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Spring 2021

## Synthesis of Novel Porphyrin Derived Molecules for the Study of Self Assembly and Photophysical Properties

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# **Honors Research Project**

## **Synthesis of Novel Porphyrin Derived Molecule for the Study of Self Assembly and Photophysical Properties**

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# Synthesis of Novel Porphyrin Derived Molecule for the Study of Self Assembly and Photophysical Properties

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**Abstract:** The photochemical potential of self-assembling porphyrins holds the potential to eliminate the use of fossil fuels. Porphyrins have the ability to absorb solar energy to excite its electrons within the highly conjugated  $\pi$  system of the porphyrin ring. The excited electron can then be donated thus created a charge separated state between the porphyrin donor and the electron acceptor. With self-assembly of porphyrin monomers into a supramolecular structure, this charge separated state can be emphasized and be prolonged so the energy potential generated can be harvested. Here, the synthesis of porphyrin derivatives substituted with biologically found molecules is described. The lysine and guanidinium substituents were chosen for their potential to enable self-assembly between porphyrin monomers. The synthetic processes for both proposed porphyrin structures are still on-going.

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## **Introduction**

Footprints are normally seen in sand, snow, or mud but the largest is the anthropological carbon footprint.<sup>1</sup> This proverbial carbon is largely defined as the quantity of carbon released within a given area of land.<sup>2</sup> The carbon is released in the form of gases such as carbon dioxide, methane, and fluorinated gases. These gases chiefly emanate from the burning of fossil fuels, such as coal and natural gas, which allows the carbon energy source to contribute to the increasing concentration of gases in Earth's atmosphere.<sup>3</sup> These gases are called greenhouse gases as they have a "greenhouse" like effect on the earth where the earth is warmed from sunlight reflecting off the surface of the earth which is absorbed and trapped by the greenhouse gases. This absorption of the sun's energy is turned into heat energy which will heat up the earth's surface and ultimately leads to global climate change.<sup>4</sup> This climate change is predicted to increase global temperature by 1-3.6°C within the century which can lead to the acidification of bodies of water, mass extinction of wildlife, the raising of global water levels, and more extreme climates worldwide.<sup>2,5</sup> The most concerning repercussion is the health risk to humans which may take form by an increase in zoological and aquatic diseases, poor air quality, and loss of agricultural viability.<sup>6</sup> Overall, global climate change is bad news for all living beings on planet earth.

With the dangers of global climate change, humans need to invest more into cleaner energy sources to circumvent the emission of greenhouse gases but still obtain energy. Green energy

sources mainly take advantage of preexisting natural mechanisms and converts it onto available energy. Preexisting natural mechanisms such as the mechanical energy from wind and water movement, geothermal heat energy from deep within the earth, and solar energy are common sources of energy that is harvested for human use.<sup>7,8</sup> Solar power has great potential to be one of the future energy providers being that sunlight is in great abundance in all areas of the world, it can be easily integrated into infrastructure, and does not require much maintenance since there are no moving parts.<sup>9</sup> In terms of advancement for photovoltaic cells, plants and cyanobacteria serve as the perfect model system to emulate or improve upon, which prevents the need to “reinvent the wheel” on how to harvest solar energy. Plants and cyanobacteria use a metabolic process called photosynthesis to convert water and carbon dioxide into high energy containing compounds using solar energy. These high energy compounds are broken down for its energy in other metabolic process.<sup>10,11</sup>

What allows plants and cyanobacteria to perform photosynthesis is the organelle called chloroplast. The chloroplast is home to the thylakoid membranes where photosystem I (PSI), photosystem II (PSII), and the light harvesting complex (LHC) are found. The active components of PSI and PSII are found in their chlorophyll reaction centers (RC), named P700 and P680, respectively.<sup>12</sup> These reaction centers absorb solar radiation, promoting electrons in the RC to a higher energy level which can be used for different means. To begin, P680 from PSII will absorb the 680 nm solar radiation energy forming the excited state P680\*. Then an electron will be donated to an electron acceptor shuttle called Pheophytin (Pheo) causing P680 to be electron deficient (P680•+). The large redox potential of P680•+, 1.17V, will drive the splitting of water which is a source of electrons to stabilize P680•+ back into P680. Having accepted an electron, Pheo•- will initiate a cascade of electron donation and acceptance leading to the P700 reaction center of PSI. After P700 accepts an electron, forming P700•-, it shall absorb the solar radiation energy at 700 nm, and be promoted to the next excitation level (P700\*•-). From there, P700\*•- will initiate another cascade of electron donation and acceptance, ultimately leading to the terminal electron acceptor, NADP+, forming NADPH which is used in further biological processes.<sup>13,14,15</sup>

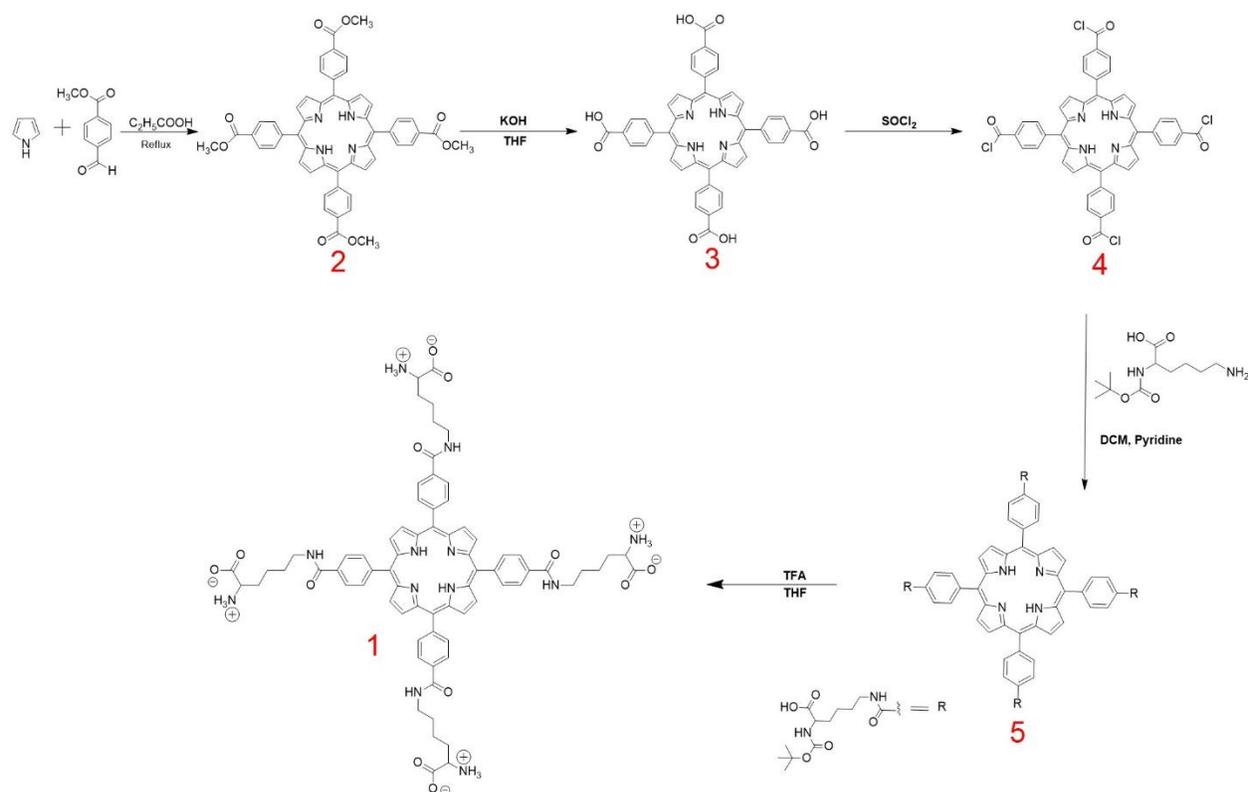
The desired property from photosynthesis is this electron transfer from molecule to molecule. A charge separated state (CSS) is created from this electron transfer process which is seen often times resulting in two oppositely species. These charges species hold an energy potential which can do further work such as splitting water as seen in photosynthesis.<sup>16</sup> The most ideal CSS is one takes place in the nanosecond time range which faster than the typical femtosecond time range. With a longer the CSS, there is more time to harvest that energy potential.<sup>17</sup>

This CSS is initiated in the chlorophyll reaction center of the LHS where a substituted porphyrin ring converts solar energy to electrical energy. Porphyrins are highly conjugated macrocyclic molecules that typically absorb light in the visible light spectrum (300 nm–800 nm) and the near-IR (>800 nm).<sup>18,19</sup> The absorbed light will excite electrons within the electron rich environment of the highly conjugated  $\pi$  system from the ground state to excited state.<sup>20</sup> The excited electron can then be transferred from the donor molecule to an acceptor molecule, thereby creating a charge separation. This charge separation is aided when the donor and acceptor molecule are assembled adjacent from each other which increases the excitonic coupling of the donating and accepting molecules.<sup>21</sup> To capitalize on the excitonic coupling, the self-assembly of monomers into a supramolecular structure is commonly sought after in the photovoltaic discipline.<sup>22</sup> Porphyrins particularly shine in self assembling due to their highly conjugated  $\pi$  system which are subject to  $\pi$ - $\pi$  stacking between the planar porphyrin faces.<sup>23</sup> In addition, porphyrins can be readily substituted to increase its self-assembling capabilities which are commonly non-covalent interactions such as ionic bonding, hydrogen bonding, Van der Waals attraction, and  $\pi$ - $\pi$  stacking.<sup>23, 24</sup>

Here, attempts were made to synthesize porphyrin derivatives with self-assembling capabilities using substituents found in biological systems. In Scheme 1, a lysine substituent is used in hopes that the terminal positive and negative charges will be able to interact with another adjacent porphyrin monomer through an ionic bond. In Scheme 2, a positively charged guanidinium substituent is used with the expectation of self-assembly with negatively charged co-aggregates also through an ionic bond. If successfully synthesized, the self-assembling properties can be analyzed using steady state absorption and emission spectroscopies, time resolved emission, transmission electron microscopy (TEM) and atomic force microscopy (AFM).

## **Results and Discussion**

The focus this project was the synthesis of a porphyrin derivative in hopes to study its photochemical and self-assembling properties. To that end, an attempt was made to synthesize a porphyrin substituted with lysine at the meso-phenyl positions of tetraphenyl porphyrin (**1**) as shown in Scheme 1.



Scheme 1. Synthesis of Bolaamphiphile (**1**).

The 5,10,15,20-tetrakis(4-methoxyphenyl) porphyrin (**2**) precursor was previously synthesized by Dr. Innocent Demshemino during his graduate and was used as a convenient steppingstone for my first reaction; the saponification of porphyrin (**2**). As seen in Figure 1, the starting material methoxy porphyrin (**2**) shows relatively pure  $^1H$ -NMR. Peaks seen at 8.816ppm represent the pyrrole hydrogens of the porphyrin ring and the peaks at 8.305ppm and 8.278ppm represent the phenyl hydrogens. At 4.111ppm are the methoxy hydrogen peaks which are an important diagnostic region for the saponification of the methoxy group in the following reaction. Similarly, the peak at -2.817ppm represent the internal pyrrole hydrogens of the porphyrin ring which characterizes the porphyrin as the free base porphyrin and not the metal coordinated porphyrin base. At 1.546ppm represents water which most likely came from the deuterated solvent,  $CDCl_3$  which is the peak at 7.256ppm. The peak at 1.250ppm is an impurity identified as hydrocarbon grease.

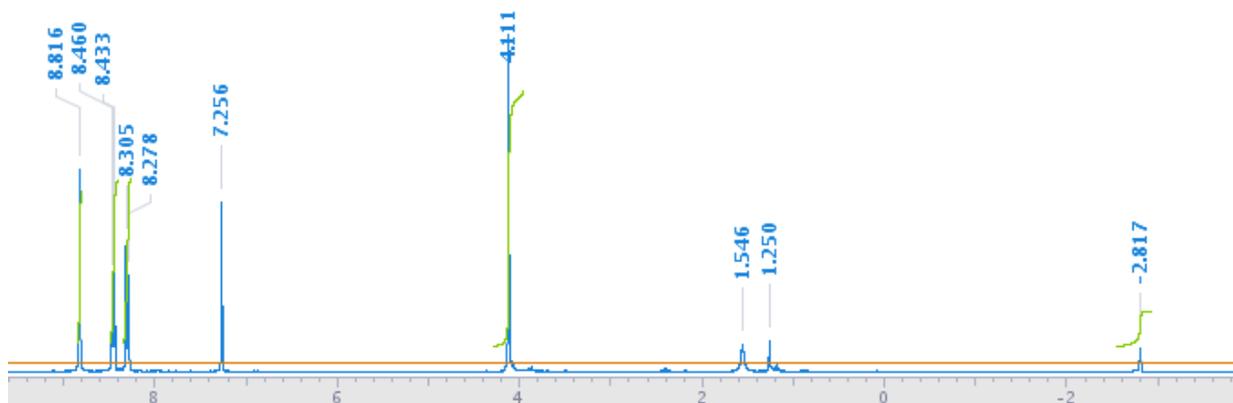


Figure 1.  $^1\text{H-NMR}$  of 5,10,15,20-tetrakis(4-methoxyphenyl) porphyrin (**2**) as synthesized by Dr. Innocent Demshemino. Solvent was deuterated chloroform.

The methoxy-porphyrin (**2**) was saponified using KOH resulting in the 5,10,15,20-tetrakis(4-carboxylphenyl) porphyrin (**3**) with a 95% yield. The  $^1\text{H-NMR}$  showed relatively pure sample with the pyrrole and phenyl peaks at 8.848 ppm and 8.392-8.321 ppm, respectively. The peaks at 2.485 ppm and 3.335 ppm represent the deuterated DMSO solvent and the water in that solvent, respectively. The peak at 2.068 ppm and 1.336 ppm are most likely solvent such as acetone and more hydrocarbon grease respectively. Given this, this sample was considered pure enough to use for the following coupling reaction with the protected lysine substituent.

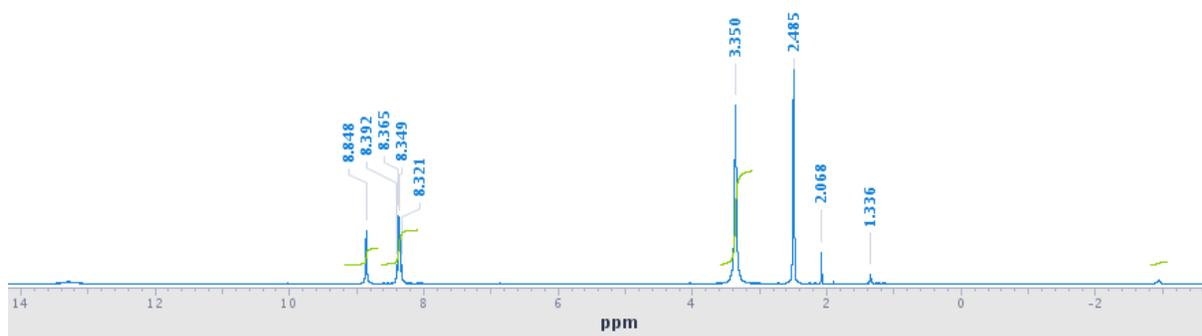


Figure 2.  $^1\text{H-NMR}$  of 5,10,15,20-tetrakis(4-carboxylphenyl) porphyrin (**3**). Solvent was deuterated DMSO.

The peptide coupling of the Boc-protected lysine was attempted by dissolving the carboxylic acid porphyrin (**3**) and Boc-protected lysine in solution and using the catalyst dicyclohexylcarbodiimide (DCC) and N-hydroxysuccinimide (NHS) which are common for peptide couplings. This reaction gave a black glossy solid that did not dissolve in any solvent. This product

was determined to not be the desired product. Subsequent reactions gave no adequate reaction, so another path was taken for the coupling.

To improve the coupling reaction, the electrophilicity of the carbonyl carbon on the carboxylic acid porphyrin (**3**) by converting it to the acid chloride porphyrin (**4**) using thionyl chloride. This would increase the reactivity of the porphyrin in order to drive the reaction more towards the products. In addition, there would be no more need for the DCC and NHS catalyst, thereby, reducing the total number of participants. According to collision theory, where the rate of reaction is dependent on the number of molecular collisions, the reaction will be faster with fewer required collisions.<sup>25</sup> This will decrease the reaction time and theoretically give a higher and more pure yield. The synthesis of the acid chloride porphyrin (**4**) proceeded by dissolving the carboxylic acid porphyrin (**3**) in thionyl chloride and allowing to react overnight. The acid chloride porphyrin (**4**) was immediately reacted with the Boc-protected lysine to avoid re-saponification of the acid chloride porphyrin (**3**) which gave a yield of 98% of the Boc-protected bolaamphiphile (**5**).

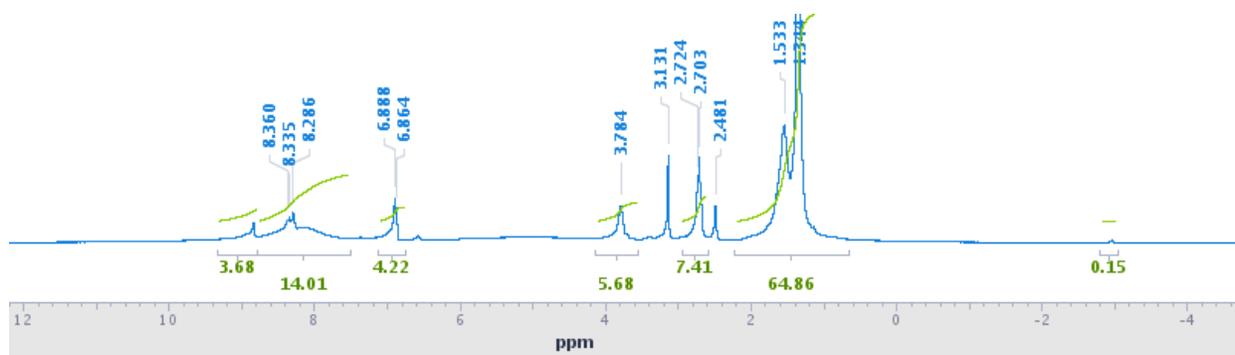


Figure 3. <sup>1</sup>H-NMR of Boc-protected bolaamphiphile. Solvent was deuterated DMSO.

As predicted, the <sup>1</sup>H-NMR gave a very clean spectrum, as seen in Figure 3. The peaks seen in the aliphatic region at 1.344, 1.533, 2.7, 3.784ppm all correspond to the hydrogens for the Boc-protected lysine. The peak at 6.8ppm is the nitrogen participating in the conjugated system of the phenyl substituted on the porphyrin. The pyrrole and phenyl hydrogen peaks of the porphyrin are seen at about 8.89ppm and 8.860-8.286ppm, as expected for typical porphyrins. The large humps seen ranging from 9.0ppm to 7.4ppm is postulated to be hydrogen exchanging. The peaks for deuterated DMSO and the water associated with that solvent are seen at 2.481ppm and 3.131ppm. The internal protons of the porphyrin ring are seen at about -3.05ppm.

With a successful coupling of the Boc-protected lysine to the acid chloride porphyrin (**4**), the final step is to deprotect the lysine which proved to be the most difficult reaction. The

deprotection of the Boc-protected bolaamphiphile (**5**) was attempted by reacting the porphyrin (**5**) in trifluoroacetic acid. This course of action gave an incomplete reaction even when left for 96 hours. The reaction was done a total of five times and each gave an  $^1\text{H-NMR}$  similar to Figure 4.

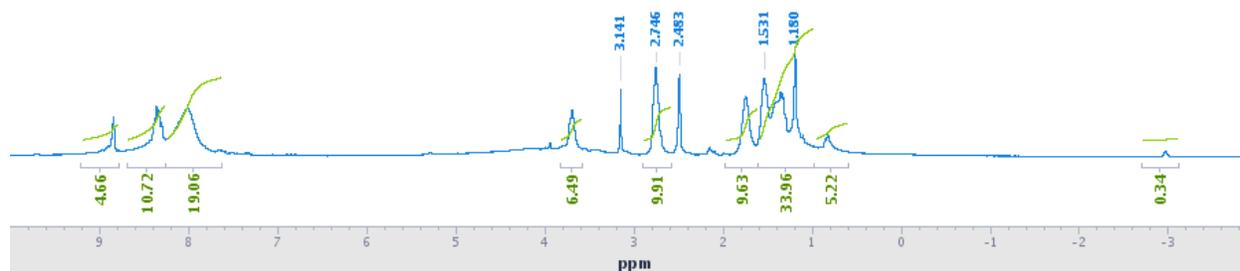


Figure 4.  $^1\text{H-NMR}$  of proposed deprotected bolaamphiphile. Solvent was deuterated DMSO.

The  $^1\text{H-NMR}$  shows the expected pyrrole and phenyl peaks of the porphyrin ring at about 8.98 and 8.37-8.15ppm, respectively. The peaks at about 3.78, 2.746, and 1.531ppm correspond to the hydrogens found on the coupled lysine substituent. From there, the impurities are plentiful seen at about 0.89, 1.180, about 1.70ppm with smaller peaks seen at 2.19ppm and 3.97ppm. These unknown peaks can line up with common solvents such as ethyl acetate (reported at 1.99, 4.03, and 1.17ppm).<sup>26</sup> In addition, a byproduct of the deprotection is the *tert*-butyl cation and, when heated, can undergo an elimination reaction to form isobutene which shows up at about 1.73ppm and 4.75ppm.<sup>27</sup> The biggest problem is that there still shows a peak at about 1.34ppm representing the hydrogens on the *tert*-butyl, which represent an incomplete deprotection. It was determined that simple laboratory purification methods were not practical for the purification of the deprotected (**1**) porphyrin. More precise methods such as a prep-HPLC would need to be used to purify the deprotected (**1**) porphyrin which the University of Akron does not provide.

With the unfinished project concerning the bolaamphiphile, a new project was started with higher prospect for a successful synthetic workup. The new project using the sample porphyrin base but uses a guanidine substituent, as shown in Scheme 2, instead of a lysine substituent.



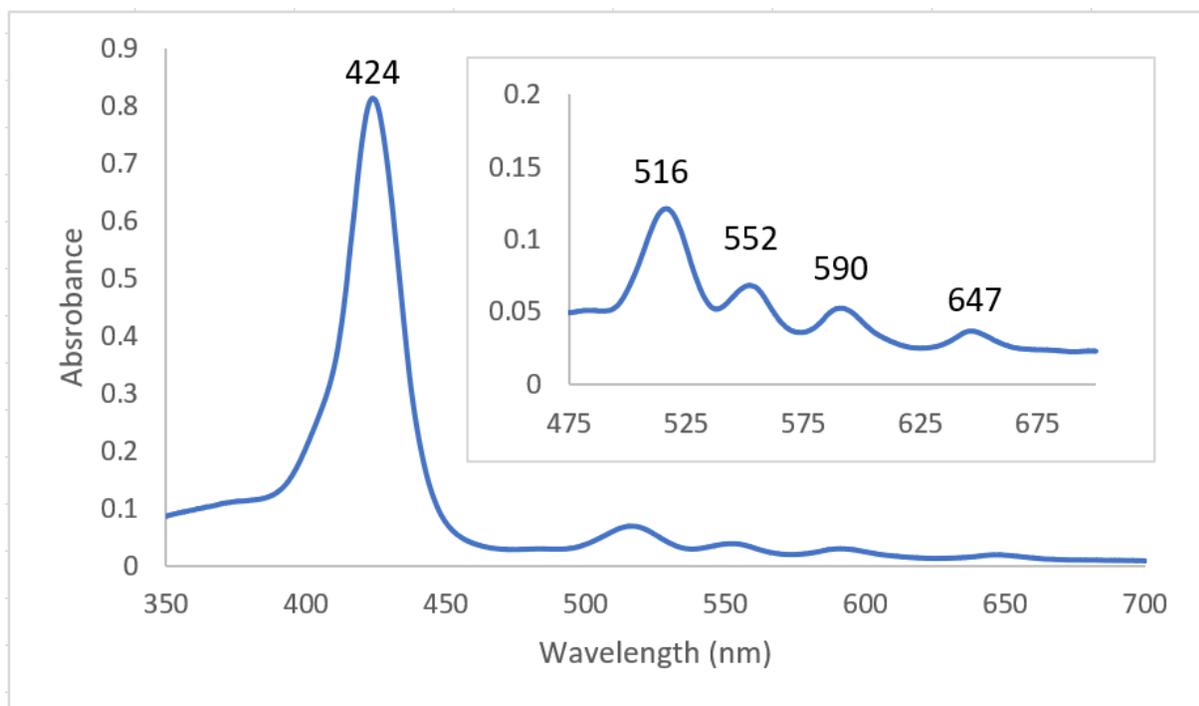


Figure 5. UV-vis spectrum of 5,10,15,20-tetrakis(4-nitrophenyl) porphyrin (**6**) in CH<sub>2</sub>Cl<sub>2</sub> with peaks labeled. Inset showed Q bands.

The UV-vis spectrum after purification by recrystallization gave the UV-vis spectrum, shown in Figure 5. This spectrum is characteristic of tetraphenyl porphyrin derivatives which have a total of 5 main features: one large Soret band and four smaller Q bands. According to previous literature, for the nitro porphyrin base (**6**), the Soret band should be seen at 425nm and the Q bands should be seen at 517nm, 552nm, 591nm, and 657nm. Since the UV-Vis spectrum of the synthesized sample is analogous to that proposed in the literature, it was concluded that the nitro porphyrin (**6**) was synthesized.

The reduction of the nitro porphyrin (**6**) to the amino porphyrin (**7**) became the bottleneck of this project with grease contamination plaguing the purity of the amino porphyrin (**7**). The reduction was completed by dissolution of the nitro porphyrin (**6**) and tin (II) chloride in concentrated HCl and allowing to reaction overnight. After purification by column chromatography twice and dried under vacuum, the <sup>1</sup>H-NMR shows the typical characteristics of a tetraphenyl porphyrin with the aromatic pyrrole peak at about 8.90ppm of the porphyrin and phenyl peaks at about 8.00ppm and 7.05ppm. The peak at 4.10ppm represents the amine hydrogens resulting from the reduction. The internal hydrogens of the porphyrin ring are represented by the peak at about -2.50ppm. The problem about this spectrum are the peaks seen at 1.54ppm, 1.25ppm, and 0.89ppm

which correspond to hydrocarbon grease and the peak at about 0.07ppm corresponds to silicone grease. This synthetic procedure was repeated a total of four times, each with the grease contamination. The grease contaminant was attempted to be removed using two purification procedures: trituration in hexane and silica column flush with hexane or petroleum ether. Both procedures failed to remove the hydrocarbon and silicone grease.

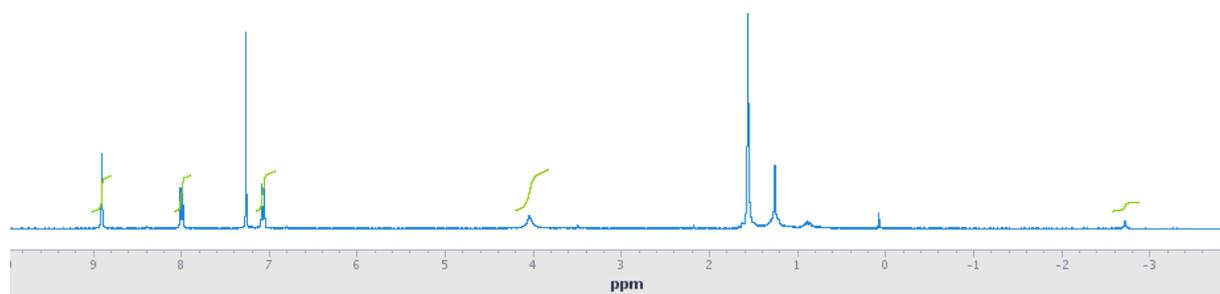


Figure 6.  $^1\text{H-NMR}$  of 5,10,15,20-tetrakis(4-aminophenyl) porphyrin (**7**). Solvent is deuterated chloroform.

Even with the presence of grease in the samples of the amino porphyrin (**7**), it can still be confidently assumed that the nitro porphyrin (**6**) was reduced to the amino porphyrin (**7**) since the  $^1\text{H-NMR}$  still showed characteristics that match the amino porphyrin (**7**) aside from the hydrocarbon and silicone grease. Ideally, the grease contaminates should be removed before further work can be done upon the porphyrin sample.

Even with the set back from grease contamination, progress of Scheme 2 was continued by the synthesis of the guanidinium derivative, 2-methylisothiuronium iodide (**8**). This was completed by refluxing thiourea with methyl iodide in methanol and purifying the product to give a fine white powder with 18% yield. This gave a very clean  $^1\text{H-NMR}$  as seen in Figure 7.

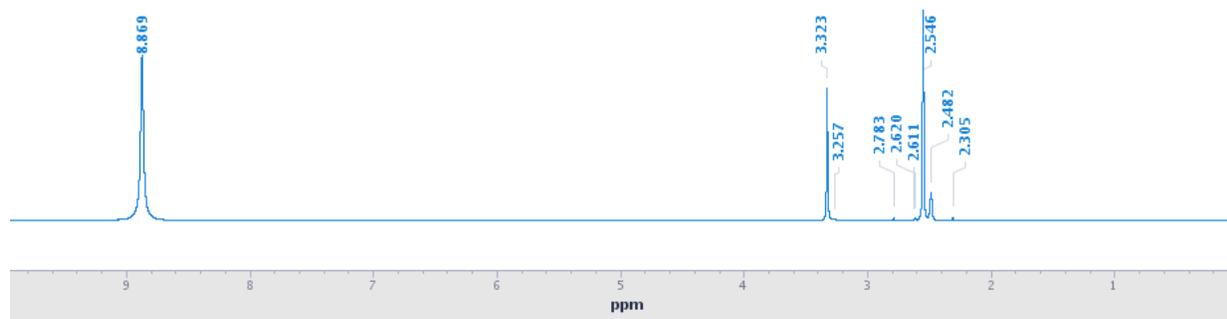


Figure 7.  $^1\text{H-NMR}$  of 2-methylisothiuronium iodide (**8**) in deuterated DMSO.

The  $^1\text{H}$ -NMR spectrum shows the conjugated amine hydrogens at 8.869ppm and the methyl hydrogens at 2.546ppm. The peaks at 3.323ppm represents water found in the deuterated DMSO solvent and the peak at 2.482ppm represents the deuterated DMSO itself. All remaining smaller labeled peaks are negligible since they represent so little of the overall sample.

Likewise, the next reaction concerning the guanidinium derivative proceeded smoothly to create N,N'-Bis(tert-butoxycarbonyl)-S-methylisothiurea (**9**). This was achieved by stirring 2-methylisothiuronium iodide (**8**) with di-tert-butyl decarbonate which will protect the amine moiety from future reactions.

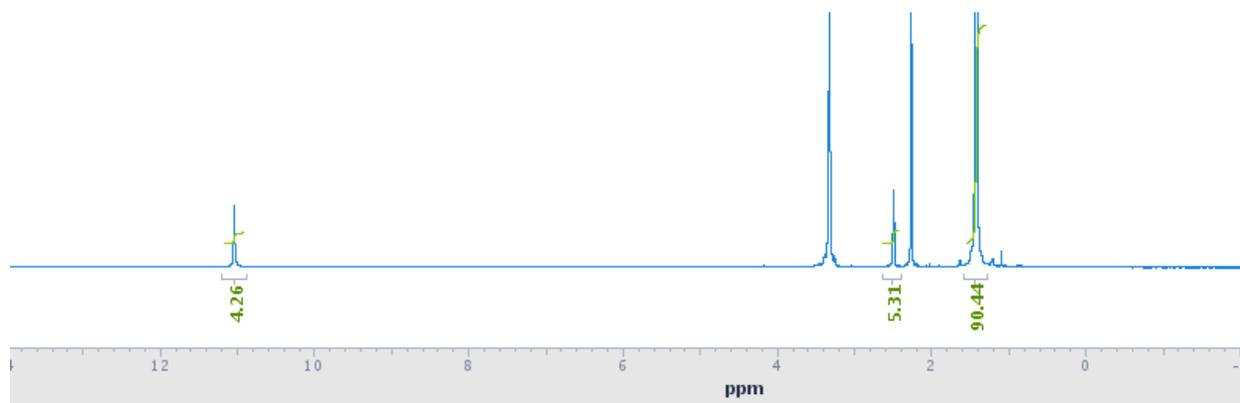


Figure 8. N,N'-Bis(tert-butoxycarbonyl)-S-methylisothiurea (**9**) in deuterated DMSO.

A successful reaction was confirmed by  $^1\text{H}$ -NMR as seen in Figure 8. The peak of the single aromatic amine hydrogen is seen at about 11.11ppm. The aliphatic thiol methyl hydrogens is the peak at about 2.25ppm and the aliphatic methyl *t*-butyl hydrogens of the Boc-protecting group is seen at about 1.50ppm. Again, the peaks at about 3.34ppm represents water found in the deuterated DMSO solvent and the peak at 2.53ppm represents the deuterated DMSO itself.

Unfortunately, due to time constraints, the remaining synthetic steps to complete Scheme 2 was not attempted. This unfinished work will potentially be completed by graduate or undergraduate students of the Modarelli group in the near future.

## Conclusion

Overall, Boc-protected bolaamphiphile (**5**), amino porphyrin (**7**), and the Boc-protected guanidinium derivative (**9**) were successfully synthesized with adequate yields. Once a clean sample of the deprotected bolaamphiphile (**1**) can be synthesized, the self-assembling properties can be studied using TEM and AFM. Similarly, once the Boc-protected guanidinium derivative (**9**) is

successfully coupled to the amino porphyrin (7), the self-assembling properties can be study with appropriate co-aggregates using TEM and AFM. Once self-assembly is confirmed and optimized, then transient absorption spectroscopy can be used to study the photovoltaic capabilities of Bolaamphiphile (1) and 5,10,15,20-tetrakis(4-phenylguanidinium) porphyrin (11).

## **Experimental**

### *General Synthetic Details*

The porphyrin derivative 5,10,15,20-tetrakis(4-methoxyphenyl) porphyrin (2) was priorly synthesized by Dr. Innocent Demshemino during his doctorate dissertation. All other materials and compounds were synthesized according to the following literature preparations:

5,10,15,20-tetrakis(4-carboxylphenyl) porphyrin (3)<sup>28</sup>, 2-Methylisothiuronium iodide (8)<sup>29</sup>, N,N'-Bis(tert-butoxycarbonyl)-S-methylisothiourea (9)<sup>30</sup>, 5,10,15,20-tetrakis(4-nitrophenyl) porphyrin (6)<sup>31</sup>, and 5,10,15,20-tetrakis(4-aminophenyl) porphyrin (7)<sup>31</sup>. Column chromatography used 230 – 400 mesh silica gel. Nuclear magnetic spectrometer was a 300MHz spectrometer by Varian Mercury.

### *General Synthetic Procedures*

#### **Synthesis of 5,10,15,20-tetrakis(4-carboxylphenyl) porphyrin (3)<sup>28</sup>**

The porphyrin 5,10,15,20-tetrakis(4-methoxyphenyl) porphyrin (2) (0.20g, 0.27mmol) was dissolved in 40mL of THF. To the mix, 30mL of 2M NaOH was added and allowed to stir under N<sub>2</sub> overnight. After the reaction period, the mixture was cooled to room temperature and cooled on ice while the mixture was acidified to pH 3. The precipitate was filtered off to yield a fine green powder (0.18g, 95%). <sup>1</sup>H-NMR: (CDCl<sub>3</sub>) (ppm) 8.83 (8H, pyrrole), 8.38-8.33 (16H, phenyl).

#### **Synthesis of Boc-protected Bolaamphiphile (5)**

Porphyrin (3) (0.25g,0.31mmol) was dissolved in thionyl chloride (25mL, 3.5mols) and stirred under N<sub>2</sub> overnight. The excess thionyl chloride was removed by evaporation under reduced pressure. The resulting dried acid chloride (4) was dissolved in 50mL of methylene chloride and cooled to 0°C. A solution of N<sub>α</sub>-(tert-Butoxycarbonyl)-L-lysine (0.54g, 2.2mmols) dissolved in 20mL of pyridine was dropped into the acid chloride solution. The mixture was stirred at room temperature for 48hours. After the reaction period, the solvent was removed by evaporation under reduced pressure. The crude product was purified using column chromatography starting with chloroform and switching to more polar methanol: chloroform (5: 95) to eluent the second band. The pure product was a dense purple solid (0.53g, 98%)

### Synthesis of Bolaamphiphile (1)

Boc-protected Bolaamphiphile (5) (0.26g, 0.16mmol) was dissolved in 8mL of THF and trifluoroacetic acid (4.5g, 39mmol). The reaction mixture was stirred in dark conditions at room temperature for four days under N<sub>2</sub> gas. After the reaction period, the solvent was evaporated under reduced pressure with gentle heating. The green crude product was dissolved in methanol and precipitated in ethyl ether. The solid was filtered by Buchner funnel and collected as a fine purple solid (0.076g, 38%).

### Synthesis of 2-Methylisothiuronium iodide (8)<sup>29</sup>

Thiourea (0.55g, 7.2mmol) was dissolved in 5mL of methanol. To that solution was added 450μL of methyl iodide (1.02g, 7.2mmol) and the reaction mixture was refluxed at 65°C overnight. The reaction mix was monitored with thin layer chromatography until completion. After the reaction period, the solvent was removed using rotary evaporator affording a yellow solid. The crude product was triturated in ethyl ether and filtered by Buchner funnel to afford a pale white product (0.38g, 18%). <sup>1</sup>H-NMR: (DMSO-d<sub>6</sub>) (ppm) 8.87 (4H, amine). 2.55 (3H, methyl).

### Synthesis of N,N'-Bis(*tert*-butoxycarbonyl)-S-methylisothiourea (9)<sup>30</sup>

2-Methylisothiuronium iodide (8) (0.17g, 0.80mmol) was dissolved in 5mL saturated NaHCO<sub>3</sub>. To that solution, (0.26g, 1.2mmol) dissolved in 10mL of methylene chloride was added. The reaction mix was stirred at room temperature for 24 hours. The organic layer was extracted with an aliquot of methylene chloride and dried with MgSO<sub>4</sub>. The solvent was removed using rotary evaporator leaving a yellow solid. The crude product was triturated in 10% ethanol: distilled water overnight. The purified product was filtered by Buchner funnel and washed with water. The product was dried under high pressure vacuum to afford a white powder (45mg, 26%). <sup>1</sup>H-NMR: (DMSO-d<sub>6</sub>) (ppm) 11.53 (1H, amine), 2.45 (3H, methyl), 1.43 (18H, *tert*-butyl).

### Synthesis of 5,10,15,20-tetrakis(4-nitrophenyl) porphyrin (6)<sup>31</sup>

4-nitrobenzaldehyde (1.57g, 10.4mmol) and acetic anhydride (2mL, 21mmol) were dissolved in 42mL of propionic acid. This mixture was allowed to reflux at 140°C for 5 minutes. Freshly distilled pyrrole (0.70g, 10.4mmol) was added slowly and the reaction mixture was stirred at 140°C overnight. After the reaction period, the reaction was slowly cooled, and the black solid product was collected by filtering with washes of water and methanol. The dense black crude product was taken into pyridine and recrystallized by refluxing for 1hour and cooled in 0°C overnight. The resulting solid is collected by gravity filtration with washes of acetone until the eluent is colorless. The pure product is a dark purple solid (1.5g, 20%). UV-Vis: (λ<sub>max</sub> nm in CH<sub>2</sub>Cl<sub>2</sub>): (Soret) 424, (Q-I) 516, (Q-II) 552, (Q-III) 590, (Q-IV) 647.

### Synthesis of 5,10,15,20-tetrakis(4-aminophenyl) porphyrin (7)<sup>32</sup>

Nitro porphyrin (6) (75mg, 0.095mmol) was dissolved in 18mL conc. HCl and brought up to 65°C for 5 minutes. Tin (II) chloride (230mg, 1.22mmol) was dissolved in conc. HCl and dropped into the dissolved nitro porphyrin (6) solution. The reaction mixture was allowed to reaction overnight under N<sub>2</sub>. After the reaction period, the mixture was adjusted to about pH 8 with ammonium hydroxide and diluted with 10mL of distilled water. The product was extracted with chloroform (3 x 30mL) and the organic phase was dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure and to afford a purple solid. The crude product was purified using column chromatography twice with 3% MeOH:DCM to elute the product. The pure product was a dark purple solid (18mg, 28% yield).

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