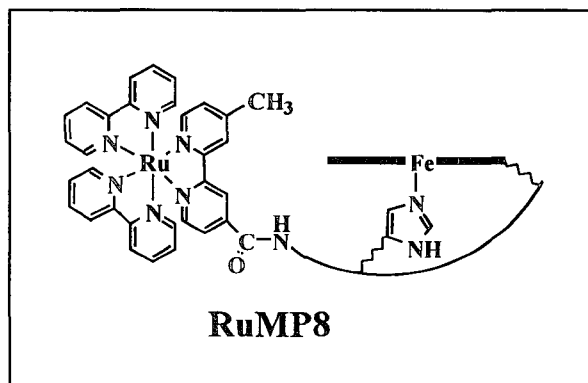


## PHOTOINDUCED ELECTRON TRANSFER AND CATALYSIS OF MICROPEROXIDE-8

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Microperoxidase 8 (MP8) has been prepared by sequential hydrolysis of cytochrome *c* by pepsin and trypsin.<sup>1</sup> This five-coordinated heme-octapeptide fragment provides a unique structure to compare the electronic coupling efficiency to the iron through the axial position and porphyrin edge. At alkali pH, Ru(bpy)<sub>2</sub>(im)<sub>2</sub><sup>2+</sup> was bound to iron through imidazolite coordination. The luminescence of Ru(bpy)<sub>2</sub>(im)<sub>2</sub><sup>2+</sup> is completely quenched in AcMP8-Ru which imply a very fast electron transfer. The transient kinetics has been measured to be greater than  $1 \times 10^{11} \text{ s}^{-1}$ . Ruthenium bipyridine complex with a carboxyl group substituted bipyridine has been prepared and reacted with the N-terminus of MP8 to yield covalent bound RuMP8 complex as shown. Photoinduced electron transfer rate of RuMP8 complex has been measured as  $1 \times 10^9 \text{ s}^{-1}$ . Marcus electron transfer theory was used to evaluate the electronic coupling for the two electron transfer pathways.



The heme environment of microperoxidase resembles

peroxidase on both structure and activities. Photoinduced oxidation of the iron ( $\text{H}_2\text{OFe}^{\text{III}} \rightarrow \text{O}=\text{Fe}^{\text{IV}}$ ) has been utilized to initiate the peroxidase catalytic cycle. Reduction of the heme center ( $\text{O}_2\text{Fe}^{\text{II}} \rightarrow \text{O}_2^{\cdot-}\text{Fe}^{\text{III}}$ ) is a key step for Monooxygenase activity.<sup>2</sup> Excitation into the MLCT band of Ru<sup>II</sup>Fe<sup>III</sup>MP8 generates reduced iron Ru<sup>III</sup>Fe<sup>II</sup>MP8. In the presence of a sacrificial donor (e.g. EDTA), the reduced form Ru<sup>II</sup>Fe<sup>II</sup>MP8 is stable for days. The RuMP8 complex provides a new route for photoinduced catalysis for MP8.

1. Low, D. W., Winkler, J. R., and Gray, H. B. *J. Am. Chem. Soc.* **1996**, *118*, 117-120.
2. Dawson, J. H. *Science*, **1988**, *240*, 433-439.