# NEW MULTICENTERED METALLOPORPHYRINS AS CATALYSTS IN HETEROGENEOUS OXIDATION REACTIONS

*by*

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*Dedicated to*
*My Parents*

# CERTIFICATE

This is to certify that the thesis entitled, **“NEW MULTICENTERED METALLOPORPHYRINS AS CATALYSTS IN HETEROGENEOUS OXIDATION REACTIONS”** being submitted by **Mr. Amit Singh** to the Indian Institute of Technology Delhi for the award of the degree of **Doctor of Philosophy** in Chemistry, is a record of bonafide research work carried out by him. **Mr. Amit Singh** has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which, to my knowledge has reached the requisite standard.

The results contained in this dissertation are original and have not been submitted, in part or full, to any other University or Institute for the award of any degree or diploma.

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# Abstract

Cytochrome P450 based model compounds have been extensively used for the oxygenation of organic substrates from past four decades. These model compounds catalyze various types of reactions such as alkene epoxidation, hydrocarbon hydroxylation, oxidative halogenation and heteroatom dealkylation. The active site of cytochrome P450 contains iron(III) porphyrin moiety which is surrounded by a long protein chain. Different types of metalloporphyrins have been used to mimic the reactions of this family of enzymes. In the major modifications in catalyst structure various metal ions ($Mn^{3+}$/ $Fe^{3+}$/ $Co^{3+}$ etc.) are used as the core and the peripheral functional groups (electronegatively substituted porphyrins) are also altered to achieve high yield oxidation. In course of desiging more robust and efficient catalyst the solid supported and covalently linked multiporphyrin frameworks have been used. Iodosylbenzene, *tert*-butyl hydroxperoxides and peracids are used as terminal oxidants in different solvents sytems. The present study in this thesis is mainly focused on the designing of new multicentered metalloporphyrins as catalysts which are used for the oxidation of organic and organometallic substrates at room temperature. Finally, we look into the structural aspects of some organometallic compounds to understand the chemical insight.

**Chapter I:** This chapter describes: (i) the structure, mechanism and functions of cytochrome P450, (ii) developments of cytochrome P450 based model compounds, (iii) latest trends of covalent and coordination apporoach to design recyclable catalysts, (iv) use catalysts in homogeneous and heterogeneous oxidation reactions and (v) motivation and evolution of the work plan.

**Chapter II:** This chapter deals with: (i) Purification methods of different solvents and reagents, (ii) Synthesis and characterization of various functional porphyrins and

metalloporphyrins, (iii) Synthesis and characterization of palladium and platinum salts, (iv) Standarization and estimation of active oxygen content in various oxidants such as *t*-BuOOH, $C_6F_5IO$, *m*-CPBA etc.

**Chapter III:** This chapter has been divided into two parts. In the first part of this chapter the reactions of 5-(4-pyridyl),10,15,20-triphenylporphinato iron(III)chloride (MPyTPPFe(III)Cl) porphyrin with Ni, Pd and Pt salts have been described. The reaction of 5-(4-pyridyl),10,15,20-triphenyl porphyrin ($MPyTPPH_2$) with *trans*-$PdCl_2(DMSO)_2$ and *cis*-2,2-bipyridyl $PdCl_2$ gives Pd-coordinated porphyrin dimers. These porphyrin dimers were characterized by UV-visible, FTIR, Elemental analysis (CHN) and Mass spectrometry.

In the next part of this chapter, synthesis and characterization of multicentered porphyrin frameworks (MPFs) based on 5,10,15,20-tetrakis-(4-pyridyl) porphinato iron(III) chloride (TPyPFe(III)Cl) with Ni(II), Pd(II) and Pt(II) salts are described. The reaction of 5,10,15,20-tetrakis-(4-pyridyl) porphinato manganese(III)chloride (TPyPMn(III)Cl) with palladium acetate in dichloromethane-methanol solvent system also gives a new material. New MPFs (**Cat.I**, **II**, **III** and **IV**) were insoluble in common organic solvents and are mesoporous or microporous in nature. New MPFs were designed and characterized by Elemental analysis, SEM, FESEM, HRTEM, EDAX, EDXRF, PXRD, Physiorption, ICP-AES, TGA and Mössbauer spectroscopy.

**Chapter IV:** This chapter describes multicentered iron(III) and manganese(III) porphyrin based frameworks catalyzed selective oxidation of norbornene. When the oxidation of this alkene was carried out under ambient conditions by using multicentered porphyrin frameworks (MPFs) such as **Cat.I**, **Cat.II**, **Cat.III** and **Cat.IV** as the catalysts and *tert*-butyl hydroperoxide (TBHP) as a terminal oxidant in dichloromethane ($CH_2Cl_2$) solvent, *exo*-2,3 epoxy norbornane was the only product. The parallel reaction with monomeric catalysts such as 5,10,15,20-tetrakis(4-pyridyl)porphinato iron(III)chloride (TPyPFe(III)Cl) and 5,10,15,20-tetrakis(4-pyridyl) porphinato manganese(III)chloride (TPyPMn(III)Cl) were also carried out for comparison. The oxidation of norbornene in presence of iron(III) porphyrin dimers was checked. Here we observed that metalloporphyrin dimers were not good catalysts for the oxidation of organic substrates w.r.t. that for monomers.

The newly designed MPFs (**Cat.I-IV**) were more efficient in catalyzing the oxidation of norbornene as compared to their monomers (TPyPFeCl and TPyPMnCl). We have successfully achieved 90-95% selective conversion of norbornene into *exo*-2,3 epoxy norbornane by MPFs **Cat.I**, **III** and **IV** in 4-12 hrs under optimized reaction conditions. The new MPFs were highly robust and recyclable with multilayered and high active surface area for catalysis. The effect of slow addition of oxidant was also studied for such reactions.

**Chapter V:** This chapter describes the iron(III)porphyrin catalyzed oxidation of organopalladium compound. The iron(III)porphyrin catalyst (TPyPFeCl) and **Cat.I.** (MPFs) were used as a catalyst and pentafluoro iodosyl benzene (PFIB) and *meta*-chloroperbenzoic acid (*m*-CPBA) were used as terminal oxidants. These organopalladium compounds were synthesized and characterized by various spectroscopic techniques.

The selective oxidation of organopalladium azo-compound was achieved in high yield when PFIB and *m*-CPBA were used as oxidants in presence of newly designed MPFs (**Cat.I**). **Cat.I** found to be more efficient than TPyPFe(III)Cl. The recyclabiilty of **Cat.I** is also more than monomeric catalyst. In case of *m*-CPBA the reaction time is only

5 minutes. **Cat.I** provides quantitative yield in all six cycles whereas TPyPFe(III)Cl provide the mixture of products *i.e,* LCOPdCl and LSOPdCl.

**Chapter VI:** This chapter has been divided into two parts. In the first part (**VI.A**): the crystal engineering aspect of the organopalladium compounds have been described with respect to anion template effect. Interestingly, the series of molecules provided a pathway to find out the link between isostructurality, polymorphism and weak interactions (C−H···X, X···X, S···S, π··· π and C−H···π etc). We have described the influence of auxiliary C–H···X interactions in dictating isostructures and polymorphs among a series of palladacycle crystals. A series of organopalladium compounds of the general formula, LPdX {L= phenyl azo-thioether based tridentate (C, N, S) ligand with different substituent and X= Cl, Br, I, $NO_3$, $ClO_4$}, have been synthesized and characterized. Methyl substituted ligand resulted in isostructural solids for all halo salts. The unsubstituted and chloro substituted ligands yielded isostructures only for chloride and bromide salts. The chloride salt of chloro substituted ligand led to a pair of concomitant polymorphs. The salts based on polyatomic anions, namely, nitrate and perchlorate resulted in different crystal packing due to dominant C–H···O interactions.

In the next part (**VI.B**): A modified ligand (phenyl azo-2-pyridine (**PAP**)) with nickel and palladium chloride salts resulted in new molecular solids; interestingly the variations of solvents lead to different crystal forms with unusual morphologies. The $(PAP)_2NiCl_2$. X (where X= $CH_2Cl_2$, $C_2H_4Cl_2$, $CHCl_3$, $CCl_4$, $CH_3CN$, $C_3H_6O$ and $C_8H_8O$ etc.) complexes show the solvent inclusion almost in every case except a few which demonstrate the role of solvent in fine-tuning of C−H···Cl, C−H···N and C−H···O weak interactions.

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