

# Project SEED 2009

## Research Report:

Synthetic Studies of Light-induced Oxidation of  
Manganese Porphyrins

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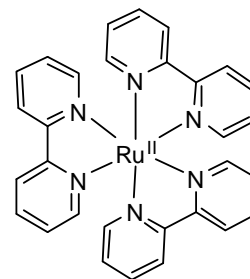
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## Introduction

The oxygen evolving complex (OEC), as found in photosystem II (PSII) of plants, is essential in the process of oxidizing water ( $\text{H}_2\text{O}$ ) to protons, electrons and dioxygen during the process of photosynthesis.<sup>1-3</sup> The active site of the OEC in the homodimeric membrane protein is made up of oxygen, calcium and manganese.

During photosynthesis, the chlorophylls in the homodimeric membrane protein absorb light to induce water oxidation and the release of dioxygen. Ruthenium polypyridine complexes, such as the one shown in Figure 1, have high molar absorptivity and photostability.<sup>4,5</sup> They have been used as artificial light-harvesting antennae for the oxidation of manganese and iron complexes.<sup>6-16</sup>



**Figure 1.** Ruthenium polypyridine

The formation of a high valent Mn-O species has been suggested as a key intermediate during the oxygen evolution of photosystem II (PSII). Manganese porphyrin complexes have been shown to catalyze water oxidation through a highly reactive  $\text{Mn}^{\text{V}}=\text{O}$  as an active intermediate created by chemical oxidation.<sup>17,18</sup> Photo-induced oxidation of  $\text{Mn}^{\text{II}}$  complex has been shown to lead to the generation of  $\text{Mn}^{\text{IV}}$  species.<sup>8</sup> However, the light-induced generation of a high valent Mn-O species has been rare except by laser flash photolysis.<sup>19-22</sup> Since a high valent  $\text{Mn}^{\text{V}}=\text{O}$  species has been proposed as a critical intermediate in water splitting by the oxygen evolving center of PSII, the possibility of generating a light-induced Mn-O species in the presence of both photoactive chromophores and manganese complexes will be investigated. This study will provide basis for the design of photocatalysts for water oxidation. The following three experiments include the synthesis of manganese<sup>III</sup>

tetraphenylporphyrin chloride, chloropentaamminecobalt(III) chloride, and photoinduced oxidation of manganese(III) porphyrin.

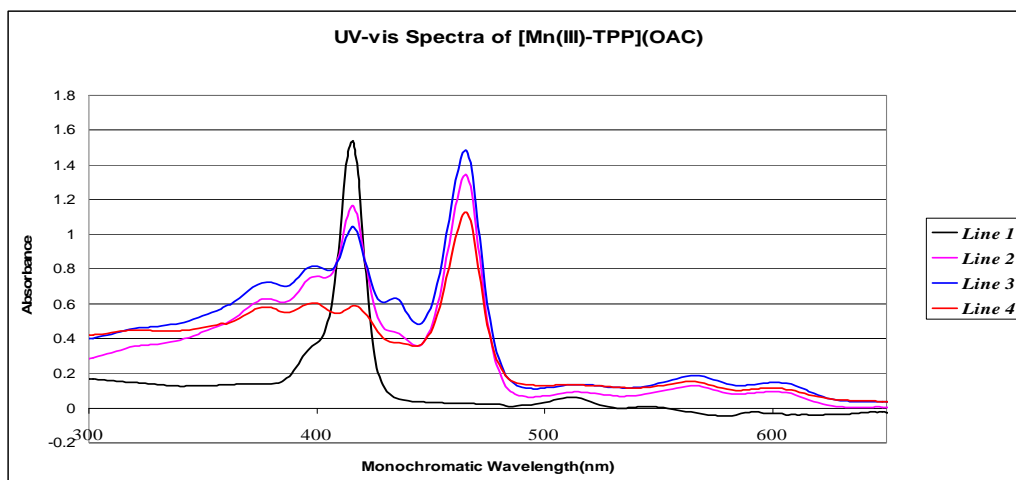
## **Experimental Section**

### **Experiment 1. Synthesis of manganese<sup>III</sup> tetraphenylporphyrin chloride**

**Materials.** manganese(II) acetate, dimethylformamide (DMF), methylene chloride, methanol (MeOH), tetraphenyl porphyrin (TPPH<sub>2</sub>), Schlenk flask, stir bar, oil bath, HP-8452A Diode Array spectrophotometer, condenser, stirring plate (heater), ice, separation funnel, vacuum flasks (Dewar flasks).

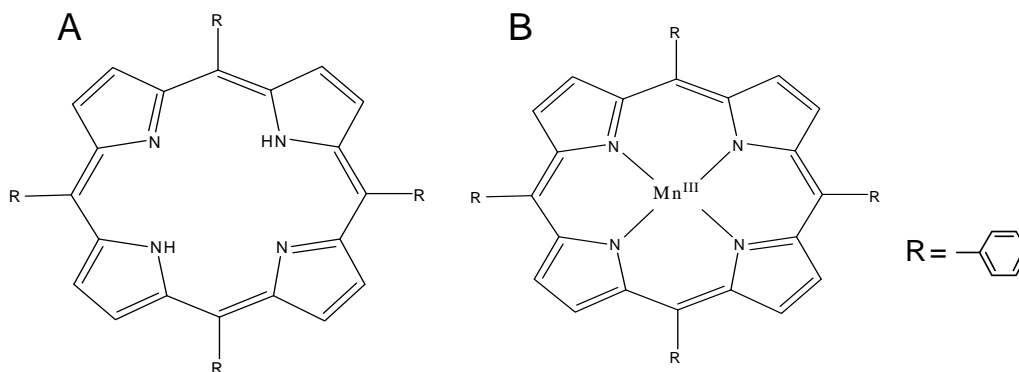
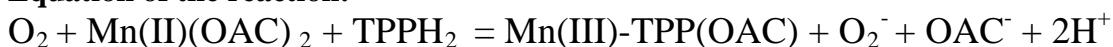
**Synthesis of manganese<sup>III</sup> tetraphenylporphyrin chloride.** TPPH<sub>2</sub> (50 mg, 0.08 mmoles) and 42 mg (0.24 mmoles) of Mn<sup>II</sup> acetate were weighed on an analytical balance and then mixed in a Schlenk flask. A stir bar was put in and 30 mL of dimethylformamide was added as a solvent. The liquid had a light purple color. Then before starting the experiment, an ultra-violet (UV-Vis) spectrum of the sample was taken as shown by line 1 in Figure 2, showing a strong absorption peak at 416 nm. The flask was then placed in a heated oil bath set to a temperature of 170 °C and a condenser was attached to the top of the flask. The condenser did not require water because the solvent (DMF) has a high boiling point, and air cools to condense it. The liquid changed to a dark purple color as the temperature increased and turned almost black at around 140 °C. Another UV-Vis spectrum was taken after half an hour as shown by line 2, with the decrease of 416 nm and the appearance of a new peak at 466 nm, and another one was taken five minutes later as shown by line 3 on the graph. The solution turned greenish-black in color when more Mn<sup>II</sup> acetate was added to help complete the reaction. After one

hour, the reaction was complete as shown by the UV-Vis spectrum in line 4. The completion of the reaction was indicated by the absorption peak at 466 nm, showing the formation of a new species. The flask was then placed in ice for it to cool down. Methylene chloride (40 mL) and an equal amount of water were added to precipitate the products. The brown-greenish solution was then put in a separatory funnel, whereby it separated into two layers after a few minutes. The first layer at the top was water and DMF while the second layer, at the bottom, was made of DMF, Methylene chloride and  $[\text{Mn}^{\text{III}}\text{-TPP}](\text{OAc})$  (acetate). The two layers were then separated and the second layer was put back in the separatory funnel. More water was added to wash the organic phase and the solution was separated again. The second layer obtained at the bottom was then put in a Schlenk flask and was attached to the vacuum pump with two Dewar flasks. They were both used to condense the solvents (DMF and methylene chloride). Liquid nitrogen was used to trap the solvents. The vacuum pump was used to evaporate the solvent and obtain the precipitate. The final product left in the flask was manganese<sup>III</sup> tetraphenylporphyrin acetate  $[\text{Mn}^{\text{III}}\text{-TPP}](\text{OAc})$ , which was then dissolved in methanol and HCl acid to form Manganese<sup>III</sup>-tetraphenyl porphyrin chloride  $[\text{Mn}^{\text{III}}\text{-TPP}](\text{Cl})$ . The product left in the flask is green in color and it weighed 46 mg.



**Figure 2.** UV-Vis spectra of the reaction of manganese acetate with tetraphenylporphyrin (line 1 – 3) and the purified [Mn(III)-TPP](OAC) (line 4).

**Equation of the reaction:**



**Figure 3.** (A) Tetraphenylporphyrin; (B)  $\text{Mn}^{\text{III}}$  tetraphenylporphyrin

**Calculating the Molecular Weight of the product:**

$$\text{Mn}^{\text{III}} = 54.9, \text{Cl} = 35.4, \text{TPP} = 613$$

$$\text{Total for all} = 703.3$$

50 mg of  $\text{TPPH}_2$  (615) was used, how much of  $[\text{Mn}^{\text{III}}\text{-TPP}]\text{Cl}$  (703) was produced?

$$\text{Theoretical yield} = 703 * 50 / 615 = 57.2 \text{ mg}$$

$$\text{Percentage yield} = (\text{Experimental amount} / \text{calculated amount}) * 100$$

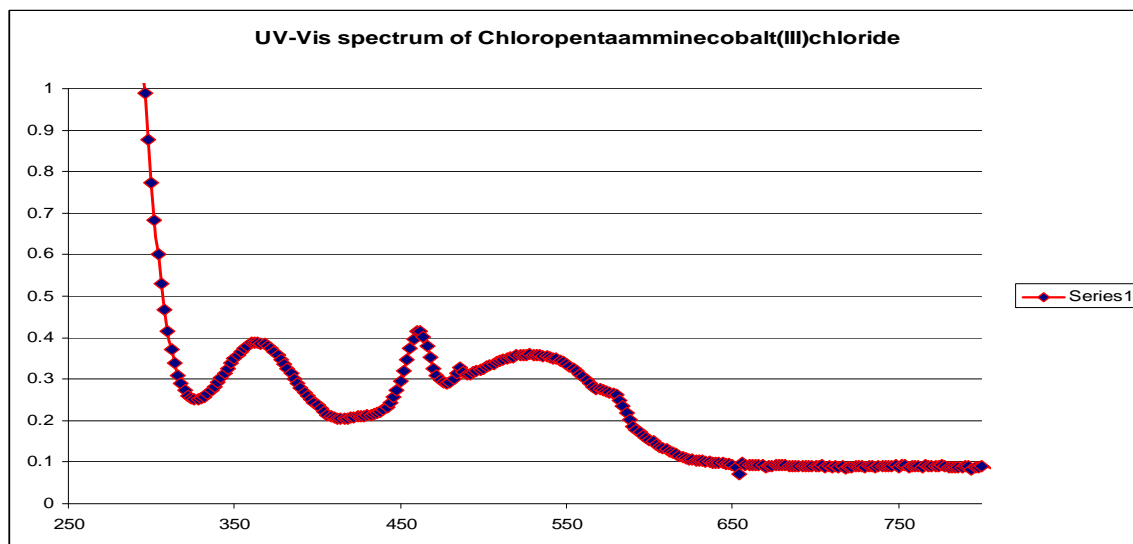
$$= 46 * 100 / 57.2 = 81\% \text{ yield}$$

## **Experiment 2: Synthesis of Chloropentaamminecobalt (III) chloride**

**Materials.** Coarsely ground  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (cobaltous chloride), water, concentrated ammonium hydroxide (28%), solid ammonium chloride, hydrogen peroxide  $\text{H}_2\text{O}_2$  (30%), filters, beakers, schlenk flask, water bath, 3M hydrochloric acid, HCl, 2M HCl acid, 1.2 M ammonium hydroxide, concentrated HCl acid, 95% alcohol (ethanol), vacuum pump, 4 to 5 portions of 25mL ether.

**Procedure.** Chloropentaamminecobalt(III) chloride was prepared following a literature method.<sup>23</sup> Eight grams of coarsely ground crystalline cobaltous chloride,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  was added to a mixture of 10 mL of water, 20 mL of concentrated (28%) ammonium hydroxide and 20 g of solid ammonium chloride in a Schlenk flask. Five mL of (30%) hydrogen peroxide was then added to the mixture while continuously stirring and was heated for an hour over a steam bath. A paste was then obtained which was treated with 100 mL of 3 M HCl acid and with continuous stirring was heated to not more than 60 °C for half an hour. The mass was filtered and washed with approximately 30 mL of 2M HCl acid. The residue was then suspended in 300 mL of 1.2 M ammonium hydroxide and heated to more than 60 °C continuously stirring it until all the purple chloride was dissolved. The liquid was then immediately filtered and the filtrate transferred to a 1000 mL three-neck round bottom flask placed on a water bath. 300 mL of concentrated HCl acid was added in three 100 mL portions at fifteen minute intervals, stirring during each addition. The heating continued for thirty minutes after the last addition, a total time of one hour. The liquid was filtered while warm and the residue first washed thoroughly with 2 N HCl acid. Next, it was washed with 95% alcohol until there were no more traces of HCl acid. (PHydrion controls (0.0 to 0.5) were used to make sure

that there were no more traces of HCl acid) in the washings and finally it was washed with four to five 25-mL portions of ether. The residue was dried for one hour using the vacuum pump. The product, chloropentaamminecobalt(III) chloride, had a light purple color. The UV-vis spectrum (Figure 4) of this compound is consistent with that reported in literature.<sup>24</sup>



**Figure 4.** UV-vis spectrum of chloropentaamminecobalt(III) chloride.

### **Experiment 3: Photoinduced oxidation of Manganese (III) Porphyrin**

**Materials and Methods.** Tris(2, 2'-bipyridine) ruthenium(II) chloride hexahydrate, chloropentaamminecobalt(III) chloride, tetra(N-methyl-4-pyridyl) porphyrinmanganese (III) chloride, phosphate (0.01 M) or acetate (0.01 M) buffers, HP-8452A Diode Array spectrophotometer, copper sulfate[CuSO<sub>4</sub>.5H<sub>2</sub>O (0.44 g/100 mL of 2.7 M NH<sub>4</sub>OH)]

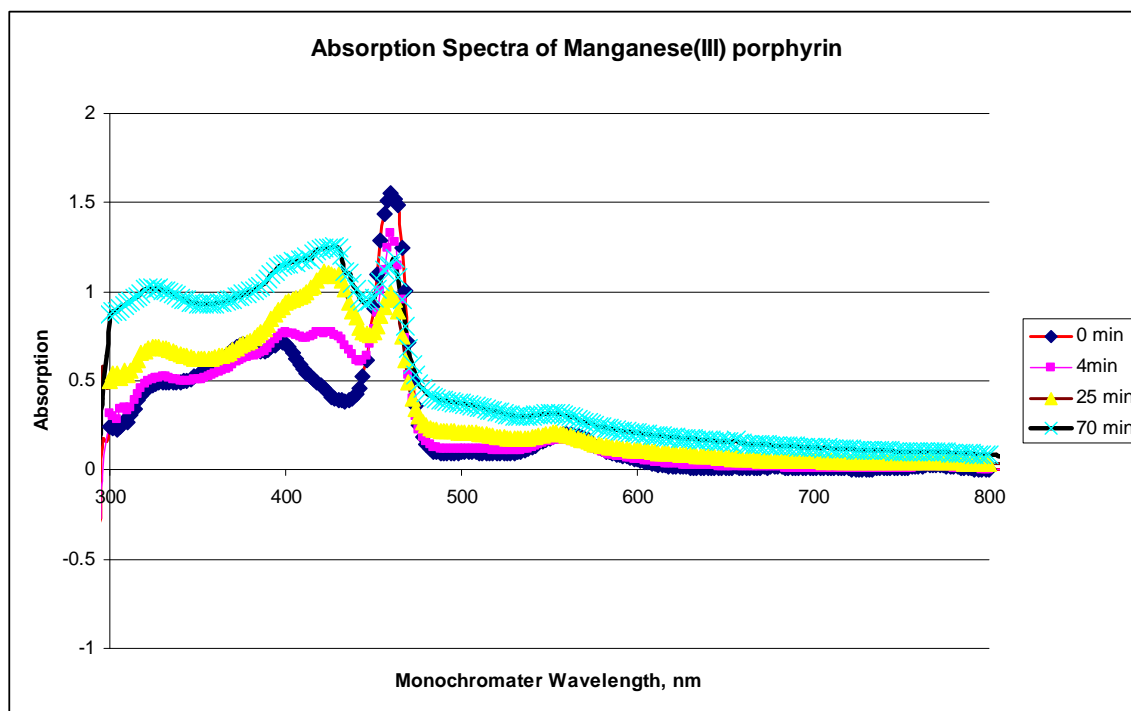
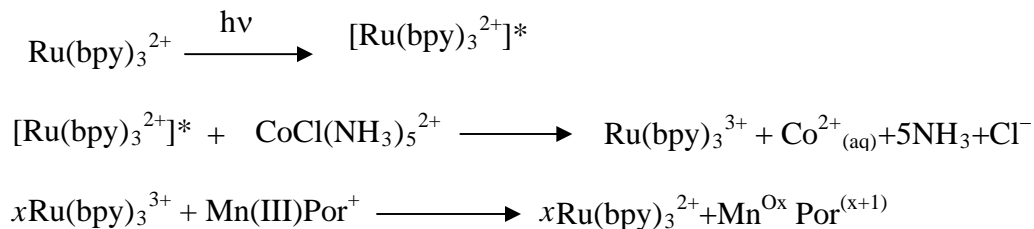
**Illumination.** The illumination of samples was performed in a 1×1cm quartz cuvette cell equipped with a glass stopcock, and a Teflon stirring bar. Simultaneous

illumination and spectrophotometric measurements were performed using the following system. A 150 W xenon lamp was passed through copper sulfate solution (a path length of 12 cm), and two glass filters to give 440 nm light. The emerging light was directed directly on the sample. The set-up was shown in Figure 5.



**Figure 5.** Illumination set-up consisting of 150 W xenon lamp, copper sulfate solution, two glass filters to give 440 nm light and the sample which contains Mn (III) Por<sup>+</sup>.

**Photoinduced oxidation of Manganese(III) porphyrin.** The oxidation of manganese porphyrins was conducted following that reported in literature.<sup>25</sup> Continuous illumination of a degassed solution containing Ru(bpy)<sub>3</sub><sup>2+</sup> (0.1 mM), CoCl(NH<sub>3</sub>)<sub>5</sub><sup>2+</sup> (1 mM), Mn(III)Por<sup>+</sup> (0.01 mM) at PH 7 (phosphate buffer) resulted in the spectral changes as shown below in Figure 6. The Mn(III)Por<sup>+</sup> forms a new single product which is its photooxidized product. The equation below shows the formation of Mn<sup>Ox</sup> Por<sup>(x+1)</sup>.



**Figure 6.** UV-Vis spectra of Manganese(III) porphyrin irradiation time at intervals of 0 min, 4 min, 25 min and 70 min.

Before the start of the experiment, the graph showed a strong absorption peak at 460 nm (Figure 6, red line). After four minutes illumination at 440 nm, the absorption at 460 nm decreased while a new absorption peak was seen at 424 nm. At the total irradiation time of 70 min a strong absorption was observed at 426 nm (Figure 6, green line), suggesting the formation of  $\text{Mn}^{\text{Ox}}\text{Por}^{(\text{x}+1)}$ . This species was unstable and changed back to its original manganese(III) porphyrin form over time.

## Conclusion

These experiments have shown that manganese(III) porphyrin can be oxidized in a three-component photochemical system, using  $\text{CoCl}(\text{NH}_3)_5^{2+}$  as the electron acceptor, consistent with that reported in literature.<sup>25</sup> The oxidized manganese porphyrin is unstable and it quickly changed back to its original manganese(III) porphyrin state. Following the same protocols as described above, the possibility of oxidation of other manganese porphyrins with different substitution groups by visible light will be investigated in future studies.

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