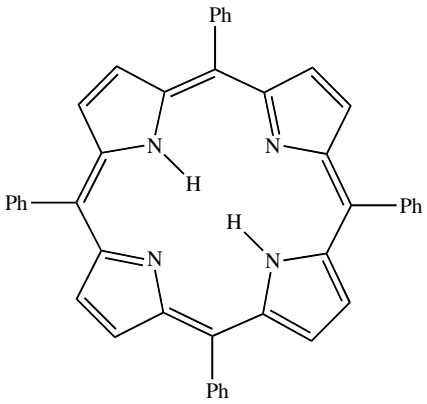
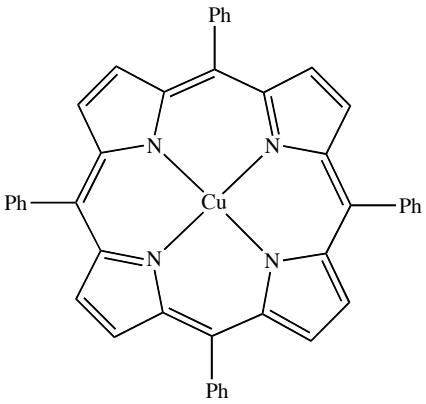
Introduction (provided by LAM)

Metalloporphyrins are important biochemical compounds. For example, iron-containing hemoglobin molecules are metalloporphyrins that bind cooperatively to oxygen and act as oxygen transporters in vertebrates.[1] Cytochrome *c* oxidase, an enzyme that contains iron-porphin units, helps to reduce oxygen to water during aerobic respiration.[2] Metalloporphyrins are also catalysts in other redox reactions involving $H_2 \rightleftharpoons H^+$, which is an important for energy source bacteria and algae, and $N_2 \rightleftharpoons NH_3$, which provides nutrients to plants.[2] Many have multiple metal centers that increase the rates of electron transfers in these reactions and reduce unwanted side reactions that form toxic products.[2]

The porphyrin, tetraphenylporphyrinate (H_2TPP), is a highly colored compound because of its completely conjugated ring structure. It was first synthesized by Rothemund in 1936.[3] However, his method, the reaction of benzaldehyde and pyrrole at 150 ˚C for 24 hours in a sealed bomb, results in low product yields and low reactivity of substituted benzaldehyde compounds. In 1967, Alder and Longo modified the reaction by carrying it out open to air and refluxing it for 30 minutes in the presence of propanoic acid.[4] These changes significantly improve the product yield and the efficiency of the reaction. The synthesis of metalloporphyrin complex, Cu(TPP), is also difficult. Although the reaction is thermodynamically favorable, it occurs slowly because the steric hindrance of the large H_2TPP ring structure makes it difficult for copper to approach the nitrogen atoms.[5]



H_2TPP



CuTPP

This report describes the efficiency of the Alder-Longo reaction method (Eq 1) for the synthesis of H_2TPP, the exchange reaction of H_2TPP with D_2O, and the reaction of H_2TPP with excess copper (II) acetate to form Cu(TPP) (Eq 2).

$$4\ C_6H_5CHO + 4\ C_4H_4NH + 3/2\ O_2 \rightarrow C_{44}H_{30}N_4 + 7\ H_2O \qquad \text{(Eq 1)}$$

$$H_2TPP + Cu(O_2CCH_3)_2(H_2O) \rightarrow Cu(TPP) + 2\ HO_2CCH_3 + H_2O \qquad \text{(Eq 2)}$$

References

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(3) Rothemund, P. A New Porphyrin Synthesis. The Synthesis of Porphin. *J. Am Chem. Soc.* **1936**, *58*, 625-627

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(where purple is background information and orange is the goal of the experiment)

The listed references are those cited in the introduction.