Synthesis and Solution Chemistry of an Octabrominated Iron (III) Porphyrin for Oxygen-Activation Catalysis

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ABSTRACT

The chemistry of water-soluble cationic porphyrins has been actively pursued in the interest of providing new materials with electronic and magnetic properties suitable for use in optical and memory devices as well as for the fabrication of metallocatalysts for the heterogeneous activation of oxygen. To this end, we have synthesized a new cationic iron(III) porphyrin bearing bromine substituents at the porphyrinic carbons.

Electrochemical studies of the iron(III) complex indicated an increase in oxidation strength by 0.33 V shift to more positive potential for the $Fe^{(III/II)}$ redox potential compared to the non-brominated iron complex. The synthesis and spectroscopic properties of the porphyrin will be presented.

INTRODUCTION

Porphyrins are cyclic organic compounds composed of four alternating pyrrole rings between methine bridges (Figure 1). Porphyrins exhibit classic aromatic characteristics obeying Huckel's rule of $(4n + 2)$ pi electrons. The highly conjugated macrocycle absorbs light strongly in the visible region with an intense Soret band around 400 nm and weaker Q-bands ranging in absorption at wavelengths of 450-700 nm. [1] Substitution at the ? and ? carbons with atoms or other functional groups is possible. The various functional groups attached to the porphyrin affect the solubility. Metal ions may also be inserted into the center of the porphyrin via chelation.
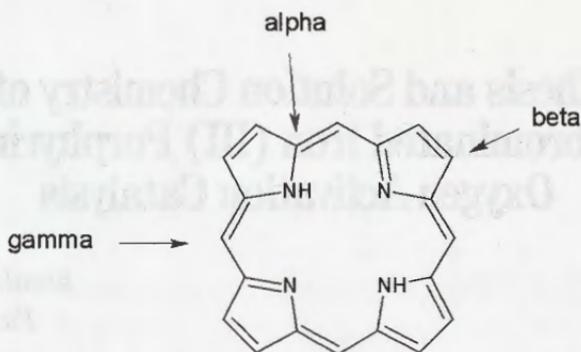
Figure 1: Chemical Structure of Porphine

Porphyrins play an integral role in biochemistry. Heme, the oxygen-carrying prosthetic group of hemoglobin and myoglobin, is an iron porphyrin. Metalloporphyrins are often utilized for catalytic purposes, for example, as catalysts for oxidation-reduction and atom transfer reactions. Specifically, porphyrin-catalyzed oxidations involve the activation of molecular oxygen for transfer to unreactive hydrocarbons. Oxidants such as peroxides and N-oxides have also been used. Since ?-halogenated porphyrins have been reported to withstand harsh oxidation conditions, the objective of this work is to synthesize the octabrominated iron (III) derivative of tetrakis(4-N-methyl)pyridiniumyl porphyrin (Figure 2) in order to develop a more profound understanding of the role of robust heterogeneous porphyrin catalysts in the activation of molecular oxygen. Applications of such metalloporphyrin catalysis include environmentally-benign synthesis, water purification, fuel-cell technology, and on-site chemical nerve-agent decomposition.[2]
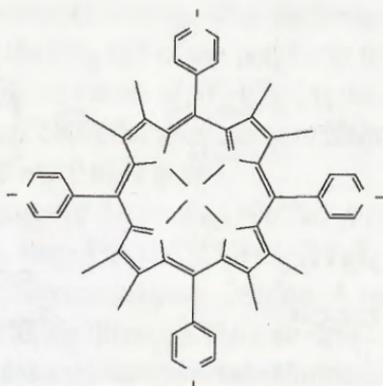
Figure 2: Chemical Structure of FeTMPyPBr$_8^{5+}$

PROCEDURE

The iron (III) porphyrin target was synthesized using several different steps. Firstly, the octabromo-derivative of the porphyrin was prepared, followed by insertion of the iron ions. [3] Ultraviolet-visible spectroscopy, using a Shimadzu UV2401PC, was then used to characterize the products.

(A) Synthesis of CuTMPyP^{4+}

Exactly 0.5194 grams of tetrakis (N-methyl-4-pyridiniumyl) porphyrin (Midcentury Chemicals) was combined with 0.5074 grams of copper (II) acetate (Fisher Scientific) in a round-bottomed flask. To that was added 50 mL of methanol and 5 mL of water were added to the round-bottomed flask. The mixture was then warmed to 40-50°C for one hour (Figure 3). The volume of the heated mixture was then reduced to dryness using vacuum distillation. No further purification was conducted.
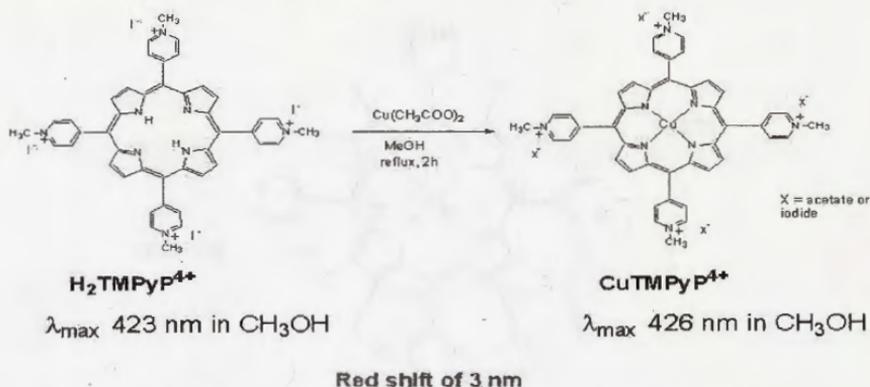
H₂TMPyP⁴⁺

λ_{max} 423 nm in CH₃OH

CuTMPyP⁴⁺

λ_{max} 426 nm in CH₃OH

Red shift of 3 nm

Figure 3: Synthesis of CuTMPyP⁴⁺

(B) Synthesis of CuTMPyPBr₈⁴⁺

Exactly 0.05487 grams of the CuTMPyPCl₄ and 25 mL of N,N-dimethylformamide (Mallinckrodt) were then added to a clean100 mL round-bottomed flask. Then 10 mL of DMF was added to a separatory funnel along with 1 mL of liquid bromine (Fluka) and mixed. The Br₂ solution was added dropwise to the round-bottomed flask and the mixture stirred using a magnetic stirring bar (Figure 4). The solution color changed from red to dark green. After the Br₂ solution was added the reaction was quenched by pouring the solution into 100 mL of distilled water. Another 50 mL of water was added and the solution was removed from stirring. A precipitate was formed and was allowed to settle. The solid was collected via suction filtration.
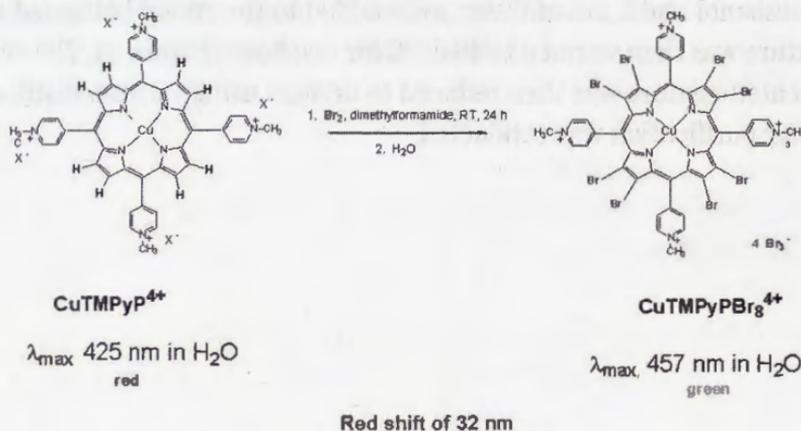

CuTMPyP⁴⁺

λ_{max} 425 nm in H₂O

red

CuTMPyPBr₈⁴⁺

λ_{max}, 457 nm in H₂O

green

Red shift of 32 nm

Figure 4: Synthesis of CuTMPyPBr₈⁴⁺

Metathesis of the counter ions was then performed. The first metathesis involved precipitating the PF_6 salt of the porphyrin from the collected solid. This was done by adding an excess of NH_4PF_6 (Acros) to the porphyrin solution. The precipitate was collected using vacuum filtration and air-dried. The mass of the precipitate was 0.6102 grams.

A total of 0.4997 grams of the product ($CuTMPyPBr_8(PF_6)_4$) was used in the second metathesis step. The $CuTMPyPBr_8(PF_6)_4$ was dissolved in acetone with excess tetrabutylammonium chloride. A new precipitate formed and was collected by suction filtration, then air-dried. A sample of the product was dissolved and determined to be the chloride salt derivative.

(C) Synthesis of $H_3TMPyPBr_8{}^{5+}$

The crystalline precipitate (0.2709 grams) was added to 15 mL of concentrated sulfuric acid (Mallinckrodt) to produce $H_3TMPyPBr_8Cl_5$ (Figure 5). The reaction was quenched after one hour with ice. The product was converted to the PF_6 salt by addition of excess NH_4PF_6. The solution was suction filtered to remove the filtrate and air-dried.

CuTMPyPBr$_8$$^{4+}$
λ_{max} 457 nm in H_2O
green

H$_3$TMPyPBr$_8$$^{5+}$
λ_{max} **497 nm in H_2O**
brown-black
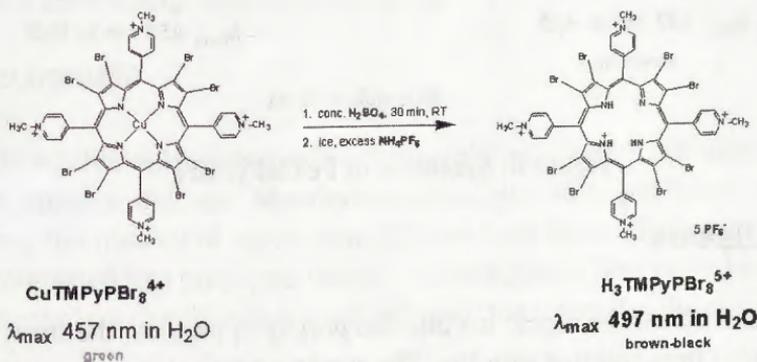
Red shift of 40 nm

Figure 5: Synthesis of $H_3TMPyPBr_8{}^{5+}$

A second metathesis was performed with 30 mL of acetone and excess NBu_4Cl (Fluka). However, the entire solid did not form. Therefore, NH_4PF_6 was added to back to the solution. The solid then redissolved in acetone so the first metathesis could then be carried out. The final product, $H_3TMPyPBr_8Cl_4$, was suction filtered to dryness.

(D) Synthesis of FeTMPyPBr$_8$$^{5+}$

The free base porphyrin was observed to react at room temperature with the iron (II) acetate. However, the reaction proceeded more rapidly when heated. The H$_3$TMPyPBr$_8$Cl$_5$ and iron (II) acetate (Aldrich) was added to a round-bottomed flask in a ratio of 1:10, respectively. 23 mL of distilled water was added to the round-bottomed flask. The solution was then refluxed and stirred (Figure 6). The solution color changed from brown to green. The porphyrin was then centrifuged and the supernatant was decanted from the precipitate.
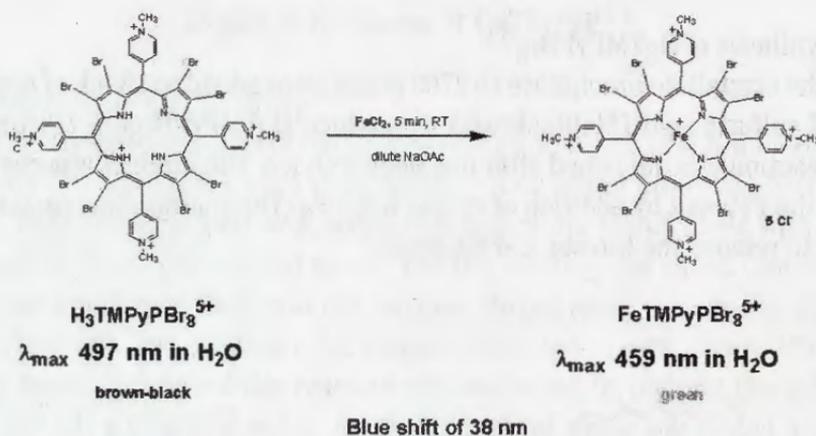

H$_3$TMPyPBr$_8$$^{5+}$

λ_{max} **497 nm in H$_2$O**

brown-black

FeTMPyPBr$_8$$^{5+}$

λ_{max} **459 nm in H$_2$O**

green

Blue shift of 38 nm

Figure 6: Synthesis of FeTMPyPBr$_8$$^{5+}$

DISCUSSION

Insertion of the cupric ion into the porphyrin protects the inner pyrole nitrogens from reacting with Br$_2$. The cupric ion was chosen because it had the highest stability constant for bonding. Characterization of the synthesis was primarily done via ultraviolet-visible spectroscopy. When Cu^{2+} was inserted, the Q-band region collapsed from four bands to two. Upon insertion, the purple solution changed to a red rust coloration.

The next step, bromination at the ?-pyrole carbons, red shifted the Soret band by 32 nanometers causing the solution to turn green. This shift is a result of the electron-withdrawing groups at the aromatic ring. During this

step, the Br_2 reacted via nucleophilic substitution at the ?-carbons. Each proton substituted for a bromine atom resulted in an additional 0.05 volt shift to more positive potential as measured by cyclic voltammetry.[4]

Once the bromination was completed, the cuprous ion was removed in order to insert the iron (II) ion. Upon demetallation, the dark green solution changed to a dark brown. Because of copper's high bonding constant, harsh acidic conditions were required. In this case, concentrated sulfuric acid was used to remove all of the copper. The copper porphyrin dissolved in concentrated sulfuric acid at room temperature and was stirred. The reaction was quenched over ice because it is an exothermic process. Excess NH_4PF_6 was added in order to precipitate out the porphyrin free base from the dilute acid solution. This step is done quickly to avoid reinsertion of copper ions into the center of the porphyrin under dilute acid. UV-Vis analysis supported the color change with a red-shift of 40 nanometers.

In the final step of the synthesis, iron (II) ions were inserted into the porphyrin. Once insertion was completed, the iron (II) oxidized to iron (III). Iron (II) ion into the porphyrin center results in a 0.33 volt shift to a more positive potential. This step is characterized by a blue shift of 38 nanometers via UV-vis and a color change from brown to green.

CONCLUSIONS

The octabrominated porphyrin complex was synthesized and ultraviolet-visible spectra indicate absorbance consistent with published data.[4] However, the removal of excess iron (II) ions from the synthetic mixture of octabrominated iron porphyrin complex is complicated. Size exclusion chromatography is currently under investigation for the removal of the excess ion.

OUTLOOK

Future experiments include complete characterization of the iron porphyrin complex. Such characterization will involve ^{13}C NMR, elemental analysis, x-ray diffraction, and pKa analysis of aquo-ligand(s) of the iron (III) metal center in aqueous phase. Once characterization is complete, the porphyrin will be sent to Coastal Carolina University where the catalytic properties will be determined.

ACKNOWLEDGEMENTS

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