# Investigation of Porphyrin-based MOFs as Porous Hosts for Generating Singlet Oxygen

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# Abstract

Porous metal-organic frameworks (MOFs) consisting of crystalline coordination polymers are of interest as host materials for molecular sorption. 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 are currently developing porous MOFs that incorporate photosensitizers 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 this goal, the work in this project focused in four areas: (1) preparation of a porous MOF containing a metalloporphyrin as the photosensitizer, (2) investigation of a method to detect formation of singlet oxygen and (3) characterization of the activity of the MOF toward generating singlet-oxygen in Organic and Aqueous environment and (4) the stability of the MOF as it generates singlet oxygen. A porous MOF containing a porphyrin as the photosensitizer was prepared via hydrothermal synthesis by reacting meso-tetra(4-carboxyphenyl)porphyrin (TCPP) with zinc nitrate and 4,4'-bipyridine (BPY) in DMF at elevated temperature. Photolytic generation of singlet oxygen by the MOF was investigated by monitoring oxidative conversion of a model contaminant, 1,3-diphenylisobenzofuran (DPBF), to the corresponding di-ketone using UV-VIS absorption spectroscopy.

# Acknowledgements

We would like to thank our Chemistry advisor, Professor John C. MacDonald, for all of his wisdom and support. During the past two years working with him, he has not only mentored us academically, but also personally. From the first Chemistry lesson up until the completion of this project, he has been almost a fatherly figure in our college careers, a gesture that we will always remember fondly. Without his guidance and friendship, this degree would have been impossible to complete. Although we regret never going ice climbing with him, we truly appreciate all the stories.

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# Introduction

Porous metal-organic frameworks (MOFs) are a class of highly-ordered crystalline solids that has attracted considerable attention over the last two decades.[1] MOFs are synthesized through the use of metal ions or clusters that coordinate to rigid organic ligands to form a continuous, multidimensional framework. These frameworks, otherwise known as coordination polymers, result in solids that are permeated by channels that impart permanent porosity.

MOFs can thought of as organic analogues of zeolites, which are inorganic porous solids usually consisting of alum-inosilicate minerals.[1] Both types of materials exhibit exceptionally high pore volumes and surface area. The contrasting factor is that MOFs, unlike zeolites, have the ability to be customized via modification to the organic ligands from which they are constructed. This key difference allows the structures and properties of MOFs (i.e. metal ions, ligand dimensions and, functional groups) to be tailored to specific applications. MOF materials and their customization seem only to be limited by the creativity and ingenuity of the chemists seeking to use these materials towards real world applications.

The MacDonald group has been focusing on the applications of MOFs towards environmental remediation by exploring the design of a class of MOFs that incorporate porphyrin ligands into the framework. Porphyrins belong to a class of compounds known as photosensitizers, which are dyes that absorb light in the UV and visible spectrum exciting them into their triplet state allowing for an energy transfer to free molecular oxygen resulting in the generation of singlet oxygen.[2] Singlet oxygen is a highly reactive species of free oxygen that is a means to oxidize or oxidatively decompose organic molecules containing susceptible unsaturated hydrocarbons. By synthesizing a sorbent material like a MOF containing theses photosensitizers built directly into the backbone of their structure, one can create a catalytic material capable of generating singlet oxygen in order to oxidatively decompose organic guest molecules that it may absorb, passively allow the product to pass through the material via its channels, and turn over to repeat the process with newly absorbed guests molecules.

It is known that porphyrins featuring four metal binding sites can form both two- and three dimensional MOFs in the presence of metals ions.[1] For example, meso-5,10,15,20-tetrakis(4- carboxyphenyl) porphyrin (TCPP) coordinates one metal ion at the center of the porphyrin ring and to two additional metal ions at each of the four carboxyl groups to form ordered sheets of porphyrin called paddlewheel layers.(11) In the absence of additional linking ligands, the paddlewheel layers stack at van der Waals contact distance to form a solid exhibiting low porosity. Addition of a linking ligand with two metal binding sites such as 4,4’bipyridine (BPY) leads to formation of highly porous three-dimensional frameworks with BPY acting as a bridging ligand between paddlewheel layers of TCPP.

Toward expanding on our research developing porous photosensitizing MOFs, this project focused on investigating generation and detection of singlet oxygen by MOFs and assessing how MOFs with different pore sizes compare in activity. Accordingly the aims of this project were the (1) preparation of porous MOFs containing a metalloporphyrin as the photosensitizer, (2) the investigation of a method to detect formation of singlet oxygen, (3) the characterization of the activity of MOFs toward generating singlet-oxygen in organic and aqueous media and (4) assessing the stability of MOFs toward degradation by singlet oxygen.

# Background

## Porous Solids

Porous Solids are a class of materials that have pores or channels permeating their structures with dimensions large enough to permit diffusion of guest molecules. These structures persist when guests or solvent molecules are completely removed. Such materials exhibit porosity (fraction of void volume to the total volume occupied by the material) that ranges widely from 0.2-0.95[3] as well as a correspondingly high surface area. These properties make porous solids the material of choice for applications involving molecular adsorption, storage and separation. One of the most well-known and widely used examples of a porous solid is Activated Carbon, which is used extensively in simple water filtration, catalysis and medical devices.

Porous solids that show irreproducible, non-repeating pores or channels are classified as disordered porous solids. Such solids have no defined structure, leaving the dimensions of their pores and void volumes as difficult to characterize. Ordered porous solids differ from disordered porous solids in that they exhibit well-defined pore structures, dimensions and topology that can be controlled and reproduced.[3]

A prime example of a class of ordered porous solids is inorganic zeolites. These materials are composed of hydrated, crystalline tectoaluminosilicates consisting of TO4 (T= Si, Al) tetrahedral bridged by oxygen atoms. Zeolites are widely regarded in the chemical industry as some of the most important heterogeneous catalysts given their selectivity character, thermal stability, ion exchange activity and crystalline properties.[4] As shown in Figure 1, zeolites have a wide variety of crystalline structures with different channel topologies as well as surface properties that can be controlled by varying the ratios of silicon to aluminum during synthesis. This variation of reagent ratios alters the arrangements of the sodalite cage, the repeating unit in zeolites. Zeolites possess a restricted range of pore sizes (4-12 Å) that only allow zeolites to act as porous hosts for ions and small organic molecules.

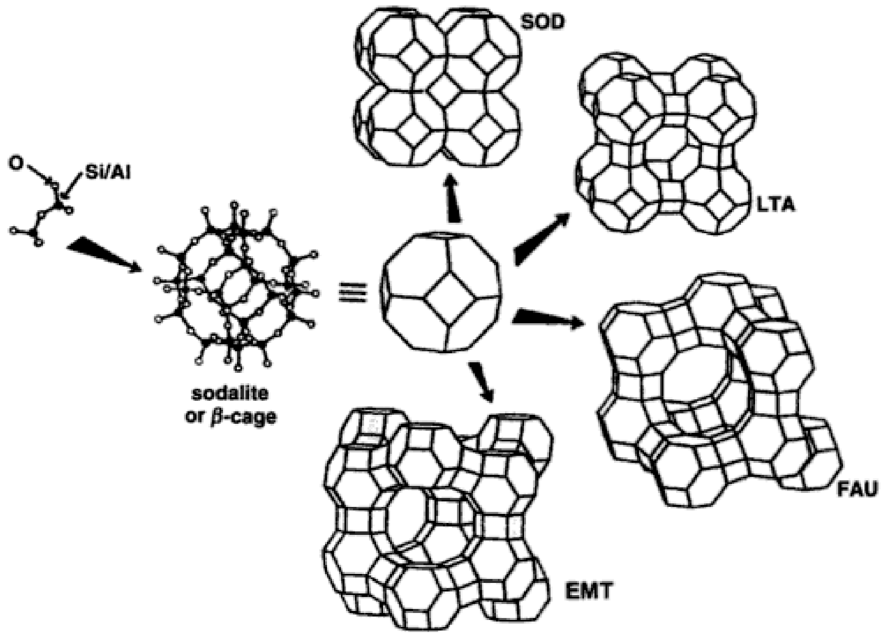

**Figure 1: Examples of several zeolite frameworks generated by different arrangements of sodalite cage**

## Metal-organic Frameworks

Metal-organic framework's (MOFs) are crystalline coordination polymers that consist of metal ions that coordinate with polyfunctional rigid organic ligands forming complexes that self-assemble into one-,two- or three dimensional frameworks. MOFs exhibit exceptional porosity and surface areas in comparison to zeolites and other porous materials. MOFs have shown to have surface areas in the range of 3000-4500 $m^2/g$ compared to most porous zeolites within the range of only 900 $m^2/g$[5]. It is these properties that allow for high accessibility for organic guest molecules within the channels of MOFs compared to zeolites.[4] Because organic molecules are the building blocks used to assemble MOFs, the structures and properties of MOFs can be tuned to a multitude of different dimensions and topologies as well as exhibit different catalytic, chemical, and physical properties. Isoreticular MOF-5 (IRMOF-5), first synthesized by Omar Yaghi in 1999, is perhaps the most well-known example of a highly porous and stable MOF with cubic architecture that serves as a standard to which the porous properties of all new MOFs are compared.[5] IRMOF-5 consists of 1,4-benzenedicarboxylic acid (BDC) ligands that coordinate to tetrahedral clusters of four zinc (II) ions. As shown in Figure 2, lengthening the di-acid ligand preserves the topology and cubic symmetry of IRMOF-5, allowing for channels with larger dimensions to be designed. This modularity with respect to the linking ligand gives rise to family of MOFs similar in crystal structure to IRMOF-5 that exhibit larger pore and channel dimensions, larger void volumes, and corresponding lower surface area. Functionality can also be introduced on the BDC ligand without altering the cube structure of IRMOF-5. Substituents such as bromine or amine groups present on the MOF backbone protrude into the channels making it possible to alter the surface properties and to introduce chemically reactive functional groups inside the void volume of the MOF where additional functionality can be introduced via post-synthetic modification.[5]

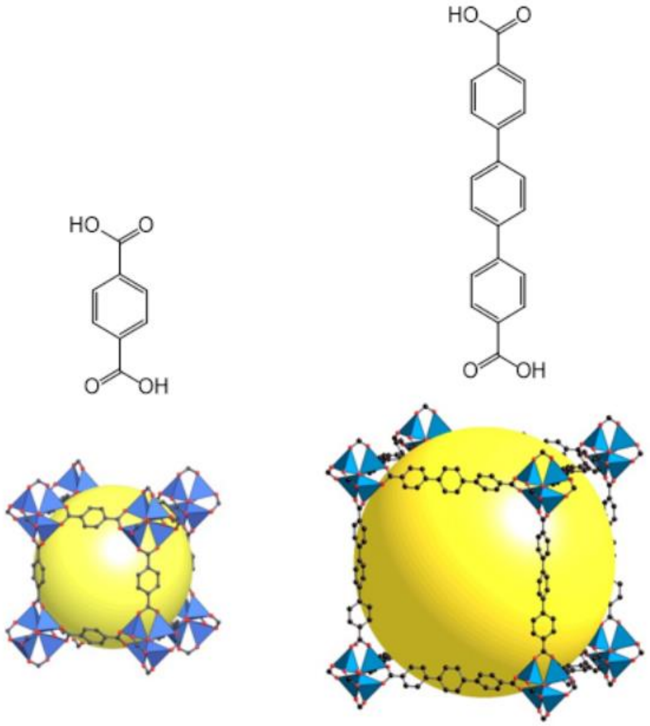

**Figure 2: Comparison of cubic structures of IRMOFs formed.**

## Singlet Oxygen

Singlet oxygen is the electronically excited state of molecular oxygen which became the focus of intense study after Khan and Kasha discovered the cause of the chemiluminescence liberating from the hypochlorite-peroxide reaction in 1963.[6] This highly reactive form of oxygen has been widely used for applications in photo oxidation, photodynamic therapy of cancer and polymer science.[2]

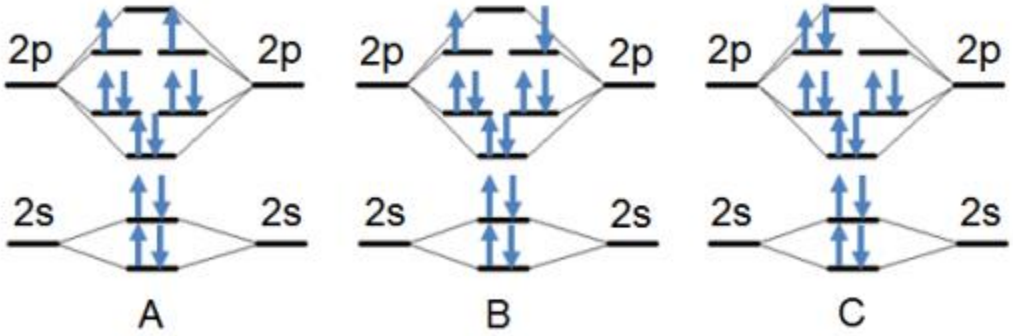

**Figure 3: Molecular Orbital Diagrams of A) Triplet Oxygen, B) Singlet Oxygen (Excited State), and C) Singlet Oxygen (Relaxed State)**

The normal and the most stable state for molecular oxygen is the ground-state, also called the triplet state. This triplet state has an electron configuration as shown in Figure 3. The point of interest is in the spin directions of the valence electrons. Singlet oxygen is created when one electron in the p-orbital of the triplet state is excited by an energy packet to cause it to flip the spin state. This causes a new total spin state of S=0, which is known as the singlet state and causes the oxygen molecule to be more unstable and therefore more reactive.[2] This excited state of oxygen has the ability to rapidly react with unsaturated carbon-carbon bonds, sulfides, amines and more. As described later in the report we take advantage of porphyrins in the backbone of MOFs to generate singlet oxygen to oxidize organic contaminants absorbed in the MOF.

## Porphyrins as Photosensitizers

Compared with other photosensitizers, porphyrins are regarded as one of the best singlet oxygen generating species. Porphyrins boast high quantum yields, long-lived triplet states and the ability to absorb various wavelengths of light in the UV and visible regions of the electromagnetic spectrum.[7] The large molecular size of porphyrins also offers the ability to synthesize MOFs with large pores, which enhances the ability to absorb organic quenchers into the MOFs' channels.[8] However, porphyrins also decompose with the appearance of singlet oxygen, a phenomenon known as photobleaching.[7]

Once oxygen is converted to its singlet excited state by the porphyrin, other molecules can deactivate it and bring it back to the triplet state. This process, known as quenching, has two main pathways: physical quenching and chemical quenching. During the physical quenching process, energy transfer reactions deactivate singlet oxygen without any new products, and during chemical quenching, singlet oxygen reacts with quenchers (e.g., organic compounds) to generate oxidation products. Chemical quenching of singlet oxygen can occur by two different pathways referred to as type I and type II mechanisms. Type I mechanism involves either the abstraction of a hydrogen atom or the transfer of an electron between the excited substrate and the substrate, yielding a free radical.[7] We are interested in the Type II mechanism, which involves the generation of singlet oxygen through an energy transfer between the excited sensitizer and triplet oxygen during a collision. We have been exploring the synthesis of MOFs that incorporate photosensitizers into the framework to take advantage of that mechanism. This would allow the backbone of the MOF itself to generate singlet oxygen through photoexcitation. The general approach utilized in this study is illustrated below in Figure 4.

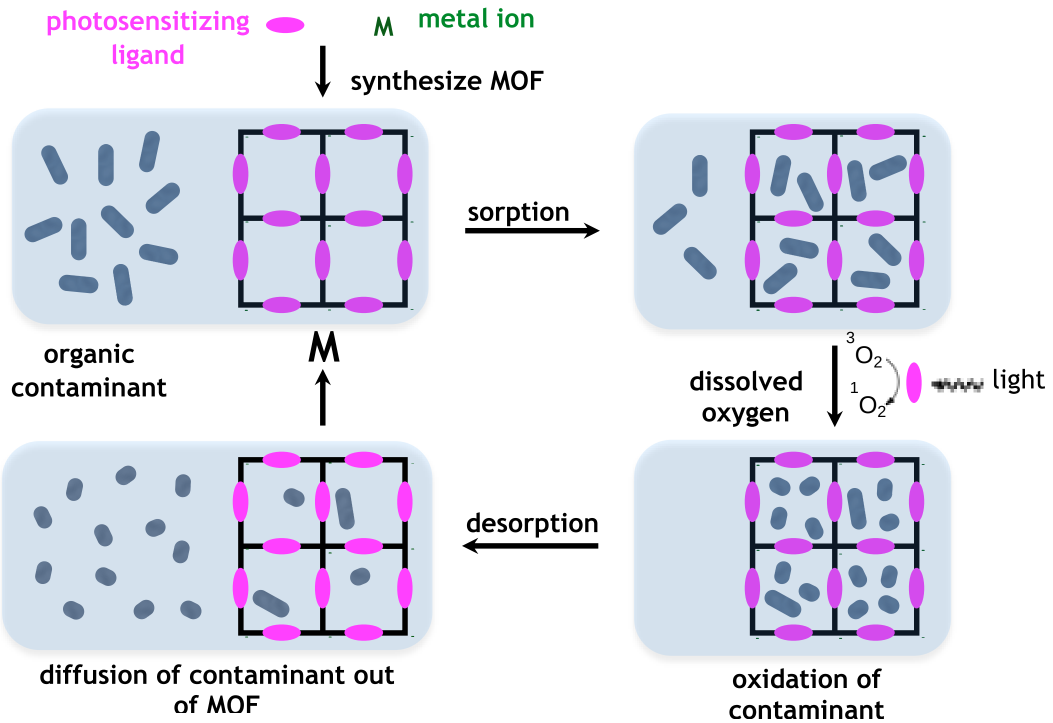

Figure 4: General approach depicting the synthesis of the MOF with a photosensitizing ligand (top left), the sorption of organic contaminants (top right), the generation of singlet oxygen and the oxidation of said organic contaminants (bottom right) and desorption of oxidized products (bottom left).

# Experimental and Characterization

## Synthesis

Reagents and solvents were purchased from Alfa Aesar, Acros, Frontier Scientific or Pharmco and used without further purification.

### Synthesis of MOFs in One Step

The following metal-organic frameworks were synthesized using the method described by Choe's group.[9],[10]

Zn-TCPP-BPY MOF 1 Synthesis (One-Step Method)

Zinc nitrate hexahydrate (8.2mg, 0.03 mmol), 5,10,15,20-tetra(4-carboxyphenyl)porphyrin (7.9 mg, 0.01 mmol), and 4,4'-bipyridine (3.1 mg, 0.02 mmol) were mixed in a molar ratio of 3:1:2 in a solution of dimethylformamide (1.5 mL) and ethanol (0.5 mL), sealed in a high-pressure glass microwave vial, heated in an oven at 80 °C for 24 hours, after which the oven was turned off and the solution allowed to cool slowly to room temperature. Deep red square blocks were formed. The crystals were filtered out using a Buchner funnel and washed with dimethylformamide until the filtrate became clear.

Co-TCPP-BPY MOF Synthesis (One-Step Method)

Cobalt (II) nitrate hexahydrate (8.7 mg, 0.03 mmol), 5,10,15,20-tetra(4-carboxyphenyl) porphyrin (7.9 mg, 0.01 mmol), and 4,4'-bipyridine (3.1 mg, 0.02 mmol) were mixed in a molar ratio of 3:1:2 in A solution of dimethylformamide (1.5 mL) and ethanol (0.5 mL), sealed in a high-pressure glass microwave vial, heated in an oven at 80 °C for 24 hours, after which the oven was turned off and the solution allowed to cool slowly to room temperature. Deep red square blocks were formed. The crystals were filtered out using a Buchner funnel and washed with dimethylformamide until the solution became clear.

### Synthesis of MOFs in Two Step

The following metal-organic frameworks were synthesized using the method described by Hupp's group.[11]

Zn-TCPP-BPY MOF 2 Synthesis (Two-Step Method)

Zinc nitrate hexahydrate (17.8 mg, 0.06 mmol), 5,10,15,20-tetra(4-carboxyphenyl) porphyrin ( 11.8 mg, 0.015 mmol) were mixed in dimethylformamide ( 2 mL) and sealed in a microwave vial. The vial was heated in an oven at 80 °C. In a small beaker, 4,4'-bipyridine (2.3 mg, 0.015 mmol) was dissolved in EtOH (2 mL). After 2 hours the vial was unsealed and the EtOH solution was added with 5 drops of Nitric Acid (HNO3). The vial was sealed again and heated in the oven at 80 °C for 24 hours, after which the oven was turned off and the solution allowed to cool slowly to room temperature. Deep red square blocks were formed. The crystals were filtered out using a Buchner funnel and washed with dimethylformamide until the solution became clear.

### Zn-TCPP-Pyrazine MOF Synthesis (Two-Step Method)

Zinc nitrate hexahydrate (17.8 mg, 0.06 mmol), 5,10,15,20-tetra(4-carboxyphenyl) porphyrin ( 11.8 mg, 0.015 mmol) was dissolved in dimethylformamide (2 mL) and sealed in a microwave vial. The vial was heated in an oven at 80 °C. In a small beaker, 4,4'-bipyridine (2.3 mg, 0.015 mmol) was dissolved in EtOH (2 mL). After 2 hours the vial was unsealed and the EtOH solution was added with 5 drops of Nitric Acid (HNO3). The vial was sealed again and heated in the oven at 80 °C for 24 hours, after which the oven was turned off and the solution allowed to cool slowly to room temperature. Large deep red square blocks were formed. The crystals were filtered out using a Buchner funnel and washed with dimethylformamide until the solution became clear.

### Zr-TCPP MOF Synthesis

The following method for synthesis was adapted from Zhao's group[12]. Zirconium(IV) chloride,anhydrate (7 mg) and 5,10,15,20-tetra(4-carboxyphenyl)porphyrin (10 mg) were and mixed into 2 mL of dimethylformamide solution in a microwave vial with 7 drops of acetic acid. The vial was sealed and was sonicated until all chemicals were dissolved. After 30 minutes of sonication, the vial was placed into an oven at 120 °C for 24 hours. The solution was then slowly cooled to room temperature until small red crystals were formed. The crystals were filtered out using a Buchner funnel and washed with dimethylformamide until the solution was clear.

## Characterization

Samples of MOF crystals were characterized using a combination of optical microscopy, thermos-gravimetric analysis (TGA) and powder X-ray diffraction (PXRD. Bulk samples of all crystals were isolated and examined under a low-power optical polarizing stereomicroscope to determine the homogeneity of samples based on crystal morphology.

### Thermogravimetric Analysis (TGA)

Samples of all crystals were analyzed by TGA to determine if crystalline samples were porous and to quantify the amount of guest solvent contained within MOFs based on loss of mass during heating. Analysis by TGA was carried out using a TA Instruments 2920 thermo-gravimetric analyzer. Bulk samples of crystals (5-10 mg) were placed in

Pt sample pans and then heated from RT to 700°C at a rate of 10 °C /min under a nitrogen atmosphere.

### Powder X-ray Diffraction Analysis

PXRD data was collected on a Bruker-AXS D8-Advance diffractometer using Cu-Kα radiation with X-rays generated at 40kV and 40mA. Bulk samples of crystals were placed in a 20 x 16 cm x 1 mm well in a glass sample holder and scanned at RT from 3-60° (2θ) in 0.05° steps at a scan rate of 2°/min.

## Methodology for Monitoring Generation and Detection of Singlet Oxygen

To determine whether irradiating the MOF produced singlet oxygen we chose 1,3-diphenylisobenzofuran (DPBF) to serve as a model contaminant. In contact with singlet oxygen, DPBF is oxidized into the endo-peroxide and ultimately into the di-keton as shown in Figure 6. The concentration of DPBF can therefore be measured by the absorbance peak at 415 nm as seen in Figure 5. As DPBF gets oxidized the amount of conjugation in the pi system is reduced such that its absorbance band undergoes a hypsochromic shift to shorter wavelength in the UV region.

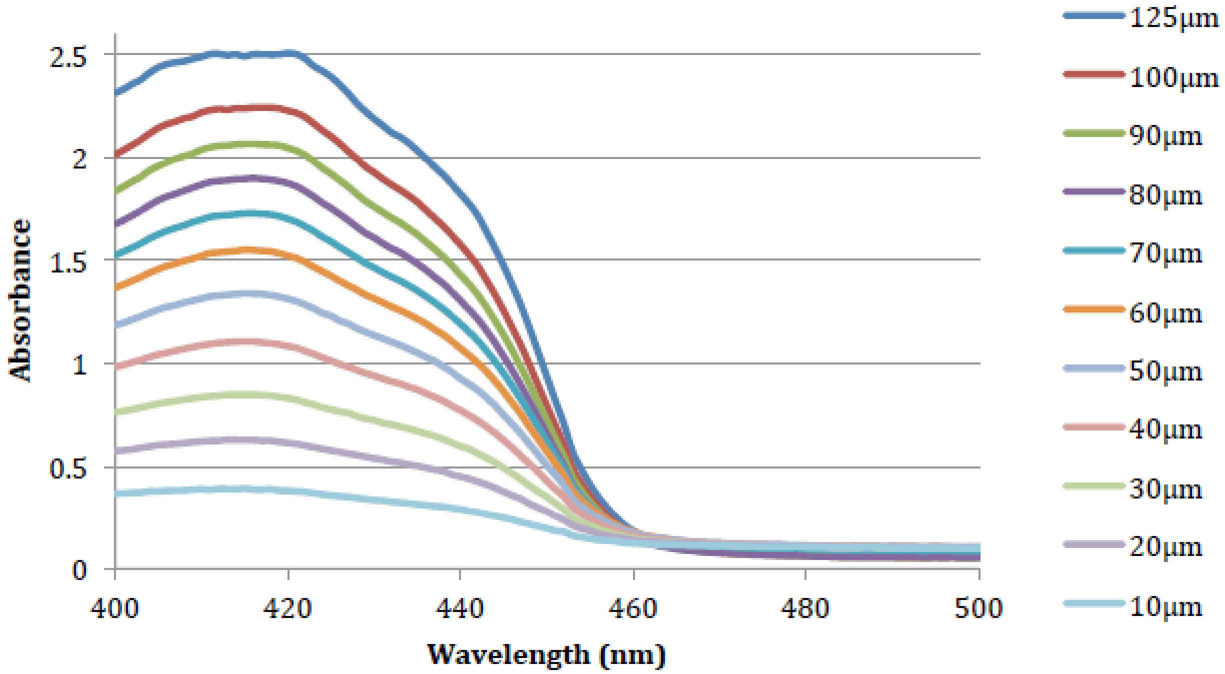

Figure 5: Calibration curve for DPBF in decreasing concentrations in DMF.

The generation of singlet oxygen can be measure indirectly as a function of the concentration of DPBF over time. For this hypothesis to be true we are assuming that singlet oxygen lifetime is fast and the overall concentration of DPBF is much larger than the concentration of singlet oxygen in any given time.

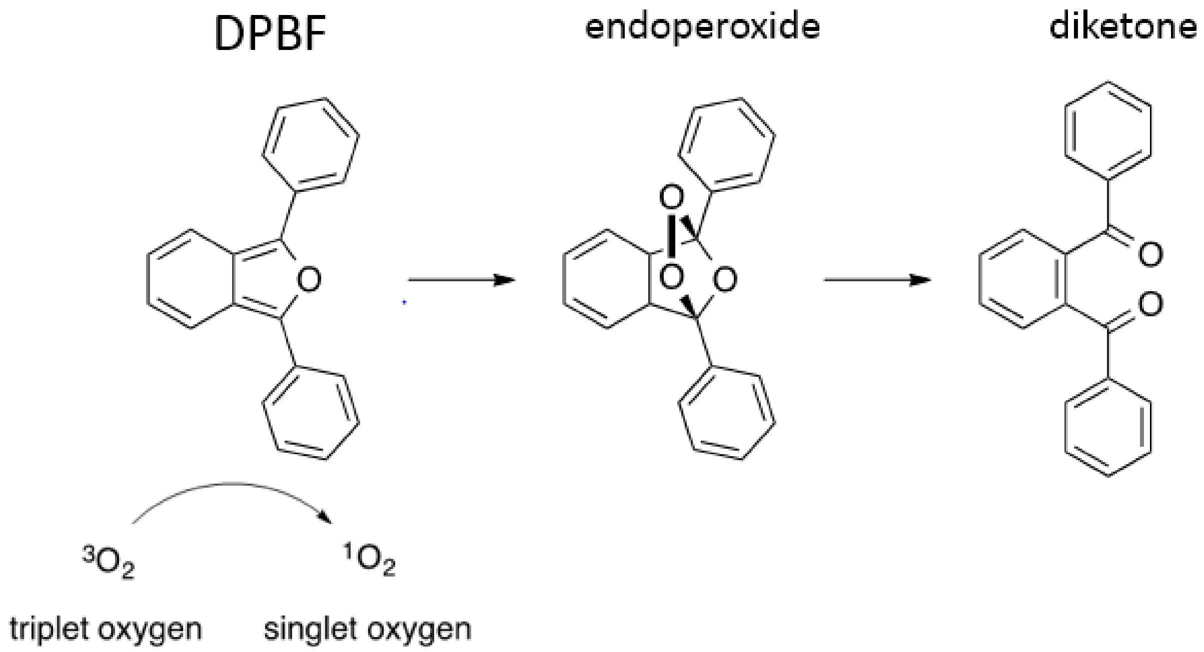

**Figure 6: Reaction pathway for DPBF in presence of singlet oxygen.**

## DPBF degradation by Light and Heat

DPBF degrades slowly upon direct exposure to ultraviolet light and temperatures above 25 °C. All beakers and vials used to handle DPBF solutions were wrapped in aluminum foil and stored in the refrigerator. Solutions of DPBF were also a periodically tested by UV-Visible spectroscopy to confirm the concentration of DPBF present in solution.

## Preparation of MOF Samples

MOF crystals recovered from solutions subjected to hydrothermal synthesis were washed with DMF until the filtrate appeared clear to residual starting materials that might affect the spectrophotometer readings. The crystals were air dried on filter paper and then crushed with a mortar and pestle to break up large crystals and form powders.

## Irradiation of Samples

As shown in Figure 7, a 60 watt Xenon lamp was used as the light source to irradiate MOF particles in solutions of DMF containing DPBF as a guest contaminant susceptible to oxidation by singlet oxygen to assess the activity of the MOF. The lamp was placed behind a 480 nm cut-off filter to prevent degradation of the DPBF through exposure to ultraviolet light. This filtered light was reflected off a right angle mirror to irradiate the surface of the solution contained in a 100 mL beaker resting on a stir plate. This experimental set up was housed in a dark, curtained room and the outside of the beaker was covered in aluminum foil to eliminate exposing the MOF and DPBF to light from outside sources.

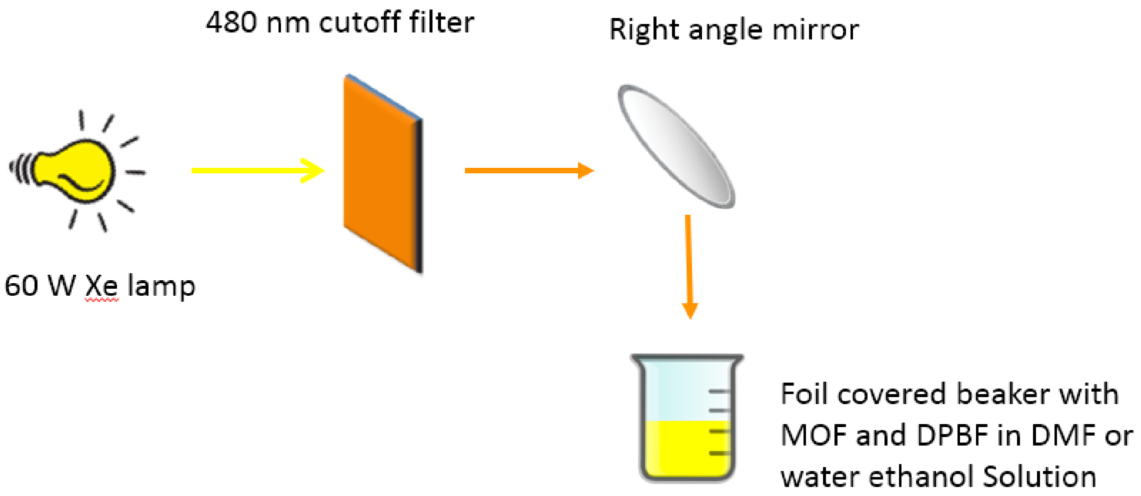

**Figure 7: Illustration for the setup used to photo-excite the MOF materials and monitor generation of Singlet Oxygen**

To determine whether irradiating the MOF produced singlet oxygen and to quantify the rate of reactivity of singlet oxygen with DPBF, 50 mL of 100 μM DPBF in DMF solution containing 40 mg of MOF crystals were irradiated and the concentration of DPBF monitored as follows. The solutions were stirred and irradiated continuously under the xenon lamp for a maximum of 140 minutes. Aliquots of 3 mL of the solution were removed by syringe at either 10 or 3 minute intervals, the solutions were passed through a 0.2 micron filter to remove MOF particles, and the absorbance was measured using UV-Visible spectroscopy to determine the concentration of DPBF remaining in solution. Upon removal from the reaction flask the samples were stored and transported in 5 dram vials covered in aluminum foil to minimize exposure to ambient UV Light prior analysis by UV-Visible spectroscopy.

To determine whether irradiating the MOF produced singlet oxygen in aqueous solution, the same set up and procedures were followed with only two differences: a 50 μM DPBF solution 8:2 EtOH/Water solution was used instead of the DMF solution and 20 mg of MOF samples instead of 40mg. As DPBF shows lower solubility in EtOH/water solution, the solution was sonicated for 30 minutes before the test to ensure that all of the DPBF had dissolved.

## Degassed Irradiation

To determine if singlet oxygen was responsible for degradation of DPBF and not by any other species, the experiments described previously were carried out in solutions degassed with nitrogen to remove dissolved oxygen. The same setup was used but instead an Erlenmeyer flask with a seal and two tubes was used as shown in Figure 8. Nitrogen gas was bubbled into the solution with DPBF and MOF crystals for one hour to remove all dissolved oxygen. For the second test, the same setup was used but the Erlenmeyer flask had no stopper to permit oxygen dissolve back into the solution.

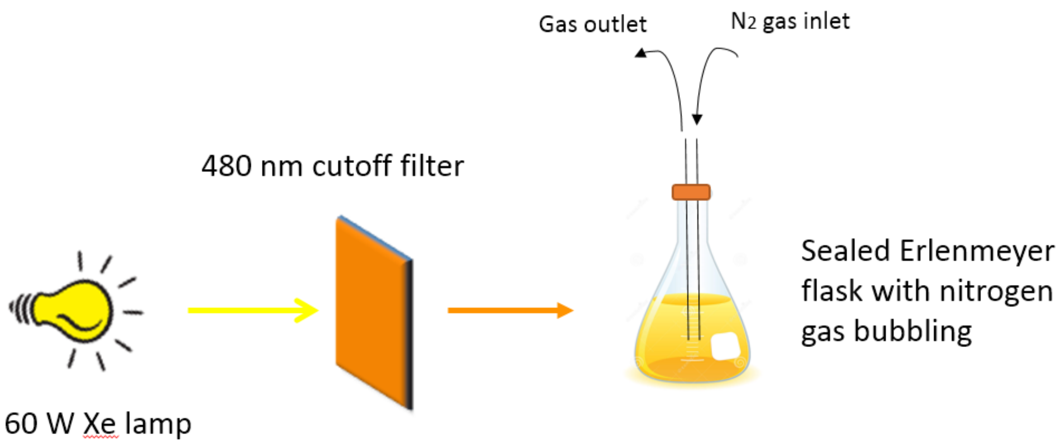

**Figure 8: Illustration for the setup used to photo-excite the MOF materials and monitor generation of Singlet Oxygen under degassed solutions.**

## Stability Studies

Two experiments were carried out to test how stable the MOFs are in regard to their singlet oxygen generating activity. It is well known that porphyrins react with the singlet oxygen they produce degrading their ability to produce singlet oxygen, a phenomenon known as photobleaching.[13] We hypothesized that embedding the porphyrin within a rigid structure such as a MOF might protect it from photo-bleaching. The first experiment consisted of irradiating a solution of 50 micro molar TCPP in DMF for 100 hours taking aliquots every 10 hours and measuring the concentration using UV-Visible spectroscopy. The test was run until the solution became clear and all of the TCPP had photo-bleached to determine the timeframe for complete degradation of TCPP free in solution.

In the second experiment, 40 mg of Zn-TCPP-BPY MOF 1 in 50 mL of DMF was irradiated continuously with the 60 Watt Xenon Lamp. For increasing periods of time an aliquot of 3 mL was extracted with a syringe and its activity was tested by putting the sample in a quartz cuvette, adding DPBF to make a 100 micro molar solution and irradiating the sample for 25 minutes. Based on the results from the singlet oxygen generation experiments for Zn-TCPP-BPY MOF 1 described above, irradiation for 25 minutes would correspond to 50% degradation of DPBF if no degradation of the embedded porphyrin occurs and full activity is maintained throughout the duration of the experiment. If the MOF loses activity due to degradation of porphyrin within the MOF by singlet oxygen, the percentage of DPBF degraded will decrease with time.

# Results and Discussion

## Zn-TCPP-BPY MOFs 1 and 2

Two methods were used to grow Zn-TCPP-BPY MOF as shown in Figure 9 and Figure 10. Choe's method used a single hydrothermal step procedure that formed thin plate crystals with large paddlewheel layers that exhibit a mixture of small channels with large channels. The BPY on this structure, according to the solved crystal structure acquired from using single-crystal X-ray diffraction (SXRD), links the Zn metal center within the porphyrin with a metal cluster and links metal cluster another metal cluster. This creates smaller channels 10 Å in diameter and larger channels 14 Å in diameter as shown in the crystal structure in Figure 9.

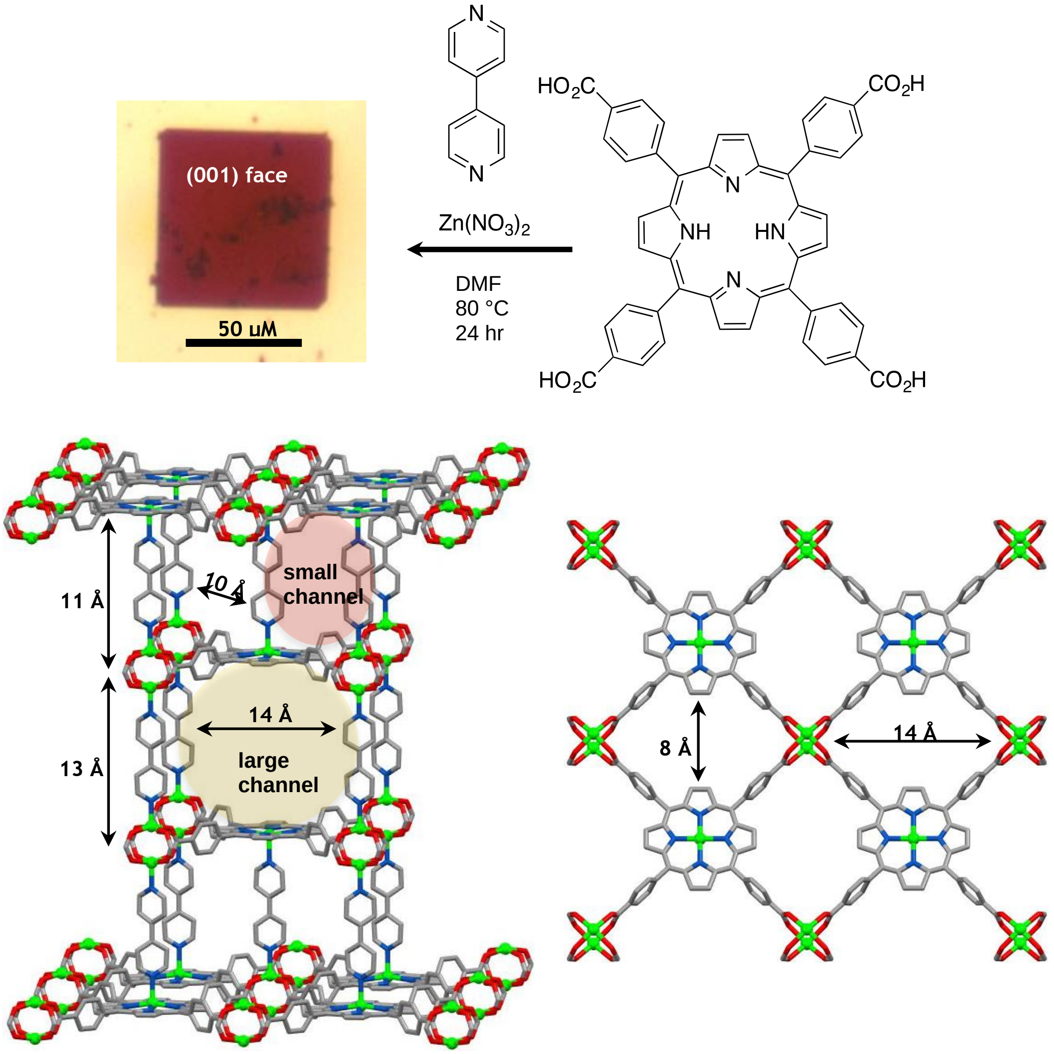

Figure 9: (Top) One step procedure for Zn-TCPP-BPY MOF used by Choe's group and (Bottom) an illustration of the two and three dimensional layers that are formed as TCPP binds with metal ions (Green) through coordination with the carboxylate groups (Red).

Hupp's method of synthesis on the other hand was a two-step hydrothermal procedure that allowed single Zn-TCPP layers to form in the first step and followed by addition of BPY to link layers of Zn-TCPP. This two-step method of synthesis generated larger crystals compared to the one-step method, and resulted in slightly different connectivity between adjacent linked layers of Zn-TCPP such that only small 10 Å channels formed as shown in Figure 10. The key difference in this structure compared to the previous structures is the Zn ion within the porphyrin coordinates to two BPY ligands, one on each side of the porphyrin ring instead of coordinating to just one BPY ligand on one side of the porphyrin ring. This difference in connectivity between the Zn ions in adjacent Zn-TCPP layers results smaller channels of uniform dimension. The layers of Zn-TCPP are offset such that the center of the porphyrin aligns with the metal cluster in adjacent layers. On Choe's method layers alternate from stacking porphyrin on top of porphyrin and porphyrin on top of metal clusters.

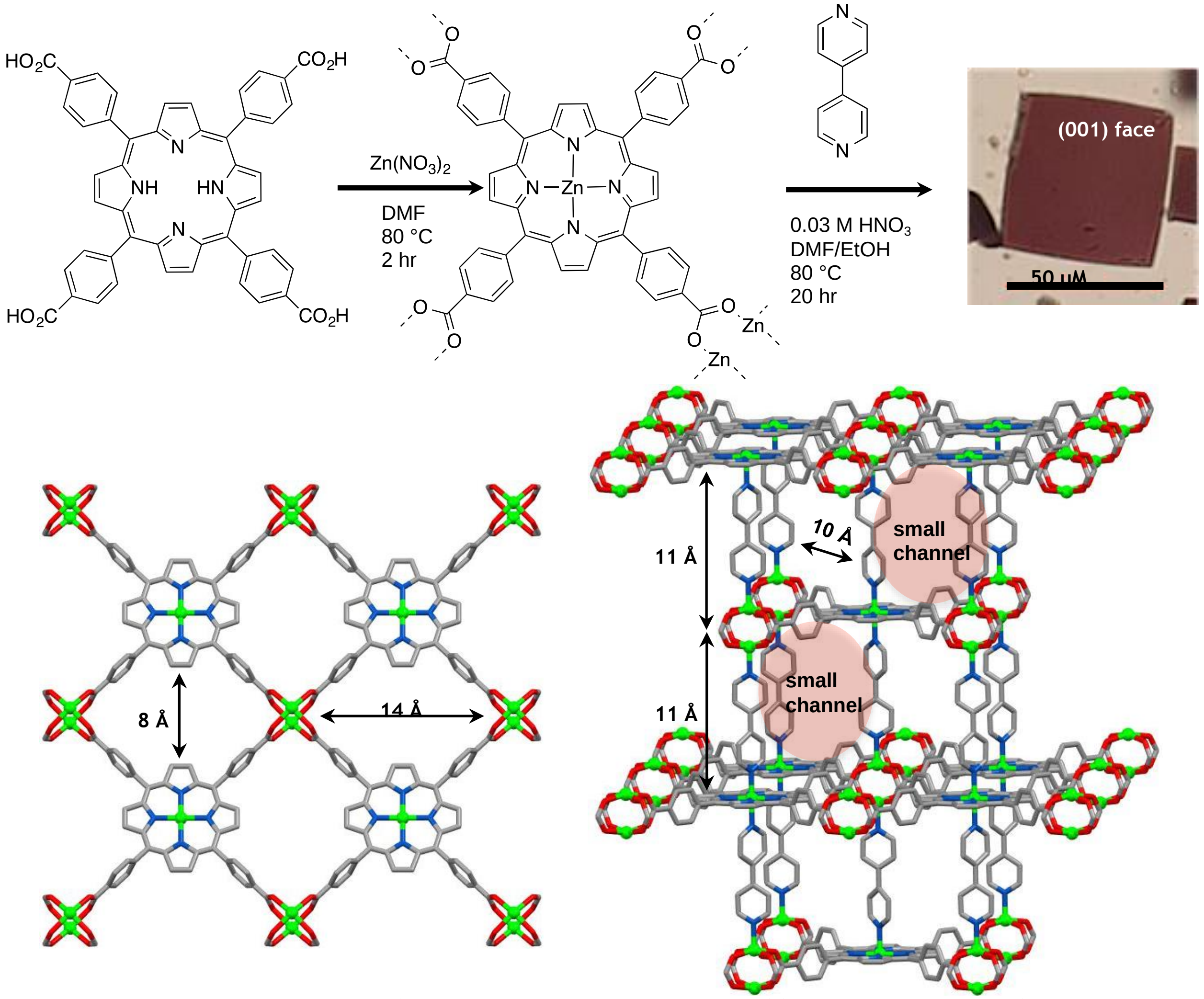

**Figure 10: (Top) One step procedure for Zn-TCPP-BPY MOF used by Hupp's group and (Bottom) an illustration of the two and three dimensional layers that are formed as TCPP binds with metal ions (Green) through coordination with the carboxylate groups (Red).**

Although the crystal structures (SXRD) of the two isomeric MOFs clearly show the porous nature of the materials, thermogravimetric analysis (TGA) was performed on both MOFs to further confirm the porosity and to assess any difference in void volume based on loss of mass of DMF solvent contained within the void spaces. As shown in Figure 11, both Zn-TCPP-BPY MOFs show an initial mass loss of approximately 55% before plateauing at 150 °C near the boiling point of DMF (153 °C) followed by an additional loss of approximately 5% of mass between 150-400 °C, and finally an additional loss of approximately 20-25% of mass above 400 °C corresponding to decomposition of the MOFs. The initial rapid mass loss of approximately 55% below 150 °C corresponds to loss of guest DMF trapped within the channels of both MOFs during synthesis and/or subsequent washing of the MOF crystals with DMF and provides direct evidence of the porous nature of both MOFs and that DMF solvent can diffuse through the void spaces created in the channels of both structures. Moreover, the data for the Zn-TCPP-BPY MOF with larger 14 Å channels shows approximately 3% greater loss in mass compared to the MOF with smaller 10 Å channels, indicating that a slightly greater void volume that accommodates more DMF as guest in accordance with the crystal structure.

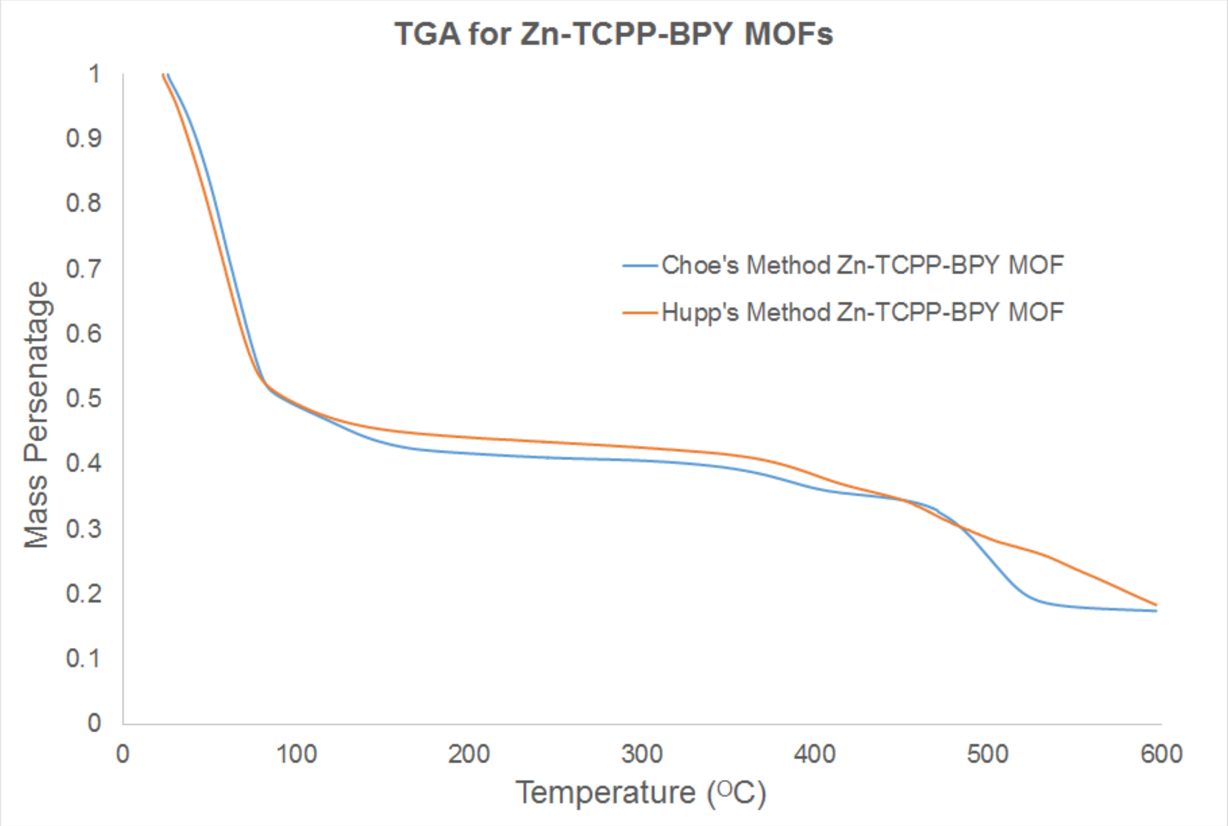

**Figure 11: Thermo-Gravimetric Analysis comparing Choe's and Hupp's method for the synthesis of Zn-TCPP-BPY**

Powder X-ray diffraction data (PXRD) was collected for both MOF’s and compared. Major peaks at 8, 10 and 13 theta match up but the overall conclusion was that the two synthesis methods did not produce structures that produce a clean PXRD, so there is not enough detail to distinguish them.

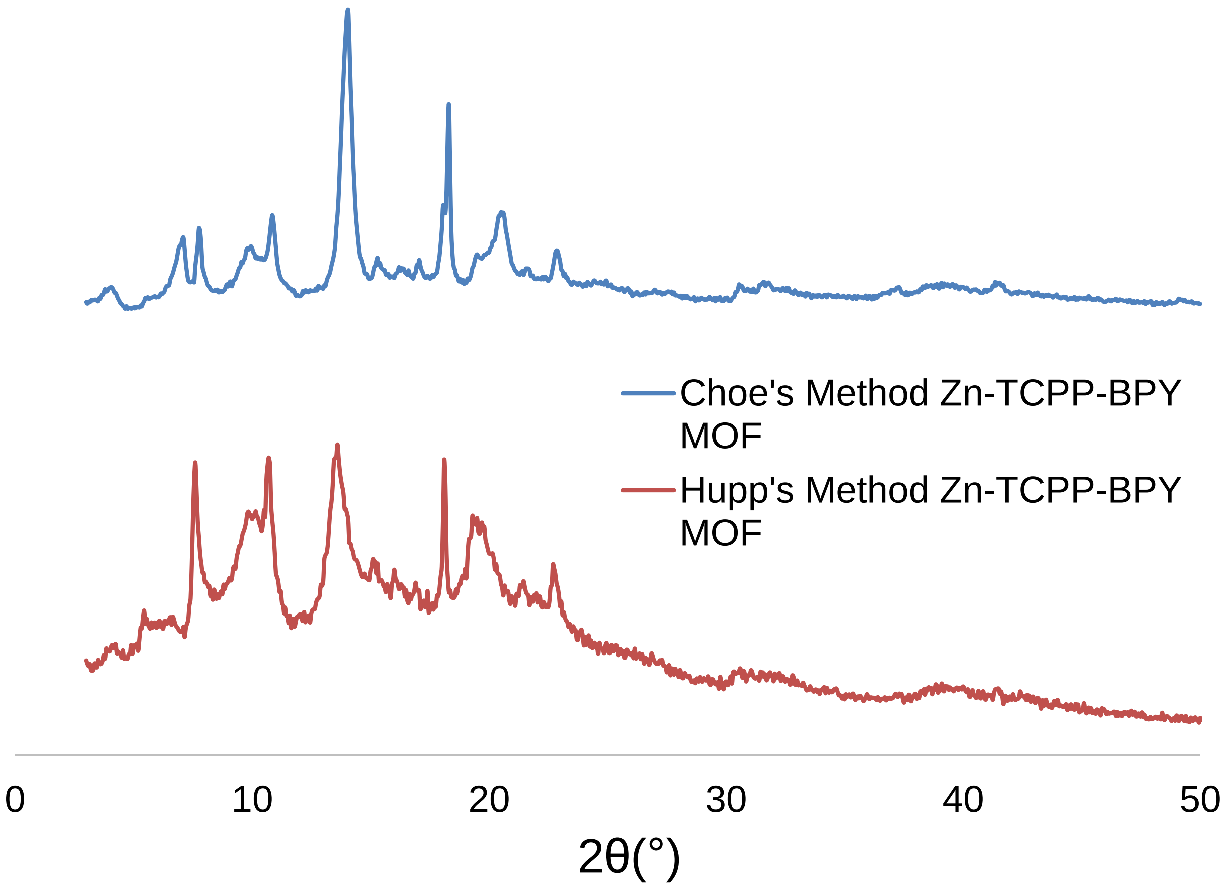

**Figure 12: Powder X-Ray Data comparing Choe's and Hupp's method for the synthesis of Zn-TCPP-BPY**

## Zn-TCPP-Pyrazine

One of the goals of this project was to grow MOFs with different size channels and compare their activity toward generating singlet oxygen. Pyrazine was chosen as ligand to link adjacent Zn-TCPP layers with smaller spacing between the layers in order to create channels with smaller diameters compared to those in the MOFs of Zn-TCPP-BPY. For the Zn-TCPP-Pyrazine the same two-step hydrothermal method was used to synthesize the MOF with pyrazine replacing BPY. This synthesis generated extremely small microcrystals that even an extended cooling down time and different solvents did not produce single crystals large enough to collect SXRD data and solve the crystal structure of the MOF.

TGA data was collected to determine if the MOF showed loss of mass corresponding to guest solvent as evidence that the MOF solid was porous. Figure 13 shows a steep decline in the first 100 C up to a mass loss of approximately 40%, could corresponds to loss of DMF solvent from the structure. Between 100C and 220C there is an additional mass loss of 10% likely indicates loss of pyrazine from the structure given the two plateaus and that the boiling point of pyrazine is 115 °C. The mass of the crystal appears constant until decomposition of the MOF occurs at 460 C. The large initial loss in mass of 40% and overall thermal stability above 400 °C provide compelling evidence that the solid is porous and likely a Zn-TCPP-Pyrazine MOF.

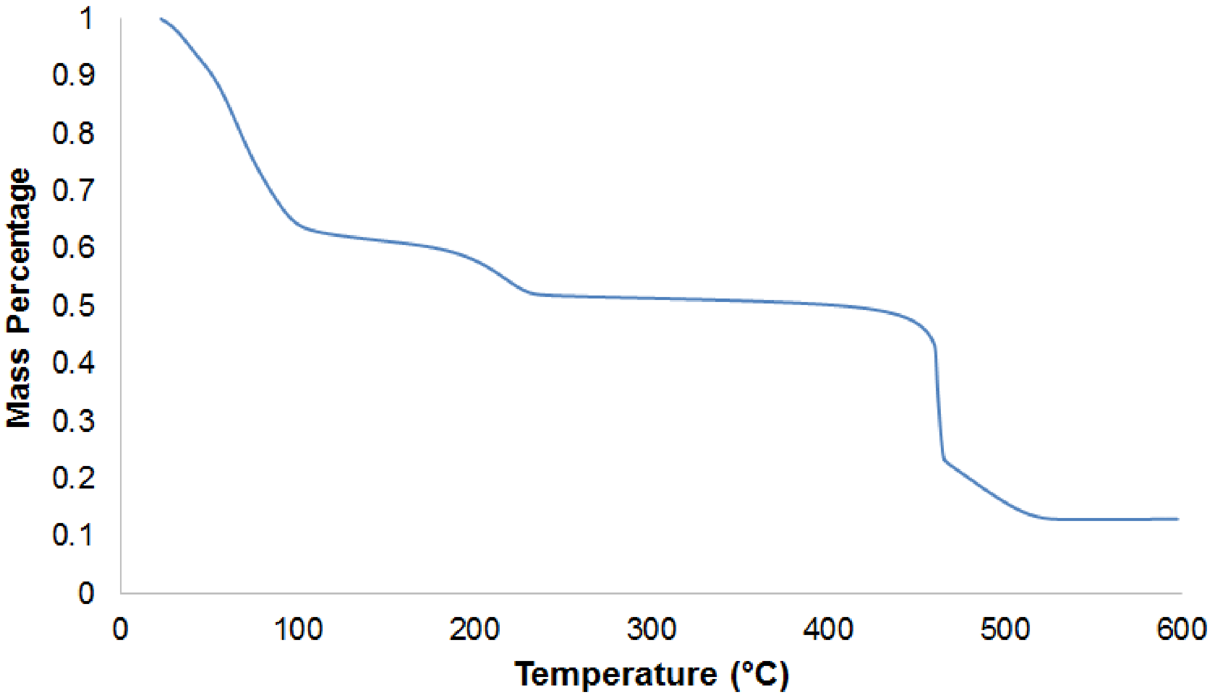

**Figure 13: Thermo-Gravimetric Analysis (TGA) for Zn-TCPP-Pyrazine MOF**

The Zn-TCPP-Pyrazine crystals were activated for 2 hours at 200 °C to examine the change that appears in the TGA data and the PXRD was gathered before and after activation. The MOF appears to go through a structure change as many of the peaks seen in Figure 14 disappear. This data further supports the hypothesis that the Zn-TCPP-Pyrazine MOF loses the pyrazine ligand upon heating and undergoes a structure change at 200C and therefore exhibits lower stability compared to the Zn-TCPP-BPY MOFs. The structure change could be due to pyrazine detaching from the structure and collapsing the Zn-TCPP layers. For this reason the Zn-TCPP-Pyrazine MOF was not chosen for further study.

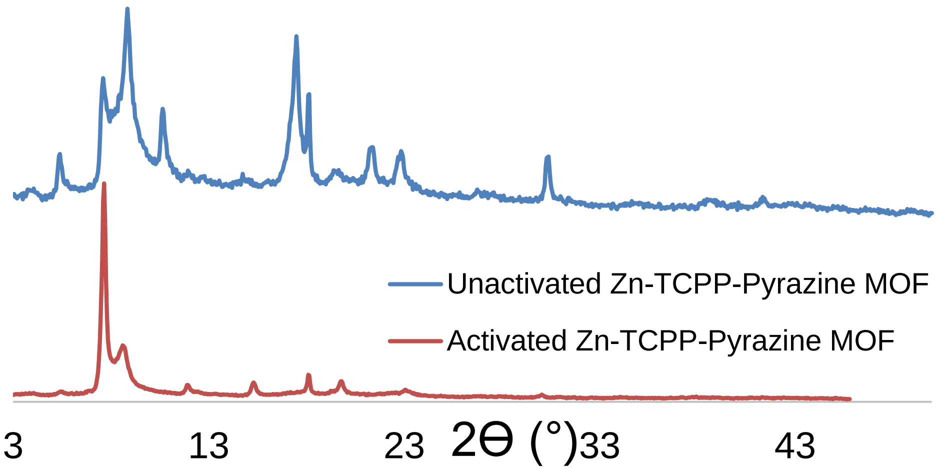

**Figure 14: Powder X-Ray Data for Zn-TCPP-Pyrazine MOF after synthesis and after being activated at 200C for two hours.**

## Zr-TCPP

The Zr-TCPP MOF was grown by Zhou's group as a more thermally stable MOF resulting from stronger binding of the carboxylate groups on the TCPP ligand to the Zr(IV) cations. The illustration in Figure 15 taken from Zhou's paper shows that the Zr-TCPP MOF exhibits a cubic structure with each red square representing a porphyrin and with an extremely large pore size of 19.5 Å. Each TCPP ligand connects with 4 zirconium metal ion clusters, resulting in channels that vary in diameter and that are 14 Å by 7 Å in the narrowest dimension.[12]

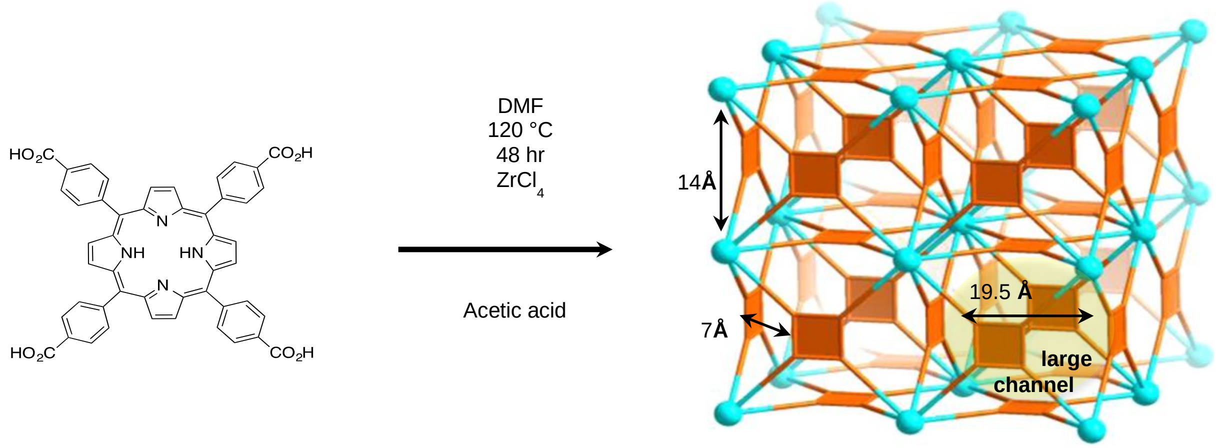

**Figure 15: Synthesis of Zr-TCPP and illustration of the cubic structure[12]**

Growth of MOF crystals following the reported method provided very small microcrystals, which made it difficult to completely dry samples of crystals free from surface-bound solvent even after drying samples for 20 minutes via vacuum filtration. For this reason the crystals were heated in an oven at 100 °C for 10 minutes to remove any surface solvent before acquiring TGA data. As shown in Figure 16, crystals of Zr-TCPP MOF lose approximately 40% of total mass as guest DMF solvent by 150 °C, followed by an additional 10% of mass until decomposition at 470 C. This date provides supporting evidence that the Zr-TCPP MOF is porous and exhibits high thermal stability.

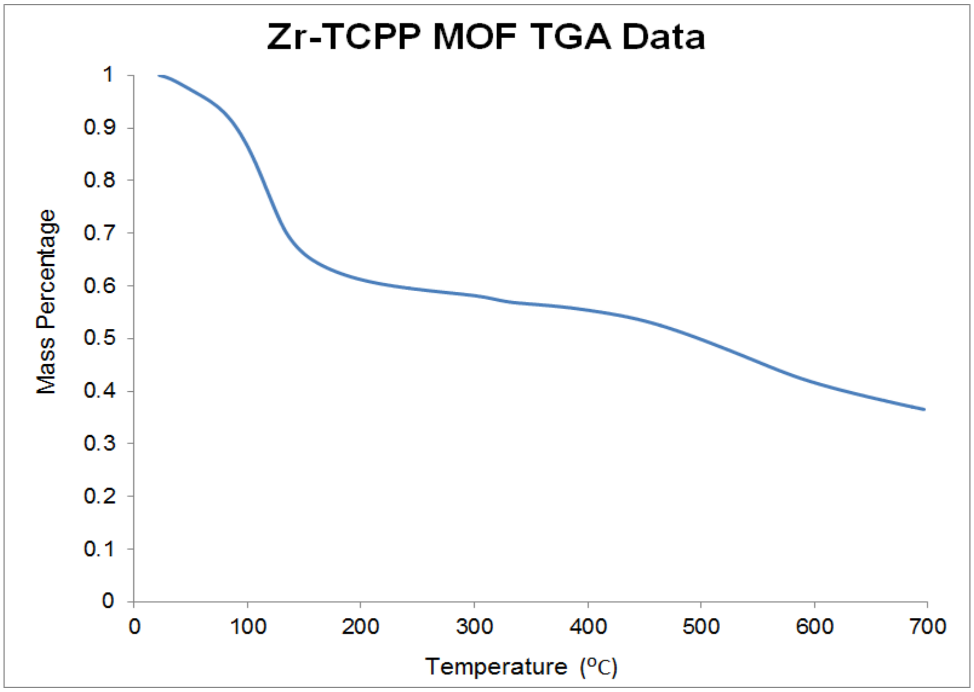

Figure 16: TGA data for Zr-TCPP after being activated for 2 hours in 100 C

The PXRD data acquired experimentally from the synthesis of Zr-TCPP was compared to the calculated PXRD data from Zhao's structure. As seen in Figure 17 most if not all of the major peaks line up with the calculated providing supporting evidence that the Crystals grown have the cubic structure shown before.

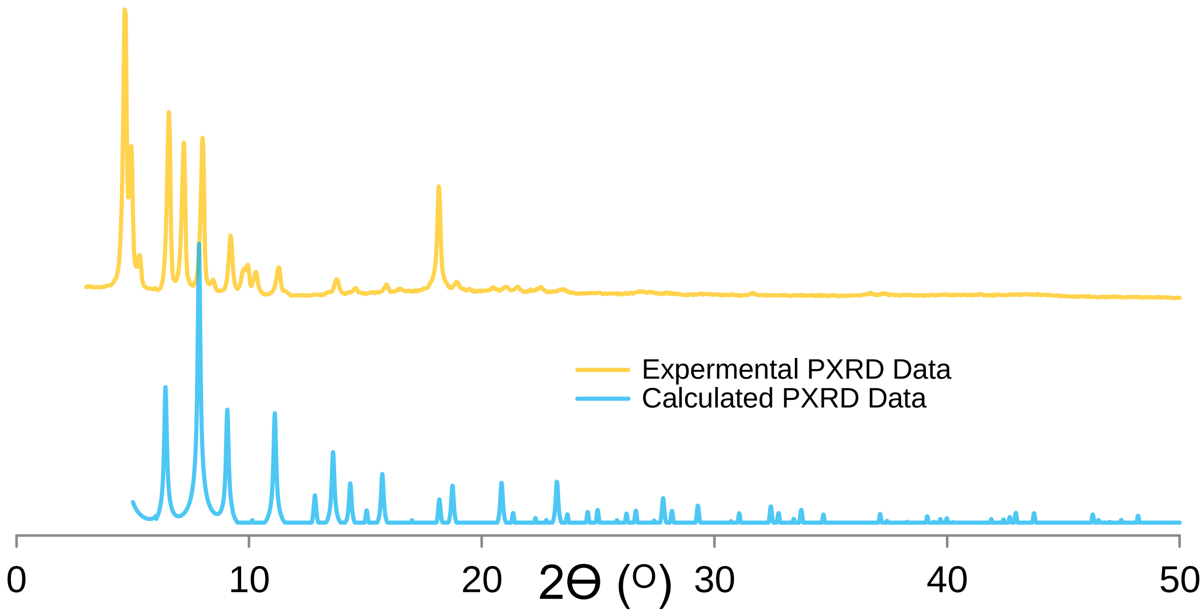

Figure 17: PXRD data for Zr-TCPP compared with the calculated PXRD data from Zhao's structure.

## Generation and Monitoring of Singlet Oxygen

Crystals of Zn-TCPP-BPY MOF 1 were the first MOF tested for singlet oxygen activity. 40 mg of air-dried MOF crystals were used to degrade 100 micro molar DPBF in 50 mL of DMF solution. Two types of control tests are carried out confirm that degradation of DPBF was caused by singlet oxygen produced when the MOF was irradiated in solutions containing DPBF and dissolve oxygen. The first control was carried out by monitoring the concentration of DPBF over time when the solution was kept in the dark to prevent photoexcitation of the MOF. The second control test was carried out by monitoring the concentration of DPBF over time in irradiated solutions containing no MOF. All of the tests were repeated in triplicate, and the results with error bars are shown in Figure 18.

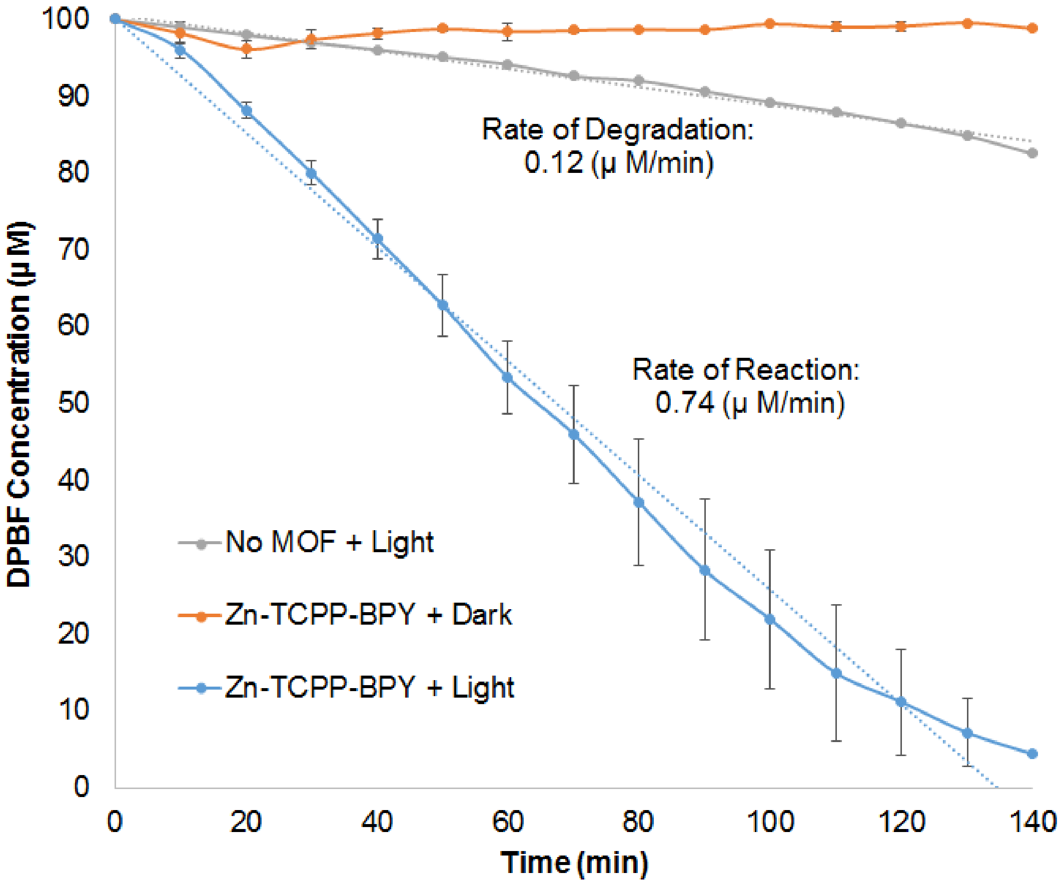

Figure 18: Degradation of DPBF by singlet oxygen generated by Zn-TCPP-BPY.

The concentration of the DPBF solution stayed constant with Zn-TCPP-BPY MOF crystals in the dark for 140 minutes. With irradiation from 60W Xe lamp, but without any MOF crystals, the concentration of DPBF decreased by only 15 micro molar after 140 minutes. Therefore the rate of degradation of DPBF under the experimental conditions used was calculated to be 0.12 micro molar per minute. Degradation of DPBF in the absence of the MOF likely is due to the 480 nm cutoff filter only stopping 50% of UV light, and to brief exposure of the solutions of DPBF to ambient light when transferring solutions.

Upon irritation in the presence of MOF crystals, DPBF was oxidized completely to the corresponding di-ketone by singlet oxygen after 140 minutes with a rate of reaction of around 0.74 micro molar per minute.

To further support the hypothesis that the degradation of DPBF was caused by singlet oxygen and not other mechanisms, a degassing test was completed. 100 micro molar DPBF in 50 mL of DMF solution with 50 mg Zn-TCPP-BPY MOF crystals was sealed in an Erlenmeyer flask with one small outlet stream. Before the test, the solution was stirred and bubbled with nitrogen gas in the dark for one hour to remove dissolved oxygen from the solution. Nitrogen gas was keeping bubbling through the solution during the 90 minutes period of the test. As a control, identical solution of DPBF and MOF crystals in DMF was sealed in an Erlenmeyer flask and stirred for one hour without degassing the solution with nitrogen. The flask was left open to the air during the 90 minutes period of the test to allow oxygen gas to dissolve back into the solution. Both tests are completed in triplicate and the results are shown with error bars below in Figure 19.

In the absence of dissolved oxygen, the concentration of DPBF remained at 100 micro molar for 90 minutes, and in the presence of dissolved oxygen 55 micro molar of DPBF was degraded in 90 minutes. These results strongly support the hypothesis that the degradation of DPBF is caused by the generation of singlet oxygen of the MOF crystals.

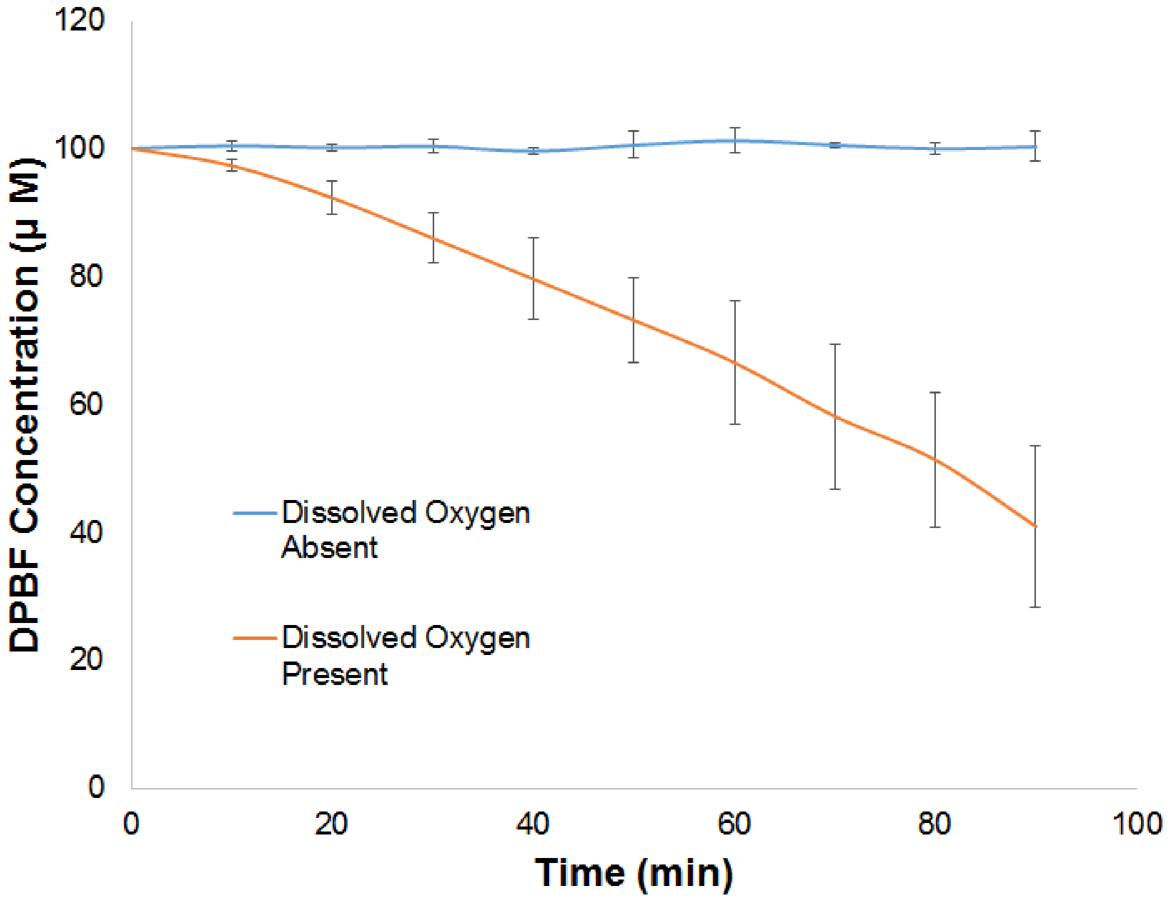

**Figure 19: Activity of Zn-TCPP-BPY MOF in a degassed solution and in an oxygen rich solution.**

The Zr-TCPP MOF exhibits singlet oxygen generation activity 10 times faster than the Zn-TCPP-BPY MOF for experiments carried out in solutions of DMF, as shown in Figure 20. The greater activity of the Zr-TCPP MOF may be a result of larger pores in the middle of cubic unit cells or the fact that the Zr-TCPP MOF contains a greater number of porphyrins per unit volume within the Zr-TCPP MOF compared to the Zr-TCPP-BPY MOF. The ability to generate singlet oxygen in aqueous solution is one of the major goals of this research in order to demonstrate that porphyrin-based MOFs might serve as effective catalytic materials for treating contaminated surface water sources. As Zr-TCPP MOF crystals have much faster generation rate, degradation of DPBF by singlet oxygen produced by the Zr-TCPP MOF were carried out in solutions containing 8:2 EtOH/$H_2O$ as solvent. It was not possible to use pure water as the solvent due to the low solubility of DPBF in water. Therefore, EtOH was added as a co-solvent. 50 micro molar DPBF in 50 mL of 8:2 EtOH/water solution was tested with 20 mg of Zr-TCPP MOF crystals. The degradation rate in solutions of water-ethanol is comparable to that observed in solutions of DMF. After 12 minutes, all of the DPBF was degraded giving a reaction rate of 7.22 micro molar per minute. This result supports the hypothesis that MOFs can be used successfully to degrade organic contaminants in water.

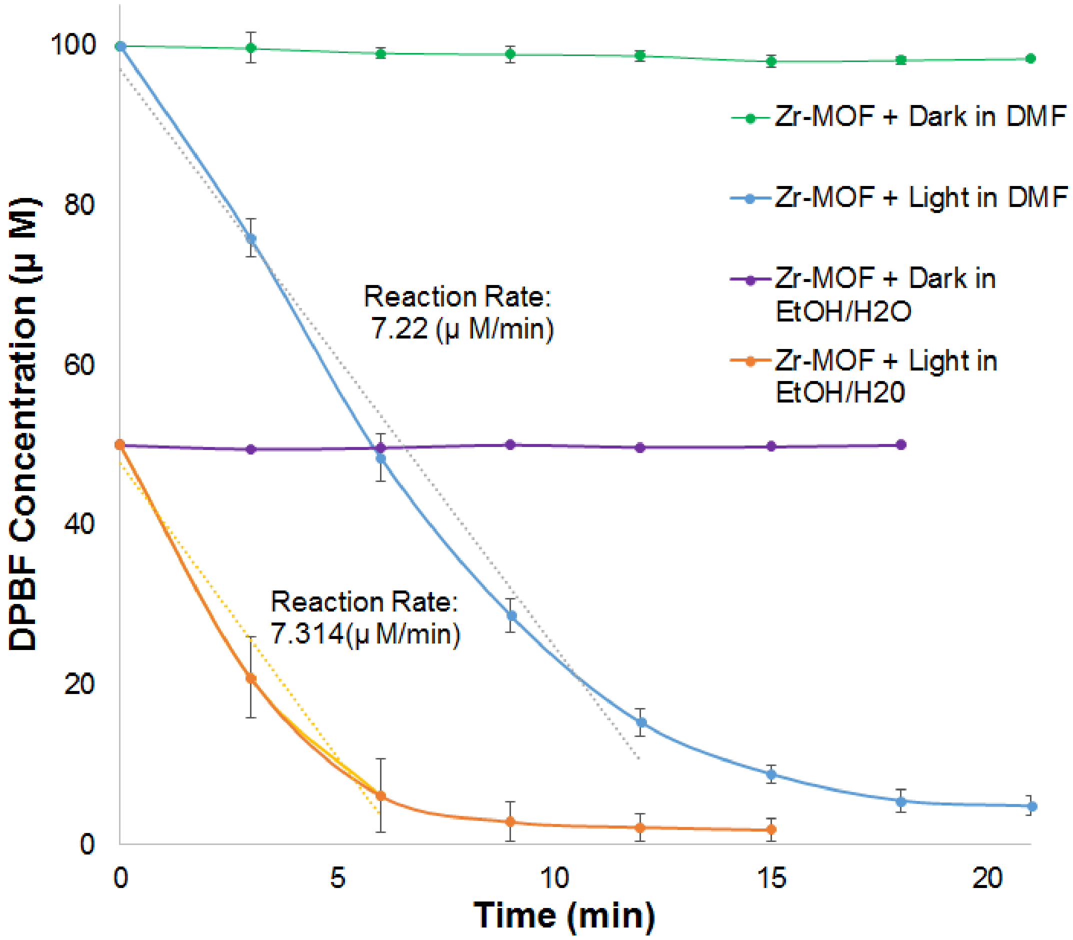

Figure 20: Singlet Oxygen generation activity of Zr-TCPP in DMF and Aqueous solution.

## Stability Studies

As mentioned previously, porphyrins free in solution react with the singlet oxygen they produce degrading their ability to produce singlet oxygen, a phenomenon known as photo-bleaching. Therefore, we wanted to determine if binding the porphyrin to a rigid structure such as a MOF might protect it from photo-bleaching We hypothesized that locking the porphyrin in the backbone of the framework would prevent the porphyrin ring form undergoing a change in conformation necessary for oxidation to occur, and thus inhibit the porphyrin ring from reacting with singlet oxygen. As shown in Figure 21, irradiating a 50 micro molar solution of free TCPP in DMF for 100 hours resulted in complete degradation of TCPP by singlet oxygen.

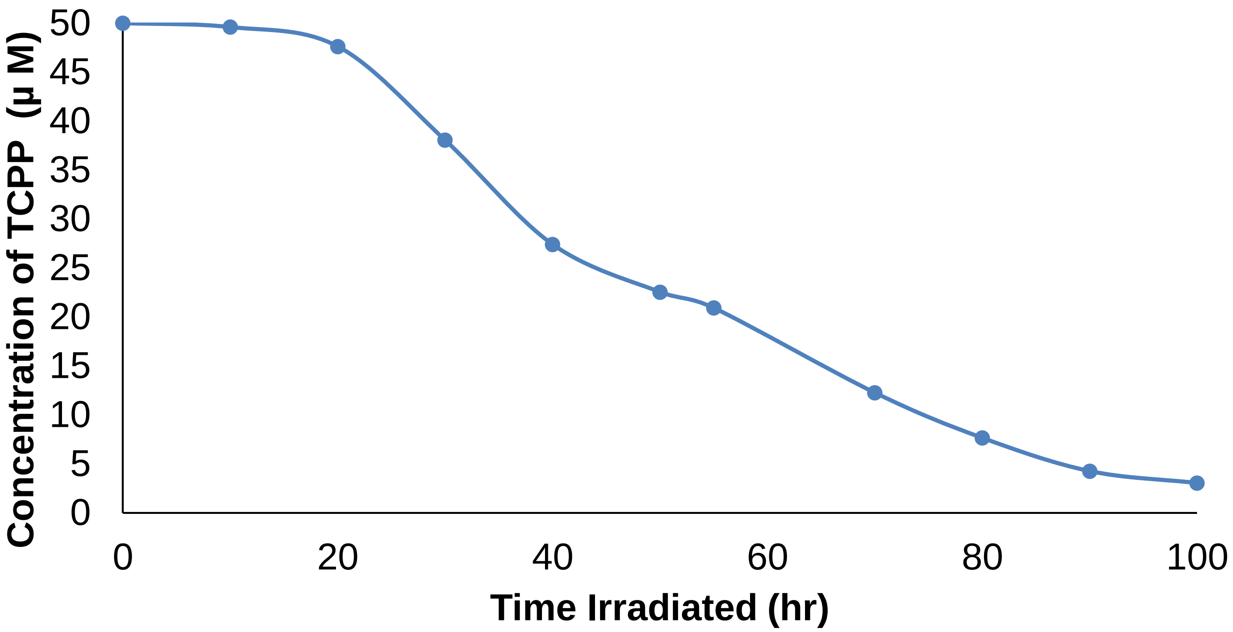

Figure 21: Photo-bleaching of TCPP by Singlet Oxygen

In contrast the Zn-TCPP-BPY MOF maintains full activity after being irradiated for over 200 hours, as shown in Figure 22. Over the course of the first 50 hours, the MOF shows an increase in activity, which likely is due to mechanical grinding of the MOF particles caused by stirring. Smaller particles have greater surface area and can absorb more light. After the initial increase in activity, the activity stabilizes and remains constant for over 200 hours indicating there is no sign of photo-bleaching. That result supports the hypothesis that the porphyrin is more stable inside the rigid structure of the MOF than free in solution. Moreover, this finding demonstrates that immobilizing porphyrins in MOFs is a convenient and viable approach for developing stable, heterogeneous materials that are useful for long=term, continuous production of singlet oxygen.

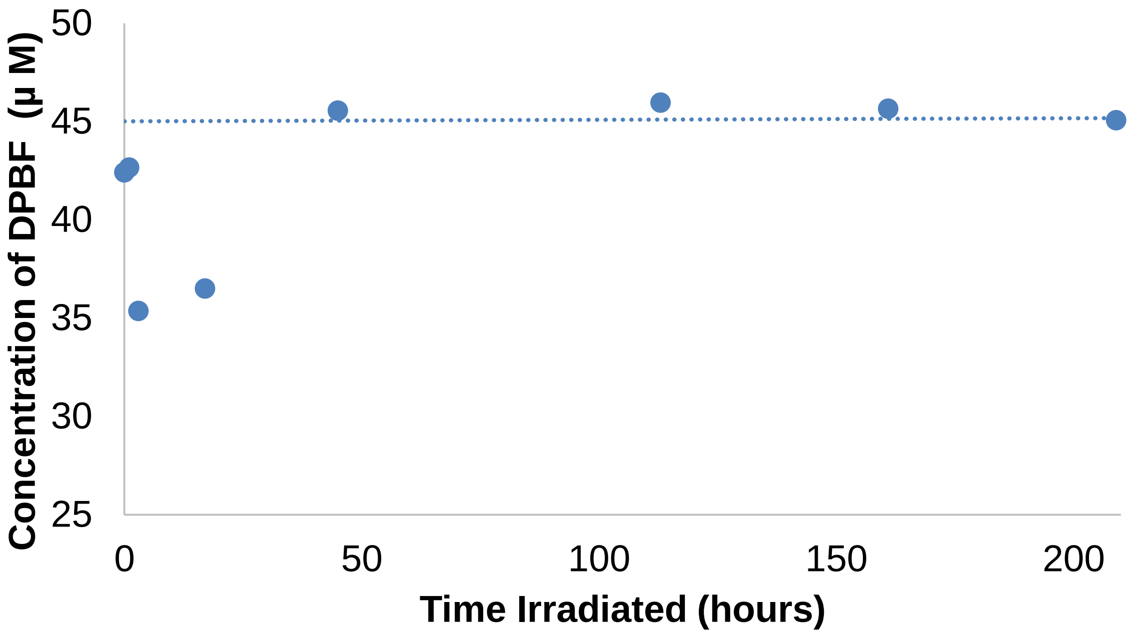

Figure 22: Activity of Zn-TCPP-BPY MOF over time

# Conclusions

- Porphyrin based Metal-organic frameworks can be synthesized with Zinc and Zirconium metal clusters.
- Zn-TCPP-Pyrazine MOF crystals are thermally unstable with activation process because of the low boiling point of pyrazine.
- Generation of singlet oxygen by MOFs was demonstrated in DMF solution and ethanol/water solution by monitoring degradation of 1, 3-Diphenylisobenzofuran (DPBF) spectroscopically.
- No activity in the absence of dissolved oxygen supports the hypothesis that singlet oxygen is responsible for the oxidation of DPBF.
- Incorporating TCPP into the rigid backbone of the Zn-TCPP-BPY MOF protects the porphyrin from degradation by singlet oxygen (photo-bleaching).
- Zr-TCPP MOF shows an enhanced activity compared to Zn-TCPP-BPY MOF.

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