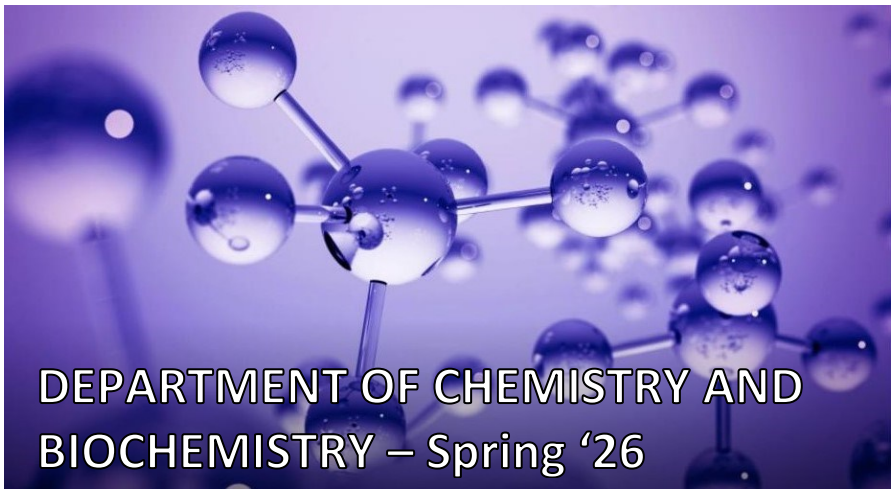

THE SALZBERG CHEMISTRY SEMINAR SERIES

The City College of New York

CREST IDEALS PHASE II

Monday, May 4 2026 @ 12:00 noon – MR1027

Detection of High Valent Intermediates in c-Type Hemes: Kinetics, Spectroscopy and Electronic Structure

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Abstract: Oxygen activation and oxidation chemistry in heme enzymes is important for many difficult chemical transformations that sustain life. The archetype enzymes are cytochrome P450 and horseradish peroxidase. A key species in the reaction process is the green intermediate compound 1, which contains a high valent state of iron (Fe^{4+}) bound to an oxygen atom and a porphyrin radical. Compound 1 is highly reactive and often short-lived which has made its characterization challenging. Prior to this work, all characterized compound 1 species were from b-type hemes, thus it was not known if enzymes with c-type hemes access the compound 1 intermediate. This has relevance to mitochondrial cytochrome *c* that shuttles electrons in electron transport chains, but gains peroxidase activity under oxidative stress conditions leading to programmed cell death. Here we discuss the first trapping and spectroscopic characterization of compound 1 from two different enzymes containing c-type hemes: bacterial cytochrome c peroxidase and cytochrome c'β. Both can function as peroxidases, but kinetic results suggest an alternative function for cytochrome c'β. New insight into the electronic structure of compound 1 implicates the propionate peripheral groups as important in stabilization of the porphyrin radical and its electronic properties, rather than the axial ligand to the heme.

Biography: Michael P. Hendrich is Professor of Chemistry at Carnegie Mellon University, which he joined in 1994. Prior to that, he was on the faculty at the University of Minnesota. He obtained his PhD at the University of Illinois in 1988. His research focus is the atomic level understanding of catalytic function of metalloenzymes, nature's catalytic centers. His group explores the isolation and spectroscopic characterization of intermediates of reaction cycles of enzymes and biomimetic complexes. The metals of interest are probed with a combination of EPR, ENDOR, Mössbauer spectroscopies, or SQUID magnetization. In the process he has developed new spectroscopic instrumentation, computer simulation software, and quantitative methodologies specifically suited to probe metalloproteins and metal complexes. His research spans the fields of physical inorganic chemistry, bioinorganic chemistry and biophysics subfields such as quantitative spectroscopy of metallocomplexes. He has published extensively and his work is highly cited by others. He has received several awards during his career, including the 1995 Searle Scholar Award.

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