

Colloquium

Developing Fe-complexes as Catalysts for Biomimetic Oxidation of Unactivated Alkyl C-H bonds

Sayam Sen Gupta

IISER-Kolkata

Chemoselective oxidation of alkyl C-H bonds in complex natural products under mild conditions have the power to reorient biomimetic natural product synthesis. Non-heme iron complexes bearing tetradentate N-donor ligands with cis labile sites, mimicking the active site of Rieske Dioxygenase enzymes, show great promise for chemoselective aliphatic C-H hydroxylation. However formidable hurdle that limits their widespread application include obtaining high levels of positional selectivity and expanding the substrate scope to include complex structures that contain more than a single polar functional group and/or arene/heteroaromatic ring(s). In this lecture, the mechanism-guided development of a peroxidase mimicking Fe-complex based on the bTAML macrocyclic ligand framework (Fe-bTAML), that perform selective oxidation of unactivated 3° bonds with unprecedented regioselectivity (3°:2° of 110:1 for adamantane oxidation), high stereoretention (99%), and high turnover numbers (TONs up to 300) using mCPBA/NaOCl as the oxidant, will be discussed. Mechanistic studies, which include correlation of product formed with Fe^V(O) reactive intermediates generated during the reaction, indicate that the major pathway involves the cleavage of C-H bonds by Fe^V(O). This methodology was then used to perform selective oxidation of several substrates including natural products with predictable selectivity, high stereoretention (>98%), and very low catalyst loadings (1-2 mol %). Finally, I will also discuss our recent efforts on using the Fe-bTAML complex to selectively catalyse the photocatalytic hydroxylation and epoxidation reactions of alkanes and alkenes respectively using water as the oxygen-atom source.

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4:00 PM (Tea/Coffee at 3:30 PM)

Auditorium, TIFR-H