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Porphyrinic Metal-Organic Frameworks for the Photocatalytic Degradation of a Mustard Gas Simulant

A Thesis

Presented to

The Honors College, California State University, Los Angeles

In Partial Fulfillment
of the requirements for graduation from the

HONORS COLLEGE

by

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ABSTRACT

Porphyrinic Metal-Organic Frameworks for the Photocatalytic Degradation of a Mustard Gas Simulant

By

Alisa S. Quon

Sulfur mustard is a toxic chemical warfare agent that is most known for its use in World War I. Today, stockpiles of sulfur mustard exist around the world and need to be safely and efficiently degraded. One efficient solution is to selectively oxidize sulfur mustard into a nontoxic product using metal-organic frameworks (MOFs). These are porous, crystalline materials that can be designed for a variety of applications such as photocatalysis. MOFs with porphyrinic linkers in particular have shown promise for the photocatalytic degradation of a simulant of sulfur mustard (CEES), into its nontoxic sulfoxide form (CEESO). In this study, four metallporphyrins and four metalloporphyrinic MOFs called PCN-222(M) were synthesized, characterized, and tested for their efficacy in converting CEES into CEESO in methanol and acetonitrile. The MOFs were made with porphyrins doped with M = manganese, copper, tin, or indium. It was determined that generally, the MOFs achieved faster rates of CEES conversion compared to their respective metalloporphyrins. In methanol, in order from fastest to slowest CEES conversion were PCN-222(Sn), PCN-222(In), PCN-222(Mn), and PCN-222(Cu). The selectivity for nontoxic sulfoxides in acetonitrile-d_3 was also determined.

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I would first like to thank my principal investigator and thesis advisor, Dr. Yangyang Liu. When I joined the Liu group three and a half years ago, I had just finished General Chemistry I and had no idea how much I would learn about chemistry, scientific thinking, and research in the next few years. I was welcomed with open arms into the world of research and learned from the other members in the lab. Dr. Liu has fostered an extremely encouraging environment on campus and has always supported me in my career goals, and I could not thank her enough for these experiences.

The people I have worked with most closely in lab have a special place in my heart. Through our ups and downs in lab, it has been great getting to know everyone in the Liu Lab and making countless good memories with them. In particular, I would like to thank Anna Nguyen, with whom I shared most struggles while working on this project together.

For always being by my side, I would like to thank my family, friends, and McMug. I could not have done any of this without their unwavering support.

Lastly, I would like to acknowledge the Department of Chemistry and Biochemistry, Early Entrance Program, and Honors College for giving me the opportunity to create this work and for providing the resources to make my time at Cal State LA unforgettable. I am excited to end my undergraduate career with this work and look forward to the next step in my career and personal growth journey.

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CHAPTER 1

INTRODUCTION

Section 1.1. Sulfur Mustard

Sulfur mustard, or bis(2-chloroethyl) sulfide, is a highly toxic chemical warfare agent (CWA) first mass produced in Germany and introduced during World War I. It can cause chronic damage to the nervous, cardiac, and respiratory systems, sometimes resulting in death.[1] Some effects of sulfur mustard include skin necrosis, second- and third-degree burns, and blisters. If sulfur mustard contacts the eyes, permanent blindness may also occur.

Today, sulfur mustard is no longer manufactured in bulk quantities in the US. However, stockpiles of sulfur mustard still exist globally as its production continued even after the CWA was banned for use in war by the 1925 Geneva Protocol.[1] Despite the passing of this protocol, there have been violations of the protocol where sulfur mustard was used. One more recent example is the Iran-Iraq war from 1980 to 1988.[2] In addition, large munitions of sulfur mustard have been disposed of at sea, which poses an environmental issue for any organisms that become exposed to the waste or water contaminated by the waste. From 2004 to 2012, there were at least three instances where military personnel and fishermen were exposed and/or harmed by these disposed munitions in Delaware and off the coast of New York.[3] There are also stockpiles of sulfur mustard that have been buried in soil or left at previous army depots in Kentucky, Alabama, Oregon, Arkansas, Utah, Colorado, Indiana, Maryland, and Johnston Atoll.[4,5] Although efforts have been taken to degrade these stockpiles of mustard gas in the past two decades (of these nine sites, detoxification remains incomplete only in Colorado and

Kentucky), it remains a significant challenge to safely and efficiently inactivate sulfur mustard.[5]

Section 1.2. Sulfur Mustard Degradation Pathways

There are three main pathways to degrade sulfur mustard: dehydrohalogenation, hydrolysis, and selective oxidation (Figure 1).[6] Of these methods, dehydrohalogenation and hydrolysis are usually ineffective because sulfur mustard is hydrophobic. Dehydrohalogenation also occurs too slowly for the purpose of degradation.[7] Both of these methods require extreme conditions and a high number of resources to produce nontoxic products. Despite these drawbacks, the U.S. army currently utilizes the hydrolysis method to detoxify existing stockpiles of sulfur mustard.[8] In this approach, the Department of Defense authorized the use of hot water and NaOH to break down sulfur mustard into thioglycol and HCl. This neutralization process was followed by biotreatment using bacteria or supercritical water oxidation, which uses water above its critical temperature and pressure to oxidize the waste products. However, hydrolysis is an ineffective approach because sulfur mustard is relatively hydrophobic (0.092 g dissolves per 100 g water at 22°C).[9] Another drawback of hydrolysis to degrade bulk sulfur mustard is that it often results in incomplete degradation; for a solid underground stockpile of sulfur mustard, water can hydrolyze the surface molecules into thiodiglycol, which may react with sulfonium (another product in the reaction) to create sulfonium salts. These stable salts form a protective layer that prevents further degradation of the interior of the bulk.[10]

One promising solution to these problems is selective oxidation of sulfur mustard into the significantly less toxic sulfoxide. In this approach, over-oxidation into the sulfone product must be avoided because the sulfone product is still significantly toxic (about half as toxic as sulfur mustard when inhaled).[10]

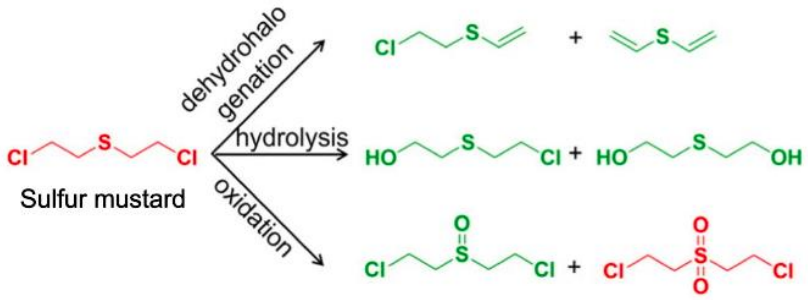


Figure 1.[6] Three pathways to degrade sulfur mustard with nontoxic products shown in green and toxic products shown in red.

Section 1.3. Sulfur Mustard Simulant

Because sulfur mustard is highly toxic, a simulant called 2-chloroethyl ethyl sulfide (CEES) is used in our experiments (Figure 2).[6] Although CEES still retains some alkylating properties, it is considerably less toxic and less regulated than sulfur mustard. CEES is commonly used in this field of research as the reactivity around the sulfur atom in CEES is very similar to that of sulfur mustard.

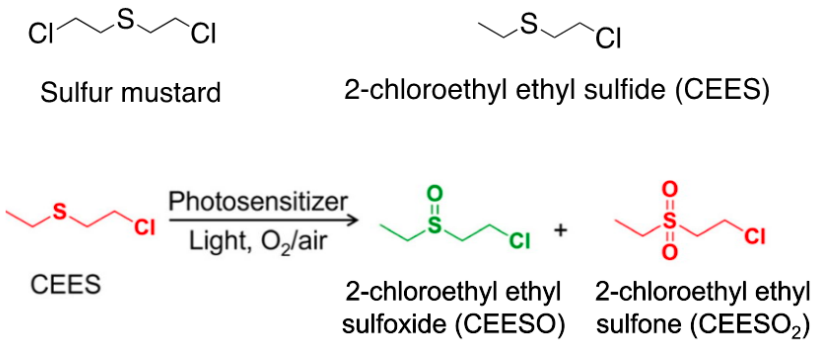


Figure 2.[6] Structural comparison of sulfur mustard and its simulant, CEES, along with the oxidation reaction of CEES into the nontoxic sulfoxide (green) and toxic sulfone (red) products.

Section 1.4. Singlet Oxygen and Photosensitizers

A mild oxidizing agent such as singlet oxygen, which can be generated by photosensitizers such as porphyrin, has been used in previous studies to achieve highly selective oxidation. Singlet oxygen is the singlet excited state of ground state triplet oxygen. It is commonly generated by irradiating a photosensitizer with light in the presence of oxygen.[11] Upon absorption of light, these organic dyes achieve their singlet excited state and then undergo intersystem crossing (ISC) to reach their triplet excited state (Figure 3). The energy from this triplet excited state photosensitizer is then transferred to ground-state triplet oxygen, which is the relatively unreactive form of oxygen that we breathe. This energy allows triplet oxygen to become singlet oxygen, which is much more reactive toward organic compounds compared to ground state triplet oxygen, which makes singlet oxygen a promising candidate for selective oxidation of CEES. The amount of singlet oxygen generated is quantified using the singlet oxygen quantum yield, which has a maximum value of one. However, it is rare for a

photosensitizer to have a singlet oxygen quantum yield of one because some of the singlet excited state photosensitizer molecules can dissipate energy through other photochemical processes, such as fluorescence, phosphorescence, and internal conversion.

The main issue with using porphyrin for this application is that it can aggregate with other porphyrin molecules, which compromises its ability to generate the maximum possible amount of singlet oxygen. Thus, it is necessary to structurally organize and stabilize porphyrin molecules in solution.

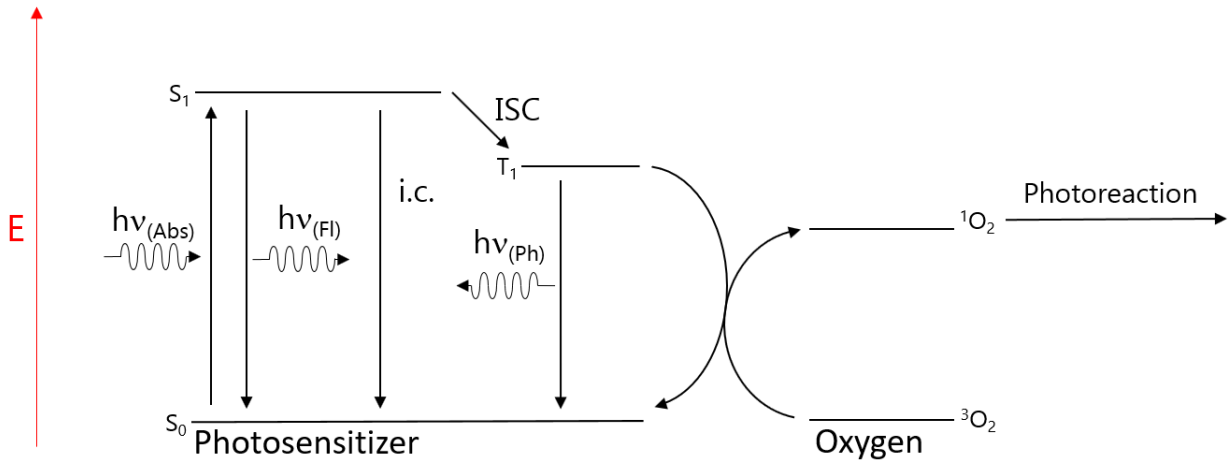


Figure 3. Jablonski diagram showing the generation of singlet oxygen ($^1O_2$) from triplet oxygen ($^3O_2$) by a photosensitizer. Fl = fluorescence, Ph = phosphorescence, i.c. = internal conversion.

Section 1.5. Metal-Organic Frameworks

Zirconium metal-organic frameworks (MOFs) have been proposed as a solution to avoid the aggregation of porphyrin.[7] MOFs are crystalline frameworks consisting of a

metal cluster and a ligand, both of which can be tuned to achieve a synergistic desired effect (Figure 4). The high porosity, surface area, and stability of MOFs makes them promising candidates to be efficient heterogeneous catalysts.

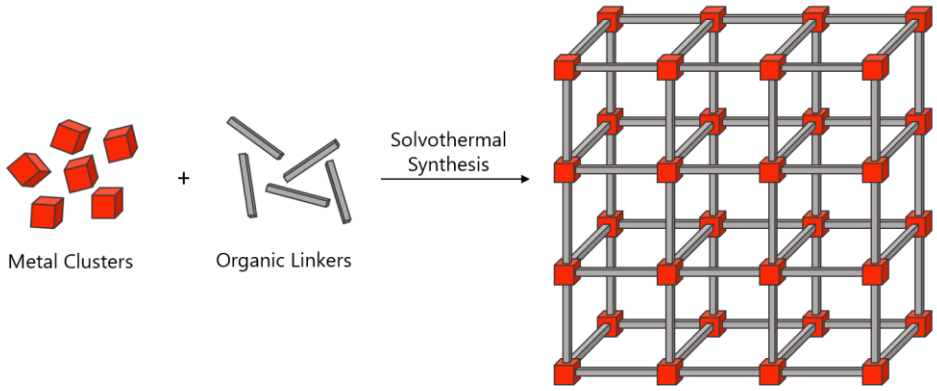


Figure 4. General structure of a metal-organic framework.

In particular, the MOF PCN-222(free base, or FB) has been shown to selectively oxidize CEES into the nontoxic product 2-chloroethyl ethyl sulfoxide (CEESO).[7] This MOF has zirconium oxide clusters that are each coordinated to six porphyrinic ligands (tetrakis(4-carboxyphenyl)porphyrin, TCPP) throughout its structure, forming pores and a channel-type topography (Figure 5). The 3.7 nm pores are large enough for the target molecules to enter the pores, where the catalysis occurs. It is hypothesized that MOFs containing porphyrin ligands with certain metals coordinated at their centers will accelerate the rate of photocatalytic activity compared to MOFs with free-base (FB) porphyrin ligands. Therefore, the purpose of this project is to study the reaction efficiency, measured in terms of the conversion rate of CEES and selectivity for sulfoxides, of the selective oxidation of CEES using PCN-222(M), where M = In, Sn, Mn, and Cu.

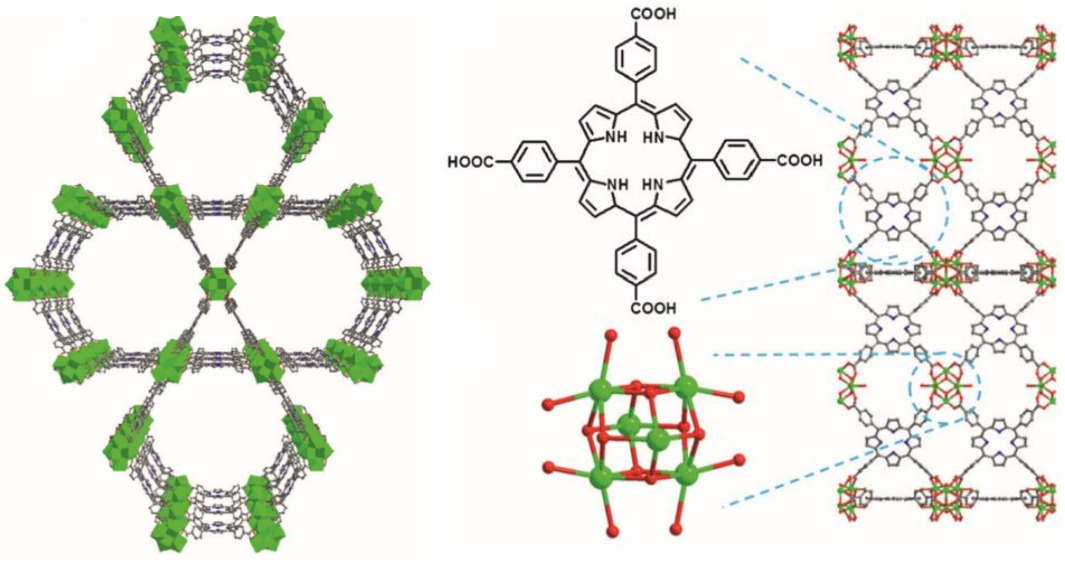


Figure 5.[7] Structure of PCN-222(FB). Left: Channel structure of PCN-222 (green = zirconium oxide clusters, gray = porphyrin linkers). Right: Chemical structure of PCN-222, showing zirconium oxide clusters connected to 6 porphyrin linkers.

CHAPTER 2

LITERATURE REVIEW

This project was designed around previous literature in an attempt to increase the reaction efficiency of the selective oxidation of a sulfur mustard simulant. Currently, the U.S. army uses hydrolysis to degrade sulfur mustard. However, because sulfur mustard is hydrophobic, this reaction is resource-wasteful, and the efficiency of this process can be improved. Recently, porphyrinic MOFs have been introduced as a class of efficient catalysts for this purpose. The mechanism and solvent-dependency of this reaction have also been elucidated, which further guided our direction in this project. Additionally, literature has shown that metalating porphyrins with metals such as tin and copper affects the singlet oxygen quantum yield of these materials, which in turn, should increase the photocatalytic potential of these materials.

Section 2.1. Recent Advances in MOF Chemistry to Degrade CEES

Because porphyrins can aggregate on top of one another, preventing the maximum generation of singlet oxygen, researchers have used MOFs to selectively oxidize the sulfur mustard simulant CEES.[12] Liu et al. investigated PCN-222(FB), which contains zirconium nodes coordinated to free base porphyrinic ligands.[7] This MOF was chosen because it exhibits many characteristics, such as high stability and porosity, that make it a promising heterogeneous catalyst. In methanol, PCN-222(FB) (4 mol % loading relative to CEES) achieved a CEES half-life of 12.0 minutes.[7] The MOF could also be reused; on the second oxidation cycle, Liu et al. observed a shorter half-life of 10.0

minutes. In this project, we aim to achieve an even shorter half-life by modifying the characteristics of PCN-222(FB).

While the study by Liu et al. focused primarily on the properties of PCN-222(FB) that made it an efficient catalyst for the selective oxidation of CEES, they did not thoroughly discuss the effects of solvent or calculations of sulfoxide selectivity. A more recent study showed that solvent plays a large role in the selectivity for sulfoxides in the oxidation of CEES. In this study, Hao et al. used three zirconium-based porphyrinic MOFs with different pore sizes, surface areas, and topologies to test the photocatalytic ability of each.[6] The reaction was performed in methanol and acetonitrile to probe the effects of solvent because it may not be practical to use methanol. While the MOFs were able to achieve 100% selectivity for sulfoxides in methanol, the selectivities in acetonitrile were around 93 to 94%. By proposing a mechanism for the oxidation of CEES, this study also provides insight as to why solvent matters; hydrogen-bonding, which is present in methanol but not in acetonitrile, facilitates the stabilization of a putative persulfoxide intermediate. This work is relevant because we also aim to use zirconium-based porphyrinic MOFs as catalysts. It has guided the direction of our project because we also performed experiments to determine the sulfoxide selectivity of our materials in acetonitrile.

Section 2.2. Effects of Metalating Porphyrins on Photocatalytic Ability

One potential way to decrease the half-life of CEES is by altering the composition of PCN-222. Metalating porphyrins seems to affect the quantum yield of singlet oxygen. For example, the singlet oxygen quantum yield of tetraphenylporphyrin (TPP) was

reported as 0.55, but metalating the same porphyrin with copper resulted in a low quantum yield of 0.03.[13] Another study found that metalating TPP with tin resulted in a quantum yield of 0.49.[13] Although these yields are lower than that of TPP, other studies have suggested Sn TCPP has many properties that make it a good photosensitizer.[14] Therefore, we chose to synthesize it and use it to make PCN-222(Sn). Due to the various literature suggesting that metalating porphyrins affects the singlet oxygen quantum yield, we decided to synthesize and test four metalloporphyrinic PCN-222 MOFs. Instead of free base TCPP, the linkers in these MOFs are metalated in their centers with tin, indium, manganese, and copper, in an attempt to increase their photosensitizing ability, and thus, the photocatalytic efficiency of these materials.

CHAPTER 3

EXPERIMENTAL METHODS

Section 3.1. Synthesis and Characterization of Porphyrins and MOFs

The metalloporphyrins M-TCPP, M = Sn, In, Mn, Cu, were synthesized according to previous literature. Sn-TCPP was synthesized in two steps to yield dark purple crystals (Figure 6).[14] M-TCPP (M = In, Mn, Cu) were synthesized in three steps to yield dark green, green, and red crystals, respectively (Figure 7).[6] Absorbance spectrophotometry data was collected using a Shimadzu UV-1800 UV-Vis Spectrophotometer.

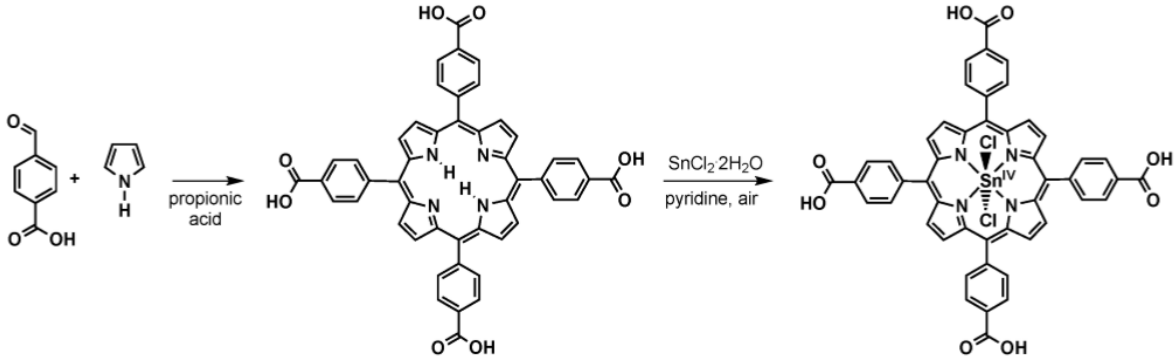


Figure 6.[14] Synthesis of Sn-TCPP.

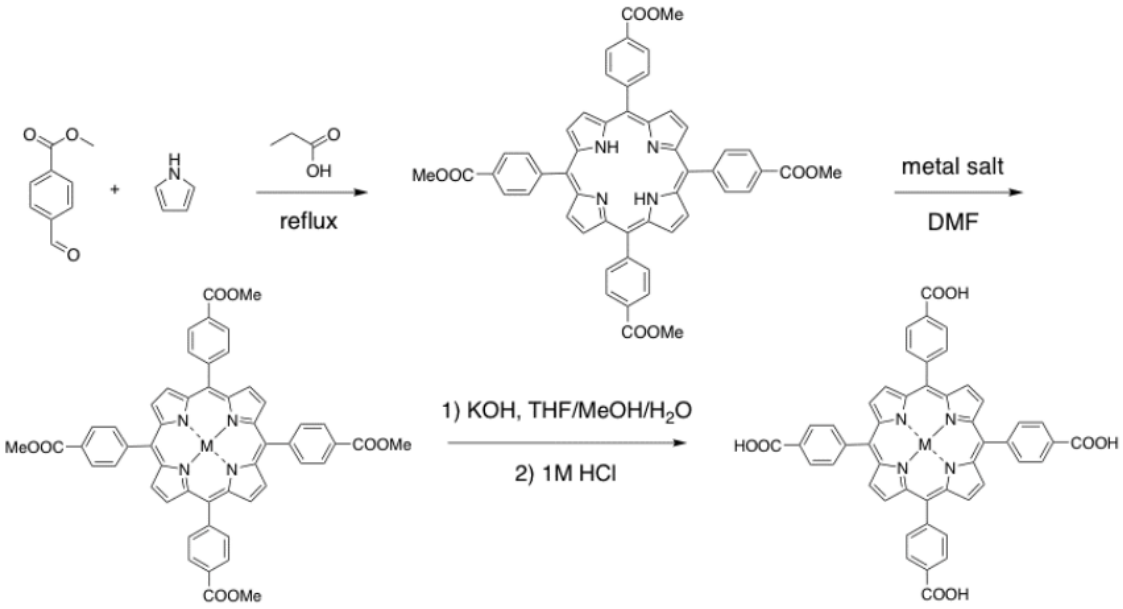


Figure 7.[16] Synthesis of M-TCPP, M = In, Mn, Cu.

After the metalloporphyrins were synthesized, they were used to synthesize their corresponding MOFs according to previously reported procedures.[16] $ZrCl_4$ (70 g) M-TCPPCl (50 mg), benzoic acid (2700 mg), and DMF (8 mL, DEF was used instead for Cu) were added to a 20 mL vial. The vials were sonicated for 30 minutes and incubated in an oven at 120°C for 48 hours. The suspensions were transferred to centrifuge vials and washed with DMF (3 x 20 mL) and acetone (3 x 20 mL). After soaking in acetone overnight, the samples were dried in a vacuum oven and activated using a gas sorption analyzer. Powder X-ray diffraction (PXRD) patterns were obtained for each sample at room temperature using a Bruker D8-Focus Bragg-Brentano X-ray powder diffractometer with a Cu sealed tube (λ = 1.54178 Å). The diffraction-crystal function in the free *Mercury* software was used to simulate the PXRD spectra. Activation and characterization with nitrogen adsorption isotherm and BET surface area was carried out

by a Smart VacPrep ASAP 2020 instrument (Micromeritics Instrument Corporation). The following suspensions were characterized using a Shimadzu UV-1800 UV-Vis spectrophotometer equipped with an integrating sphere: 0.002 mmol PCN-222(Mn) in 3 mL MeOH, 0.002 mmol PCN-222(Sn) in 2 mL MeOH, 0.002 mmol PCN-222(In) in 3 mL MeOH, 0.002 mmol PCN-222(Cu) in 4 mL MeOH.

Section 3.2. Photocatalytic Testing[6]

To a microwave vial, 1 mL of methanol and 0.5 mol % (0.001 mmol) of catalyst were added. O_2 gas was bubbled into the vial for 20 minutes followed by blue LED irradiation for 20 minutes. Blue light (~450 nm) is used because the UV-vis spectra of TCPP show maximum absorption of energy around 420 nm. An internal standard, 1-dibromo-3,5-difluorobenzene (5 µL), and CEES (23 µL, 0.02 mmol) were added at t = 0 min. A sample from the vial was taken and diluted with 0.5 mL of dichloromethane (DCM) in a gas chromatography (GC) vial. The vial was irradiated with blue light again. GC samples were taken every few minutes depending on the catalyst, and all samples were analyzed with gas chromatography-mass spectrometry (GC-MS). The spectra were analyzed to calculate percent conversion of CEES at each time point. These experiments were repeated in triplicate or until consistent data were obtained, and the average percent conversion of CEES at each time point was plotted against time for each catalyst.

3.3. GC-MS Analysis

GC-MS was used to calculate the percent conversion of CEES into products at each time point. Three sample chromatograms over the course of an experiment are shown in

Figure 8. The relative concentration of CEES decreases and the concentration of CEESO increases over time. The first peak corresponds to the internal standard (IS, 1-bromo-3,5-difluorobenzene), which allows us to calculate the relative amount of CEES left in each sample. If $CEESO_2$ is present, another peak would be present around the CEESO peak. From the integrations of each of these peaks, we can calculate the percent CEES conversion at time *i* using the following equation and plot percent conversion over time:

$$\%\ conversion\ at\ time\ t = \frac{\frac{CEES}{IS}_{t=0} - \frac{CEES}{IS}_{t=i}}{\frac{CEES}{IS}_{t=0}} \times 100\%$$

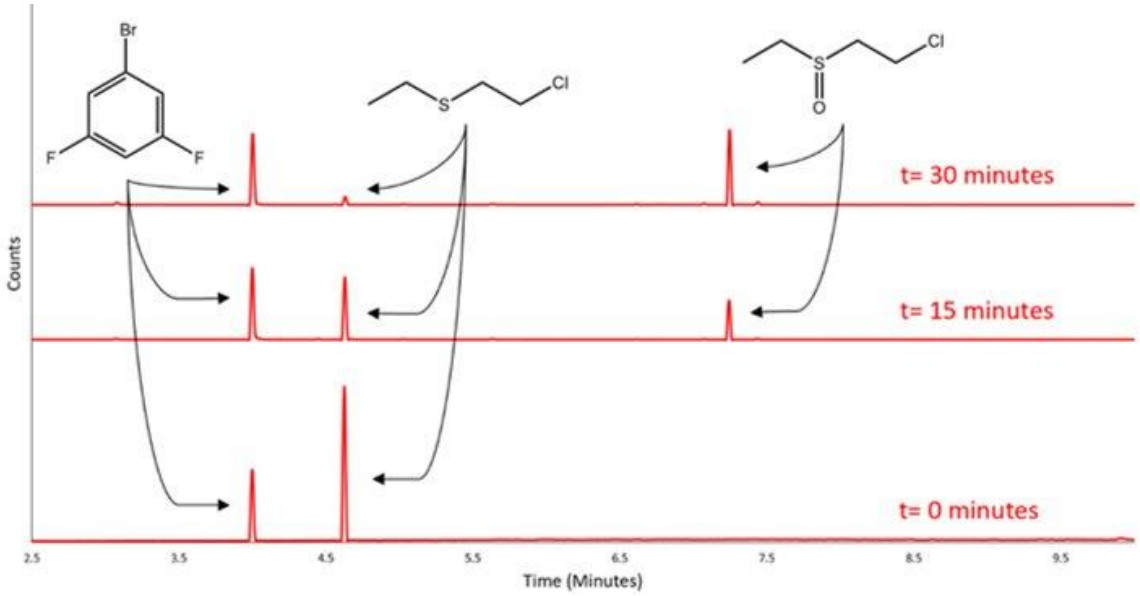


Figure 8. Sample GC-MS chromatograms at t = 0, 15, and 30 minutes.

3.4. Sulfoxide Selectivity Experiments and ^{1}H NMR Analysis.

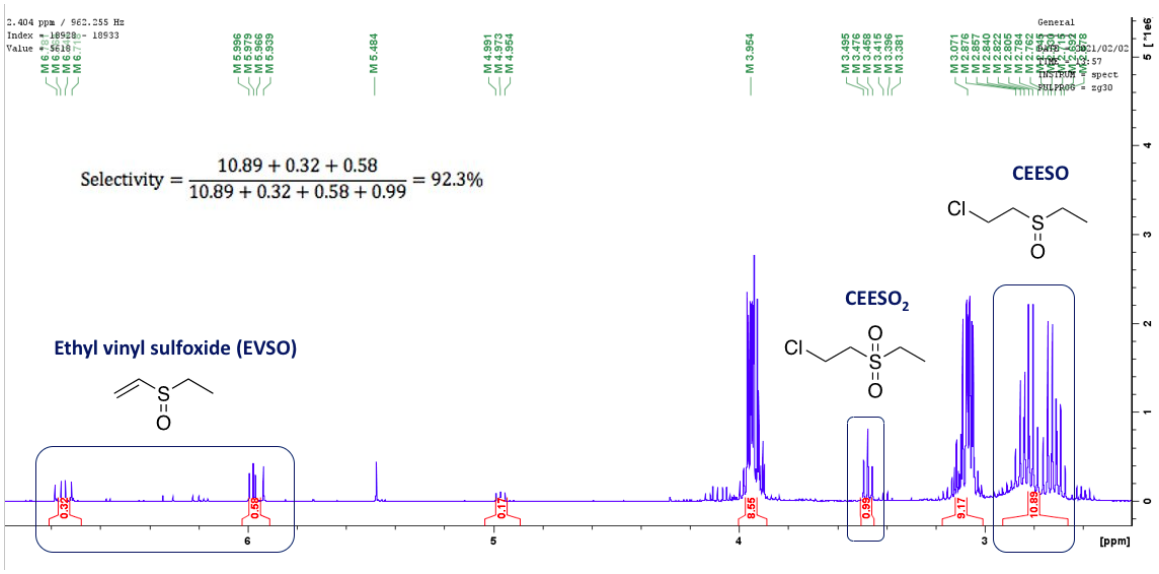
To a microwave vial, 1 mL of acetonitrile-d_3 and 0.5 mol % (0.001 mmol) of catalyst were added. O_2 gas was bubbled into the microwave vial for 20 minutes followed

by irradiation with a blue LED light for 20 minutes. CEES (23 µL, 0.02 mmol) was added at t = 0 minutes. The microwave vial was irradiated with blue light again until 100% CEES conversion was reached, which was confirmed by GC-MS analysis on a sample taken from the vial. The solution was filtered to remove MOF and then analyzed using ^{1}H NMR to determine the sulfoxide selectivity:

$$sulfoxide\ selectivity = \frac{int_{sulfoxides}}{int_{sulfoxides} + int_{sulfone}} \times 100\%$$

One example sulfoxide selectivity calculation for PCN-222(Sn) is shown below in Figure 9. We found that another sulfoxide besides CEESO was generated: ethyl vinyl sulfoxide (EVSO). Since this product should also be nontoxic, we included it in our calculations.

Figure 9. Sample calculation for sulfoxide selectivity using PCN-222(Sn) in acetonitrile-d_3.



CHAPTER 4

RESULTS

After synthesizing the porphyrins and characterizing them using UV-Vis spectroscopy, we used the porphyrins to synthesize their respective MOFs. These MOFs were characterized using PXRD (Figure 10) and UV-Vis spectroscopy (Figure 11).

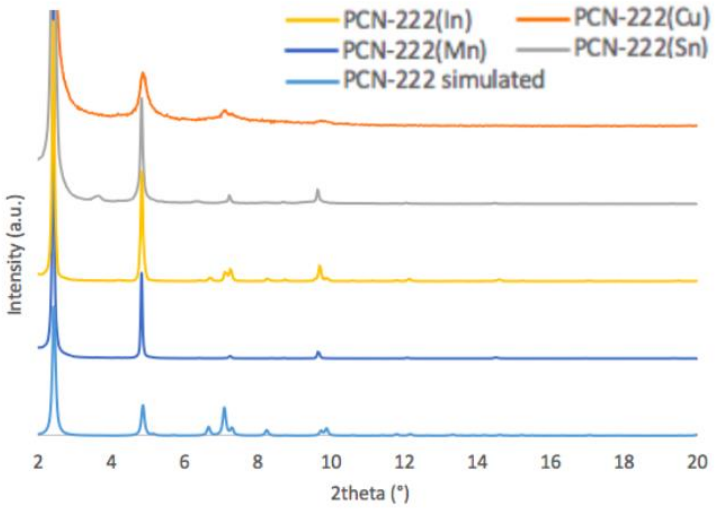


Figure 10. Powder X-ray diffraction spectra of PCN-222(M), M = FB, Sn, In, Mn, Cu.

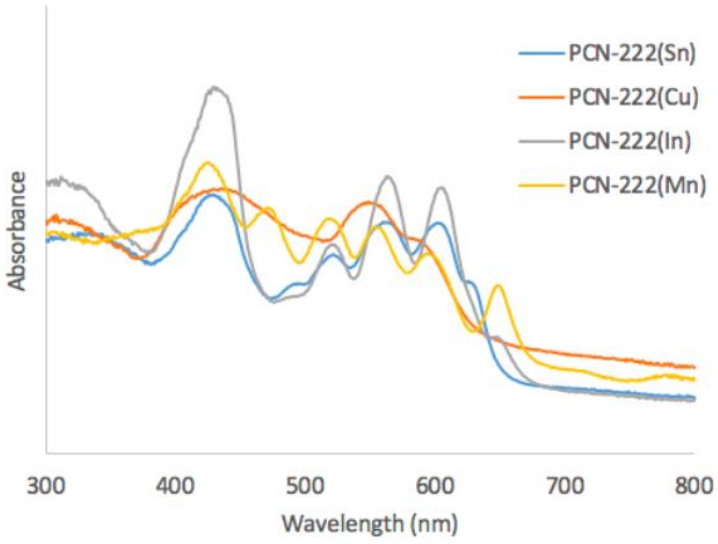


Figure 11. Overlayed UV-Vis spectra of PCN-222(M), M = Sn, In, Mn, Cu.

The first objective of the photocatalytic experiments was to determine if 0.5 mol % or 1.0 mol % of catalyst relative to CEES would yield faster conversion. For all four metalloporphyrins, the conversion rate of CEES into CEESO was slower at 1.0 mol % catalyst compared to 0.5 mol % catalyst (Figure 3). Thus, 0.5 mol % catalyst was used for the remainder of the trials.

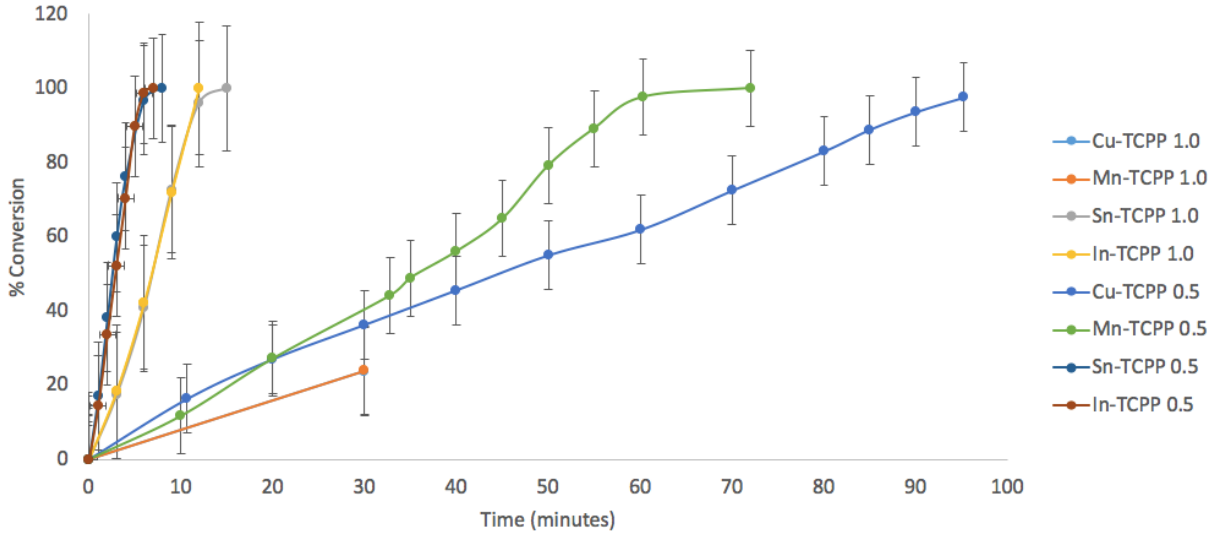


Figure 12. Percent conversion of CEES over time with standard error bars using 0.5 and 1.0 mol % of M-TCPP (M = Sn, In, Mn, or Cu) as catalysts in methanol.

The results for the 0.5 mol % catalyst experiments are zoomed in on to compare the kinetics using different metalloporphyrins (Figure 13). These data were used to calculate the half-lives of CEES. In order from fastest to slowest to reach 100% conversion of CEES were In-TCPP (half-life of CEES = 2.5 minutes), Sn-TCPP (2.6 minutes), Mn-TCPP (32 minutes), and Cu-TCPP (45 minutes).

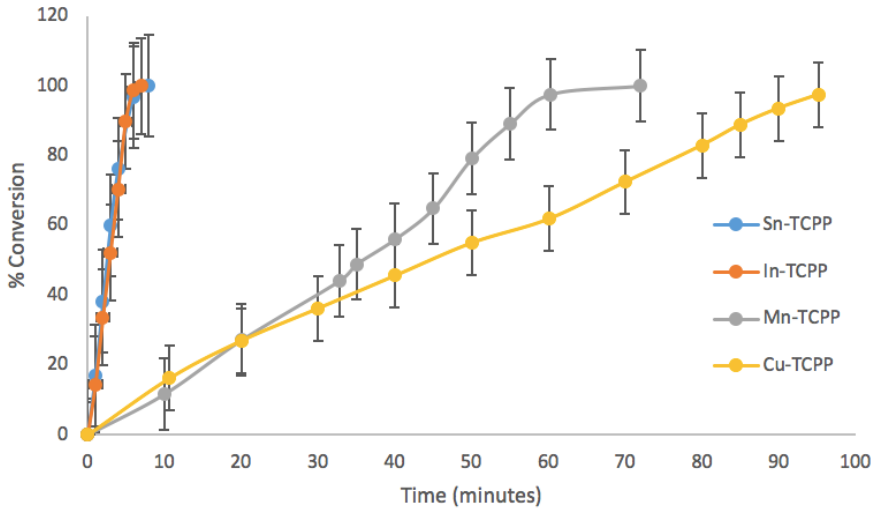


Figure 13. Percent conversion of CEES over time with standard error bars using 0.5 mol % of M-TCPP (M = Sn, In, Mn, or Cu) as catalysts in methanol.

Another objective of this project was to determine the kinetics of the reaction using PCN-222(M) and to compare the effect of (Figure 14).

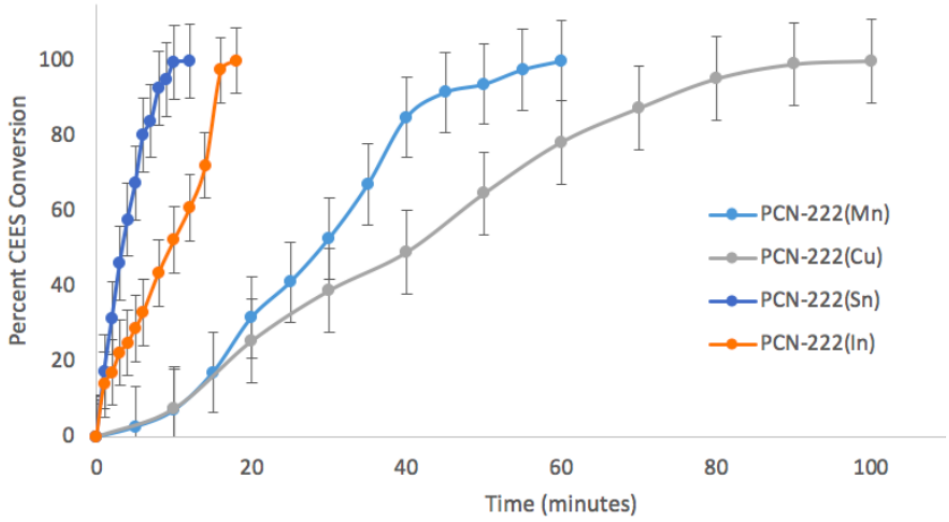


Figure 14. Percent conversion of CEES over time with standard error bars using PCN-222(M) (M = Sn, In, Mn, or Cu) as catalysts in methanol.

PCN-222(M) (M = Mn, Cu, and Sn) reached 100% conversion of CEES faster than their respective metalloporphyrins, suggesting that the oxidation of CEES into CEESO is faster using porphyrinic MOFs compared to free porphyrin. PCN-222(In), however, had a longer half-life than In-TCPP.

From these data, we calculated the half-lives of CEES using PCN-222(M) in methanol (Table 1). CEES half-lives and sulfoxide selectivities in acetonitrile were also determined and are shown in Table 1.

Table 1. Half-life of CEES in methanol and acetonitrile, and sulfoxide selectivity in acetonitrile for photocatalytic experiments using 0.5 mol% PCN-222(M) (M = free base, Sn, In, Mn, or Cu) as catalyst. [(a)] Trials were run but GC-MS was not in operation. [(b)] Trials were run but NMR was not in proper operation for quantitative analysis. [(c)] Only one trial was performed. Repeated trials are necessary to confirm result.

MOF	CEES Half-life in Methanol	CEES Half-life in Acetonitrile	Sulfoxide Selectivity in Acetonitrile
PCN-222(free base)[6]	12.0 min	7.4 min	93%
PCN-222(Sn)	3.4 min	13.8 min[c]	92%[c]
PCN-222(In)	9.5 min	N/A[a]	N/A[b]
PCN-222(Mn)	28.8 min	N/A[a]	80%[c]
PCN-222(Cu)	40.3 min	N/A[a]	N/A[b]

CHAPTER 5

DISCUSSION AND CONCLUSION

DISCUSSION

The four MOFs were characterized using PXRD (Figure 10) and UV-Vis spectroscopy (Figure 11). PXRD can be used to determine the crystalline structure of materials. This technique works by irradiating a material with X-rays and measuring the intensity of the diffracted X-rays. The PXRD patterns of the four MOFs match the simulated pattern of PCN-222(FB), indicating that the four MOFs were successfully synthesized. In the UV-Vis spectra, the large Soret band around 420 nm and smaller Q-bands from 500-700 nm result from the metalloporphyrin ligands in the MOFs. Because the Q-bands are present at different wavelengths when comparing among MOFs, we can conclude that there are different metal-doped porphyrins present in each MOF.

Photocatalytic runs were performed for each of the porphyrins and porphyrinic MOFs. Comparison between CEES conversion rates using 0.5 mol % and 1.0 mol % of catalyst relative to CEES reveals that the lower percentage of catalyst yields faster conversion (Figure 12). With 1.0 mol % catalyst, it is likely that more porphyrins aggregated with one another, which may have blocked some catalytic sites. With 0.5 mol % catalyst, there should be less aggregation, leading to more catalytic sites being exposed and thus, faster conversion rates.

For experiments conducted using M-TCPP in methanol, in order of fastest to slowest to reach 100% conversion of CEES were In-TCPP (half-life of CEES = 2.5 minutes), Sn-TCPP (2.6 minutes), Mn-TCPP (32 minutes), and Cu-TCPP (45 minutes)

(Figure 13). This trend also held true for PCN-222(M), except the reaction using PCN-222(In) was slightly slower than that using PCN-222(Sn) (Figure 14).

When comparing conversion rates using PCN-222(M) and M-TCPP, PCN-222(M) tends to catalyze the reaction at a faster rate. This may be due to a similar phenomenon that explains the difference in conversion rates between 0.5 mol % and 1.0 mol %: higher exposure of catalytic sites with less catalyst due to less porphyrin stacking. The MOFs provide a rigid structure that exposes the metalloporphyrin linkers to CEES and $^3O_2$ in the pores and prevents the porphyrins from aggregating.

Figure 14 shows the average percent conversion of CEES into products over time using each catalyst in methanol. From these data, we calculated the half-lives of CEES to be 3.4 minutes, 9.5 minutes, 28.8 minutes, and 40.3 minutes for PCN-222(M) (M = Sn, In, Mn, Cu), respectively (Table 1). Table 1 also shows the previously reported CEES half-life using PCN-222(free base or H_2): 12.0 minutes.[7] PCN-222(Sn) and PCN-222(In) exhibited significantly shorter CEES half-lives, which suggests that doping the porphyrinic ligands with these metals increased the efficiency of the selective oxidation reaction.

Currently, there is not much literature that explains the effect of these metals on catalytic activity. One possible explanation is that PCN-222(Sn) and PCN-222(In) promote higher rates of intersystem crossing (ISC) than PCN-222(FB). ISC is a spin forbidden, non-radiative transition from an excited singlet state to an excited triplet state. Higher rates of ISC are associated with more generation of singlet oxygen and thus, faster rates of oxidation of CEES. Based on this idea, it is likely that In and Sn have faster rates of intersystem crossing than Mn and Cu.

Another factor we investigated was the selectivity for nontoxic sulfoxide products in aprotic solvents such as acetonitrile. This is because hydrogen-bonding in methanol facilitates 100% or near 100% selectivity for sulfoxide; however, a protic, organic solvent like methanol may not be the most practical choice of solvent in mass degradation. Thus, acetonitrile is an alternative aprotic solvent that has been previously studied for this purpose.[6] Previous studies found that sulfoxide selectivity was primarily affected by solvent choice rather than MOF structure, so we expected the selectivity to be lower in acetonitrile than in methanol.[6] After 100% conversion of CEES was reached in CD_3CN using PCN-222(Sn) as a catalyst, a ^1H NMR spectrum of the reaction mixture was taken and analyzed to calculate the sulfoxide selectivity. PCN-222(Sn), had 92% selectivity, which was very high compared to that of PCN-222(free base), 93% (Table 1).[6] Based on one trial, PCN-222(Mn) was found to oxidize CEES with a sulfoxide selectivity of 80%. This is relatively low, and further literature analysis and repeated trials will be necessary to explain this result.

CONCLUSION

In this study, we aimed to improve the photocatalytic activity of materials that could degrade a sulfur mustard simulant via selective oxidation. Four porphyrinic MOFs, namely PCN-222(M) (M = Sn, In, Mn, Cu) were synthesized, characterized, and tested for their efficacy in this reaction. Photocatalytic experiments were performed to determine the CEES half-life in methanol. PCN-222(Sn) and PCN-222(In) exhibited significantly faster CEES half-lives in methanol than the previously reported PCN-222(free base). Notably, compared to currently used materials, PCN-222(Sn) exhibited

one of the fastest reported CEES half-lives under these conditions as well as a very high selectivity for nontoxic sulfoxides in acetonitrile.

Future work includes further characterizing each PCN-222(M) sample by obtaining gas sorption isotherms and calculating the percent selectivity for CEESO using ^{1}H NMR after 100% conversion of CEES in methanol-d_4 has been reached. Based on the GC-MS spectra, the selectivities in methanol were observed to be 100% or near 100%, but NMR analysis will confirm these observations. Photocatalytic runs will also be conducted in triplicate in acetonitrile for all remaining MOFs to analyze the effect of solvent on conversion rate. Since the NMR was not in working condition for quantitative analysis, the remaining sulfoxide selectivity samples will be analyzed once the NMR is in proper working condition. Then, we may be able to determine which metals promote the most selectivity in acetonitrile and attempt to explain the results. An extension of this project would be to create MOF textiles using the best performing MOF(s) in this study to provide a more practical application of these MOFs; a textile allows for solid-state catalysis, which could be useful for integration into everyday textiles such as personal protective equipment or cleaning wipes.[2,6] Another set of experiments would involve sending our best-performing MOF to an organization that can test its catalytic abilities on actual sulfur mustard. Because sulfur mustard is less soluble than CEES in methanol, this may slightly affect the reaction efficiency reported in our study.

This project builds upon a growing collection of important literature on degrading toxic chemicals and tells us more about MOFs and photocatalysis. The MOFs we made and tested have not been tested for this reaction before, and at least one of them yielded

very promising results. This work lends way to future studies that may improve selectivity in aprotic systems and further explain the effects of different metals on catalytic activity, with the overarching goal to degrade stockpiles of nerve agents. Hopefully, we will be able to finish this project and publish it in a scientific journal soon.

In the process of completing this thesis, I have greatly improved my laboratory and writing skills. When I joined the Liu lab group three and a half years ago, I had no idea how much I would learn and grow as both a chemist and researcher. In the lab, I performed organic synthesis, inorganic synthesis, compound separation, MOF characterization, and photocatalysis experiments. I learned how to use multiple analytical instruments such as the GC-MS, UV-Vis, PXRD, gas sorption, and more. After obtaining raw data, I also learned how to present it in the best way and analyze it from different perspectives with the help of lab mates and my advisor. One of my favorite realizations about research is that there is always more to learn, from younger and older scientists alike, and that no one has all the answers.

Furthermore, I was able to develop a closer connection with my thesis advisor by having weekly meetings. During these meetings, I shared my research progress, and she would encourage me to think in different ways and read literature to explain my results. In this process, I became a lot quicker at reading and understanding scientific journal articles. Although my time doing basic science research is almost over, I am forever grateful that I have been able to develop a strong, professional connection with my advisor and to know that she is always willing to support me in my career goals.

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