

Design of New Photoactive Ruthenium Complexes to Study Rapid Electron Transfer in Cytochrome Oxidase

Francis Millett, Sue E. Brand, Sany Rajagukguk, Lois Geren, and Bill Durham, University of Arkansas, Fayetteville, AR

Background and Objective: Cytochrome oxidase transfers electrons from cytochrome c to molecular oxygen and conserves the energy by pumping protons across the mitochondrial membrane during respiration. However, the rate of electron transfer and proton pumping is too fast to resolve by traditional techniques.

Methods: We have introduced a new method to study biological electron transfer that utilizes a photoactive ruthenium complex, Ru(II), which is covalently attached to Cc.

Results: Photoexcitation of Ru(II) to Ru(II*), leads to rapid electron transfer to the ferric heme group in Cc, followed by electron transfer to Cu_A, heme a, and heme a₃ in cytochrome oxidase. A high-yield ruthenium dimer has also been developed to rapidly inject electrons directly into CcO, allowing measurement of the kinetics of electron transfer and proton release at each step in the oxygen reduction mechanism.

Discussion and Conclusions: Important goals are to determine the location of the proton “pump site” above heme a₃, and what controls proton transfer from Glu-286 to the pump site and proton release to the exit channel. The role of electrostatics in controlling electron transfer and proton pumping in cytochrome oxidase are also examined.

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