# ABSTRACT

A brief overview of polydentate ligands and their metal complexes, with special emphasis on their photophysical and catalytic behaviour, has been made. In this background, the objective, scope, and application of the present investigation have been described in Chapter I.

A series of novel polydentate macrocyclic corrole ligands has been synthesized and described in chapter II. The photophysical properties of the newly synthesized family of substituted nitrophenyl free base $A_2B$-corroles have been studied. The metal ion sensing abilities of the free base ligands are explored. The $A_2B$ corroles emerge as efficient polydentate fluorophore system for selective Hg(II) ion detection in solution. Among all the corroles, the free base 10-(tridecyloxyphenyl)-5,15-bis(nitrophenyl)corrole substituted with a long chain has been found to exhibit the highest Hg(II) sensing ability. High guest count (up to three mercuric ions per corrole) with a high association constant is observed. The experimental evidences show that the emission intensity quenches with the addition of Hg(II) ion, initially *via* metal coordination and subsequently through exciplex formation. This is the first report of exciplex formation of corroles with mercury ions. The results obtained will help to improve the design of sensors for the direct determination of Hg(II) ions present in ultra low concentration.

The synthesis and characterization of new iron complex of 5,10,15 *tris*-(difluorophenyl)corrole have been described in chapter III. The catalytic properties of newly synthesized 5,10,15-*tris*(difluorophenyl)iron(IV)chloride complex [(tdfc)$Fe^{IV}$Cl] with benign *tert*-butylhydroperoxide as the terminal oxidant has been evaluated. The [(tdfc)$Fe^{IV}$Cl] /*t*-BuOOH system has been found to efficiently catalyze the oxidation of alkanes, alkenes, alkylbenzene and alcohols at room temperature. The homolytic cleavage of the O-O bond of *tert*-butylhydroperoxide by the catalyst is observed and the oxygenates have been shown to be derived from organoperoxides. The results clearly indicates that the main role of the iron(IV) corrole complex is the activation of alkyl hydroperoxide rather than oxygen atom transfer (OAT). Selective hydroxylation of unactivated C-H bonds of alkanes has also been realized using catalyst [(tdfc)$Fe^{IV}$Cl] with *m*-chloroperbenzoic acid as the terminal oxidant.

Chapter IV describes iron-corrole complex 5,10,15-*tris*(pentafluorophenyl) iron(IV) chloride [(tpfc)$Fe^{IV}$Cl] catalyzed epoxidation of olefins in ionic liquid [BMIM]$PF_6$ medium at room temperature with different terminal oxidants. For the first time, metallocorrole catalyzed epoxidation of a series of conjugated and non-conjugated olefins has been undertaken in ionic liquid ([BMIM]$PF_6$) medium at room temperature using different terminal oxidants such as *t*-BuOOH, PhIO and aqueous NaOCl. The product selectivity achieved in ionic liquid medium shows remarkable improvement over those obtained in molecular solvents. The highest product yield is achieved by a biphasic system involving ionic liquid with aqueous NaOCl as the terminal oxidant. The biphasic system provides easy recovery and recycling of the catalysts without any modification of structure.

The studies of homoleptic copper dipyrromethene complex has been discussed in Chapter V. The bidentate dipyrromethene complex of Cu(II) has been synthesized. The X-ray crystal structure of [Cu(II)$(dpm)_2$] has been determined. The neutral bis(5-(4-nitrophenyl)dipyrromethene)Cu(II) complex [Cu(II)$(dpm)_2$] is found to undergo ligand centred oxidation process to give [Cu(II)$(dpm)_2^{\bullet +}$], which has been substantiated by combined experimental and theoretical investigation. The metal bound ligand centred oxidation at high potential is of irreversible nature. The DFT calculation reveals increase in spin density over ligand moiety in the one electron oxidized [Cu(II)$(dpm)_2$] complex, suggesting radical character of the ligand. Complex [Cu(II)$(dpm)_2$] is found to catalyze C-H activation of alkanes and alkenes with *tert*-butylhydroperoxide at room temperature. The oxidation under ambient condition with benign terminal oxidant clearly indicates the involvement of the ligand based oxidation of [Cu(II)$(dpm)_2$] in catalyzing C-H activation at room temperature.

Chapter VI presents the ligand co-opertative effect in metal complex catalyzed oxidation elaborating the role of redox-neutral or redox-innocent cyclam ligand (1,4,8,11-tetraazacyclotetradecane) in C-H bond activation. The chapter describes efficient and selective hydroxylation of cycloalkanes (R-H→R-OH) catalyzed by high spin non-heme iron(III) cyclam complex [$Fe^{III}$(cyclam)$(OTf)_2$]OTf with hydrogen peroxide under mild condition. Remarkable increase in conversion and selectivity has been achieved by the addition of acid suggesting acid promoted O-O bond heterolysis. The efficient functional model of monoxygenase group of enzyme based on a high-spin iron(III) complex of cyclam [$Fe^{III}$(cyclam)$(OTf)_2$]OTf provides the first example wherein a non-heme iron complex catalyzes alkane hydroxylation with 100% selectivity.

The intercalation of *cis*-[Fe(III)(cyclam)$Cl_2$]Cl (cyclam = 1,4,8,11-tetraazacyclo- tetradecane) complex on smectite montmorillonite K-10 is described in chapter VII. The intercalated solid is fully characterized using powder EDXRF, XRD, TGA, IR and UV-Visible analysis. Complex *cis*-[Fe(III)(cyclam)$Cl_2$]Cl intercalated into Montmorillonite K-10 emerges as an efficient catalyst for selective hydroxylation (R-H→R-OH) of alkanes using environmentally benign $H_2O_2$ at room temperature. Cyclohexane and adamantane are selectively oxidized to their corresponding alcohols with remarkably high turnover number (198 and 265 respectively). Relative reaction without the clay matrix proves that a cooperative effect between the constituents of the intercalated catalyst is responsible for the enhanced selectivity.