Abstract for the Oesper Award Lecture

Steady-State 4-Electron Reduction of Oxygen by a Synthetic Analog of Cytochrome C Oxidase under Rate-Limiting Electron Flux

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A functional analog of the active site in the respiratory enzyme, cytochrome c oxidase (CcO) has been synthesized in 35 steps. This bio-mimetic analog reproduces every feature in CcO's active site: a myoglobin-like heme (heme a3), a distal tridentate imidazole ligand set bound to copper (Cub), a phenol (tyr-244), and a proximal imidazole. When covalently attached to a SAM liquid-crystalline film on an Au electrode (via "click chemistry"), this functional model continuously catalyzes the selective 4-electron reduction of oxygen at physiological potential and pH, under conditions where electron delivery is rate-limiting (as it is in CcO). By selectively blocking each redox center, while measuring partially-reduced-oxygen-species (PROS), Cub, and Tyr-244 are shown to be essential for selective 4-electron oxygen reduction.

James P. Collman
Biography

James Collman is emeritus Daubert Professor in the Department of Chemistry, Stanford University. He was born on Halloween, October 31, 1932 in Beatrice, Nebraska and is a graduate of the University of Nebraska, where he received his B.S. in 1954, and an M.S. in 1956, in chemistry. In 1958 Collman received his Ph.D. in Organic Chemistry from the University of Illinois, Champaign Urbana and proceeded directly to the University of North Carolina, Chapel Hill, as an instructor, becoming an assistant professor in 1959, an associate professor in 1962 and a full professor (of both organic and inorganic chemistry) in 1966. In 1967 he moved to Stanford University as a professor of chemistry. Collman was appointed Daubert Professor of Chemistry in 1980.

At North Carolina Collman's research focused on reactions of both coordination and organometallic compounds of the transition elements. He developed concepts such as oxidative-addition, reductive-elimination, and migratory insertion and invented a cobalt complex that hydrolyzes amide bonds at the N-terminus of peptides at physiological pH and room temperature. At Stanford, Collman continued his research on organometallic chemistry, but, inspired by the late Henry Taube, he became interested in dioxygen complexes and catalytic multi-electron redox reactions. This lead Collman to invent **functional** mimics of heme-proteins such as the "picket fence porphyrin" and more recently biomimetic analogs of the active site in the respiratory enzyme, cytochrome c oxidase. Collman's other research interests encompass diverse topics: catalytic oxygenation, multiple metal-metal bonds, dihydrogen, and dinitrogen complexes, and superconductivity.

Collman has received several national awards, two honorary degrees, and in 1974 he was elected to the NAS and the AAS. In

1983 he was named California Scientist of the Year. Collman has held several fellowships: NSF Senior Postdoctoral, two Guggenheims, Visiting Erskine (New Zealand), and Churchill (Cambridge). He has won two undergraduate teaching awards at Stanford. Collman has directed many successful students and postdoctorals; several are better known that he is. Over 40 of Collman's former coworkers hold academic positions around the World.