

**The Synthesis of a  $\pi$ -Extended Tetrathiafulvalene Porphyrin for MOF Formation and Use in Solar Cells**

Presented by Alec Lucas

In partial fulfillment of the requirements for graduation with the  
Dean's Scholars Honors Degree in Chemistry

---

**Jonathan Sessler**

**Supervising Professor**

---

**Graeme Henkelman**

**Honors Adviser in Chemistry**

---

**Date**

---

**Date**

I grant the Dean's Scholars Program permission to post a copy of my thesis on the Texas ScholarWorks. For more information, visit <https://repositories.lib.utexas.edu/>.

**The Synthesis of a  $\pi$ -Extended Tetrathiafulvalene Porphyrin for MOF Formation and Use in Solar Cells**

**Department: Chemistry**

---

**(Your name, printed)**

---

**Signature**

**Date**

---

**(Supervising professor's name, printed)**

---

**Signature**

**Date**

## Abstract

With the purpose of creating a conjugated system for potential experiments in solar cell applications, the first  $\pi$ -extended TTF (ExTTF) porphyrin with a functionalizable handle (carboxylic ester) was synthesized. The overall yield was 0.249%. This compound will then be incorporated into a 2-D metal-organic framework using zinc and bispyridine as the linkers. Assuming the synthesis of this sheet will later be successful, it can be tested for its redox properties using CV and its absorption properties to assess its feasibility in a solar cell. It is believed that these sheets of ExTTF porphyrin and zinc will have long-lived charge separated states when paired with  $C_{60}$  and will improve the efficiency of solar cells.

## Introduction

As the population of the earth grows energy needs continue to rise. With the volumetric decline and environmental hazards associated with fossil fuels, alternative energy sources (i.e. Solar energy) are growing in popularity.<sup>1</sup> Harnessing the abundant solar energy that radiates onto the surface of the earth is becoming heavily researched.<sup>2</sup> In recent years, interest in organic photovoltaics has increased dramatically.<sup>2</sup> While organic solar cells have not yet achieved the same efficiency or stability of their inorganic counterparts, the potential to synthesize the cells more cost-effectively and make cells which are very lightweight remains appealing.<sup>3</sup> Improving efficiency and stability will allow for the growth of research for organic solar cells and eventual utilization to meet the growing energy crisis.

The ability to absorb lower energy light and maintain long-lived charge separated states are two important characteristics of photovoltaic cells. When a photon is absorbed, its energy excites the electron from the valence band into the conduction band.<sup>4</sup> The network of covalent bonds that the electron previously belonged to now has one fewer electron. The presence of a missing electron allows the bonded electrons of neighboring atoms to move into the "hole," which then sets off a chain movement of holes.<sup>5</sup> Photons absorbed in the semiconductor create electron-hole pairs. The greater the mobility of these charge carriers, the greater voltage that will be produced.<sup>5</sup> In organic PV systems, the electron donating capabilities can be altered by changing the size of the conjugated system or by changing the functional groups that are attached to these systems.<sup>3</sup>

Tetrathiafulvalene (TTF) has tunable redox properties with three different stable oxidation states. As demonstrated in the work of Nathan Bill (former PhD student in Dr. Sessler's research group), his  $\pi$ -extended TTF-boradiazaindacene chimera (ex-TTF-BODIPY) fluoresced at 803 nm TTF was not oxidized, no fluorescence when in the mono-oxidized state, and fluoresced at 1185 nm.<sup>9</sup> These redox properties can be significantly altered by the insertion of a conjugated system in between the dithiolene rings because it reduces the coulombic repulsion between the positive cations, and can, thus, lead to higher conductivities which will optimize its interactions with various electron acceptors.<sup>6</sup> A porphyrin is a conjugated system that could work due to the promising research by Nathan Bill and others.<sup>7</sup>

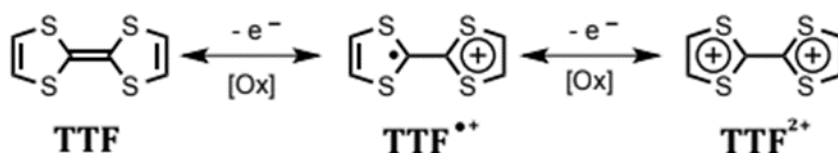
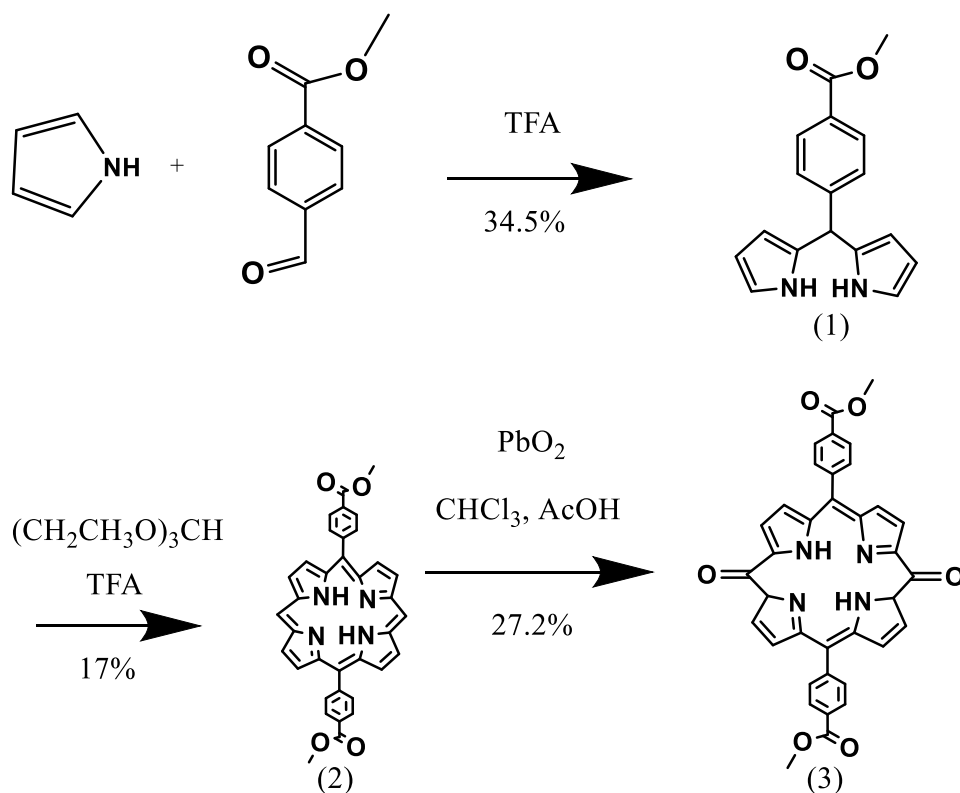


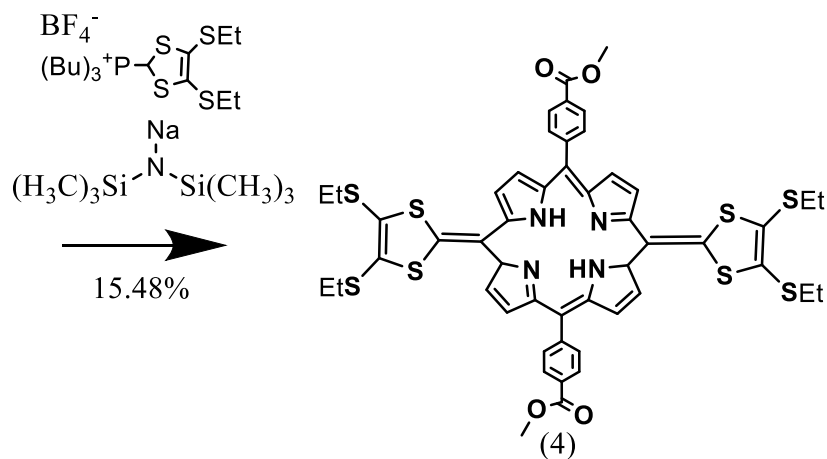
Figure 1: TTF Oxidation States<sup>6</sup>

Porphyrins are a group of heterocyclic conjugated organic compounds, composed of four modified pyrrole subunits connected at their alpha carbons by methine.<sup>8</sup> Porphyrins typically absorb strongly in the visible region of the electromagnetic spectrum because of this large conjugated system.<sup>8</sup> The porphyrin will serve as a chromophore when serving as the linker between the dithiolene rings. A porphyrin core would allow for better electronic communication upon excitation with wavelengths above 500 nm that would not occur solely with TTF.<sup>6</sup>

My current work in the Sessler group has focused on the synthesis of a  $\pi$ -extended TTF (ExTTF) porphyrin with carboxylic ester functional groups on the meso positions. By adding carboxylic ester groups to the ExTTF, the compound contains a functionalizable handle which can be readily modified to utilize this system in a myriad of applications. This compound will then be incorporated into a metal-organic framework (MOF) using zinc as the metal linker between the carboxylates and bispyridine as the linker between the thiol rings. This 2-dimensional sheet can be tested for its redox properties using cyclic voltammetry and its absorption properties to assess its potential applications in solar cells. Future work would be to attempt to attach C<sub>60</sub> to the framework and perform photovoltaic tests on this novel material. It is believed that these sheets of ExTTF porphyrin and zinc will have long-lived charge separated states and improve efficiency of solar cells.

## Methods





The desired exTTF porphyrin was synthesized in 4 steps with an overall yield of 0.249%. Acid catalyzed coupling of pyrrole with 4-formylbenzoate yielded the dipyrromethene (1). Macrocyclization with triethylorthoformate with trifluoroacetic acid as a catalyst yielded the bis-substituted porphyrin. Oxidation of the free meso positions using lead oxide and acetic acid gave the diketoporphyrin (3) and coupling of the dithiafulvalene ((4,5-bis(ethylthio)-1,3-dithiol-2-yl)tributylphosphonium) with the porphyrin yielded the ExTTF porphyrin (4). The percent yields for compounds (1-4) were 34.80%, 17.00%, 27.20%, and 15.48%, respectively.

### Synthesis of Dipyrromethene<sup>10</sup>

Methyl 4-formylbenzoate (4.84 g) was added to 75 mL pyrrole while under nitrogen and stirred for 15 minutes. TFA (0.225 mL) was then added into the mixture. When using the rotovap, a temperature between 50-60°C was appropriate. Using flash chromatography, the major fraction containing compound (1) and higher oligomers with was eluted with DCM. Compound (1) appeared bright red and orange on TLC using Br<sub>2</sub> vapor.

### Synthesis of Porphyrin<sup>11</sup>

Compound (1) (500 mg) was added to 600 mL DCM in a round bottom flask. Then, 18.2 mL triethylorthoformate was added and stirred in the mixture until dissolved. TFA (3.1 mL) in 125 mL DCM was added dropwise to the reaction mixture over the course of 20 minutes. The round bottom flask was covered in aluminum foil to keep out light and was under nitrogen. The reaction was stirred for 4 hours before adding 15.6 mL pyridine to quench the reaction. It was allowed to stir for 17 hours in the dark. The solution was then purged with air for 10 minutes and stirred under ambient light for 4 hours. The DCM was evaporated using a rotovap. The resulting black solid was pre-absorbed onto celite before using flash chromatography with DCM as the eluent. The purple product was triturated with methanol and recrystallized with toluene and 1% pyridine.

### Oxidation of Porphyrin<sup>12</sup>

Compound (2) (50 mg) was dissolved in 1.1 mL acetic acid and 5.4 mL chloroform. Then, 214 mg lead dioxide was added to the mixture. The mixture was heated at 60 degrees Celsius for 5 hours to ensure both meso positions are oxidized. The reaction was quenched using 16.2 mL of sodium bicarbonate

solution. The product was extracted with DCM using a short plug of celite after collecting the organic layer from the separation funnel. The product has a slight tint of dark blue.

### **Coupling of TTF and Porphyrin<sup>13</sup>**

A solution containing 0.17g phosphonium and dry THF (10 mL) was made in a round bottom flask. After degassing with nitrogen for 15 minutes, the solution was cooled to -78°C using an ice bath made from dry ice and isopropanol. A 0.6 M solution of NaMDS in toluene was added dropwise. The NaHMDS must be collected using a glove box and it must be in minimal contact with oxygen. The mixture was stirred for 10 minutes and a solution of (3) in 25 mL dry THF or (3) in powder form was added to the reaction mixture over the course of 20 minutes. After stirring for 30 minutes, the reaction was brought to room temperature and stirred for 3-5 hours before being poured onto saturated NH<sub>4</sub>Cl (10 mL). The product was extracted with DCM, washed with brine, and dried with Na<sub>2</sub>SO<sub>4</sub>. The column used DCM as the eluent and the product appears green.

### **Results and Discussion**

In the Appendix, there are NMR spectra for each reaction that confirm the synthesis of product for each step. The solvent used in the NMR was deuterated chloroform. NH peaks are excluded from the spectra as only shifts left of zero were included.

After successfully synthesizing compound (2) using TFA as the catalyst, the reaction was attempted again but with propionic acid as the catalyst, however, the conditions were probably too harsh and degraded the porphyrin during the reaction. To lose a minimal amount of product during the steps of recrystallization for the porphyrin synthesis, it was found that it must be triturated with methanol and recrystallized with toluene and 1% pyridine. When using flash chromatography, it was important to wait for it to slowly elute with DCM rather than ruin separation by adding a squirt of acetone to speed up the elution. Minimizing the risk of the separation not running well could have possibly eliminated the need to recrystallize.

The first attempt at oxidizing compound (2) was not successful as the TLC revealed that there was a lot of un-oxidized and mono-oxidized porphyrin. This porphyrin was difficult to oxidize because the carboxylic esters deactivate the porphyrin which makes the loss of electrons more difficult to achieve. Thus, the reaction had to be under reflux at 50-60°C to raise the energy of the reagents.

The first attempt to couple the TTF to compound (3) was successful but the yield was low likely due to degradation and not letting the reaction run long enough. NaHMDS degrades when exposed to air for a while and it was exposed for a length of time while setting up the addition funnel. The product is not stable in this form so it is possible that the TTF decoupled from the porphyrin over time. This reaction is not very kinetic so it is possible that letting the reaction run for 3 hours was not long enough. LDA is another base that could have worked for this reaction and it will likely be used to try to attain higher yields.

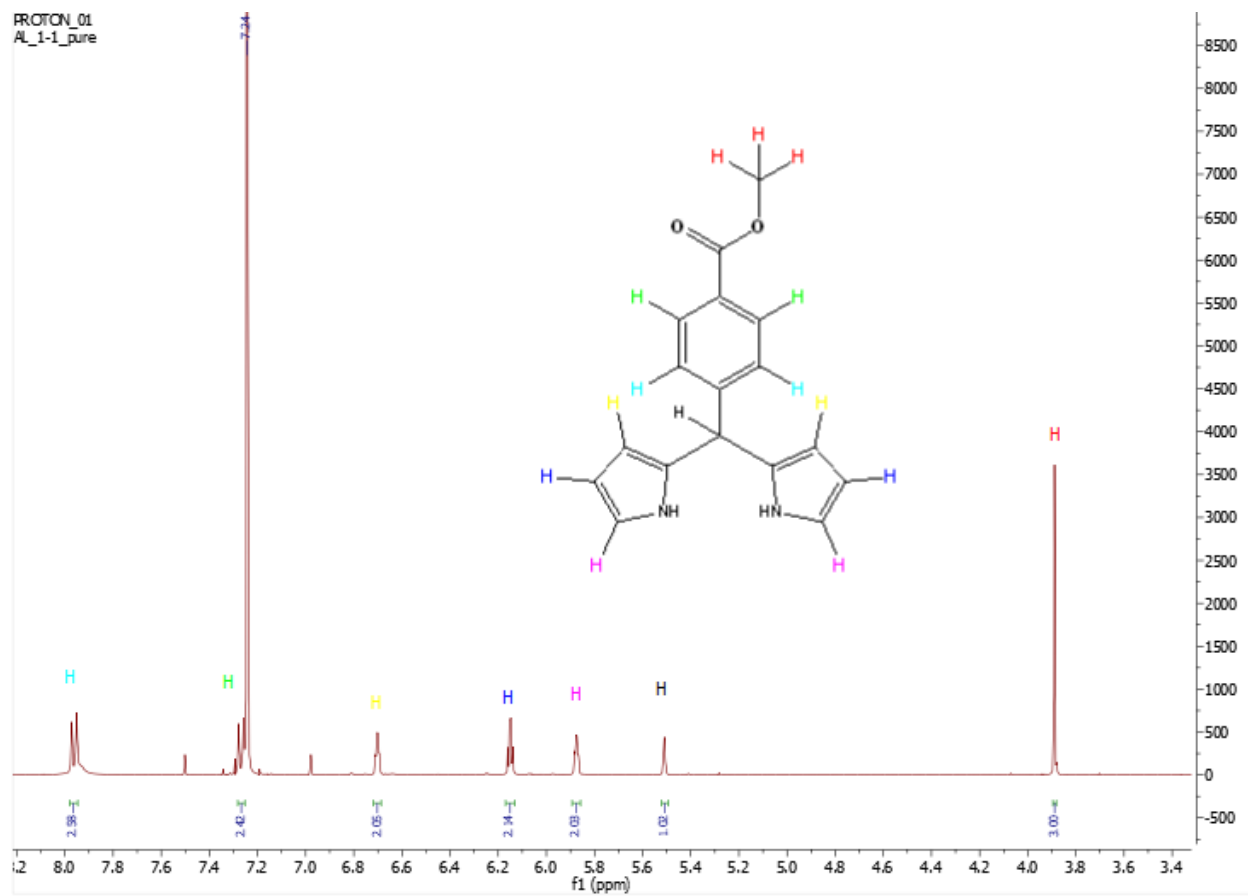
The significance of synthesizing this Ex-TTF porphyrin is that this is the first Ex-TTF porphyrin with a functionalizable handle that can potentially allow it to be transformed into a MOF or be used in other applications. Nathan Bill's work corroborated that an Ex-TTFP can be synthesized but this work

expanded on that finding by including a functionalizable handle onto the porphyrin. While there wasn't enough time to attempt to create the MOF using zinc and bis-pyridine as the linkers, saponifying the carboxylic ester with NaOH, creating the MOF, and attaching it to buckminsterfullerene would be the immediate next steps. Making a 2-D MOF is interesting for electronic applications because its charge separation could be tested using cyclic voltammetry and its electron donating capability could be tested by collaborating with a physical chemistry group. If it can be demonstrated that this MOF paired with C<sub>60</sub> has a long-lived charge separated state, it would be a worthy candidate for solar cell experimentation. And more generally, if the MOF can be synthesized and it can remain stable, it can be tested for a number of applications, such as, a "molecular muscle" that could experience expansion and contraction on the contingency of the redox conditions. Lastly, I am confident that the MOF will form using zinc linkers because the zinc will form a planar conformation with the four oxygen ligands, and according to Nathan Bill's work, zinc paired with TTF porphyrin was stable and demonstrated strong electron donating ability.<sup>9</sup>

## Conclusion

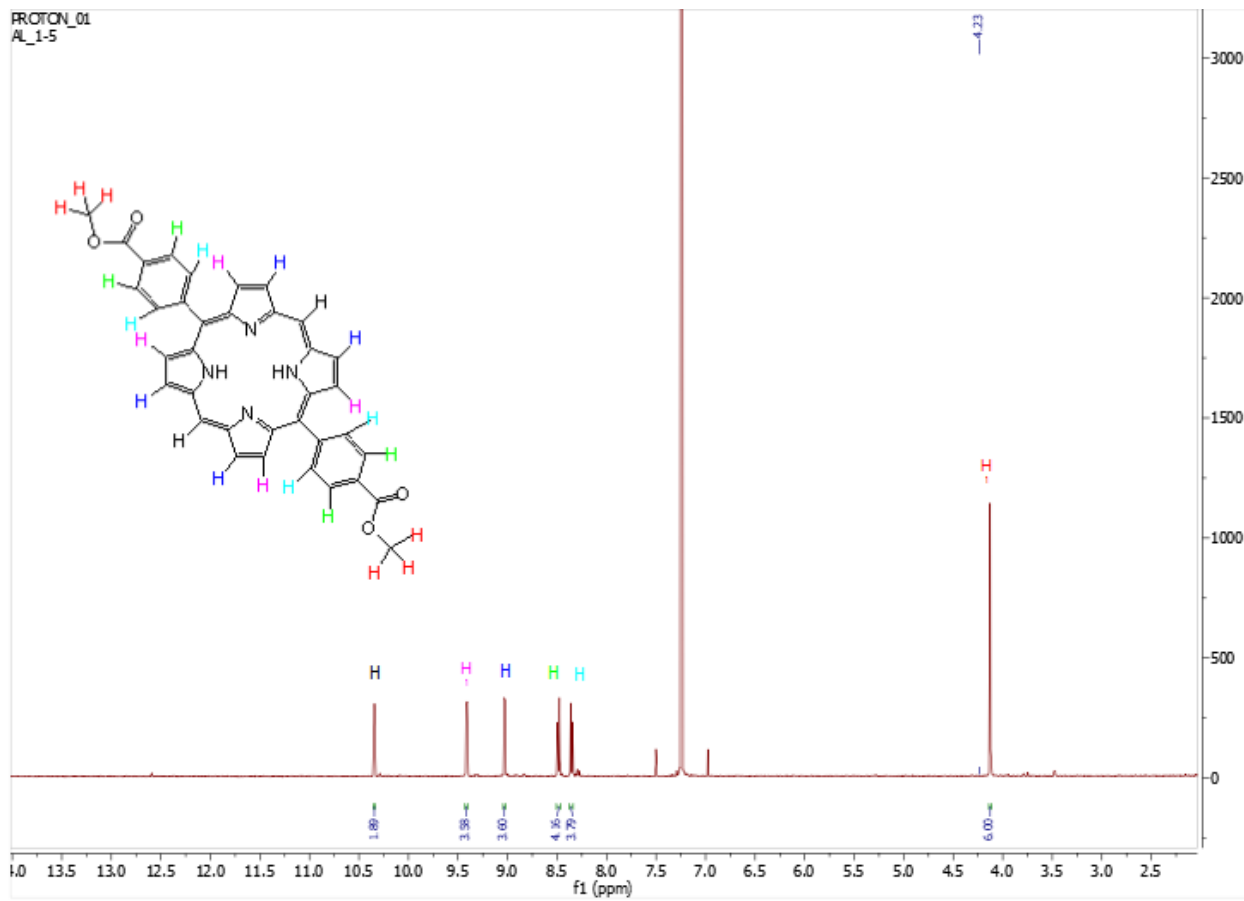
The desired ExTTF porphyrin was synthesized in 4 steps with an overall yield of 0.249%. This low yield has room for improvement. The individual yields could be improved by properly recrystallizing compound (2) with toluene and 1%, minimizing air exposure to NaHMDS in production of compound (4), allowing the coupling reaction to run for 5 hours, and by using a different base, such as, LDA for catalyzing the coupling reaction. The significance of the synthesis of this ExTTF porphyrin is that it is the first ExTTF porphyrin with a functionalizable handle- carboxylic ester. After saponification, the compound will be ready for attempted MOF synthesis. This is predicted to be successful, and if so, this will be the first ExTTF porphyrin MOF. Such a success would open up a frontier of experiments to be performed with the most obvious one being to test its electron donating capabilities and how long-lived its charge separated state is when paired with C<sub>60</sub>.

## Appendix

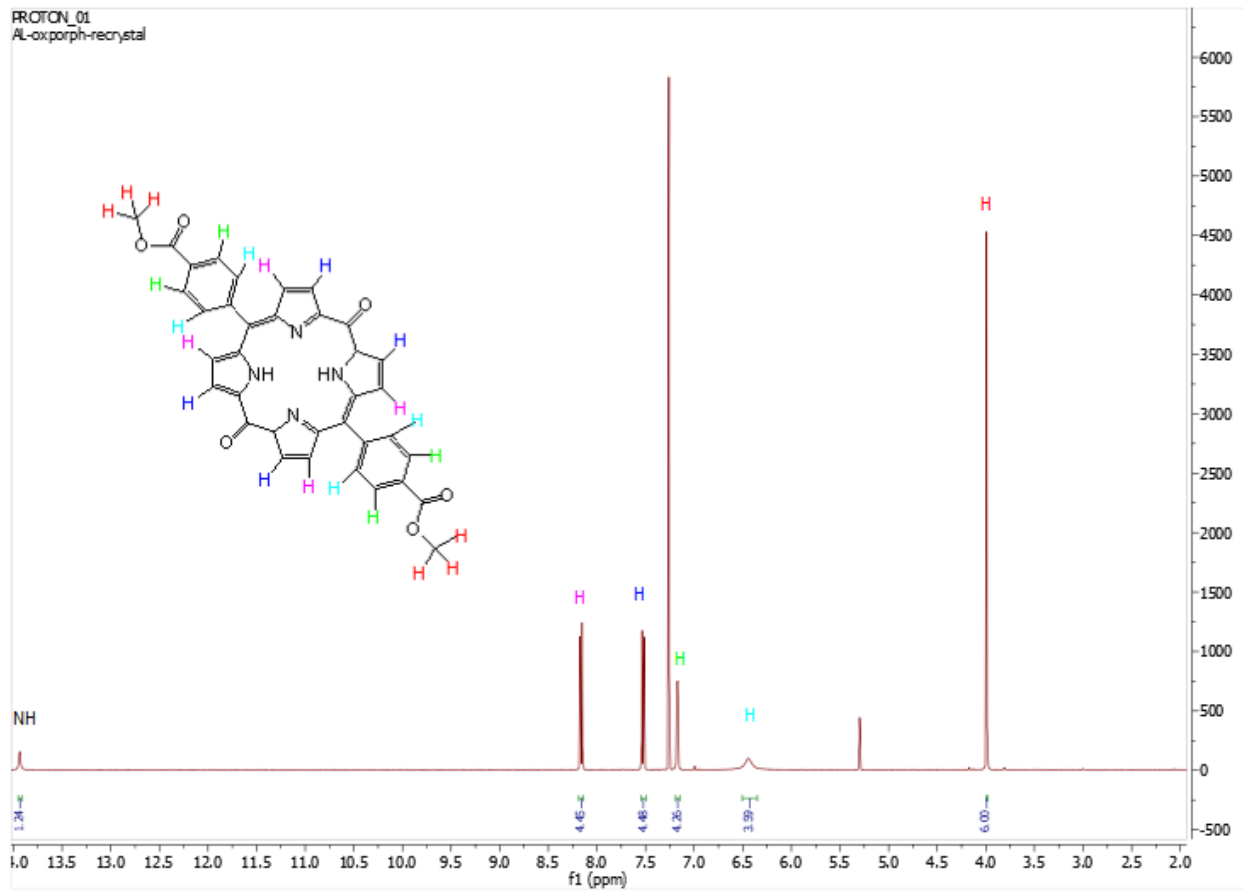


NMR for Compound (1)

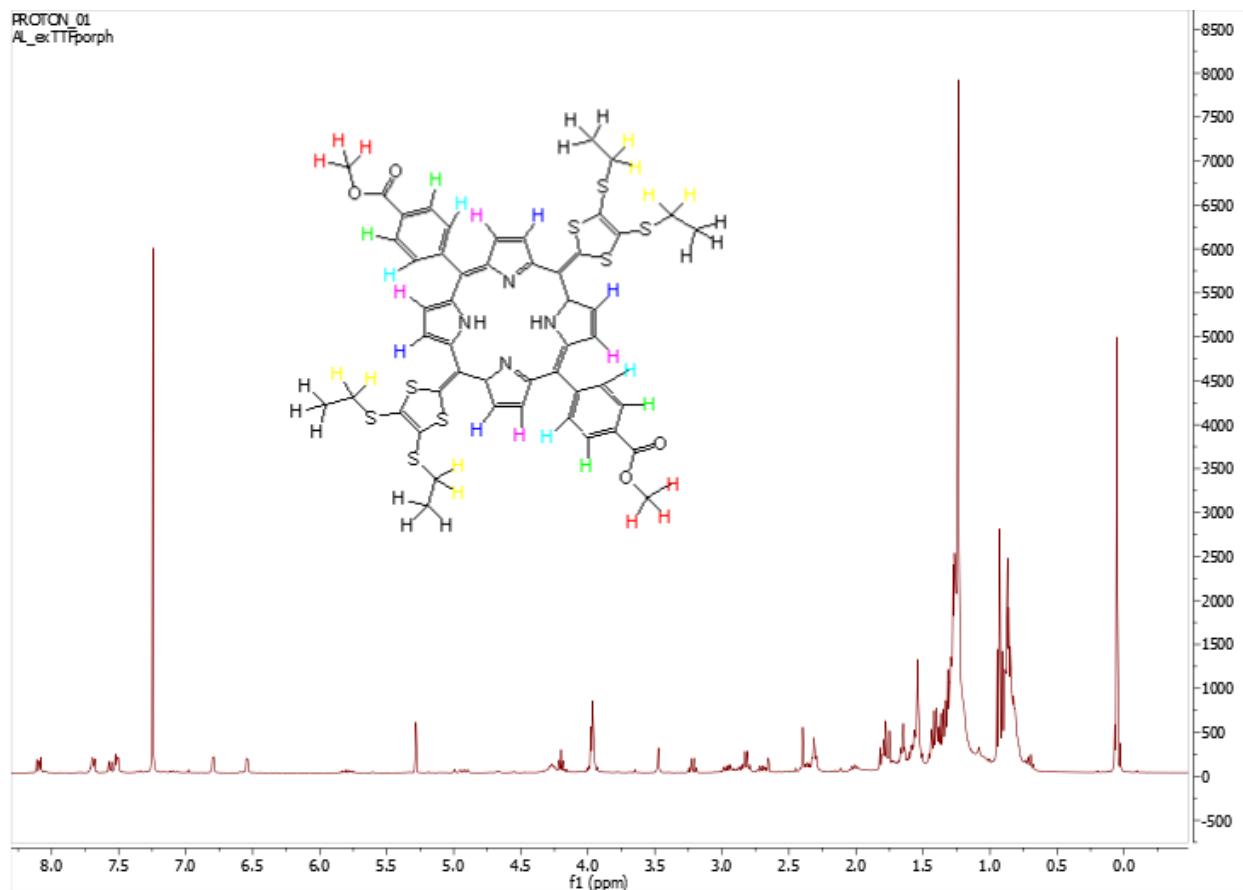




NMR for Compound (2)



NMR for Compound (3)



### NMR for Compound (4)

Note that the peaks for the thiol ethyl can't be completely identified given the contamination of this reading in the 2 to 0.5 ppm range but it is with high confidence that I can claim this spectrum confirms the synthesis of Compound (4).

### References:

1. "Snapshot of Global Photovoltaic Markets 2016". *International Energy Agency*. **2016**.  
[http://www.iea-pvps.org/fileadmin/dam/public/report/statistics/IEA-PVPS -  
\\_A\\_Snapshot\\_of\\_Global\\_PV\\_-\\_1992-2016\\_1.pdf](http://www.iea-pvps.org/fileadmin/dam/public/report/statistics/IEA-PVPS_-_A_Snapshot_of_Global_PV_-_1992-2016_1.pdf)
2. Best Research Cells Efficiency. *National Renewable Energy Laboratory*.  
<https://www.nrel.gov/pv/assets/images/efficiency-chart.png>
3. Po, R., Carbonera, C., Bernardi, A., Tinti, F., Camaioni, N., "Polymer- and carbon-based electrodes for polymer solar cells: Toward low-cost, continuous fabrication over large area". *Solar Energy Materials and Solar Cells*. **2012**
4. Nelson, J. "The Physics of Solar Cells". *Imperial College Press*. **2003**
5. Lorenzo, E. "Solar Electricity: Engineering of Photovoltaic Systems". *Progensa*. **2004**.
6. Bill, N. "Extension of Tetrathiafulvalene Conjugation Through Pyrrolic-Based Dyes: ExTTF Porphyrin and ExTTF BODIPY". *The University of Texas at Austin*. **2013**
7. Li, L., Diau, E. "Porphyrin-sensitized Solar Cells". *Chemical Society Reviews*. **2013**

8. Ivanov, A.; Boldyrev, A. "Deciphering aromaticity in porphyrinoids via adaptive natural density partitioning". *Organic & Biomolecular Chemistry*. **2014**
9. Bill, N. "π-Extended tetrathiafulvalene BODIPY (ex-TTF-BODIPY): a redox switched "on-off-on" electrochromic system with two near-infrared fluorescent outputs". *Chemical Communications*. **2013**
10. Brueckner, J., Jeff. J., Posakony. C., Johnson. R, James, B., Dolfin, D., *Org. Synth.* **1999**, 76, 287
11. Brueckner, J., Jeff. J., Posakony. C., Johnson. R, James, B., Dolfin, D., *J. Porphyrins Phthalocyanines*. **1998**. 2, 455–465
12. Lahaye, D.; Muthukumaran, K.; Hung, C-H.; Gryko, D; Reboucas, J. S.; Spasojevic, I.; Batinic-Haberle, I.; Lindsey, J. S. *Bioorg. Med. Chem.* **2007**, 15,7066-6086.
13. *J. Am. Chem. Soc.* **2014**, 136, 16497