Investigation of Metal-Organic Frameworks as Materials for Generating Singlet Oxygen

A Major Qualifying Project Report
Submitted to the Faculty
of the
WORCESTER POLYTECHNIC INSTITUTE
in partial fulfillment of the requirements for the
Degree of Bachelor of Science
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Date: April 25, 2013

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Abstract

Porous metal-organic frameworks (MOFs) consisting of crystalline coordination polymers are of interest as host materials for molecular sorption because MOFs exhibit permanent porosity, high thermal stability, and feature pores with high surface areas, large pore volumes, and properties that can be modified through synthesis. We currently are developing porous MOFs that incorporate photosensitizers (organic dyes) in the MOF backbone in an effort to develop highly sorbent materials that generate singlet oxygen in order to oxidatively decompose adsorbed organic guest molecules present in the MOF. Ultimately, these materials will be used for applications involving environmental remediation and treatment of contaminated water sources. Toward that goal, the work in this project focused in two areas: (1) preparation of a porous MOF containing a metalloporphyrin as the photosensitizer, and (2) investigation of a method to detect formation of singlet oxygen. A porous MOF was synthesized hydrothermally by reacting *meso*-tetra(4-carboxyphenyl)porphyrin (TCPP) with cobalt chloride in pyridine at elevated temperature and its porous behavior characterized thermally by TGA. In addition, a solution-based electrochemical method to monitor production of singlet oxygen was explored that measures oxidative degradation of diphenylisobenzofuran (DPBF) to the corresponding dibenzoylbenzene.

Acknowledgments

I would like to greatly thank my chemistry Professor, Dr. John C. MacDonald, who allowed me to work on his research that has been progressing for years. He has been a great influence throughout my time at WPI and spent hours mentoring me through my first piece of technical research. Without his commitment to the research and me growing into a scientist, this project wouldn't have been possible.

I would also like to Dr. Chris Lambert and PHD student Morgan Stanton for the access to their laboratory equipment and sharing their knowledge with our group on electrochemistry; their partnership proved to be invaluable.

Lastly, I would like to thank Francisco Espinoza, an undergrad who voluntarily has been working on this research for a couple of years now. Thank you for all your time instructing me on how to use the instruments and on laboratory procedures. Good luck continuing this research.

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Introduction

Water pollution is an ongoing problem that affects the health of people worldwide both in developed countries due to industry and in developing nations that lack or fail to enforce regulation of water management and resource policies. Contamination of water sources by organic compounds used in manufacturing and energy production is increasingly problematic because many common organic contaminants (e.g., polychlorinated biphenyls, polyvinyl chloride, phthalates, dioxin, furans, fire retardants, parabens, hormones, detergents, fire retardants, polyaromatic hydrocarbons, industrial solvents, etc.) are harmful to humans even at very low concentrations (Edward T. Furlong, 2002). Accordingly, there is a growing need to develop new technologies and materials that can remove or reduce the level of organic contaminants present in water.

Metal-organic frameworks (MOFs) are a new class of porous materials composed of coordination polymers that form crystalline solids permeated by channels with high surface areas and pore volumes (Voskian, 2011). As such, MOFs are promising host materials for molecular storage and separation because they are known to absorb a variety of organic guest compounds in a manner similar to porous inorganic zeolites. Unlike zeolites, however, MOFs are derived from organic building blocks such that the structures and porous properties of MOFs can be modified through organic synthesis. Therefore, MOFs offer a significant advantage over zeolites as sorbent materials because the dimensions, topologies, void volumes, surface areas and surface properties can be tailored to maximize sorption of a particular guest.

The MacDonald research group has been investigating the design and porous properties of a new family of coordination polymers in an effort to develop MOFs that exhibit high specificity for absorbing hydrophobic organic guests. That research has shown that MOFs containing aromatic ligands in the backbone of the framework selectively absorb greater amounts of hydrophobic aromatic guests (e.g., naphthalene, phenanthrene, and pyrane) compared to polar aromatic guests (e.g., ibuprofen, acetaminophen and aspirin), and that selectivity increases as the size of the guest increases.

The overall goal of this project was to develop a MOF containing a photosensitizer in the backbone in order to create a highly sorbent porous solid that converts triplet oxygen into reactive singlet oxygen catalytically as a means to oxidatively decompose organic guest molecules absorbed by the MOF. Ultimately, we hope to use these materials to treat water sources polluted with organic contaminants. This research expanded on our previous research in two areas. The first phase of this project focused on synthesis of a porous MOF containing a metalloporphyrin as the photosensitizer and characterization of the porous behavior using thermogravimetric analysis (TGA). We chose a metalloporphyrin as the photosensitizer because porphyrins have high absorption coefficients (0.85-0.95) and are known to produce singlet oxygen with high efficiency in solution. The target ligand, *meso* tetra(4-carboxyphenyl)porphyrin (TCPP), was selected because it contained the requisite carboxylic acid groups necessary to coordinate to cobalt ions and form the corresponding Co-TCPP MOF. The second phase of this product involved investigating a method to detect and quantify the production of singlet oxygen. The goals of this phase of the research were to identify a suitable organic compound, diphenylisobenzofuran (DPBF), to serve as a representative contaminant that would react with singlet oxygen, and then measure production of singlet oxygen electrochemically using voltammetry to monitor oxidative degradation of DPBF into dibenzoylbenzene.

Background

Metal Organic Frameworks (MOFs)

Over the past twenty years, MOFs have become of great interest to researchers who are investigating porous materials. MOFs are crystalline coordination polymers with organic building blocks (bi-, tri-, or polyfunctional ligands) coordinated to transition metal ions or clusters of metal ions that self-assemble in solution to form open, three-dimensional networks exhibiting long-range order (Voskian, 2011). A hallmark of MOFs is the formation of continuous channels throughout the crystalline solid with pore diameters that vary between 4-20 Å. The constituents of the framework typically occupy just 10-50% of the volume of the solid, with the remaining 90-50% of the volume occupied by mobile guest solvent that can be removed easily by heat or vacuum. As a result, MOFs have remarkably high internal surface areas on the exposed framework that typically range from 1000-6000 m^2/gram of material, and pores that are highly accessible to organic guests (Czaja, Trukhan, & Müller, 2009). Despite the large void volumes present in the channels of MOF when guest solvent is removed, MOFs often are thermally stable to temperatures exceeding 400 °C and exhibit permanent porosity—that is, the framework does not collapse or undergo structural rearrangement when guests are removed. An attractive feature of MOFs is that they are molecular materials constructed using organic molecules as the basic building blocks. The structures, dimensions, and surface properties of the channels in MOFs can be tailored readily through organic synthesis, which in turn permits the sorbent properties of the MOF to be modified by design to favor absorption of different organic compounds based on their size, structure, and functional groups. Examples of MOFs prepared from dipyridines and dicarboxylic acids coordinated to indium ions are shown in Figure 1 (Voskian, 2011).

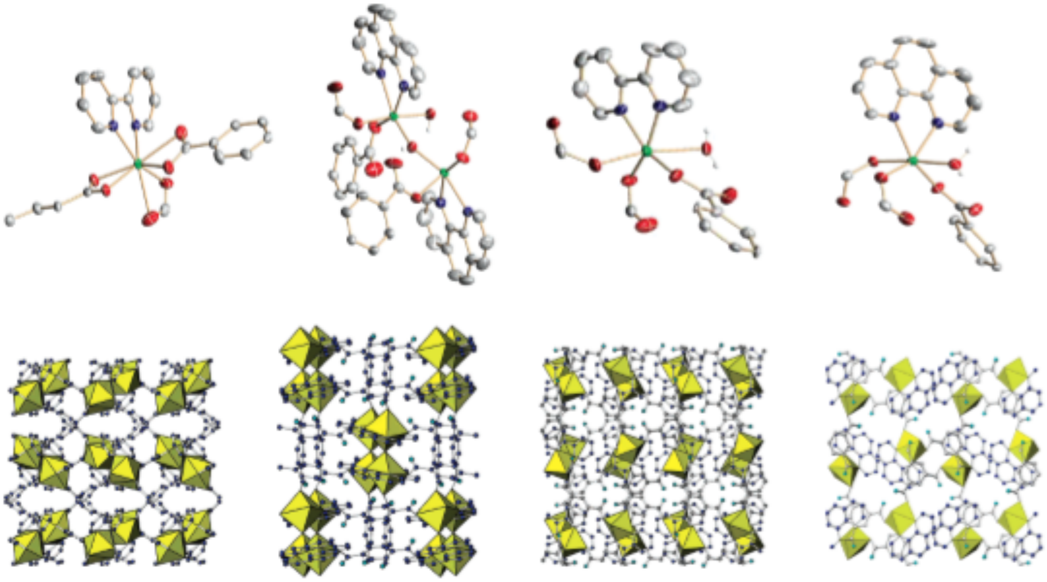

Figure 1. Examples of MOFs composed of aromatic dipyridines and dicarboxylic acids coordinated to indium ions.

MOFs vs Zeolites as Porous Hosts

Zeolites are crystalline inorganic solids that exhibit porous behavior analogous to MOFs. Zeolites are composed of tetrahedral clusters of TO_4 (T = Si, Al) bridged by oxygen atoms that feature well defined channels with structures and pore topologies that can be controlled based on the ratio of Si and Al atoms present in the crystalline lattice. Today, zeolites are used broadly as porous hosts in many applications because of the wide range of channel topologies arising from variation in the arrangements of the sodalite cage, which serves as the basic building block in zeolites. (Auerbach, Carrado, & Dutta, 2003). Figure 2 shows examples of several common zeolite structures that result from different arrangements of the sodalite cage.

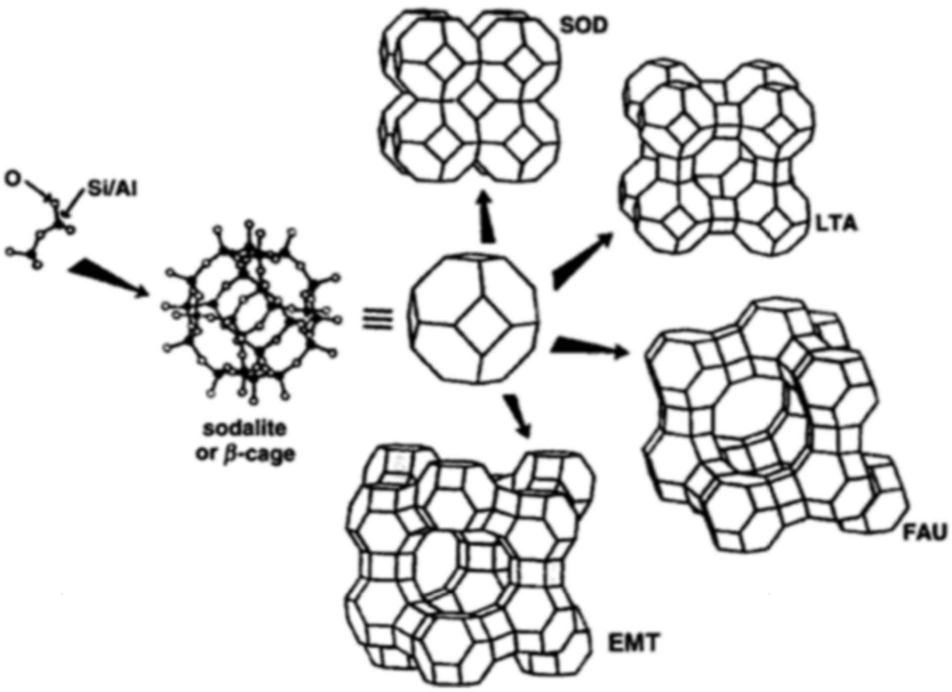

Figure 1. Examples of several zeolite frameworks generated by different arrangements of the sodalite cage (Auerbach, Carrado, & Dutta, 2003).

Unlike MOFs where the building blocks are organic ligands whose structures and properties can be modified synthetically, the building blocks of zeolites are atoms, which makes the pore structures and properties of zeolites difficult to "tune". In addition, zeolites feature pore openings ranging from 4 to 12 Å, which are smaller that those observed in MOFs (4 to 20 Å). Consequently, MOFs can have void volumes and surface areas that far exceed those of zeolites. In addition, the surface properties of the channels in MOFs may be modified without altering the architecture or framework of the MOF either by appending different organic substituents onto the ligand backbone or by increasing the length of the ligand backbone (Eddaoudi, et al., 2002). For example, shown in Figure 3 are the structures of a family of structurally related MOFs with consistent cubic framework architectures resulting from coordination of linear aromatic dicarboxylic acids to tetrahedral clusters of Zn ions (Eddaoudi, et al., 2002). By varying the length of the dicarboxylic acid (i.e., benzene, naphthalene, biphenyl, etc.) or by introducing different substituents (i.e., halogen, amino group, alkyl group, etc.) onto the dicarboxylic acid, it was possible to systematically expand the dimensions of the channels and the hydrophicity/hydrophilicity of the channel walls.

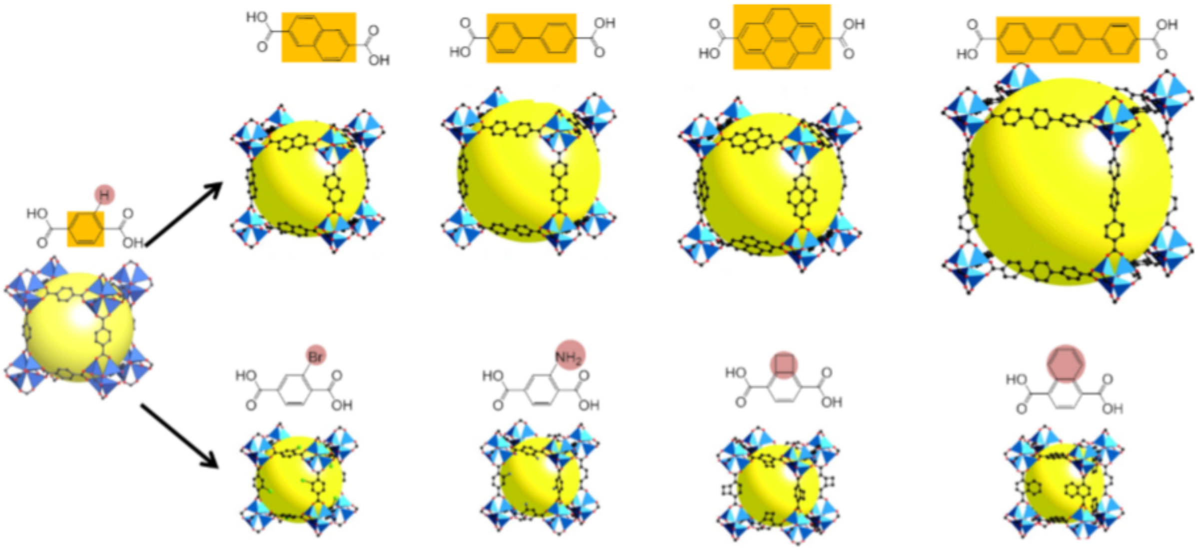

Figure 3. Top: The orange boxes show aromatic dicarboxylic acids of different lengths that were used in the synthesis of the MOF resulting in different pore sizes. Bottom: The maroon circles show different substituents appended on to 1,4-benzenedicarboxylic acid that were used to generate MOFs with the same cubic framework as the original on the far left. (Eddaoudi, et al., 2002).

To meet the goals of this project, it was important to choose a porous host material capable of absorbing organic compounds (contaminants) with a range of structures and sizes. A previous study in our group of the sorption behavior of MOF-5 (shown on the left in Figure 3) revealed that the MOF actively absorb significant amounts of large polyaromatic hydrocarbons (PAHs) such as naphthalene, phenanthrene and pyrene when the MOF solids are placed into ethanolic solutions containing those guests. Competition studies examining sorption from solutions containing equimolar mixtures of those guests showed that MOF-5 selectively absorbs larger PAHs. For example, we found that MOF-5 preferentially absorbs phenanthrene in an 8:1 ratio over naphthalene across a range of concentrations, as shown in Figure 4. That study revealed that selective absorption of larger PAH guests resulted from tighter binding of guests with dimensions that more closely match the channel dimensions of the MOF.

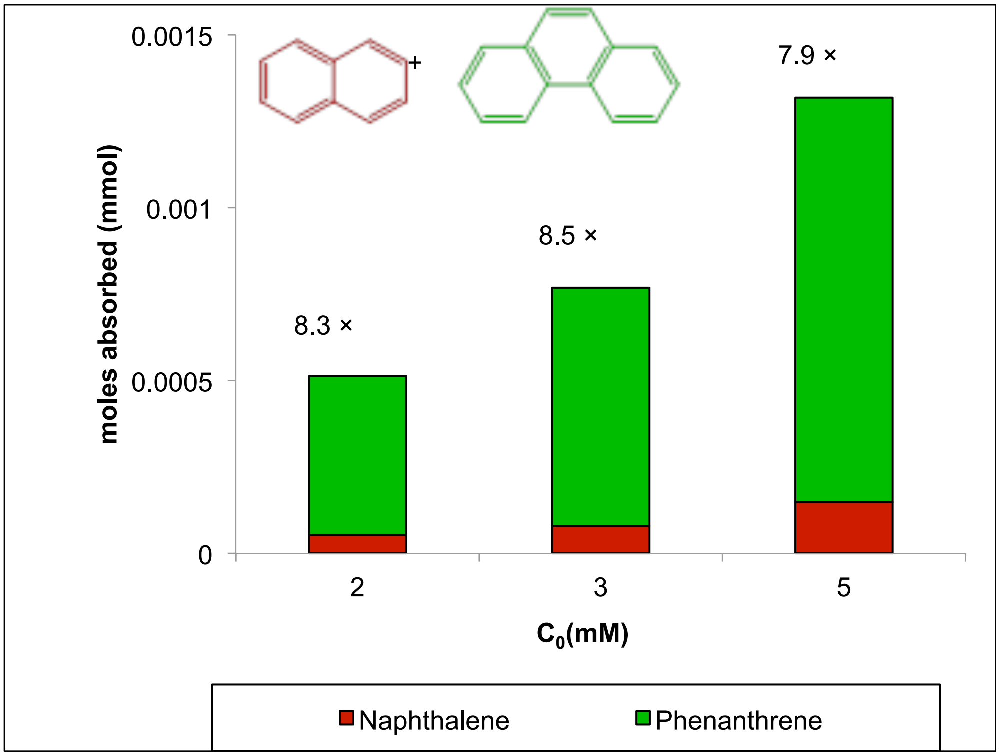

Figure 2. Phenanthrene was selectively absorbed 8:1 over naphthalene by MOF-5 at different concentrations in ethanol.

Not only do differing organic ligands change the framework of the MOF, but changing the metal ions and coordination geometry will also change the structure of the porous material. Many of the reported MOFs have ligands coordinated to transition metals anywhere from linear to octahedral geometries but MOFs derived from lanthanide metal ions have coordinated with up to nine ligands bound to the metal ion (Ma, Yuan, Wang, & Zhou, 2009).

Although zeolites exhibit higher thermal stability up to 1200°C compared to the typical thermal stability of MOFs up to 400°C (Auerbach, Carrado, & Dutta, 2003), MOFs still are useful as sorbent materials for multitude of applications where elevated temperatures are not a factor.

For the purposes of this project, MOFs were more suitable than zeolites as the porous host for the following reasons: (1) a ligand containing a suitable photosensitizer can be incorporated into the backbone of a MOF but not a zeolite, and (2) the pore openings of MOFs are larger than those of zeolites, allowing larger organic guests (contaminants) to diffuse into the porous host.

Singlet Oxygen

The oxygen that is in our atmosphere and water is in the ground state form of molecular oxygen. The molecular orbital electron configuration contains two unpaired valence electrons and is shown below.

$O_2 \rightarrow (\mathrm{core})(\pi_x\uparrow\downarrow)(\pi_y\uparrow\downarrow)(\pi_x{*}\uparrow)(\pi_y{*}\uparrow)$

In order to best describe singlet oxygen, only the two anti-bonding π electrons are of importance, therefore, ignoring everything but said two electrons the configuration is portrayed below;

$O_2 \rightarrow (\pi_x{*}\uparrow)(\pi_y{*}\uparrow)$

Triplet state oxygen, or it's ground state has two electrons in its highest energy level aligned in the same direction. This ground state is given the notation $^3\Sigma$. There are also two low energy excited states in which the highest level electrons have opposite spins. These have the ability to be paired or unpaired. The molecular orbital configuration for these two excited states are as follows;

$^1\Delta O_2 \rightarrow (\pi_x^*\uparrow\downarrow)$ or $(\pi_y^*\uparrow\downarrow)$

$^1\Sigma O_2 \rightarrow (\pi_x^*\uparrow)(\pi_y^*\downarrow)$

Where $^1\Delta$ denotes the paired form and $^1\Sigma$ denotes the unpaired form. Even though $^1\Delta$ is lower than energy than $^1\Sigma$, both are referred to as ‘singlet oxygen’ (Daniel Carney, 2009).

Singlet Oxygen is of interest for this research because of its strong oxidative properties. It has the ability decompose organic contaminants such as polychlorinated biphenyls, polyvinyl chloride, phthalates, dioxin, furans, fire retardants, parabens, hormones, detergents, fire retardants, polyaromatic hydrocarbons, industrial solvents, etc. in water (Zoltán Bénia, 2013) (Edward T. Furlong, 2002).

There are many different methods to generate singlet oxygen. Direct excitation of oxygen is possible but difficult. The most common route is through an energy transfer from a photosensitizer such as *meso* tetra(4-carboxyphenyl)porphyrin (TCPP) shown in Figure 5.

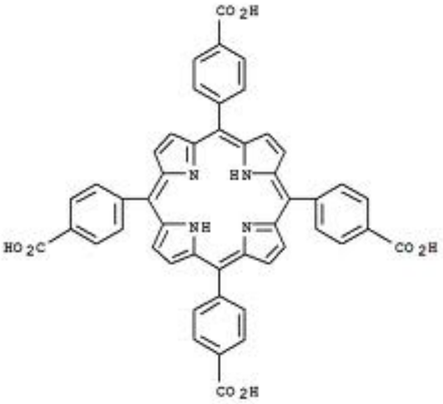

Figure 3. Chemical structure of tetra(4-carboxyphenyl)porphyrin (TCPP).

Singlet oxygen is generated from the ground state oxygen found in the photosensitizer ligand through energy transfer of light. This singlet oxygen then undergoes transformation to the first excited triplet state. Through collision, the ground state triplet oxygen in the environment, in the surrounding air or water, undergoes an energy transfer to produce singlet oxygen (Daniel Carney, 2009). This is the mechanism we have chosen to exploit.

Experimental

Synthesis of the Co-TCPP MOF

Meso tetra(4-carboxyphenyl)porphyrin (TCPP) (0.160g, 0.20mmol) $CoCl_2$ (0.117g, 0.50mmol) and 12 mL of a 0.1 M pyridine/KOH solution were sealed in a 25 mL microwave vial and then heated in an oven at 150 ° C for 48 hours, then cooled to RT to yield a microcrystalline sample of reddish-purple crystals of the Co-TCPP MOF. The crystals were then washed with pyridine to remove any residual unreacted starting materials and allowed to dry in air. The 2.5:1 metal to ligand ratio used in this synthesis was modified from the 3:1 ratio reported previously (Kosal, Chou, Wilson, & Suslick, 2002).

Analysis of the Co-TCPP MOF by TGA

Thermogravimetric analysis (TGA) was used in order to characterize the thermal stability and porous behavior of Co-TCPP MOFF. TGA data were collected using a TA instrument, Hi-Res TGA 2950 Thermo Gravimetric Analyzer. A sample of 0.05 g of Co-TCPP MOF was loaded into a Pt TGA pan and then heated at a rate of 5 ° C per minute from RT to 500 ° C.

Generation and Detection of Singlet Oxygen

The detection of singlet oxygen was be monitored using three electrode, electrochemical solvent analysis through excitation via the photosensitizing method described during the background section. Diphenylisobenzofuran (DPBF) was chosen as a representative contaminant because it is known to react with single oxygen to form the corresponding endoperoxide, which undergoes further oxidation to form the dibenzoylbenzene as shown in the reaction scheme in Figure 6.

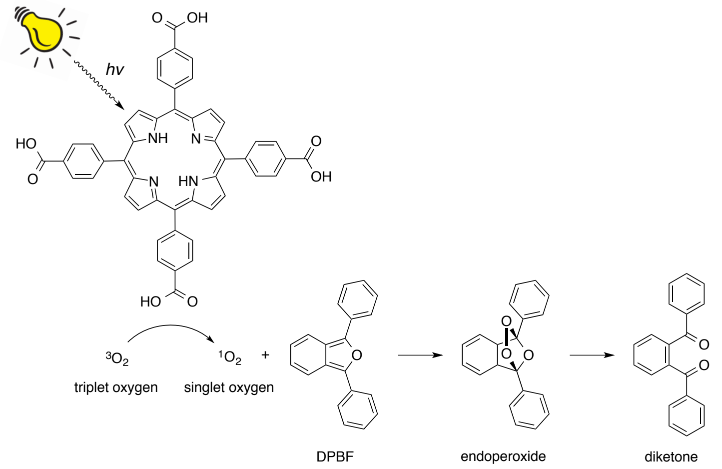

Figure 4. Mechanism of oxidation of DPBF by singlet oxygen. Singlet oxygen formed by photoexcitation of TCPP and subsequent energy transfer to triplet oxygen then oxidizes DPBF to the endoperoxide followed by rearrangement to dibenzoylbenzene.

The electrochemical setup consisted of three electrodes connected to a potentiostat with glassy carbon as the working electrode, Ag/AgCl as the reference electrode and Pt wire as the counter electrode. The electrodes were placed in a quartz cuvette containing a solution of the photosensitizer, DPBF, DMF and supporting LiCl as electrolyte, and then covered by a box to eliminate ambient light. Photoexcitation was carried out by shining light from a 60 W lamp at a distance of 15 cm from the box through a HOYA orange filter in the side of the box as shown in Figure 7 (Sharp, Forsythe, & Davis, 2009).

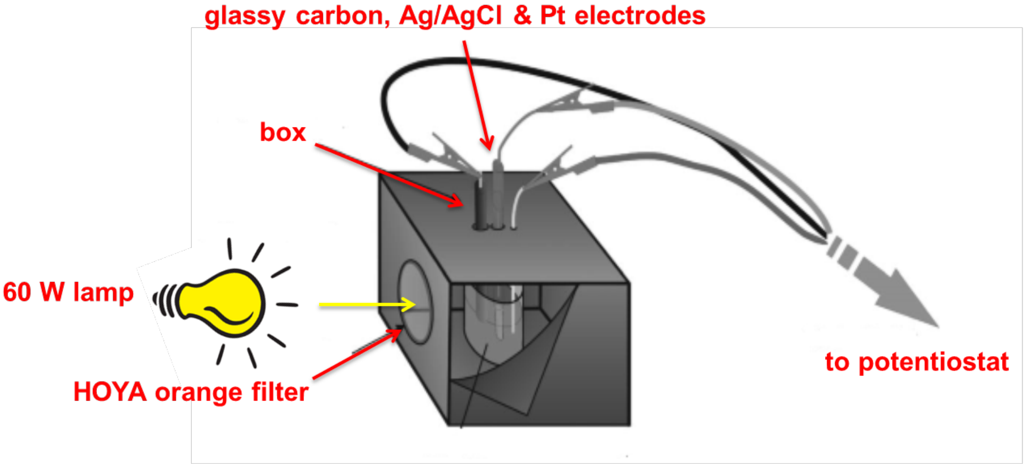

Figure 5. Illustration of the electrochemical setup used to photoexcite TCPP and monitor generation of singlet oxygen.

Square-wave voltammetry was used to measure the concentration of the DPBF in solution in the presence of the TCPP photosensitizer with the light on. A stock solution containing 0.0307 g of DPBF and 200 mL of dimethylformide (DMF) was prepared, serially diluted to make 60 mL solutions containing 0, 50, 100, 150, 200, 250 µM DPBF containing 50 µM LiCl and 200 µM TCPP (Kosal, Chou, Wilson, & Suslick, 2002). Square-wave voltammetry was carried out on each solution with the light on using the following experimental parameters: pulse size 5, frequency 25 Hz, step size 2 mV, sweep width 0 V to 0.9 V. The results showing oxidation of DPBF are shown in Figure 12 in the Results and Discusson.

Control experiments were carried out to monitor the response of DPBF to light in the absence of the photosensitizer, to TCPP in the absence of light, and to the presence of TCPP and light. Square-wave voltammetry was conducted to measure the concentration of DBPF at two-minute intervals on stock solutions of 200 µM DPBF in DMF under the following conditions: 1) DPBF, light on, no TCPP: 54 mL 200 µM DPBF solution with 0.1 M LiCl was monitored with the light on for 20 minutes; 2) DPBF, TCPP, light off: 6 mL of 500 µM TCPP in DMF was added to 54 mL 200 µM DPBF and the solution monitored for 20 minutes in the dark; 3) Using the previous solution containing DPBF and TCPP, the light was turned and monitored for 20 minutes. The results of those experiments are shown in Figure 13 in the Results and Discussion.

Results and Discussion

Synthesis and Thermal Analysis of the Co-TCPP MOF

Reaction of the TCPP ligand with $CoCl_2$ in pyridine under hydrothermal conditions at 150 °C for 48 hours produced the Co-TCPP MOF as a microcrystalline sample of reddish purple crystals, as shown in the optical micrograph in Figure 8. Considering that the TCPP ligand is a white solid and that $CoCl_2$ is a dark purple solid, the reddish-purple color of solid obtained from the reaction provided evidence that a coordination polymer formed. The fact that the solid did not dissolve when washed with pyridine provided further evidence that the product was a MOF because both starting materials are soluble in pyridine. MOFs generally are not soluble in organic solvents due to their high molecular weight and high strength of the coordination bonds between the metal ions and carboxylate groups on the ligand. When a single large crystal ~0.5 mm in length was removed from solution, blotted dry on filter paper, and observed under a polarizing stereomicroscope, the crystal initially appeared clear with well-developed faces and edges. Over the course of 30 minutes, the crystal slowly turned translucent, then opaque with cracks appearing in the crystal and the odor of pyridine evident. Under crossed polarizing lenses, the crystal extinguished light uniformly when rotated, indicating a single, continuous crystalline phase. After 30 minutes, different regions of the crystal extinguished light at different times when rotated. Those observations indicated that the crystal had broken up into smaller microcrystals and no longer was a single, continuous crystalline phase. The noticeable smell of pyridine and the fact that the single crystal turned opaque and became microcrystalline all strongly suggested that the crystal was composed of a porous MOF with pyridine present in the channels. We and others frequently have observed such behavior with MOF crystals as guest solvent in the channels diffuses out of the MOF lattice and is lost via evaporation.

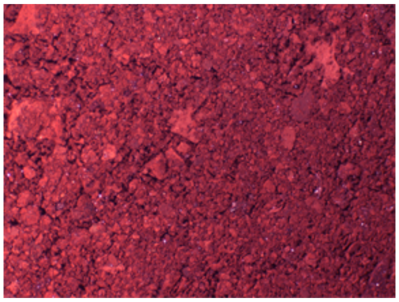

Figure 6. Polycrystalline sample of the Co-TCPP MOF prepared by hydrothermal synthesis.

Shown in Figure 9 is the proposed mechanism by which we expected the TCPP ligand to coordinate to the Co ions during the hydrothermal reaction between TCPP and $CoCl_2$. Yaghi has shown previously that aromatic dicarboxylic acids act as bidentate ligands where both carboxylate oxygen atoms coordinate to Zn ions (Figure 3) in forming coordination polymers (Eddaoudi, et al., 2002). Given that TCPP ligand contains four carboxylic acid groups capable of binding to Co ions, we expected all four acid groups to react in forming the MOF.

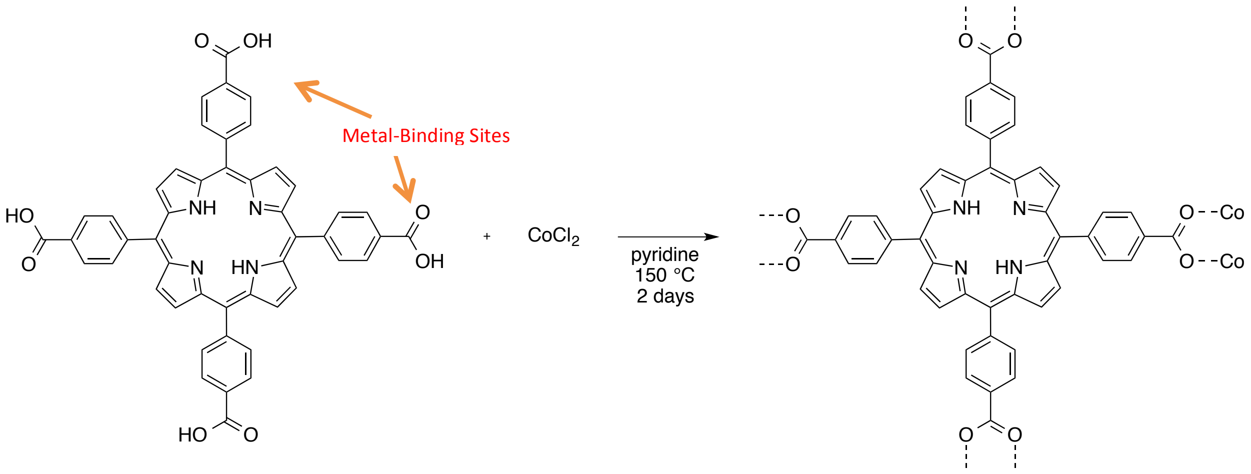

Figure 7. Proposed mechanism for the reaction between TCPP ligands and Co ions in forming the Co-TCPP MOF.

The crystal structure of the Co-TCPP MOF is shown in Figure 10 (Kosal, Chou, Wilson, & Suslick, 2002). All four carboxylate groups on the TCPP ligand are involved in coordinating to Co ions with two carboxylate groups coordinating via bidentate interactions at both oxygen atoms and two carboxylate groups coordinating via monodentate interactions via just one oxygen atom. In addition, Co ions also re coordinated by the four nitrogen atoms at the center of the porphyrin ring that are not involved in forming the MOF framework. The net result of coordination by the carboxylate groups is a MOF framework resembling Yaghi's cubic MOFs that features large 12 Å x 12 Å channels. An important feature of the Co-TCPP MOF structure is that the TCPP ligands are exposed within the framework such that oxygen present in solution can diffuse easily in the channels to react with the TCPP photosensitizer.

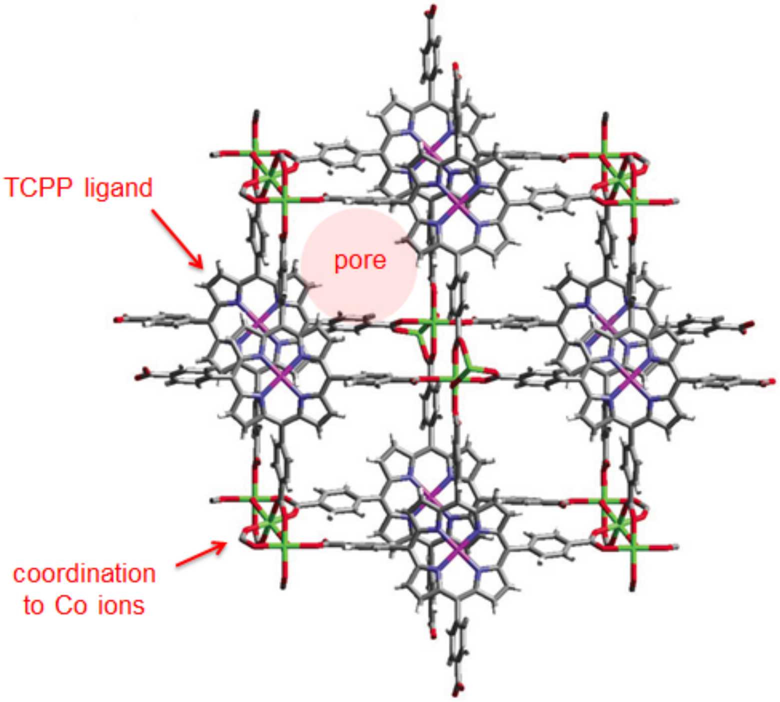

Figure 8. Crystal structure of the Co-TCPP MOF with Co ions coordinated to carboxylate groups shown in green, Co ions at the center of the porphyrin ring shown in purple, and carboxylate groups shown in red.

Thermogravimetric analysis (TGA) was carried out by heating a 0.05 g sample of the Co-TCPP MOF to characterize the thermal stability of the MOF, to confirm that pyridine solvent was present as a guest in crystals of the MOF, and to determine if the pyridine guest could be removed. Shown in Figure 11 is the TGA thermogram detailing loss of mass from the sample as a function of heating. The Co-TCPP MOF lost approximately 17% of its mass across a very broad temperature range spanning from RT to 400 °C before finally rapidly decomposing as signified by the sharp loss of mass at ~420 °C. The TGA data revealed several important findings. First, the loss of mass of 17% indicated that guest solvent was present in the MOF, which confirmed that the MOF was porous and that it was capable of absorbing a significant amount of pyridine within the channels. Given that fact that the crystals lost mass immediately starting at RT suggests that the crystals likely contained an even higher percentage of pyridine than could be measured by TGA. Previous studies of solvent loss by MOFs in our group has shown that MOFs with pore openings greater than 10 Å frequently lose significant amounts of guest solvent within a few minutes. In one case, we found that a MOF containing a mixture of ethanol and water lost greater than 40% of its mass within 15 minutes in the TGA on standing at RT. Therefore, it is likely that the Co-TCPP MOF takes up more than 17% of pyridine by mass and that we are not able to accurately measure the exact amount by TGA due to the time (~5 minutes) it takes to prepare, load and starting measuring loss of mass. The TGA curve also shows a slight change in slope at approximately 115 °C, which corresponds to the boiling point of pure pyridine, with the slope become slightly steeper after 115 °C. That data indicates that the MOF loses guest solvent at a slightly faster rate upon reaching the boiling point of pure pyridine, which is not surprising. What is surprising is that the MOF continues to lose guest pyridine out to 400 °C, or 285 °C above the boiling point of pyridine. That result is important because it suggests that even a relatively small aromatic guest such as pyridine interacts strongly with the TCPP ligands in the MOF framework and that the Co-TCPP MOF should exhibit strong sorption behavior toward contaminents. Lastly, the TGA data shows that decomposition of the Co-TCPP MOF does not occur until above 400 °C indicating that MOF has high thermal stability comparable to Yaghi's MOF-5 (Tranchemontagne, 2007).

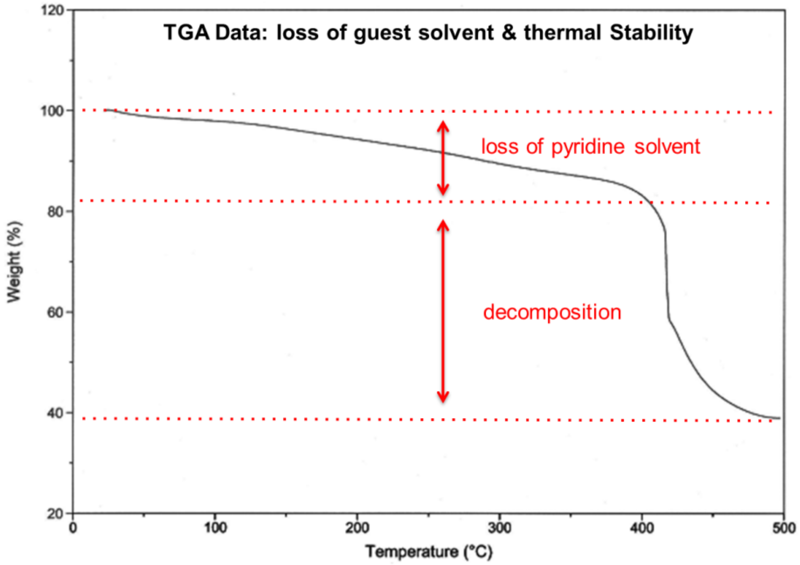

Figure 9. TGA data for Co-TCPP MOF showing loss of pyridine solvent between RT and 400 °C and thermal decomposition of the MOF at 420 °C.

Generation and Detection of Singlet Oxygen

Using the electrochemical method described in the experimental section, we examined the ability of the TCPP ligand to act as a photosensitizer for converting triplet oxygen into singlet oxygen. It was important to confirm that the free TCPP ligand would generate singlet oxygen before testing the Co-TCPP MOF for several reasons. First, we wanted to quantify the activity of the photosensitizer in solution at known concentrations to establish solution data that could be compared to the activity observed for the Co-TCPP MOF. We anticipated that it would be difficult to assess the activity of the Co-TCPP MOF in generating singlet activity because the MOF particles are not soluble, and therefore calculating the effective concentration of TCPP ligand participating in generating singlet oxygen is not possible. Therefore, comparing the activity of the MOF to the activity of the TCPP ligand was necessary. Second, we did not know if incorporating a photosensitizer such as TCPP into the rigid backbone of a MOF would affect the ability of the ligand to act as a photosensitizer. For example, a number of organic dyes that fluoresce strongly in solution exhibit no fluorescence in the solid state due to quenching cause by the solid. Therefore, it was necessary to evaluate the photosensitization with the free ligand prior to testing the MOF. We chose to monitor oxidation of diphenylisobenzofuran (DPBF) as a representative organic contaminant because DPBF readily undergoes oxidation by singlet oxygen.

Shown in Figure 12 is an overlay of the square-wave voltammograms measuring oxidation of DPBF by singlet oxygen generated by 50 μM TCPP in DMF with 0.1 M LiCl as supporting electrolyte. The voltammograms show well-defined peaks at +0.69 V resulting from oxidation of DPBF (the intermediate and diketone product are not electrochemically active in the region from 0 to 1 V that was scanned).

The data clearly indicates that the free TCPP ligand acts as a photosensitizer in solution and that oxidation of the DPBF "contaminant" can be monitored readily across the range of concentrations tested.

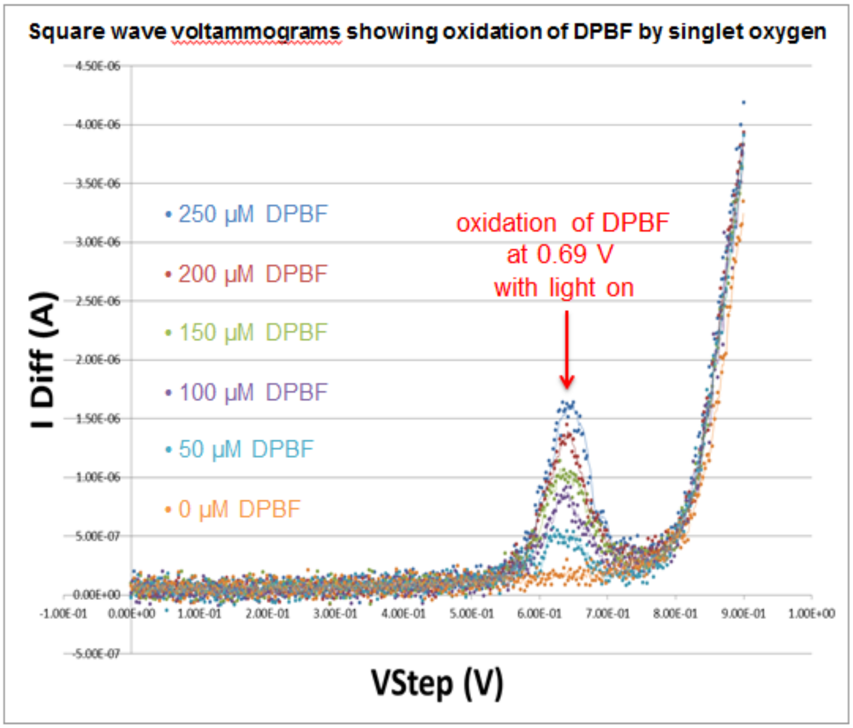

Figure 10. Square-wave volammograms showing oxidation of DPBP by singlet oxygen in the presence of 50 μM TCPP with 0.1 M LiCl supporting electrolyte in DMF with concentrations of DPBF varying from 0-250 μM.

Having confirmed that TCPP generates singlet oxygen and that oxidation of DPBF could be quantified electrochemically, it was important to establish that singlet oxygen was responsible for oxidation of DPBF. Shown in Figure 13 is the response of 200 μM DPBF over time in the presence and absence of the 50 μM TCPP photosensitizer and with the light on and off in DMF containing 0.1 M LiCl. The top (blue) data in Figure 13 shows that in the absence of the TCPP ligand, no oxidation of DPBF occurs when exposed to light. The middle (red) data shows that in the absence of light, no oxidation of DPBF occurs in the presence of the TCPP photosensitizer. The bottom (green) data shows that oxidation of DPBF only occurs in the presence of TCPP when the light is turned. The data also indicates that oxidation of DPBF is evident immediately when the light is turned on and is complete after 20 minutes. Oxidation of DPBF also could be followed qualitatively as the initially yellow solution turned colorless when oxidation was complete.

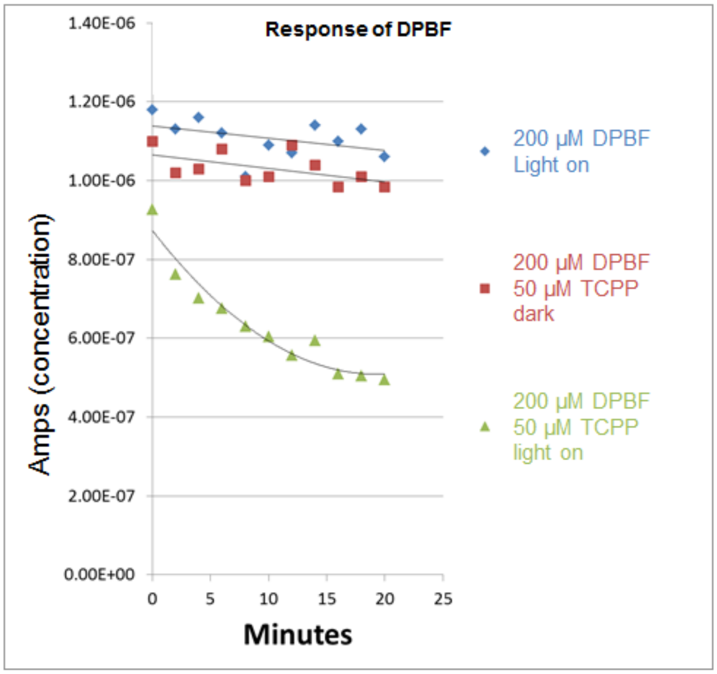

Figure 11. Response of DPBF toward oxidation by singlet oxygen in the presence and absence of TCPP and light.

Key Findings

We were able to accomplish two of the major goals of this project—namely (1) to prepare and characterize a MOF containing an organic photosensitizer in the backbone of the framework, and (2) to investigate a method to monitor production of singlet oxygen by the photosensitizer. We successfully synthesized the Co-TCPP MOF and showed that it is porous, thermally stable to above 400 °C, absorbs a significant amount of guest pyridine as solvent, and that the pyridine guest interacts strongly with the TCPP ligands within the channels of the MOF. In addition, we were able to prove that the free TCPP ligand acts as a photosensitizer by generating singlet oxygen that can be quantified electrochemically using square-wave voltammetry to monitor oxidation of a test contaminant, DPBF. The next step of this research will be to investigate the ability of the Co-TCPP MOF to generate singlet oxidation and monitor oxidative degradation of DPBF by the MOF. Although we have not yet tested the activity of the Co-TCPP MOF, we are confident that the MOF likely will exhibit enhanced activity due to the relative high concentration of TCPP ligands present in the MOF, and the fact that absorption by the MOF should generate a local high concentration of contaminants such as DPBF in the channels in near proximity to the TCPP ligands.

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