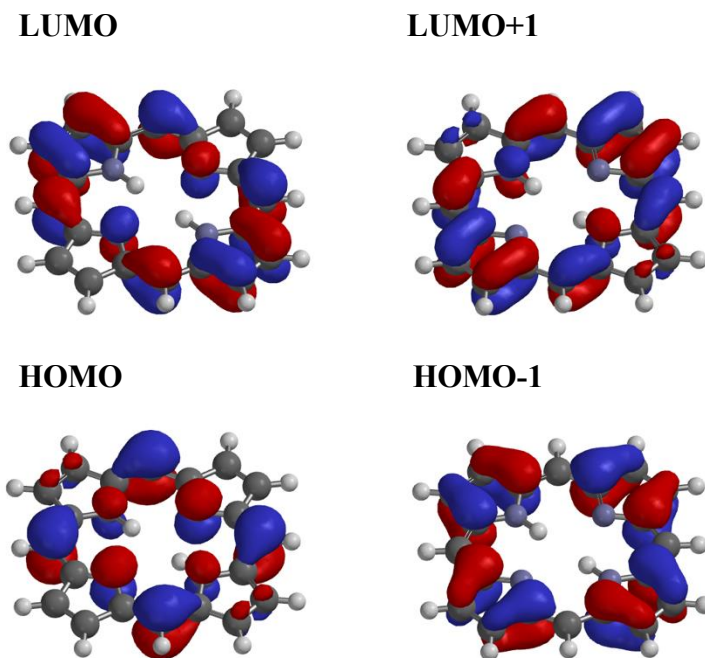
is interesting, it is the location of the vibrational fundamental of the Q band that contains information relevant to the particle-on-a-ring experiment.



**Figure 6.** UV/Vis spectrum collected for octaethylporphyrin. The band of lowest wavelength is the Soret band, while the band in the visible region is the Q band. A.) Scaled spectrum of the Soret band for octaethylporphyrin. The red and green peaks highlighted within the Soret band are the HOMO to LUMO+1 and HOMO-1 to LUMO+1 transitions identified by peak fitting. B.) Scaled spectrum of the Q band for octaethylporphyrin with vibrational transitions labeled.

The position and shape of the Q band is unique to the substituted porphyrin and gives the porphyrin its distinct color, as it is in the visible region. The effect of the substitution of the porphyrin could be determined by the difference in position of the Q band. The Q band has four distinct peaks within the band that can be clearly observed when no metal is present (see Figure 6). It was determined that the lowest energy peak, representing the true HOMO to LUMO transition, within the band is the transition that is most applicable to the particle-on-a-ring model. According to density functional calculations ( $\omega$ B97X-D method with a basis set of 6-31 G\*) run in Spartan (Spartan '20 V1.0.0), it was found that the orbitals comprising the  $\pi$  system are in the correct orientation for the particle-on-a-ring model in the HOMO orbital transitioning to the LUMO. This is illustrated in the images of the molecular orbitals shown in Figure 7. The orbitals of the porphyrin appear to match in orientation around the inner conjugated ring in the HOMO and LUMO orbitals. Since this transition is between the highest occupied and lowest unoccupied

molecular orbitals, it must be the reddest peak of the Q band that is used to apply the particle-on-a-ring model to the porphyrin. Since the HOMO-1 orbital follows the conjugated  $\pi$  system along the outside of the porphyrin ring, it doesn't capture the conjugated  $\pi$  system quite as well.



**Figure 7.** Images of molecular orbitals generated by Spartan.

The wavelength of maximum absorbance for this HOMO to LUMO transition (also known as a  $\pi$  to  $\pi^*$  transition in conjugated molecules) was used to calculate the energy of the transition using the following equation:

$$\Delta E = \frac{hc}{\lambda} \quad (5)$$

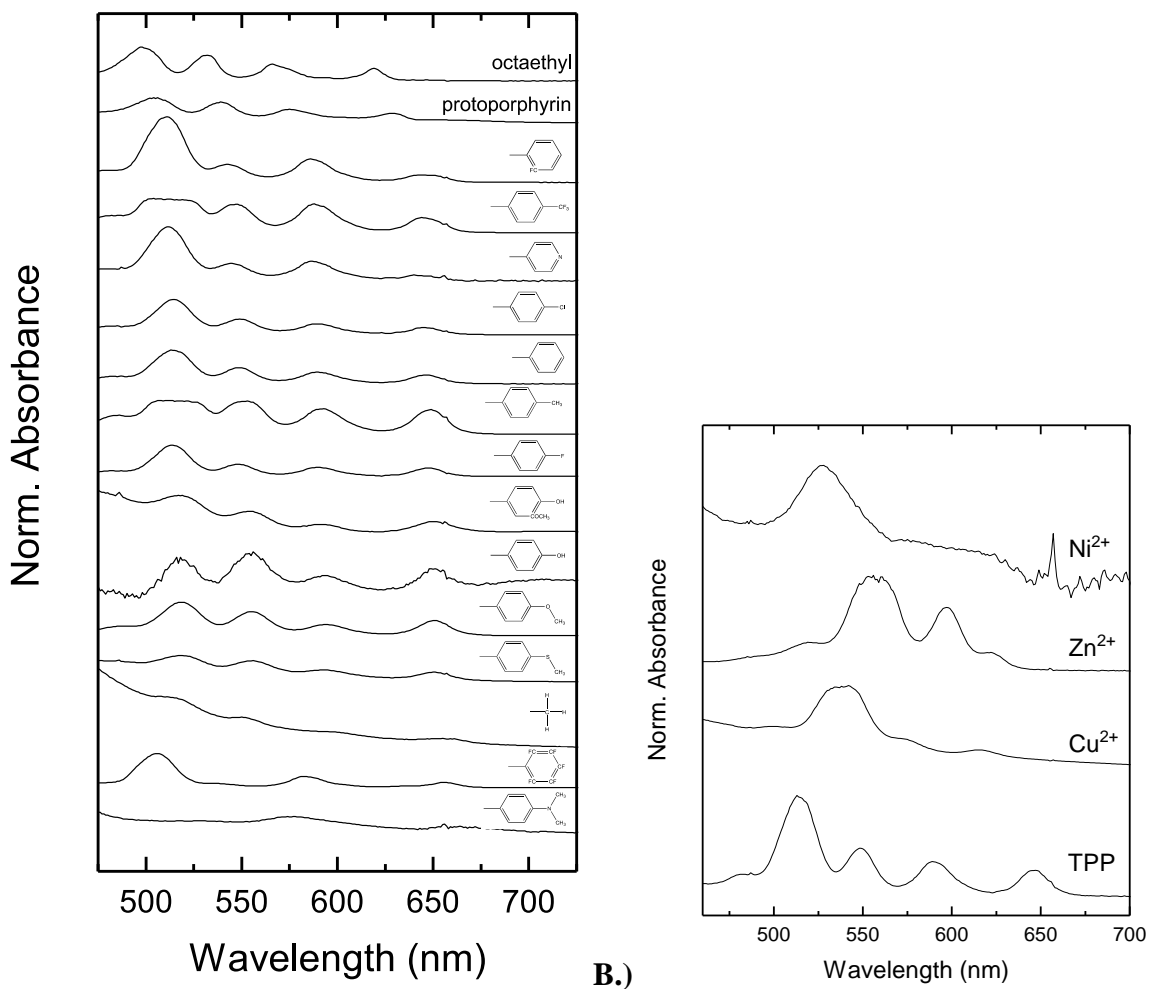
where  $\Delta E$  is the energy of the transition,  $h$  is Planck's constant ( $6.626 \times 10^{-34}$  J·s),  $c$  is the speed of light ( $2.998 \times 10^8$  m/s), and  $\lambda$  is the wavelength of maximum absorbance for the peak (in m). The energy of the transition can then be used to calculate the approximate radius of the "ring" of the porphyrin using the following equation:

$$\Delta E = \frac{\hbar^2}{2mr^2} (2m_l + 1) \quad (6)$$

where  $\hbar$  is Planck's constant divided by  $2\pi$ ,  $m$  is the mass of an electron,  $r$  is the radius of the ring, and  $m_l$  is the angular momentum quantum number. In the case of porphyrins,  $m_l$  is equal to 4. Since two electrons can fit into an orbital and  $m_l$  values that describe the different orbitals can be 0 and positive or negative integers, the 18 electrons in the  $\pi$  system fit into the 0,  $\pm 1$ ,  $\pm 2$ ,  $\pm 3$ , and  $\pm 4$  orbitals, filling nine orbitals in total. When an electron is excited, as in UV/Vis, it is promoted out of the HOMO. This molecular orbital mirrors the conjugated  $\pi$  system, which follows the perimeter of the porphyrin molecule, but cuts in along the inside of the pyrrole rings containing deprotonated nitrogen atoms. The radius of the ring can then be used to calculate the approximate circumference of the ring using the equation for the circumference of a circle:

$$C = 2\pi r \quad (7)$$

where  $C$  is the approximate circumference of the ring. From this circumference, the average bond length for a conjugated carbon-carbon bond can be found by dividing the calculated circumference by the number of bonds in the system. In the case of this experiment, it was determined that there were 18 bonds in the inner ring system, so the calculated circumference for each substituted porphyrin was divided by 18 bonds. A total of 18 bonds was used in the calculation rather than the 20 that comprise the outer ring because the inner conjugated  $\pi$  system is where the Q band transitions occur. While the outer ring  $\pi$  system is properly oriented for the HOMO wave function to potentially disperse into it, any effects of this nature would be expected to be revealed when comparing calculated bond length to actual values for conjugated C-C bonds. The following results in Table 2 show the calculated average C-C conjugated bond length found for each of the synthesized porphyrins using experimental data from UV/Vis spectra. The positions of the Q bands were determined from the UV/Vis spectra for each porphyrin, shown below in Figure 8.



**Figure 8.** (A) The UV/Vis spectra for each of the *meso*-substituted porphyrins synthesized, normalized so that the position of the Q band is highlighted. (B) The UV/Vis spectra for each of the metal complex porphyrins, including TPP for comparison, normalized so that the position of the Q band is highlighted. A spectrum for nickel complexed into tetraphenylporphyrin is included, but the position of the vibrational fundamental is not reported because no peak could be easily identified.



**Table 2.** Calculated values for the average conjugated C-C bond length for each of the porphyrins that were synthesized based on the UV/Vis spectra collected. For comparison, the literature value for the length of a conjugated C-C bond is 1.39 Å.<sup>11</sup>

Porphyrins	Q Band Position (nm)	Circumference (Å)	C-C Bond Length (Å)
5,10,15,20-tetra(4-dimethylaminophenyl)porphyrin	663.6	26.916	1.495
5,10,15,20-tetrakis(pentafluorophenyl)porphyrin	655.5	26.751	1.486
5,10,15,20-tetramethylporphyrin	655.5	26.751	1.486
5,10,15,20-tetrakis(4-methylthiophenyl)porphyrin	650.7	26.653	1.481
5,10,15,20-tetrakis(4-methoxyphenyl)porphyrin	650.2	26.643	1.480
5,10,15,20-(4-hydroxy-3-methoxyphenyl)porphyrin	649.0	26.618	1.479
5,10,15,20-tetrakis(4-hydroxyphenyl)porphyrin	648.3	26.604	1.478
5,10,15,20-tetrakis(4-fluorophenyl)porphyrin	647.4	26.585	1.477
5,10,15,20-tetra-p-tolylporphyrin	647.1	26.579	1.477
5,10,15,20-tetraphenylporphyrin	646.0	26.557	1.475
5,10,15,20-tetrakis(4-chlorophenyl)porphyrin	645.8	26.553	1.475
5,10,15,20-tetra(4-pyridyl)porphyrin (purchased)	644.6	26.528	1.474
5,10,15,20-tetrakis(4-(trifluoromethyl)phenyl)porphyrin	644.2	26.520	1.473
5,10,15,20-tetrakis(2-fluorophenyl)porphyrin	643.2	26.499	1.472
Protoporphyrin IX disodium salt	627.5	26.174	1.454
5,10,15,20-tetraphenyl-21H,23H-porphine zinc (II)	622.2	26.063	1.448
2,3,7,8,12,13,17,18-octaethylporphyrin (purchased)	619.1	25.998	1.444
5,10,15,20-tetraphenyl-21H,23H-porphine copper (II)	615.6	25.924	1.440

Based on the results contained in Table 2, there were a significant number of porphyrins that demonstrated excellent agreement with the particle-on-a-ring model. This was determined by comparing the calculated C-C bond length to the literature value for a conjugated C-C bond, 1.39 Å.<sup>11</sup> All of the porphyrins tested predicted a C-C bond length longer than was expected. This result was anticipated due to the presence of the two additional  $\pi$  bonds not in the conjugated system but in the ring and properly oriented to give the HOMO and LUMO wave functions room to delocalize outward, thus expanding the ring. It was determined that, aside from the metal complexes, the *meso*-unsubstituted octaethylporphyrin yielded a bond length that was the most accurate. This is likely because the substituents on the ring are in the  $\beta$  rather than *meso* positions, and because the substituents do not contain  $\pi$ -orbitals themselves (see Figure 4). As a result, the substituents are

far enough away from the conjugated  $\pi$  system that they do not interact, resulting in a relatively unaffected system that models the particle-on-a-ring theory quite accurately (see Table 2). This result also is in agreement with the measured spectrum of the protoporphyrin IX (see Figure 4 for structures).

The model appears to break for other substituted porphyrins as a result of the presence of available orbitals in the substituents that allow for further delocalization of the HOMO and LUMO wave functions. By drawing some of the electron density (i.e., wave function) outside the ring, using the particle-on-a-ring model would make it appear as though the ring has simply become larger, increasing the radius, and therefore the circumference, causing the bond length to increase since the number of bonds has not changed. This effect can be amplified by some of the properties of the atoms present in the substituent groups, such as electronegativity. Similar to the earlier discussion of the base porphyrin, when additional orbitals of correct orientation are present (i.e., another  $\pi$  system) on the *meso*-substituents, the HOMO and LUMO wave functions are able to delocalize into them, thus increasing the size of the ring and the predicted C-C bond length. When the substituent contains more electronegative species (e.g., 4-fluorophenyl, 4-methoxyphenyl, and even more so with pentafluorophenyl) the electrons within the  $\pi$  system are partially withdrawn creating even more probability for the HOMO and LUMO wave functions to delocalize outward. However, electronegativity is not the only property that can influence the degree of delocalization into the substituent orbitals. If the accuracy of the model were based solely on the presence of additional  $\pi$  orbitals and a simple consideration of the electronegativity of the substituent, then it would seem that the tetramethylporphyrin would have one of the shortest calculated bond lengths. Since there is no additional  $\pi$  system or electronegative species present at the *meso* positions, it would not be initially expected that the HOMO/LUMO wave functions would be able to delocalize

into the added methyl groups. Instead, the calculated bond length from the synthesized tetramethylporphyrin was one of the longest compared to the other synthesized porphyrins.

It appears that when substituents in the *meso* positions of the synthesized porphyrin contain molecular orbitals, although not necessarily  $\pi$  orbitals, that are of a similar energy to the HOMO or LUMO and are in an orientation that would allow them to interact with the HOMO/LUMO orbitals of the ring, more than expected delocalization can occur. In other words, the interactions of the orbitals on the substituents allow conjugation out of the ring including through hyperconjugation, like in the case of the tetramethylporphyrin. If the orbitals of the substituents can interact with the orbitals within the ring, there is a potential that the electrons within the conjugated  $\pi$  system of the ring could also be found in the orbitals of the substituents. Because this would draw some of the electron density outside of the ring, one of the boundary conditions of the particle-on-a-ring model would be broken, and the model would be worse at yielding an accurate bond length. The hyperconjugation of the substituent molecular orbitals into the molecular orbitals of the ring provides an explanation for the inaccuracy of the calculated bond length for tetramethylporphyrin and tetra-*p*-tolylporphyrin. Since the methyl substituents are not electronegative compared to the porphyrin ring, nor have a  $\pi$  system, tetramethylporphyrin was expected to have one of the most accurate calculated bond lengths. However, the bond length is actually quite inaccurate relative to other porphyrins. Based on calculations performed in Spartan, it is expected that this is due to hyperconjugation, in which the  $sp^3$  orbitals on the carbon atoms of the methyl groups interact with the HOMO orbitals of the porphyrin ring. It is expected that the accuracy of the model depends on both the possibility of the substituent providing orbital space to further accommodate the HOMO and LUMO of the ring and is amplified by some of the substituent properties.

After accounting for issues arising due to solubility, the syntheses for most of the porphyrins reported in Table 2 are feasible for an undergraduate student to reproduce individually. There were five porphyrins for which a synthesis was attempted (occasionally somewhat successfully) using similar procedures, but were unsuccessful in yielding satisfactory spectra. The porphyrins that would be produced from these syntheses did not present any new or interesting points to provide to the experiment compared to the porphyrins in Table 2, so these were not included. One of these porphyrins was tetraethylporphyrin, which was synthesized from propionaldehyde. The synthesis was initially run using the same generalized procedure, however, no crystals were precipitated. Water was added to the reaction mixture and the flask was placed in an ice bath, which resulted in a product with a tar-like appearance that could be gravity filtered out. However, this product did not yield a UV/Vis spectrum that resembled a porphyrin spectrum. The synthesis was attempted two more times, once with mild heating rather than boiling propionic acid, which resulted in a more gradual color change than the immediate and drastic color change that occurred with the first attempt, however there was still no precipitate. The reaction mixture was then neutralized, which did result in a precipitate, although it did not resemble porphyrin crystals and gave the same UV/Vis spectrum as the first synthesis. The synthesis was then attempted a final time in a more organic solvent, isobutyric acid, to reduce solubility. This synthesis resulted in the same product and therefore the same non-porphyrin appearing UV/Vis spectrum.

The second of these porphyrins is (4-pyridyl)porphyrin, which was synthesized from 4-pyridinecarboxaldehyde. This synthesis was also attempted multiple times. The first attempt was performed using the generalized synthesis, however there were no crystals present in the reaction mixture, even after the addition of water and the use of an ice bath. A UV/Vis spectrum was collected of the reaction mixture itself, which contained a Soret band and a potential Q band. An

attempt at extracting the porphyrin was made using diethyl ether and sodium bicarbonate, which resulted in a few crystals on the surface of the reaction mixture after partial neutralization and sitting for 48 hours. These crystals did not easily dissolve in either dichloromethane or methanol, but did finally dissolve partially in dichloromethane with sonification. This dichloromethane solution resulted in a usable UV/Vis spectrum, but the results did not provide any particularly interesting points that made the troublesome synthesis necessary. Instead, the data from the purchased porphyrin are included in Table 2 for reference.

The third of these porphyrins is tetrakis(2-hydroxyphenyl)porphyrin, which was synthesized from salicylaldehyde. The first attempt for this synthesis was also performed using the generalized synthesis procedure. This synthesis did result in a precipitate, although this precipitate resembled black tar and clumped together during filtration, significantly increasing the time required to filter. The solid did not dissolve in dichloromethane and dissolved poorly in methanol, resulting in a poor UV/Vis spectrum with very low absorbances. The second and final synthesis for this porphyrin was performed using isobutyric acid rather than propionic acid. This synthesis produced crystals, from which a UV/Vis spectrum could be collected. The UV/Vis spectrum contained a potentially decent Soret band, however, there was no indication of a possible Q band. Additionally, the spectrum for this porphyrin did not seem to provide any particularly interesting results that would make the problematic synthesis worth performing in an undergraduate laboratory.

The fourth of these porphyrins is the unsubstituted porphine, which was synthesized from formaldehyde. The first attempt using the generalized synthesis procedure did not yield crystal products. A second attempt was then made using mild heating rather than boiling propionic acid, which produced a thick solid product, which was then gravity filtered overnight. The product changed color from red to black overnight and did not dissolve in dichloromethane, methanol, or

acetone for UV/Vis analysis. A third synthesis attempt was made using boiling isobutyric acid rather than propionic acid. The addition of formaldehyde and pyrrole reacted violently upon contact with the boiling isobutyric acid, immediately bubbling back up through the reflux condenser and out through the top. This synthesis produced a large yield of spongy black solid which also could not be dissolved in dichloromethane, methanol, or acetone for UV/Vis analysis. A fourth and final attempt was made by performing the synthesis in isobutyric acid again with no heat for about 20 minutes. This synthesis also produced solid, which also did not dissolve in any solvent for analysis. The filtrate also did not produce a spectrum.

The last of these porphyrins is tetrakis(4-(trifluoromethyl)phenyl)porphyrin, which was synthesized from 4-(trifluoromethyl)benzaldehyde. The first attempt at this synthesis was made using the generalized synthesis procedure, however, no porphyrin crystals were produced. The reaction mixture was then split in half; water was added to one part, which resulted in crystals, but vacuum filtration failed to pull liquid through a Buchner funnel. Equal parts of water and diethyl ether were added to the other half of the reaction mixture, and the porphyrin was extracted first into the diethyl ether, and then was washed with sodium bicarbonate to remove excess acid, and dried with calcium chloride. The solid that was collected as a result yielded an excellent porphyrin spectrum, however, similar to the synthesis for tetrakis(2-hydroxyphenyl)porphyrin, the spectrum did not provide any new interesting points to justify the use of a more complicated procedure. The synthesis is feasible for an undergraduate upper-level chemistry student, but due to time constraints for the laboratory period, may not be reasonable for an undergraduate experiment. The data from the ultimate success of this synthesis is included in Table 2 for reference, but the synthesis could not be reproduced.

## **V. Proposal of Student Experiment**

The goal of this thesis project was to design and propose an undergraduate laboratory experiment for physical chemistry students to enhance their understanding of a fundamental quantum mechanical system: the particle-on-a-ring. The experiment consists of students synthesizing their own porphyrins, analyzing their porphyrins using UV/Vis spectroscopy, and employing relevant quantum mechanical equations to evaluate the particle-on-a-ring model. Since each synthesis takes approximately 1-2 hours, it would be beneficial to assign students to groups, and assign each group a porphyrin to synthesize. Depending on the size of the class, a variety of porphyrins could be assigned that will produce significant differences in carbon-carbon conjugated bond lengths that must later be analyzed. Allowing students to synthesize their own porphyrin products is a valuable component to the experiment in that it requires the students to recall and utilize skills learned in organic chemistry courses. Recalling skills from a previous course is an excellent way to strengthen and enhance those abilities, while also showing their relevance to current material.

Once the porphyrins have been synthesized, each group should collect a UV/Vis spectrum for each of the porphyrins synthesized in the class. The yields of each of the porphyrins are generally large enough that the products can then be shared among groups, such that each group can still collect their own data for each porphyrin. Additionally, each group would not need a large portion of the product. Only a few crystals need to be dissolved in dichloromethane to obtain a UV/Vis spectrum from which a wavelength of maximum absorbance of the fairly intense and colorful Q band can be determined. Given the particle-on-a-ring equation (using the wavelength value from each spectrum), students should calculate the carbon-carbon bond length predicted using the particle-on-a-ring equation for the transition energy. Once students have determined how to solve for the bond length, calculations can be performed using Excel.

Some of the syntheses are more straightforward than others, as discussed in the Results and Discussion section. Depending on the number of students and number of groups in the laboratory section, the instructor should choose which porphyrins to synthesize based on availability or accessibility of reactants, time constraints, and points of interest provided by each porphyrin. Seven key porphyrins are listed in the student handout (see Appendix A), but these may be adjusted as needed to accommodate class size. The instructor should exercise discretion in choosing porphyrins to include, such that a variety of results are obtained and so that students are still given the opportunity to discuss the effects of different substituents on the model. It is suggested that TPP, (4-dimethylaminophenyl)porphyrin, and (4-fluorophenyl)porphyrin should be included, at a minimum. Since the synthesis procedure for TPP often requires less time than either (4-dimethylaminophenyl)porphyrin or (4-fluorophenyl)porphyrin, it is also suggested that the group responsible for the synthesis of TPP might also be responsible for the complexation of a metal into the center of TPP.

Regarding the analysis component of the experiment, there is a significant pedagogical advantage to having students explain the difference between the experimental calculated bond lengths for each porphyrin and the literature value. Asking students to describe how the model works and why the model breaks under certain conditions requires the students to explore the details of the model and how it applies to molecules. For example, asking students to explain the hyperconjugation of the substituent orbitals into the ring, and then describe why this causes the model to break requires one to evaluate the effect of hyperconjugation on the conjugated  $\pi$  system and the subsequent effect this has on the particle-on-a-ring calculations. By describing these cause-and-effect relationships, such as the one in the previous example, the student begins to gain a deeper understanding of the quantum model and how it works. A complete sample student handout is included in Appendix A.



## VI. Conclusion

It was determined that there are several *meso*-substituted porphyrins that can be successfully synthesized by undergraduate chemistry students using the skills they would have learned in their organic chemistry courses. Porphyrins were shown to be an excellent model of the particle-on-a-ring theory via analysis with UV/Vis spectroscopy. The bond lengths that result from calculations using the particle-on-a-ring model differed slightly from the literature value for a conjugated carbon-carbon bond, but overall exhibit an excellent agreement. The difference between the values provides students with an opportunity to explore the model on a deeper level and investigate how it works and at what point it breaks.

The implementation of a laboratory experiment such as this one into undergraduate physical chemistry courses would provide students with the opportunity to gain a deeper understanding of such a fundamental theory of quantum mechanics. It would provide students with experience working with concepts such as waves and wave functions, boundary conditions, and quantization. Physical chemistry students are often taught the related particle-in-a-box theory in a more in-depth manner, including coverage during the lecture course and a corresponding laboratory experiment, however, the particle-on-a-ring model is then often covered more quickly. It is often glossed over as a theory that is essentially the particle-in-a-box theory applied to a different type of molecule and with different boundary conditions. However, there is a greater difference between the two theories than the type of molecule and the boundary conditions, and the models are often too abstract for students to rationalize the differences on their own. Therefore, a laboratory experiment is needed to deepen students' understanding of the particle-on-a-ring model, as well as quantum mechanics as a whole. While porphyrins may not be a perfect model,

it is precisely this imperfection and the ease of their synthesis that makes them excellent laboratory models for student experimentation.

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## VIII. Appendix A: Sample Student Handout

### Experiment: Porphyrins on a Ring

#### Purpose

The purpose of this experiment is to explore the particle-on-a-ring system by using actual molecules to simulate electrons trapped in a 2D ring.

#### Pre-Lab Questions

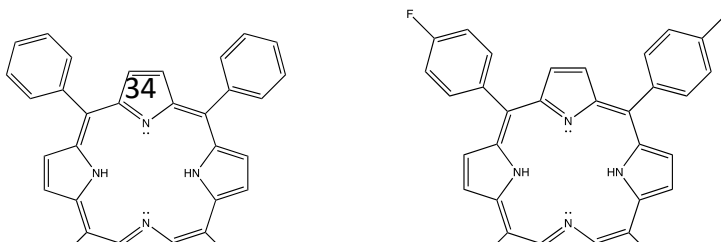
Complete the following questions in your lab notebook and hand them in when you get to lab.

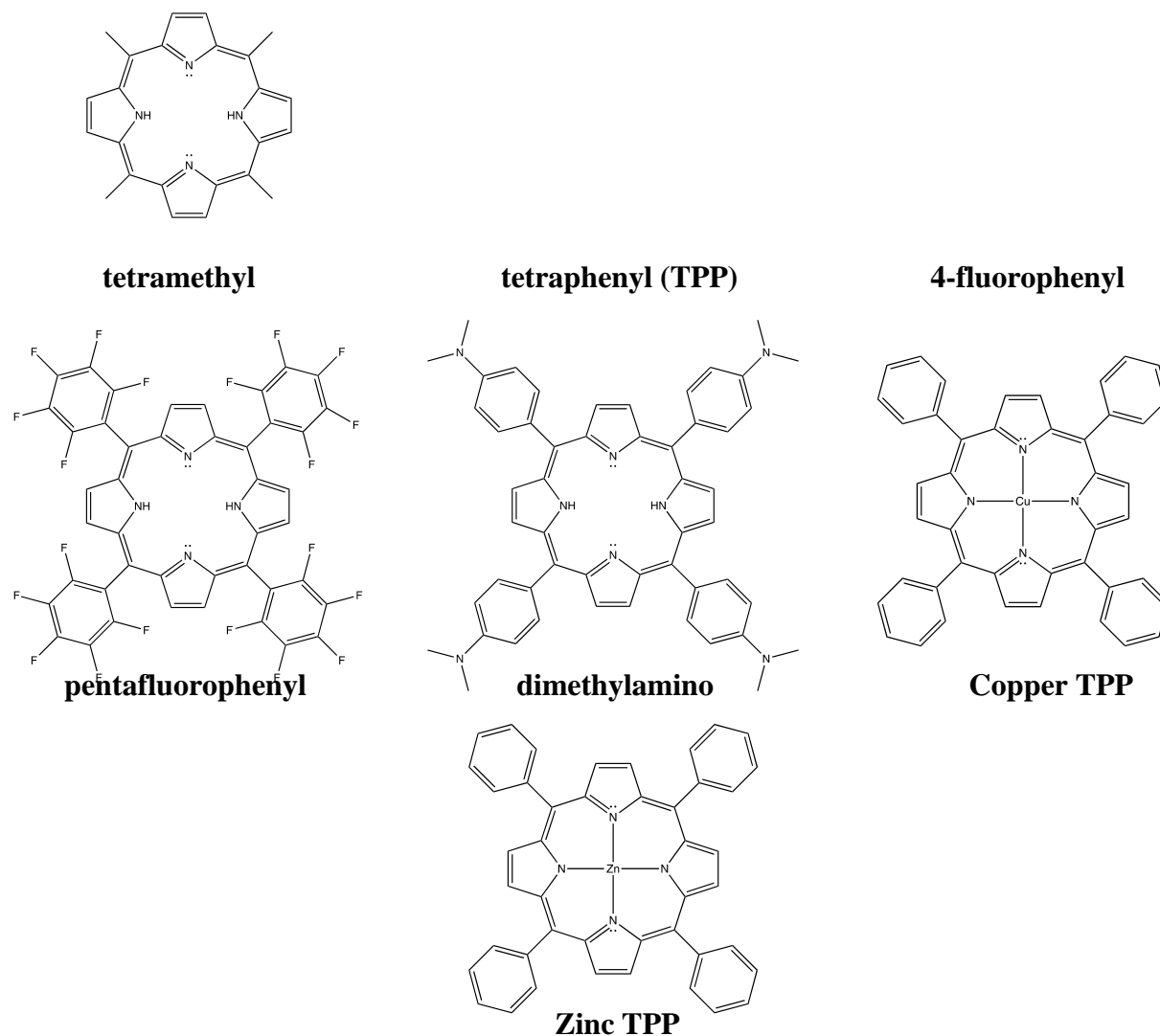
1. Define the number of  $\pi$  electrons in a molecule of benzene and the corresponding  $m_l$  value.
2. If the  $\pi$  system of benzene exhibits a  $\pi - \pi^*$  transition with maximum absorbance at 255 nm ( $\lambda_{max}$ ), use equations 4, 5, and 6 to calculate the radius of the molecule (in nm), and calculate the average bond length of the carbon-carbon conjugated bonds.

#### Background

Porphyrin molecules exist as vibrantly colored molecules that are common in nature, such as in hemoglobin or chlorophyll. The color of a porphyrin results from its interactions with visible electromagnetic radiation. The reflection of the color of light that is observed and the absorption of the opposite color of light determines the apparent color of the molecule. This is true for the observed colors in any object, for example, if something appears blue, then it is mostly yellow or orange light that is being absorbed. Objects that appear to be black suggest that all of the light is absorbed, and none is reflected, while objects that appear to be white suggest that all of the light is reflected and none of it is absorbed. The colors of light, and therefore specific frequencies of light, that can be absorbed by a certain molecule are determined primarily by the electronic structure of the molecule. Electronic excitations typically occur in the UV and visible regions, sometimes resulting in observable colors.

The 2-D particle-on-a-ring model can be used to describe the motion of an electron along a conjugated  $\pi$  system. Since a conjugated  $\pi$  system, by definition, contains multiple  $\pi$  electrons that are in resonance with each other, they are free to travel through the entire  $\pi$  system. Since electrons exhibit wave-particle duality, they can be conceptualized as a wave traversing around the entire system. In the case of this experiment, the  $\pi$  system is the “ring” along the perimeter of the porphyrin ring, excluding any substituents, and following the interior of the pyrrole rings with deprotonated nitrogen atoms to include the lone pairs of electrons. The *meso*-substituted porphyrins shown in Figure 1 exhibit this type of conjugated  $\pi$  system. The chemical names of the porphyrins in Figure 1 are as follows: tetramethylporphyrin, tetraphenylporphyrin (TPP), tetrakis(4-fluorophenyl)porphyrin, tetrakis(pentafluorophenyl)porphyrin, tetra(4-dimethylaminophenyl)porphyrin, tetraphenyl-21H, 23H-porphine copper (II) (copper TPP), tetraphenyl-21H, 23H-porphine zinc (II) (zinc TPP). For example, the conjugated  $\pi$  system in tetramethylporphyrin includes 9  $\pi$  bonds and 2 lone pairs spanned across the ring structure (see Figure 1).





**Figure 1.** Structures for each of the seven porphyrins used in this experiment. The two deprotonated nitrogen atoms in the pyrrole rings are included in the  $\pi$  system, while the nitrogen atoms in the protonated pyrrole rings are not.

A particle on a 2D ring with radius  $r$  must satisfy the 2D Schrödinger equation:

$$\frac{-\hbar^2}{2mr^2} \frac{\partial^2}{\partial \phi^2} \psi = E\psi \quad (1)$$

where  $\hbar$  is Planck's constant divided by  $2\pi$ ,  $m$  is the mass of the particle (in kg),  $r$  is the radius of the ring, and the potential energy term is infinite everywhere outside of the conjugated  $\pi$  system of the ring and zero on the ring. The solution to this equation is as follows:

$$\psi_{m_l} = \sqrt{\frac{1}{2\pi}} e^{im_l\phi} \quad (2)$$

where  $m_l$  is the angular momentum quantum number,  $i$  is the imaginary number  $i^2 = -1$ , and  $\phi$  is the angular position of the particle on the ring. The energies of the system can be found by solving this Schrödinger equation:

$$E_{m_l} = \frac{m_l^2 \hbar^2}{2mr^2}, \quad m_l = 0, \pm 1, \pm 2, \pm 3, \dots \quad (3)$$

The sign of  $m_l$  indicates the direction of rotation around the ring. However, in spectroscopic experiments such as this one, it is the energy difference from one energy level to the next energy level that is measured. The difference between the adjacent  $m_l$  energy level and the  $m_l+1$  energy level can be found by taking the difference of the energy equations for each level:

$$\Delta E = E_{m_l+1} - E_{m_l} = \frac{(m_l+1)^2 \hbar^2}{2mr^2} - \frac{m_l^2 \hbar^2}{2mr^2} = \frac{\hbar^2}{2mr^2} (2m_l + 1) \quad (4)$$

Unlike the basic particle-on-a-ring model, the porphyrin molecule contains multiple electrons rather than a single particle. Since Pauli's Exclusion Principle states that no two electrons can have the same set of quantum numbers, each  $m_l$  value should represent two electrons, one with  $m_s$  equal to  $+1/2$  and one with  $m_s$  equal to  $-1/2$ . For example, in a molecule such as benzene, which has 6  $\pi$  electrons, the occupied  $m_l$  orbitals would be 0,  $+1$ , and  $-1$ . The electronic excitation of each porphyrin molecule will excite an electron from the highest occupied  $m_l$  level to the lowest unoccupied  $m_l$  level. For example, an electron in benzene would be promoted from  $m_l = +1$  to  $m_l = +2$ .

This method of determining  $m_l$  levels can be applied to each of the porphyrin molecules in this experiment. The radius of the ring can be determined by determining the energy of the transition from one  $m_l$  level to the adjacent  $m_l$  level spectroscopically, using the wavelength of maximum absorption ( $\lambda_{max}$ ) and solving Equation 4 for  $r$ . The length of an average carbon-carbon conjugated bond length for the porphyrin molecule can then be calculated by finding the circumference of the molecule and dividing that value by the number of bonds in the ring:

$$b = \frac{C}{q}, \quad C = 2\pi r \quad (5, 6)$$

where  $b$  is the average length of each bond in the system,  $C$  is the circumference of the ring, and  $q$  is the total number of bonds in the system. Since the conjugated  $\pi$  system of the porphyrin excludes the exterior bonds of the two pyrrole rings with deprotonated nitrogen atoms, the system includes the interior bonds of each of the deprotonated pyrrole rings, and follows the exterior of the remainder of the ring. The calculated value for  $q$  can then be compared to the literature value for the average length of a conjugated carbon-carbon bond, 1.39 Å.

Porphyrins tend to yield a distinct UV/Vis spectrum, which contains two primary bands: the Soret band and the Q band. The Soret band contains two peaks, although they may appear as one due to peak broadening, in the UV region (ca. 400 nm). The Q band appears generally as our distinct peaks in the visible region. Since the Q band is found at a longer wavelength, it represents the lower energy transitions, from the HOMO and HOMO-1 orbitals to the LUMO orbital. Based on geometry calculations, the molecular orbitals are in the correct orientation for interaction with the HOMO/LUMO transition (the classic  $\pi$ - $\pi^*$  transition). Therefore, it is the lowest energy, or reddest, peak of the Q band that is most applicable to the particle-on-a-ring model.

## Procedure

### Necessary Materials:

#### Part A:

- Appropriate substituted aldehyde(s)
- Pyrrole

- Propionic or isobutyric acid
- Appropriate solvent for washing
- 100 mL round-bottom flask
- Buchner funnel and filter paper
- Vacuum tubing
- Vacuum flask
- Small beaker
- Magnetic stir bar and stir plate
- Heating mantle and temperature adjustment controller
- Reflux condenser and tubing

*Part B:*

- Synthesized TPP
- *N, N*-dimethylformamide (DMF)
- 100 mL round-bottom flask
- Magnetic stir bar and stir plate
- Appropriate metal acetate compound
- Heating mantle and temperature adjustment controller
- Reflux condenser and tubing

*Part C:*

- Solvent for UV/Vis analysis (dichloromethane or methanol, see Table 1)

**Procedural Detail:**

*Part A: Porphyrin Synthesis*

1. Assemble a reflux apparatus
2. Add a magnetic stir bar and 40 mL of the appropriate organic acid to a 100 mL round-bottom flask.
3. Heat the acid under reflux with a heating mantle until vigorously boiling.
4. Create a mixture of 15.75 mmol of appropriate aldehyde and 1.0 mL of pyrrole in a small beaker.
5. Add the mixture of aldehyde and pyrrole to the boiling acid by pouring it down the reflux condenser.
6. Rinse the walls of the condenser with a few mL of acid to ensure all of the aldehyde and pyrrole mixes with the acid.
7. Heat under reflux for 30 minutes.
8. Assemble the vacuum filtration apparatus using a Buchner funnel and vacuum flask.
9. Remove heat from the reaction mixture and cool until the flask can be held comfortably, or for about 15 minutes. An ice bath can be used to cool the mixture faster.
10. Vacuum filter through a Buchner funnel.
11. Wash the crystals with the appropriate solvent for washing by pouring it onto the filter, rinsing the walls and the filter itself, until the washings are relatively clear.
12. If no crystals have precipitated out of the solution, add about 50 mL of water to reduce solubility and filter again.

13. If there are still no crystals, separate about half of the reaction mixture into a large, clean beaker. Using a saturated sodium bicarbonate solution, neutralize this portion of the filtrate and filter again.

*Part B: Complexing a Metal into TPP*

1. Add 0.1 g of TPP and 20 mL DMF to a 100-mL round-bottom flask with a magnetic stir bar and stir.
2. Add 0.80 mmol of the appropriate metal acetate compound to the purple mixture.
3. Heat under reflux for 30 minutes, then cool to room temperature. An ice bath can be used to cool the solution faster.
4. Collect a UV/Vis spectrum (see Part C).
5. If the spectrum does not appear any different from the spectrum for TPP, continue heating under reflux for about 20 minutes and collect the spectrum again.

*Part C: Spectrophotometric Analysis:*

1. Turn on and warm up the UV/Vis spectrometer.
2. Dissolve the synthesized porphyrin crystals into enough dichloromethane to make a solution of about  $1 \times 10^{-5}$  M. If collecting a spectrum of a metal complex, add a few drops of the solution to a cuvette with dichloromethane and mix well.
3. Set the spectrometer to manual and take an absorbance spectrum of the porphyrin solution. Dilute the solution in the cuvette until the lowest energy peak of the Q band (ca. 500 - 700 nm) has an absorbance of less than 2.
4. Save the spectrum as a .csv file to a flash drive or email them to yourself and your partner so you can access it.
5. Repeat steps 2-4 using the appropriate solvent for each of the synthesized porphyrins to be analyzed.
6. Empty all used solvent and porphyrin waste into a labeled waste container.

## Results

### Calculations

Based on your measured values, determine or calculate the following quantities for each porphyrin:

1. The energy of the  $\lambda_{max}$  transition
2. The radius of the ring
3. The circumference of the ring
4. The carbon-carbon bond length (in Å)

### Report Guidelines

Be sure to address/include the following in the appropriate sections of your lab report:

1. A single graph with the absorption spectra for each of the 7 porphyrin molecules. It may be helpful to vertically offset the spectra from one another so that all the bands are clearly visible on the same graph.
2. A table including the wavelengths of maximum absorption for the lowest energy transition of the Q band and the radius and calculated bond length of each porphyrin.
3. Do the calculated bond lengths for each of the porphyrin molecules match the literature value for a conjugated carbon-carbon bond? Why or why not?
4. Discuss the difference between calculated bond lengths for *meso*-substituted porphyrins versus the metalloporphyrins. Is this what you would expect?



5. Discuss the validity of the particle-on-a-ring model for the porphyrin system.