

Development of new photocatalysts for pharmaceuticals photodegradation by advanced oxidation processes

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KEYWORDS

Wastewater treatment
Pharmaceutical pollutants
Advanced Oxidation Processes (AOPs)
Photocatalysis
Metal-Organic Frameworks (MOFs)
Porphyrins

ABSTRACT

Pharmaceutical pollutants, present in waste, surface, and ground waters, constitute nowadays a serious hazard for human health, as well as a threat to the environment. It is therefore imperative to develop green methods for the treatment of these water bodies, in order to eliminate or at least transform these pollutants into less hazardous compounds. The goal of this dissertation was to develop new porphyrin based MOFs (Por-MOFs) capable of acting as photocatalysts in Advanced Oxidation Processes (AOPs) for the degradation of two pharmaceutical compounds: paracetamol and 17 β -estradiol. AOPs have shown the capacity to oxidize most organic compounds, without forming hazardous secondary products, constituting a green method of wastewater treatment. Por-MOFs are a class of materials with a myriad of unique properties which has applications in multiple scientific and technological fields, including photocatalysis. In this project we developed two zirconium Por-MOFs based on tetrakis(4-carboxyphenyl)porphyrin which were characterized by Powder X-Ray diffraction and then tested as (photo)catalysts in the oxidation of the aforementioned pharmaceuticals. The catalytic studies investigated the influence of parameters such as the load of catalyst, the effect of an oxidant agent and the pH. Results indicated that the oxidation of the pharmaceutical substrates was favoured in alkaline reaction medium. We also reported the preparation of tetra-pyridyl and tetra-S-pyridyl based MOFs, characterized by Powder X-Ray diffraction, for catalytic micro-wave assisted oxidation of secondary alcohols. Preliminary results showed that the hybrid materials have little chemical stability under the reaction conditions used, indicating the necessity for further investigation of optimum reactions conditions.

1 Introduction

1.1 Pharmaceuticals in aquatic environment

The continuous technological and scientific advances the world as witness in recent decades, have allowed the existence of a wide range of pharmaceuticals used to treat many different types of medical conditions. Despite being an overwhelmingly positive aspect of modern society, it also represents an environmental problem since an increasing volume of pharmaceutical compounds is being detected in aquatic environments.¹⁻³ Pharmaceutical compounds (PCs) are considered to be pseudopersistent organic pollutants as a result of their continuous discharge into the environment as well as how difficult their removal by common water treatment methods tends to be.^{3,4} Despite being found in relatively low concentrations, usually from ng/L to μ g/L, in both surface and wastewaters, as well as in groundwater, they can be harmful to both the environment and to human health.⁵⁻¹¹ Based on this it is possible to affirm that there is a necessity of treating surface, waste and groundwaters in order to transform these organic pollutants into less hazardous compounds or remove them completely from the aquatic environment.

The array of conventional water treatment processes can be classified as primary, secondary, or tertiary (Figure 1.1). Primary treatments are based in

physical separation processes designed to remove large sediments, heavier solids, oils, and greases. Secondary treatments consist of biological processes, capable of removing organic pollutants both soluble and insoluble. Tertiary treatments are essentially chemical processes with the goal of disinfecting water so it can be safely utilized for human consumption.¹²⁻¹⁴ The primary and secondary treatments are not ideal to remove or decompose PCs, whereas chemical processes are the most effective of the methods and chlorination is the most common, mainly due to its low cost. Advanced oxidation Processes (AOPs) represent an interesting alternative chemical treatment with tremendous potential for this application.

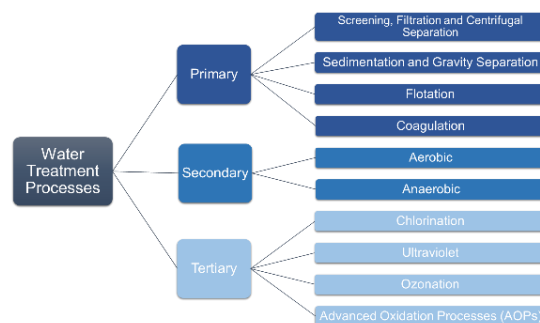


Figure 1.1. Classification of Water Treatment Processes.

AOPs consist of chemical reactions capable of producing highly reactive oxidizing species, which have the capacity to oxidize and mineralize most organic compounds.^{15,16} There is a wide range of AOPs in existence that goes from ozone-based methods to UV-based, as well as electrochemical, physical and catalytic AOPs.¹⁵ The treatment of organic wastewater is the main application of this type of process and, when compared to other methods, AOPs demonstrate advantages such as high efficiency of mineralization as well as the limited formation of secondary pollutants. Nevertheless, AOPs are not yet established as a treatment for large industrial scale due to its relative high costs.^{17,18}

Heterogeneous photocatalytic AOPs have been widely explored recently, in various applications.¹⁹ One method of photocatalysis consists of utilizing photosensitizers (PS) which absorb visible light and can react with molecular oxygen to form reactive oxygen species (ROS).^{20,21} The process starts by exposing the PS to irradiation, which will promote an electron to an excited energy level. From there, transference of electrons from the PS to molecular oxygen (Type I mechanism), or energy transfer from the PS to molecular oxygen upon collision between the two (Type II mechanism) can yield different ROS. This process is accurately described by the famous *Jablonski Diagram* (**Figure 1.2**).^{20,21}

This methodology has been widely explored in multiple applications, particularly in cancer photodynamic therapy (PDT).²² Furthermore, it is considered a green method of chemical wastewater treatment due to its capacity of oxidizing organic compounds without originating other hazardous sub products, as well as the fact that multiple PS can be activated with sunlight avoiding the use of UV-lamps which have much higher rates of energy consumption.^{12,21}

The preparation of efficient and inexpensive catalysts is utterly essential to the development of photocatalytic AOPs for wastewater treatment. Amongst the multiple possible PS that have been explored, porphyrins have been piquing the interest of

the scientific community, due to their unique photochemical properties which can be easily manipulated.²³ In addition, porphyrins can be immobilized on solid materials to form heterogeneous catalysts which conjugates their photochemical properties with the possibility of their reuse in multiple catalytic cycles. Porphyrins can be supported in materials such as zeolites or metal-organic frameworks (MOFs), to name a few.²⁴ The latter of these two will be highlighted.

1.2 Metal-Organic Frameworks (MOFs)

MOFs are crystalline, porous materials formed by organic linkers coordinated with metal ions.^{25,26} The metallic centers and the organic linkers are considered to be the MOFs' primary building units (PBU) and the number of possible combinations between these are nearly endless.²⁷ As a consequence, it is possible to prepare MOFs with characteristics specifically useful for predetermined applications. This constitutes the primary motive which explains the exponential growth in interest for this class of materials in the last two decades.

This class of materials has been significantly explored in multiple fields from gas storage and capture,²⁸ luminescence,²⁹ electrochemistry,³⁰ catalysis,³¹ or as metal corrosion inhibitors.³² With regards to photocatalysis, MOFs have attracted the scientific community's attention, as of late, due to the possibility of combining the effects of adsorbent and photocatalyst in the removal of dyes and other organic contaminants from waste waters, including pharmaceutical compounds.³³

The preparation of a MOF is a complex process involving multiple pieces. The proper selection of the PBUs is of crucial importance. In addition, parameters such as the pressure, the temperature, the reaction time, and pH, all play an essential role in the synthesis of a MOF. Solvothermal synthesis is the default method of MOF preparation, with the majority of MOFs being prepared via this method. The procedure starts by preparing the reaction mixture with the PBUs as well as

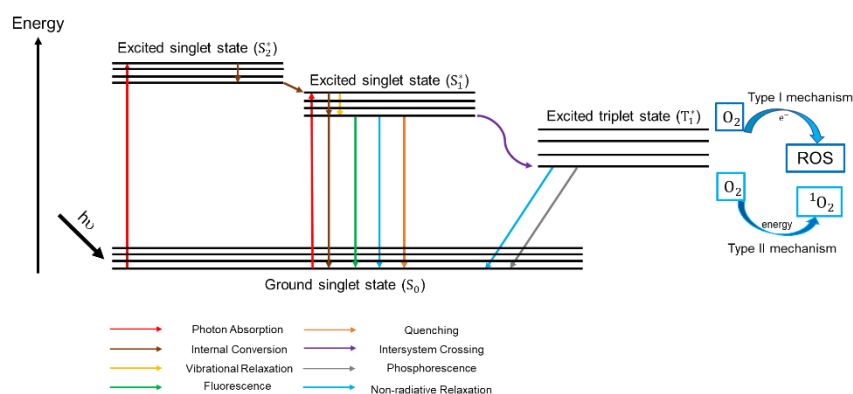


Figure 1.2. Modified Jablonski diagram, schematically demonstrating the mechanism of photocatalysis using a PS as catalyst.^{20,21}

a solvent, hence, the name. The most commonly used solvents are water, and some organic solvents as for instance, N,N-dimethylformamide (DMF). The mixture is transferred to a closed system, usually an autoclave, and put in an oven for a predetermined period of time, often multiple days. The temperatures in this type of synthesis range between 80 and 250 °C.³⁰

Amongst the multiple types of MOFs, porphyrin based MOFs (Por-MOFs) are a unique class of materials in which porphyrins are the organic PBU of the hybrid structure. The properties of a MOF are closely related to the organic PBU and porphyrins are fascinating organic molecules, who all share a core unit which consists of an aromatic macrocyclic ring composed by four modified pyrrole subunits linked together by four methine bridging groups (**Figure 1.3**).³⁴ They are pigments with crystalline and fluorescent character, which can be found in nature or synthesized in laboratorial settings.³⁴ Furthermore, porphyrins have a wide range of properties that are not only incredibly compatible with MOF construction (as for instance their rigid molecular structure and large dimensions) but also confer the MOF with unique capabilities, as a consequence of their tunable substituents and metalation site in their core.

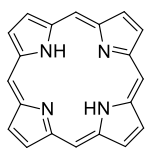


Figure 1.3. The Porphyrin macrocycle.

Por-MOFs have been explored in the fields of guest molecules adsorption, separation, and storage, as well as in the fields of nano-thin film, light harvesting, and catalysis.³⁵ Por-MOFs are particularly interesting materials in photocatalytic applications since porphyrins and metalloporphyrins have great photocatalytic activity, as a consequence of their conjugated aromatic electron system.³⁵ When these properties are combined with the MOFs' typical high porosity and surface area, as well as the possibility of being reutilized in multiple catalytic cycles, it becomes simple to understand the growing interest surrounding this class of material for photocatalytic applications.

Herein we report the synthesis of zirconium based Por-MOFs and the catalytic assays investigating their effectiveness as heterogeneous catalysts in AOPs for the photodegradation of pharmaceutical compounds.

2 Synthesis of porphyrin based MOFs

The main goal of this project was to synthesize new porphyrin-based zirconium MOFs in which the organic linkers would be the porphyrins **H₂TPPF₁₆(SC₂H₄COOH)₄** (**1**) and **H₂TPPF₁₆(SC₆H₄COOH)₄** (**2**) (**Figure 2.1**). Another

objective was the synthesis of the previously reported PCN-222 which consists of a class of zirconium MOFs with porphyrin **H₂TPP(COOH)₄** (**3**) or derivatives as the organic linkers. These materials would then be tested and compared as photocatalysts in the photodegradation of pharmaceutical compounds in water. For that reason, we started by synthesizing **1** and **2** from the commercially available **H₂TPPF₂₀** (**4**) porphyrin.

The synthesis of porphyrins **1** and **2** consisted of the nucleophilic aromatic substitution of the four *para*-fluorine atoms of porphyrin **4** by 3-mercaptopropionic acid and 4-mercaptopbenzoic acid, respectively. The experimental procedure utilized was adapted from Lourenço *et al.* (2014)³⁶ (**Scheme 2.1**). Characterization of the obtained porphyrins was performed by ¹H NMR, UV-Vis and mass spectroscopies, with results aligned with the literature.³⁶

The synthesis of some zinc, manganese, and iron metalloporphyrins from the aforementioned free base porphyrins **1-3** was also attempted. From this work resulted two metalloporphyrins from **1** with zinc and iron, as well as two manganese metalloporphyrins from **2** and **3**, respectively. All metalloporphyrins prepared were characterized by UV-Vis and the results were in alignment with what can be found in the literature.^{37,38}

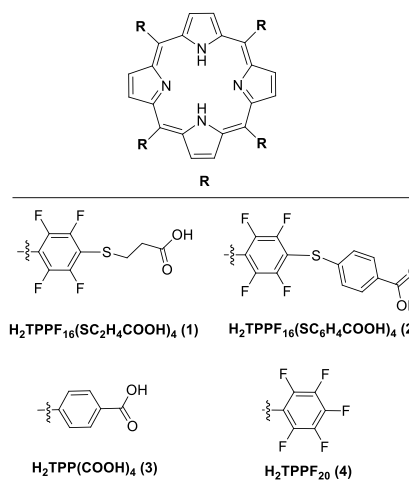
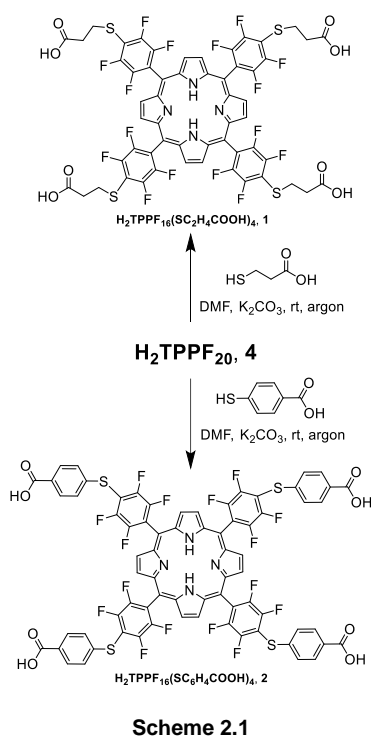


Figure 2.1. Structures and designations of the porphyrins explored in this project.

The preparation of MOFs consisted of a solvothermal method, in which the reaction mixture was left in a glass reactor with slow agitation. The reactions took place in an oil bath at temperatures ranging from 120 to 140 °C. Typically, solvothermal synthesis of MOFs is performed in autoclaves inside ovens, however it was decided to perform the reactions in glass reactors, in an oil bath, to easily follow the evolution of the reactions visually and decide when to finish them.

The general procedure followed was adapted from Feng, D. *et al.* (2012)³⁹ (**Scheme 2.2**). However, during the preparation of the different MOFs we faced multiple obstacles which were tackled by changing

experimental conditions such as the temperature or the duration of the reactions, the solvent and other reagents. Despite all these variables two things were deemed essential and were performed for every reaction. One of them was to assure that all the reactants were thoroughly dissolved before heating the reaction mixture. In order to accomplish this, all reaction mixtures were put in an ultrasonic bath for a few seconds prior to their heating. The other was to thoroughly wash the obtained solid after the reaction was finished with solvents which could dissolve the base porphyrin and metal salts. This way it was ensured that there would not be a mixture of porphyrin, salts, and MOF in the obtained solid.



Two zirconium based MOFs were successfully obtained from porphyrin **3** and its manganese complex **Mn(III)TPP(COOH)₄**, respectively designated **H₂TPP(COOH)₄Zr₄** and **Mn(III)TPP(COOH)₄Zr₄**. These materials were washed four times with ethanol, being centrifuged and decanted each time. The solids were then left in acetone for a night before finally being harvested with quantitative yields.

Both the free base and Mn(III) solids (**Figure 2.2** and **Figure 2.3**, respectively) were characterized by Powder XRD and by UV-Vis spectroscopy. This data shows crystalline materials that kept the porphyrin's absorption characteristics, which means the synthesis of these Por-MOFs was successful.

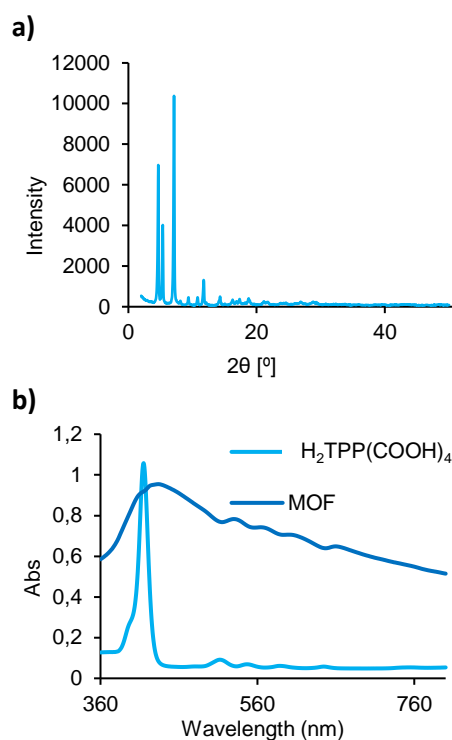
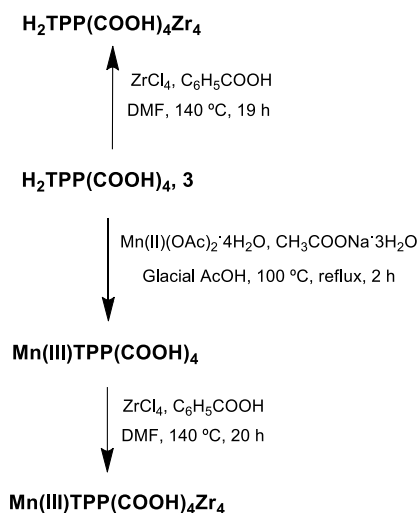


Figure 2.2. a): Powder X-ray diffraction data of MOF **H₂TPP(COOH)₄Zr₄**; **b):** UV-Vis spectra of porphyrin **H₂TPP(COOH)₄** (**3**) and its respective zirconium MOF, both in methanol.

Unfortunately, it was not possible to come up with definitive procedures for the syntheses of MOFs based on porphyrins **1** and **2** nor on their metallic complexes.

During the development of this project, it was possible to understand that the synthesis of MOFs, specially from large organic ligands, such as porphyrins, is incredibly complex with a wide range of variables being crucial to the success of the reaction, from temperature to time of reaction or even the acid utilized. However, an extensive range of attempts varying multiple reaction conditions could possibly result in more successful outcomes.

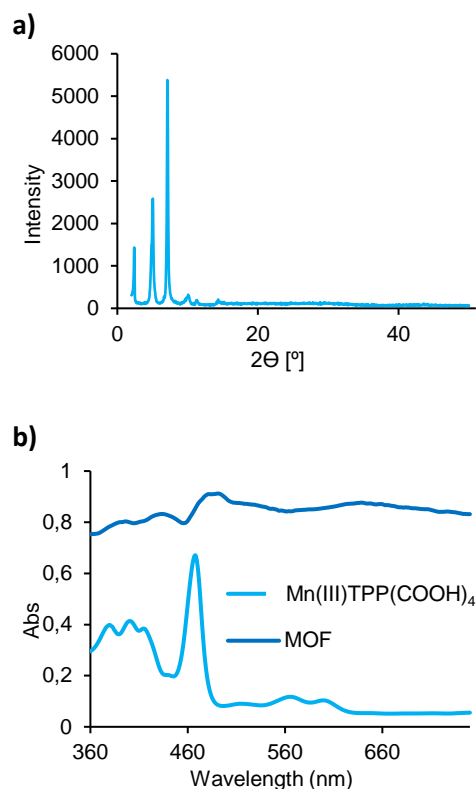


Figure 2.3. a): Powder X-ray diffraction data of MOF $\text{Mn(III)TPP(COOH)}_4\text{Zr}_4$; b): UV-Vis spectra of porphyrin $\text{Mn(III)TPP(COOH)}_4$ and its respective zirconium MOF, both in methanol.

3 Oxidation of pharmaceuticals by Advanced Oxidation Processes (AOPs)

Pharmaceuticals such as paracetamol (PCM) and 17β -estradiol (E2) are fairly widespread in modern society and for that reason it is becoming increasingly common to find them in waste and surface waters alike.^{21,40–43} In addition, the accumulation of this type of pollutants in aquatic environment represents dangerous potential effects on both fauna and flora, as well as to human health. For those reasons, these two compounds were applied as models of pharmaceutical pollutants to test the activity of the synthesized porphyrins and zirconium Por-MOFs as catalysts for their photodegradation. The photooxidation of these

pharmaceuticals was explored in batch mode.

Prior to the photocatalytic studies, a singlet oxygen assay was performed using 1,3-diphenylisobenzofuran (DPBF) as a $^1\text{O}_2$ scavenger. DPBF reacts with $^1\text{O}_2$ and is oxidized to o-dibenzoylbenzene (DBB) losing its characteristic yellow color and becoming colorless during the process. Furthermore, DPBF has its peak absorption at approximately 415 nm which means the depletion of DPBF can be followed by UV-Vis analysis by comparing its absorption before and after irradiation.²¹

The results show that $\text{H}_2\text{TPP(COOH)}_4$ (**3**) has the capacity to generate $^1\text{O}_2$ since in its presence, approximately 50% of DPBF was decomposed (**Figure 3.1**). On the other hand, $\text{Mn(III)TPP(COOH)}_4$ does not have the capacity to generate $^1\text{O}_2$ based on the residual depletion of DPBF during the reaction in its presence. Regarding the MOFs, the results are in line with their respective base porphyrins. $\text{H}_2\text{TPP(COOH)}_4\text{Zr}_4$ shows capacity to generate $^1\text{O}_2$ albeit less than its base porphyrin, since during the same period and with a bigger concentration of catalyst the depletion of DPBF remained at approximately 34%. $\text{Mn(III)TPP(COOH)}_4\text{Zr}_4$ showed no capacity to generate $^1\text{O}_2$ as shown by the residual depletion of DPBF.

3.1 Photooxidation of paracetamol

The photooxidation of paracetamol was firstly tested with porphyrin $\text{H}_2\text{TPP(COOH)}_4$ (**3**). The studies consisted in a first assessment of whether or not the porphyrin was capable of oxidizing the medicinal substrate, followed by a study of potential degradation mechanisms as well as an investigation of the effect the solution's pH has in the reaction. Once these studies were concluded the MOF catalyst $\text{H}_2\text{TPP(COOH)}_4\text{Zr}_4$ was tested, and the studies focused on finding optimum reaction conditions.

To evaluate the photocatalytic performance of $\text{H}_2\text{TPP(COOH)}_4$ (**3**) in PCM oxidation, an aqueous solution of the later ($130\ \mu\text{M}$) and the porphyrin ($13\ \mu\text{M}$) was irradiated with white light ($18\ \text{mW/cm}^2$) for 50 minutes and followed by UV-Vis spectroscopy (**Figure 3.2**). After only five minutes, the degradation of PCM seemed complete and a subproduct, P1, was formed. P1 was also oxidized, after 15 minutes, into subproduct P2 which remained in solution for the remaining time of reaction. The results allowed the conclusion that

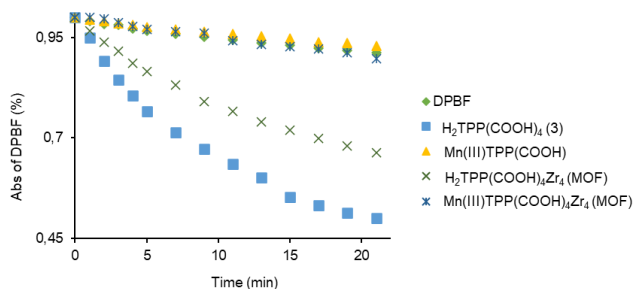


Figure 3.1. Comparative photooxidation of DPBF with or without homogeneous and heterogeneous photosensitizers

porphyrin $\text{H}_2\text{TPP}(\text{COOH})_4$ is able to decompose PCM in aqueous solution under white light irradiation in just 5

minutes and that two different sub products are formed during the first 50 minutes of reaction.

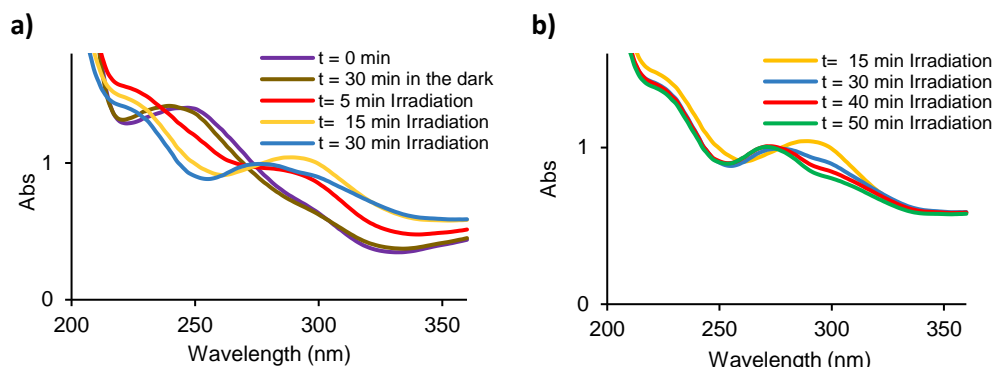
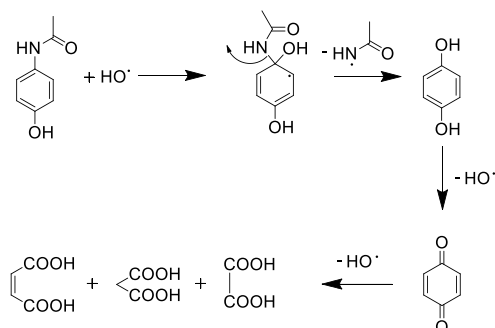


Figure 3.2. UV-Vis spectra of the reaction mixture of paracetamol (130 μM) and $\text{H}_2\text{TPP}(\text{COOH})_4$ (3) (13 μM) (pH = 8.5) analyzed after predetermined periods of irradiation with white light (18 mW/cm^2), for **a)** the first 30 minutes of irradiation; and **b)** the last 35 minutes of irradiation.

The identification of subproducts P1 and P2 could potentially allow for the formulation of a PCM degradation mechanism. With that in mind, previously reported subproducts of photodegradation of PCM, benzoquinone, hydroquinone, *p*-aminophenol and *p*-nitrophenol, were analyzed by UV-Vis spectroscopy.^{42,44} The analysis indicated that both hydroquinone and *p*-aminophenol were a possible match to P1. Subproduct P2 on the other hand, could not be matched with none of the analyzed compounds. With this information it was possible to infer two potential previously described reaction mechanisms, with the most likely match consisting in the oxidation of PCM to hydroquinone as a consequence of the attack of $\cdot\text{OH}$ radicals onto the aromatic ring of paracetamol in the *para*- position and subsequent elimination of the acetamide radical.^{45,46} The sequence of oxidative reactions would continue originating simple dicarboxylic acids (**Scheme 3.1**). Despite this evaluation, without further studies of identification of intermediate and final subproducts of PCM's degradation it is not possible to affirm with certainty what reaction mechanism takes place.



Scheme 3.1

The studies to evaluate the effect of the pH were conducted using Britton-Robson buffer solutions of appropriate values of pH to regulate the reaction mixtures' pH. The values studied were 2.5, 5.5, 7.0, 8.9,

9.5 and 11.0. Oxidation of PCM was only verified with alkaline solutions. **Table 3.1** summarizes the main results of this study.

Table 3.1. Values of pH before and after irradiation for each study, as well as the main results from each reaction.

| Initial pH | Final pH | Catalyst stability | PCM degradation |
|------------|----------|--------------------|-----------------|
| 2.53 | 2.57 | No | No |
| 5.71 | 6.2 | Yes | No |
| 7.40 | 7.45 | Yes | No |
| 8.9 | 8.82 | Yes | Yes |
| 9.45 | 9.48 | Yes | Yes |
| 10.92 | 10.46 | Yes | Yes |

The study of photooxidation of paracetamol using the $\text{H}_2\text{TPP}(\text{COOH})_4\text{Zr}_4$ MOF consisted in multiple different experiments, in pursue of the optimum reactions conditions. Firstly, the effect of catalyst concentration was evaluated. Then, the addition of an oxidant agent was attested and finally the effect of pH in heterogeneous catalysis was also investigated.

The results of the multiple reactions showed once again the importance of alkaline values of pH in the reaction mixture for the photo degradation of paracetamol with this catalyst. Catalyst loads of up to 50% the molar amount of substrate with or without the effect of hydrogen peroxide showed to be incapable of oxidizing PCM. With reaction at pH = 8, however, oxidation of PCM was verified. Unfortunately, the MOF catalyst showed to lose its stability in these conditions since a small part of it was dissolved into its porphyrin precursor, hindering the possibility of recycling studies.

3.2 Photooxidation of 17 β -estradiol

The photocatalytic studies using 17 β -estradiol as substrate started by testing the catalytic activity of

porphyrin $\text{H}_2\text{TPP}(\text{COOH})_4$, followed by testing the respective Por-MOF. Unlike the studies with PCM however, this time, the studies focused on a quantitative analysis of the oxidation of the substrate. For that, high performance liquid chromatography (HPLC) analysis was performed, in addition to following each reaction by UV-Vis spectroscopy.

The photocatalytic performance of porphyrin $\text{H}_2\text{TPP}(\text{COOH})_4$ (**3**) in the degradation of E2 was tested by irradiating with white light (18 mW/cm^2), a reaction mixture consisting of both reagents dissolved in methanol, for 180 minutes. The reaction was controlled by UV-Vis spectroscopy and samples were analyzed at predetermined periods of time. The results show that after 30 minutes of irradiation, E2 is significantly oxidized given that its absorbance band is all but depleted. Additionally, subproducts of the degradation of E2 seem to be formed (**Figure 3.3.a**). In order to follow the degradation of E2 over time, this reaction was repeated using shorter irradiation intervals, with samples being analyzed, both by UV-Vis spectroscopy and HPLC, every 5 minutes, for the first 45 minutes of the reaction. The HPLC analysis reveals that the period the solution was left in dark conditions resulted in a slight decrease in E2 concentration (only 5%). Once the solution was irradiated, photodegradation occurred,

with approximately 45% of E2 being oxidized (**Figure 3.3.b**).

For the exploration of the photocatalytic activity of the MOF catalyst $\text{H}_2\text{TPP}(\text{COOH})_4\text{Zr}_4$ in the oxidation of E2 multiple studies were performed, in search for the optimum reaction conditions, investigating the influence of the same parameters previously tested during the photocatalytic studies for PCM degradation.

Once again, oxidation of the substrate was only verified in the reaction with $\text{pH} = 8$. The MOF catalyst was able to oxidize the substrate even if not completely. It is possible to see how after 180 minutes of irradiation, E2's characteristic absorbance band loses its shape which indicates its photodegradation (**Figure 3.4.a**). Moreover, HPLC results indicate that by the end of the reaction most of the substrate has been decomposed with a degradation of E2 up to 83% (**Figure 3.4.b**). It is also possible to verify that before the start of the irradiation, the concentration of the substrate in the solution has dropped approximately 42%. This can be explained by adsorption of the E2 by the MOF catalyst. This result is on pair with previous studies of heterogeneous photooxidation of E2 with MOFs.^{21,41,47}

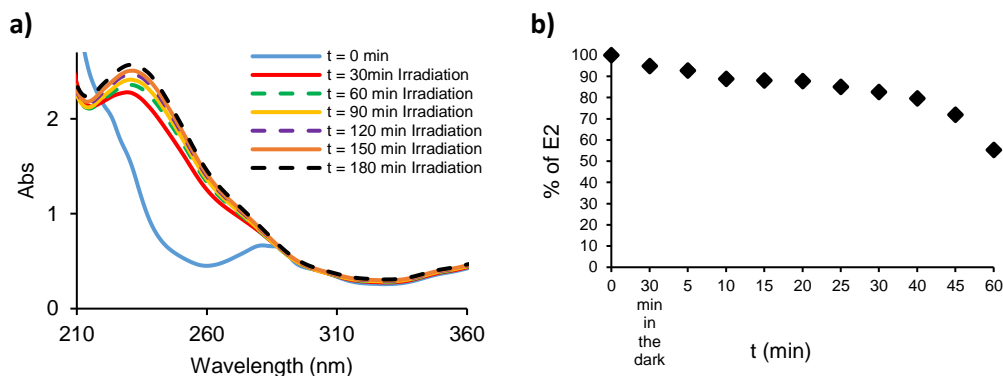


Figure 3.3. a): UV-Vis spectra of the reaction mixture of E2 ($147 \mu\text{M}$) and $\text{H}_2\text{TPP}(\text{COOH})_4$ (**3**) ($14.7 \mu\text{M}$) under white light irradiation (18 mW/cm^2), for 180 minutes; **b):** Evolution of the concentration of E2 in the reaction mixture over time.

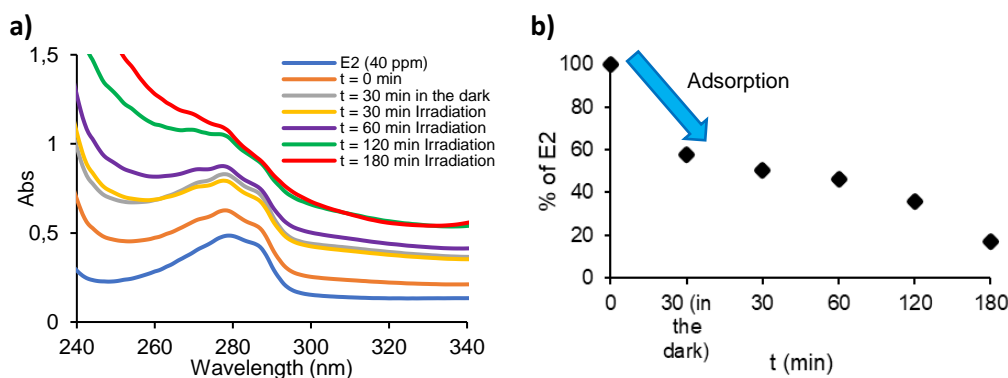


Figure 3.4. a): UV-Vis spectra of the reaction mixture of E2 ($147 \mu\text{M}$) and $\text{H}_2\text{TPP}(\text{COOH})_4\text{Zr}_4$ ($73.5 \mu\text{M}$) ($\text{pH} \sim 8$) under white light irradiation (18 mW/cm^2), for 180 minutes; **b):** Evolution of E2 concentration in the reaction mixture over time.

3.3 Oxidation of pharmaceuticals in dark conditions

Since the manganese porphyrin and respective Por-MOF revealed to be incapable of producing singlet oxygen during our assays, these catalysts were tested in the absence of light and in the presence of an oxidant agent, in this case hydrogen peroxide.

The procedure consisted in adding the catalyst and the oxidant to the aqueous solution of PCM (130 μM , 20 ppm) and to the solution of E2 (147 μM , 40 ppm) in methanol. The reaction solution would then be left in the dark with stirring and samples would be analyzed by UV-Vis spectroscopy in pre-determined intervals. The reaction mixtures had a catalyst/substrate molar ratio of 0.1 for the stock solution (the same solution utilized in the photocatalytic studies) of porphyrin **Mn(III)TPP(COOH)₄** and of 0.5 for the MOF **Mn(III)TPP(COOH)₄Zr₄**. As per hydrogen peroxide the oxidant/substrate molar ratio was 10.

The results of the reactions with the porphyrin as catalyst show that under the described conditions the porphyrin is oxidized, and the substrate is not. This can be concluded based on the fact that while the absorbance band of the pharmaceutical substrates suffered no significant decrease, the Soret Band, characteristic of the porphyrin, suffered a very significant decrease over time (**Figure 3.5**).

The reactions utilizing the Por-MOF as heterogeneous catalyst showed the latter's stability under the reaction conditions. However, it is also possible to conclude that under the tested reaction conditions the catalyst was not able to oxidize neither PCM nor E2 (**Figure 3.6**). These results were somewhat unexpected. Despite not being able to generate singlet oxygen, manganese metalloporphyrins have shown catalytic activity in dark conditions in previous reported work.^{31,48} This leads us to believe that the conditions under which the reactions were conducted were not ideal for the degradation of the pollutants.

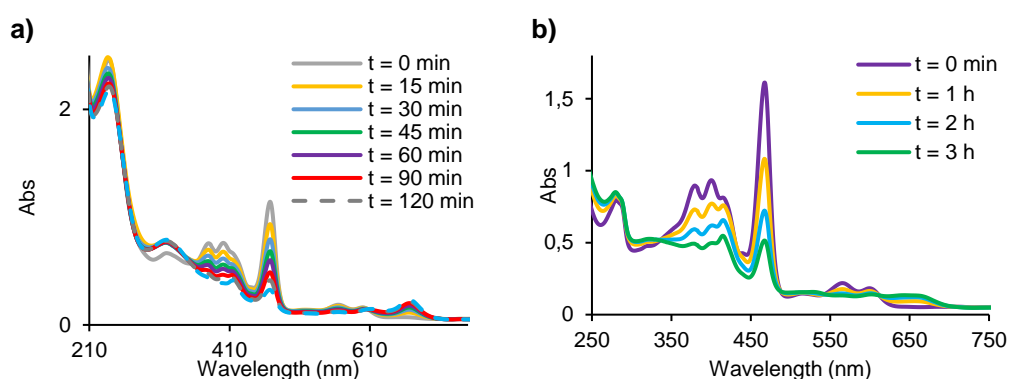


Figure 3.5. UV-Vis spectra of the reaction mixture of **Mn(III)TPP(COOH)₄** (molar ratio catalyst/substrate = 0.1) and H_2O_2 (molar ratio oxidant/substrate = 10) and **a)** PCM (130 μM , 20 ppm), **b)** E2 (40 ppm, 147 μM). The reactions were left in the dark with stirring for 180 min.

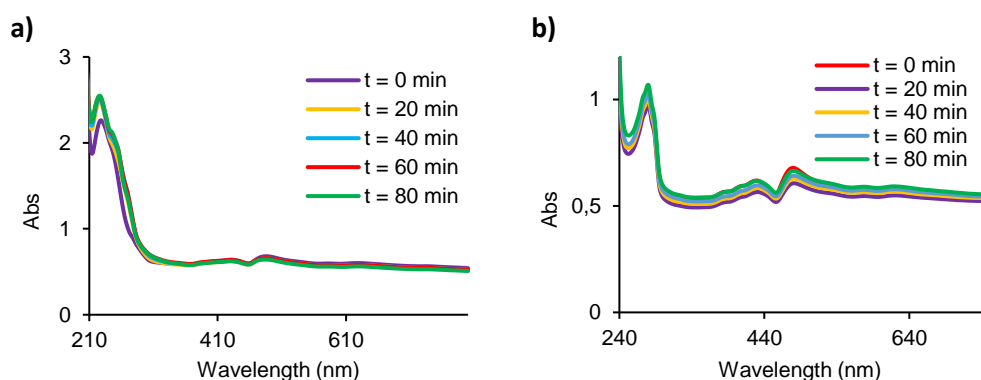


Figure 3.6. UV-Vis spectra of the reaction mixture of **Mn(III)TPP(COOH)₄Zr₄** (molar ratio catalyst/substrate = 0.5) and H_2O_2 (molar ratio oxidant/substrate = 10) and **a)** PCM (130 μM , 20 ppm), **b)** E2 (40 ppm, 147 μM). The reactions were left in the dark with stirring for 80 min.

4 Tetra-pyridyl and tetra-S-pyridyl porphyrin based MOFs as catalysts for micro-wave assisted oxidation of secondary alcohols

While developing the previously described materials and performing the catalytic studies which constituted the main focus of this dissertation, tetra-pyridyl and tetra-S-pyridyl based MOFs were also prepared with the goal of complementing a different project. The intent of this project was to develop porphyrin based MOFs which could then be utilized as catalysts for micro-wave assisted oxidation of secondary alcohols.

The goal was to develop mixed and single metal Por-MOFs with copper and zinc from the base porphyrins 5,10,15,20-tetrakis(4-pyridyl)porphyrin (**H₂TPyP**, **5**) and 5,10,15,20-tetrakis[2,3,5,6-tetrafluoro-4-(4-pyridylsulfanyl)phenyl]porphyrin (**H₂TPPF₁₆(SPy)**, **6**) (Figure 4.1).

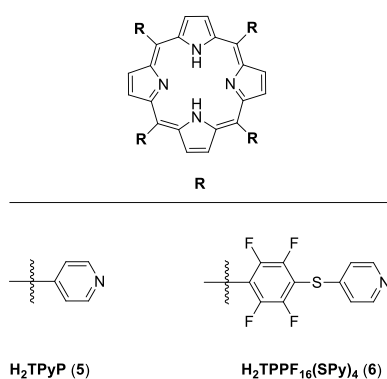
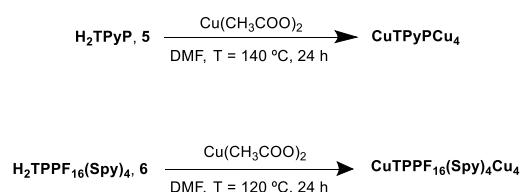


Figure 4.1. Structure and designation of the porphyrins explored in this section

From the multiple attempts were yielded the copper-copper MOFs **CuTPyPCu₄** and **CuTPPF₁₆(SPy)₄Cu₄**. The synthesizes of these MOFs was performed via the same solvothermal method applied to the preparation of the **H₂TTP(COOH)₄** based MOFs, with the general procedure being adapted from Castro, Kelly *et al.* (2017)⁴⁹ (Scheme 4.1).



Scheme 4.1

The materials were obtained with satisfactory yields and after being thoroughly washed and dried were characterized by Powder-XRD (Figure 4.2 and Figure 4.3). The analysis showed the materials had

crystalline character, which indicates the success of the synthesis.

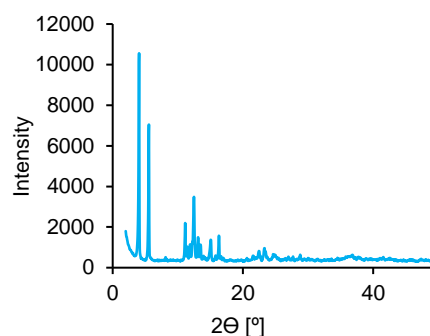


Figure 4.2. Powder X-ray diffraction data of MOF **CuTPyPCu₄**

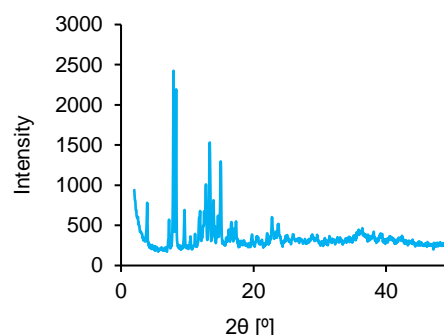


Figure 4.3. Powder X-ray diffraction data of MOF **CuTPPF₁₆(SPy)₄Cu₄**

It was not possible to obtain mixed metal Por-MOFs despite multiple attempts at obtaining such materials from both porphyrins. We believed this is related with the known difficulty of Por-MOFs to retain their structure upon solvent removal. This was probably originated due to the thorough washing of the materials with a solvent in which the porphyrin precursor was very soluble. With the intent of avoiding the problem of possible mixtures between the MOF and unreacted porphyrin in the final powder, a different problem might have been inadvertently created. Furthermore, zinc based secondary building units are more labile, which directly contributes to the fact that the zinc based MOFs are significantly more prone to lose their structural integrity and collapse upon solvent removal.

5 Conclusion and Outlook

Unfortunately, it was not possible to find reproducible synthetic pathways to prepare MOFs based on porphyrins **H₂TPPF₁₆(SC₂H₄COOH)₄** and **H₂TPPF₁₆(SC₆H₄COOH)₄**, which could originate novel MOFs useful in a myriad of applications, including photocatalysis. However, two MOFs from the free base porphyrin **H₂TTP(COOH)₄** were reproduced with success.

Furthermore, the capacity of the aforementioned free base porphyrin and its respective MOF to oxidize both PCM and E2 was demonstrated. However, optimum reaction conditions were not found in the case of the heterogeneous study which meant that the MOF's activity over multiple catalytic cycles was not evaluated. This is something worth further exploration since this is the main feature of a MOF which qualifies its sustainability as a catalyst at industrial scale.

The manganese materials had negative results in all the catalytic studies in which they were utilized. As previously mentioned, this is an unexpected result and is likely due to the fact that the manganese ion was probably not available as an active site, plus the reaction conditions can certainly be improved as well.

Finally, two copper based MOFs were prepared from porphyrins H_2TPyP and $H_2TPPF_{16}(SPy)_4$. The materials were obtained with satisfactory yields and their catalytic ability will be tested in another project.

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