SYNTHESIS, CHARACTERIZATION AND THE CATALYTIC ACTIVITY OF NEW COVALENT METALLOPORPHYRIN FRAMEWORKS

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by

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CERTIFICATE

This is to certify that the thesis entitled, **"SYNTHESIS, CHARACTERIZATION AND THE CATALYTIC ACTIVITY OF NEW COVALENT METALLOPORPHYRIN FRAMEWORKS"** being submitted by **Mr. Manoj Kumar 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. Manoj Kumar 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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Dedicated
to
My Parents

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Abstract

The thesis entitled ‘Synthesis, characterization and the catalytic activity of new covalent metalloporphyrin frameworks’ presents the research work carried out on model compounds based on heme enzymes. Heme enzymes, such as cytochrome P450 (CYP 450), peroxidase, catalase, heme oxygenase, and nitric oxide synthase catalyze a diverse array of important metabolic transformations that require the binding and activation of dioxygen. The dioxygen activation catalyzed by heme enzymes and model compounds has been extensively explored. The active site of the enzyme contains an iron(III) porphyrin, thus several metalloporphyrins are used as cytochrome P450 models. In the model compounds various metal ions (Fe^{3+}, Mn^{3+}, Co^{3+}, Ru^{3+} etc.) are used as the core and the peripheral functional groups (electronegatively substituted porphyrins) are also altered to achieve high yield oxidation of organic molecules. The solid supported and metal coordinated multinuclear metalloporphyrins have been prepared along these lines to gain greater catalyst survival. The *t*-BuOOH, H_2O_2, CumOOH, *m*-CPBA, C_6F_5IO are used as terminal oxidants in different solvents systems. The work presented in this thesis is mainly focused on the design of new covalently linked multicentered metalloporphyrins as catalysts, their synthesis, characterization and catalytic activity. On catalytic activity the oxidation of organic substrates at room temperature and the [4+2] cycloaddition reaction for unactivated aldehydes with simple dienes in the presence of catalytic quantities of those new metalloporphyrins are addressed.

Chapter I described the literature on: (i) the known basic structural and functional information of cytochrome P450, (ii) the historical development of the model compounds of cytochrome P450. (iii) the recent approach of covalent metalloporphyrin frameworks, (iv) the use of such catalysts as homogeneous and heterogeneous catalysts in oxidizing reactions and (v) the motivation and evolution of the present work plan.

Chapter II deals with: (i) purification methods of different solvents and reagents, (ii) synthesis and characterization of various functional porphyrins and metalloporphyrins, (iii) synthesis of some palladium and platinum salts, (iv) standardization and estimation of active oxygen content in various oxidants such as *t*-BuOOH, H_2O_2, CumOOH, *m*-CPBA.

Chapter III described the details of the transformation of tetrakis (5,10,15,20-p-bromophenyl) iron (III) and manganese (III) porphyrins to the respective mesoporous materials of variable surface areas by Suzuki coupling. Four materials, all mesoporous, were thus isolated with surface areas of 159 m^2/g; 263 m^2/g; 702 m^2/g; and 1301 m^2/g. All the materials were tested for their oxidizing ability of cycloalkenes/alkane by *t*-BuOOH, H_2O_2, CumOOH and *m*-CPBA. All the catalysts were found to oxidize various alkenes selectively and the material with highest surface area (1301 m^2/g) was found to be the most efficient one. This material with surface area of 1301 m^2/g was not destroyed even 5% in 10 cycles of successive oxidation processes of norbornene conducted in one pot.

Chapter IV gives the details of the synthesis of two nanoporous perylene bis-imide linked metalloporphyrin framework catalysts via condensation of 5,10,15,20-tetrakis-(4′-aminophenyl) iron(III) porphyrin chloride or 5,10,15,20-tetrakis-(4′-aminophenyl) manganese(III) porphyrin chloride with perylene-3,4,9,10-tetracarboxylic dianhydride. Both the materials were crystalline in nature and were characterized by electron microscopy techniques, the solid-state ^{1}H-^{13}C CP/MS NMR, powder X-ray diffraction (PXRD), and magnetic susceptibility measurements. The nitrogen gas physisorption study has indicated that both materials are porous in nature and have BET surface areas of 653 m^2/g and 974 m^2/g respectively with uniform pore size of 2.8-3.0 nm. These materials act as heterogeneous catalysts for selective oxidation of alkanes/ alkenes with

tert-butyl hydroperoxide and are not degraded even after multiple uses up to a minimum of 10 cycles in one pot.

Chapter V described how the two iron(III) tetraphenyl porphyrin catalytic units are connected by an azo-link to form the dimeric compound **A**. Compound **A** was then reacted with Pd^{2+} to make a tetrameric iron(III) porphyrin complex **B** with all four iron(III) catalytic sites open to the substrates and reactants. Both the compounds were characterized spectroscopically and the morphology of **B** was established by SEM and AFM images. The results of homogeneous oxidation of some alkanes and alkenes with *t*-BuOOH in presence of catalytic quantities of **A** and **B** has indicated remarkable improvement in the selectivity and efficiency of **B** over **A** and **A** over the monomeric catalyst.

The last chapter has results on one-pot efficient reaction of several unactivated aldehydes with a simple diene to their corresponding pyran derivatives in the presence of catalytic quantities of nanoporous iron(III) porphyrin frameworks. This heterogeneous catalyst has been readily synthesized from 5,10,15,20-tetrakis(4-cycnophenyl)porphyrin iron(III)chloride with the help of Pinnar type synthesis. The elucidation of the structure of the amorphous materials were tried by using different characterization techniques including fourier transform infrared spectroscopy (FT-IR), powder X-ray diffraction (PXRD), CHN, atomic absorption (AAS), scanning electron microscopy (SEM). The surface areas of the materials were measured by physisorption study of N_2 at 77K. The standard conditions for the catalytic hetero Diels-Alder reaction of a series of compounds in high yield is also described. In all these reactions it has been noted that the catalyst remains active for at least 8 cycles without any significant degradation. The catalytic reactions of PFeX with variable P and X for [4+2] cycloaddition of different benzaldehydes with a diene has been added up to understand the mechanistic aspects.

Table of contents

List of schemes and figures

Abbreviations

COFs	Covalent Organic frameworks
CMFs	Covalent Metalloporphyrin Frameworks
CYP450	Cytochrome P450
DCM	Dichloromethane
EDX	Energy dispersive X-ray
$F_{20}TPP$	*meso*-tetrakis(pentafluorophenyl)porphinato
FESEM	Field emission scanning electron microscopy
GC	Gas chromatography
HRMS	High resolution mass spectrometry
ICP-AES	Inductively coupled plasma atomic emission spectroscopy
ICP-AAS	Inductively coupled plasma atomic absorption spectroscopy
IR	Infra-red
SQUID	Superconducting Quantum Interference Device
m-CPBA	*meta*-chloroperoxybenzoic acid
MOFs	Metal organic frameworks
$TPPH_2$	5,10,15,20-tetraphenyl porphyrin
NMR	Nuclear magnetic resonance
P	General notation for porphyrin ligand
CumOOH	Cumyl Hydroperoxide
PXRD	Powder X-ray diffraction
TBHP	*Tert*-butyl hydroperoxide
TGA	Thermo- gravimetric analysis
$(NH_4)_4TPPH_2$	*meso*-tetrakis(4-aminophenyl)porphinato
$(Br)_4TPPH_2$	*meso*-tetrabromophenyl-porphinato
$(NH_2)_4TPPFe(III)Cl$	5,10,15,20-*tetrakis*(4-amino)porphinato iron(III) chloride
$1\text{-}NO_2TPPH_2$	5-(4-nitrophenyl)10,15,20-triphenylporphyrin
$(NH_2)_4TPPMn(III)Cl$	5,10,15,20-*tetrakis*(4-amino)porphinato manganese(III) chloride
UV-vis	Ultra-violet visible
PXRD	Powder X-ray Spectroscopy
ESI-Mass	Electrospray Ionization- Mass
TEM	Transmission electron microscopy