# CHAPTER 8

# CHEMISTRY

## Doctoral Theses

01. AGARWAL (Pallavi)

**Six-Membered Cyclopalladated N, N’, N”- Triarylguanidines Ligated with Pyrazole and Substituted Pyrazoles and Cadmium (II) Pivalate Complexes. Syntheses, Structural Aspects and Catalysis.**

Supervisor: Prof. N. Thirupathi

Th 23087

*Abstract*

*(Not Verified)*

Six-membered cyclopalladated N,N',N"-triarylguanidines, $[\{k^2(C,N)Pd\}_2(m\text{-}OAc)(m\text{-}Pz)]$ (I–IV), $[k^2(C,N)Pd(m\text{-}Pz)]_2$ (V–XI), and $[AgNO_3$Ì$\{\{k^2(C,N)Pd\}_2(m\text{-}NO_3)(m\text{-}Pz)\}]$(XII) have been isolated in good yields and characterized by micro-analytical, IR, and NMR ($^1H$, $^{19}F$, and $^{13}C$) spectroscopic techniques. Molecular structures of ten complexes were determined by SCXRD. The reactions of six-membered cyclopalladated N,N',N"-triarylguanidines, $[k^2(C,N)Pd(m\text{-}X)]_2$ (97, 99, 104, 105 and XIII) with two equiv. of pyrazole (pzH) and 3,5-dimethyl pyrazole (3,5-dmpzH) in $CH_2Cl_2$ at RT for 24 h afforded a new class of cyclopalladated N,N',N"-triarylguanidines, $[k^2(C,N)Pd(PzH)_2X]$ (Ar = 2-$MeC_6H_4$; X = Br; PzH = 3,5-dmpzH (XIV), pzH (XV); X = $OC(O)CF_3$; PzH = 3,5-dmpzH (XVI); Ar = 2-$(MeO)C_6H_4$; X = Br; PzH = 3,5-dmpzH (XVII); $OC(O)CF_3$ (XVIII); Ar = Ph; X = $OC(O)CF_3$; PzH = 3,5-dmpzH (XIX)) in good yields. The reaction of XIV with $NH_4PF_6$ in $CH_2Cl_2$ at RT for 24 h afforded $[k^2(C,N)Pd(3,5\text{-}dmpzH)_2(PF_6)]$ (XX) in 83% yield. Complexes XIV–XX were characterized by elemental analyses, IR, NMR ($^1H$, $^{13}C$ and $^{19}F$) spectroscopic techniques, and conductivity measurements. The catalytic efficacy of XIV–XX in Suzuki-Miyaura coupling reactions of various aryl bromides with $PhB(OH)_2$ was evaluated and these cyclopalladated guanidines showed a wide substrate scope in the coupling reactions with low catalyst loadings (1.00, 0.1 and 0.01 mol%) under mild reaction conditions. The reaction of $CdCl_2\cdot 2.5H_2O$ with two equiv of aq. NaOH followed by treatment of the resulting solution with two equiv of pivalic acid gave $[Cd(k^2\text{-}OC(O)^tBu)_2(H_2O)_2]$ (XXI) while the reaction of $Cd(OAc)_2\cdot 2H_2O$ with two equiv of aq. NaOH followed by treatment of the resulting solution with two equiv of pivalic acid gave a heterobimetallic one dimensional coordination polymer (1D-CP), $\{Na_2[Cd(m_5\text{-}k^3\text{:}k^3\text{-}OAc)(m_3\text{-}k^2\text{:}k^3\text{-}OC(O)^tBu)(m_3\text{-}k^1\text{:}k^2\text{-}OC(O)^tBu)_2]\cdot 2^tBuC(O)OH\}_{¥}$ (XXII). Complexes XXI and XXII were characterized by microanalytical data, IR spectroscopy, solution $^1H$ and $^{13}C$ $\{^1H\}$ NMR spectroscopy and solid state CP-MAS $^{13}C\{^1H\}$ NMR spectroscopy, TG-DTA analyses and single crystal X-ray diffraction.

*Contents*

1. Introduction. 2. Results and discussion. 3. Experimental section.

02. ALKA DEVI

**Novel Approaches for Synthesis of Quinazolines, Quinazolinones and 3-Aryl-3, 4-Dihydro-(2H)-1, 2, 4-Benzothiadiazine 1, 1-Dioxides from Benzylamines.**

Supervisor: Dr. K. Gopalaiah

Th 23088

*Abstract*
*(Not Verified)*

The thesis entitled “Novel Approaches for Synthesis of Quinazolines, Quinazolinones and 3-Aryl-3,4-Dihydro-(2H)-1,2,4-Benzothiadiazine 1,1-Dioxides from Benzylamines” is to be submitted to the University of Delhi. The thesis deals with the studies related to the oxidative coupling methods with a variety of nitrogen nucleophiles to produce six-membered nitrogen heterocycles in the presence of sustainable metal catalysts. The thesis consists of five chapters. Chapter 1 deals with the conceptual aspects of oxidative coupling transformations. Several named reactions in this field such as Negishi reaction, Suzuki reaction, Stille reaction, Hiyama reaction and Buchwald–Hartwig reaction have been explored and widely applied in industry. By variation of the coupling partners, coupling reactions can be classified into three types: traditional coupling, oxidative coupling, and reductive coupling. Chapter 2 deals with the development of novel, efficient and practical approach for synthesis of quinazolines by oxidative cross-coupling of benzylamines with ortho-aminobenzylamine. Based on recent studies from our laboratory, it was envisaged that the reaction could be carried out between benzylamines and o-aminobenzylamine to give the 2-substituted quinazolines. Reactions were feasible with electron-donating and electron-withdrawing substituents on the phenyl ring of benzylamine. Chapter 3 describes studies aimed towards the exploration of cascade synthesis of quinazolines from benzylamines and o-aminobenzylalcohol. In the perspective of atom economy and green chemical synthesis, we have screened various iron salts and solvents to optimize the reaction conditions. The reaction proceeds smoothly at 110 °C in the presence of oxone as an oxidant. Chapter 4 describes attempts to develop a novel and efficient approach for synthesis of 2-substituted quinazolinones from readily available benzylamines and anthranilamide in a simple and one-pot procedure. Chapter 5 deals with the development of a new approach based on the oxidative coupling methodology for synthesis of 3-aryl-3,4-dihydro-(2H)-1,2,4-benzothiadiazine 1,1-dioxides from 2-aminobenzenesulfonamide and benzylamines.

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1. Oxidative coupling reactions for carbon-carbon and carbon-heteroatom bond formations 2. Iron-catalyzed oxidative cross—coupling of Benzylamines and o-aminobenzylamine for synthesis of quinazolines 3. Iron-catalyzed cascade synthesis of quinazolines and o-aminobenzylalcohol 4. Copper-catalyzed oxidative reaction for synthesis of quinazolinones from anthranilamide andbenzyamines 5.Coppr-catalyzed oxidative coupling of benzylamines and 2-aminobenzenesulfonamide for synthesis of 3-Aryl-3, 4-dihydro-(2H)-1,2,4-benzothiadiazine 1,1-dioxide. Summary and publications.

03. ANJEETA RANI

**Divulging the Biomolecular Interactions between the Proteins and Osmolytes**

Supervisor: Dr. P. Venkatesu

Th 22997

*Abstract*
*(Not Verified)*

The marginal stability of protein can easily lead to denatured conformation of protein which may not function properly resulting in physiological malfunctioning. This situation cannot be avoided as the surrounding is full of a number of harsh conditions such as temperature, pressure, pH etc. The osmolytes are assumed to be derived through natural selection due to their ability to protect proteins of the organism from the various stresses. The study of interactions of protein and osmolytes may be lead to get insight into the mechanism by which these osmolytes stabilize the proteins. It may be emphasized here in the present work that sucrose and trehalose have stabilizing and activating impacts on stem bromelain (BM) at all concentrations except at their lower concentration where both are behaving as destabilizers as well as deactivators. Urea and GdnHCl, both show same trends as a function of concentration but vice versa to the trehalose and sucrose. Hydrated trehalose and poorly hydrated or bare GdnHCl is playing a key role in counteraction of adverse effect of GdnHCl on BM. Sorbitol is found to show unanticipated behaviour for BM stability that is poor stabilizer as compared to other small sized polyols. It can be concluded here that direct binding of osmolyte to the active site of BM may be the

leading factor for decrease in activity of BM except proline where high rigidity of active site may be responsible. Proline possesses utmost efficacy to increase the thermal stability among all studied osmolytes attributing to preferential exclusion. The interaction between sugar and catechin may diminish the fruitful impacts of catechin on In. The preferential binding of sugar is playing role behind the unfavourable impacts of catechin on In in the presence of sugars.

*Contents*

1. Introduction and review of the literature 2. Materials and experimental techniques 3. Influence of a series of structurally related polyols on the stability and activity of stem bromelain 4 (a). Influence of sugars and classical denaturants on the stability and activity of stem bromelain. 4(b). Counteraction effects of trehalose on denaturant-induced unfolding of stem bromelain 5. Influence of methylamines and amino acids on the stability and activity of stem bromelain 6. Influence of sugars on the structure and stability of insulin in the presence of green tea. 7. Conclusions.

04. ARORA (Ritu)
**DFT Mechanistic Studies on Some Important Organic Rearrangements**
Supervisor: Prof. Rita Kakkar
Th 23016

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1. Diazoketones and their reactions 2. Computational methods 3. Schmidt rearrangement of some protonated acyl azides 4. Wolff rearrangement of some diazocarbonyl compounds 5. Negative ion wolff rearrangement of some diazoketones 6. Rearrangements in radical cations of diazoketones 7. Concluding remarks.

05. ARUN KANT
**Montmorillonite and its Polymer Composites for Extended Release of Drugs.**
Supervisor: Prof. Monika Datta
Th 23008

*Abstract*
*(Not Verified)*

ABSTRACT In detail, the term Drug Delivery Systems was referred to the construction of delivery vehicle for drug and method of its administration in the human as well as animal body. Overall the challenge of increasing the therapeutic effect of drugs and concurrent minimization of side effects, can be tackled through proper design and engineering of the DDS in a case to case manner. The problem with the use of such dosages is the fluctuations in drug concentration in blood plasma resulting in serious undesirable side effects. Extended drug delivery system can control the effective required concentration of the drug in the blood plasma for the required period of the time. This can also improve bioavailability by preventing premature degradation. Montmorillonite is FDA approved excipient material has attracted great interest from researchers all over the world. Mt, organo Mt and Mt in combination with polymers (PLGA and Alginate) to form composite materials are used as drug carrier. In the present thesis efforts has been made for the development of methodology for the synthesis of Mt based drug delivery for three drug, Metronidazole (antibiotic drug), Metoprolol tartrate (antihypertensive drug) and Hydrochlorothiazide (antihypertensive drug). The work can be divided into two, Section-I and section-II. SECTION I: This section further divided in five chapters. CHAPTER 1: DRUG DELIVERY SYSTEM CHAPTER 2: DRUGS USED IN THE PRESENT WORK CHAPTER 3: METHODOLOGIES CHAPTER 4: THEORY OF ADSORPTION ISOTHERM MODELS CHAPTER 5: THEORY OF KINETIC MODELS SECTION II: This section further divided in six chapters CHAPTER 1: PRISTINE Mt AS DRUG DELIVERY VEHICLE CHAPTER 2: ORGANO Mt AS DRUG DELIVERY VEHICLE CHAPTER 3: Mt - PLGA COMPOSITE AS DRUG DELIVERY VEHICLE CHAPTER 4: Mt-ALGINATE BEADS AS DRUG DELIVERY VEHICLE CHAPTER 5: SUMMARY OF THE WORK REPORTED CHAPTER 6: FUTURE PROSPECTS OF THE WORK REPORTED

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1. Drug delivery system. 2. Drugs used in the present work. 3. Methodologies. 4. Theory of adsorption isotherm models. 5. Theory of kinetic models. Section II: 1. Pristine Mt as drug delivery vehicle. 2. Organo Mt as drug delivery vehicle. 3. Mt-PLGA composite as drug delivery vehicle. 3. Mt-alginate beads as drug delivery vehicle. 5. Summary of the work reported. 6. Future prospects of the work reported.

06. BANSAL (Deepak)
**Coordination Chemistry with Amide- Based Ligands Containing Additional Thiazole, Thiazoline, Benzothiazole and Benzimidazole Donors.**
Supervisor: Prof. Rajeev Gupta
Th 23021

*Abstract*
*(Not Verified)*

This dissertation is divided into six chapters. Chapter 1, introductory in nature, presents an overview of various amide-based ligands and their coordination aspects with different metal ion. Subsequent chapters discuss the coordination chemistry of several amide-based ligands containing appended thiazole, thiazoline, benzothiazole and benzimidazole rings. In particular, chapter 2 presents a few mononuclear metal complexes in which the appended heterocyclic rings create H-bonding based secondary coordination sphere which assist in binding and orienting the substrate(s) closer to the catalytic metal ion. In chapter 3, sensing properties of several amide-based ligands, appended with different heterocyclic rings, was evaluated towards various metal ions with notable sensing of Cu(II) and Zn(II) ions. Chapter 4 presents a series of hydroxide-bridged dizinc(II) complexes containing H-bonding cavities. Depending on cavity structure and therefore secondary coordination sphere, these complexes showed remarkable recognition abilities toward assorted phosphates with significant sensing of ATP. Chapter 5 presents a series of hydroxide-bridged dicopper(II) complexes with the focus to evaluate their role in catecholase activity where parameters, such as extent of H-bonding and cavity structure, were found to influence the catecholase activity. The last chapter explores several μ-oxo bridged tri- and tetra-nuclear cobalt and manganese complexes in which appended thiazole, thiazoline, benzothiazole and benzimidazole rings play significant roles in controlling formation of tri- versus tetra-nuclear core.

*Contents*

1. Introduction: Survey of amide-based Ligands containing appended heterocyclic rings and their coordination complexes 2. Mononuclear complexes of amide-based ligands containing appended functional groups: Role of secondary coordination spheres on substrate binding and catalysis 3. Cavity based coordination complexes of amide-based Ligands containing appended benzothiazole rings: Selective binding of Cu (II) and Zn (II) ions 4. Hydroxide- bridges dinuclear Zinc complexes in hydrogen bond surroundings: Selective binding of assorted phosphates. 5. Hydroxide-bridged dinuclear copper cores within hydrogen bonding cavities: modelling catacholase activity 6. Oxo-bridged trinuclear and tetranuclear manganese and cobalt complexes with amide-based Ligands containing appended heterocyclic rings. List of publications.

07. BISHNOI (Swati)
**Design, Synthesis and Characterization of Some Novel Heterocyclic Compounds and their Applications.**
Supervisor: Prof. Marilyn Daisy Milton
Th 23165

*Contents*

Part A. Design, synthesis and characterization of novel phenothiazine-based compounds: photophysical, thermal and computational studies and their applications 1. Novel tunable phenthiazine hydrazones as colour displaying, ratiometric and reversible pH sensors 2. Synthesis and characterization of novel brominated phenothiazine-5-oxide scaffolds 3. Synthesis and characterization of novel diaryl-phenothiazine-5oxides: potential candidates for optoelectronic materials Part B. Design, synthesis and characterization of novel benzimidazolium salts and their applications 4. Design, synthesis and characterization of novel unsymmetrically N, N'-disubstituted benzimidazolium salts 5. Application of benzimidazolium salts as fluorescent probes for micromolar detection of Fe (III) ions in aqueous media and as preligands for suzuki-miyaura coupling 6. Summary and conclusions. Publications.

08. BHATTACHARYA (Soumee)
**Synthesis of Selected Core-Modified Porphyrinoids in Sensing, Photodynamic Therapy and Development of Newer Materials.**
Supervisor: Prof. S.M.S. Chauhan
Th 23019

*Abstract*
*(Not Verified)*

ABSTRACT The thesis entitled "Synthesis of selected core-modified porphyrinoids in sensing, photodynamic therapy and development of newer materials" has been divided into five chapters. CHAPTER-1 Brønsted acidic ionic liquids catalyzed efficient synthesis of symmetrical and unsymmetrical core modified porphyrins and its application for the detection of toxic metals. Porphyrins are a class of conjugated macrocyclic compounds in which four pyrrole rings are interconnected to each other in cyclic fashion through meso-carbon bridges. Replacement of pyrrole by other heterocycles, such as furan, thiophene, selenophene and tellurophene in a porphyrin ring leads to new macrocyclic systems referred to as core-modified porphyrins or heteroatom substituted porphyrins. CHAPTER-2 Synthesis of different calix[4]phyrins and their interaction with mercury. Calix[4]phyrins consist of the intermediate structure of porphyrins and calix[4]pyrroles and, they have properties analogous to those of both porphyrins and calix[4]pyrroles and play diverse roles as metal ion receptors and anion complexing agents and form a rich coordination chemistry. CHAPTER-3 Synthesis of expanded core modified porphyrinoids and their application in the sensing and photodynamic therapy Expanded porphyrins are synthetic analogues of the porphyrins and differ from porphyrins by containing more than 18p electrons in the conjugated pathway either due to an increased number of heterocyclic rings or due to multiple meso carbon bridges. CHAPTER-4 Synthesis of carbaporphyrins and N-confused porphyrins as well as their interaction with mercury Benziporphyrins were synthesised using the [3+1]methodology with hetero-tripyrrane and benzene 1,3 or 1,4-dicarbinol in dichloromethane using boron trifluoride etherate as catalyst. N-confused porphyrin (NCP) has a confused (i.e., a,b'-linked) pyrrole ring, and thus possesses a reactive inner carbon and a peripheral nitrogen . CHAPTER-5 Synthesis of core-modified azuliporphyrinogen and its interaction with polyaromatic hydrocarbon Porphyrinogen are a class of macrocycles composed of four pyrrole units linked through four meso- carbon bridges. Porphyrinogen exists in four isomeric forms.

*Contents*

1. Bronsted acidic ionic liquids catalyzed efficient synthesis of symmetrical and unsymmetrical core-modified porphyrins and its application in the detection of toxic metals 2. Synthesis of different core-modified calyx [4] phyrins and their interaction with mercury 3. Synthesis of core-modified expanded porphyrinoids and their application in sensing and photodynamic therapy 4. Synthesis of hetero-carbaporphyrins and N-confused porphyrins as well as their interaction with

mercury and other toxic metals 5. Synthesis of core-modified azuliporphyrinogen and their interaction with polyaromatic hydrocarbon. List of publications.

09. CHOUDHARY (Deepak)

**Novel Approaches for the Synthesis of Structurally Diversified N/S/O-Heterocyclic Compounds.**

Supervisor: Prof. Akhilesh K. Verma

Th 23166

*Abstract*

*(Not Verified)*

The thesis entitled “Novel Approaches for the Synthesis of Structurally Diversified N/S/O-Heterocyclic Compounds” describes a versatile and an efficient synthetic methodology to produce a broad range of biologically important variety of benzoxazines/oxazines fused isoquinolines and naphthyridines, pyrazolylanilines, pyrazole, pyrazoloquinolines and annulated carbazoles. The designedAg(I)-catalyzed domino protocol in water which allowed a facile access to an impressive variety of benzoxazines/oxazines-fused N-Heterocyles in good yields with high regioselectivity. The reaction proceeded with high 6-endo-dig regioselectivity and confirmed by X-ray crystallographic studies. The competitive experiments demonstrated that intramolecular nucleophilic attack over intermolecular attack. The product formation was also found to be higher in case of aromatic amine over aliphatic amine. The method appeared to be very general and compatible with differently substituted starting materials having different electronic properties increasing its applicability to various functional groups. Further, a novel H-bond directed, catalyst-free approach for the chemoselective synthesis of functionalized pyrazoles with a free amino group has been developed. The presence of H-bonding was confirmed by control experiments, deuterium labeling studies and X-ray crystallographic studies. The efficiency of this environmentally friendly method combined with its operational simplicity (majority of pyrazoles were purified by recyrstallization without using chromatography) make it attractive for the construction of variety of heterocyclic compounds and also expand the application of H-bonding in the organic synthesis. The synthesized pyrazolines were further oxidized with IBX to produce pyrazoles and demonstrated their utility in organic synthesis. Pyrazoles with free amino groups were further transformed into pharmaceutically important pyrazoloquinolines. Copper-mediated approach for the synthesis of aryl and hetero-aryl annulated carbazole (AHACs) through [1,5]-Hydride shift and [1,3]-Methyl shift have been investigated. The scope of ortho-alkynylaldehyde was extended with a range of differnt heterocyclic moiety with amino-hydrazone. A deuterium labeling experiment supports the source of methyl source, mechanistic studies and further confirmed by their X-ray crystallographic studies.

*Contents*

1. On water: ag-catalyzed domino approach for the synthesis of benzoxazine/oxazine-fused n-heterocycle 2. H-bond directed: protection and catalyst-free chemoselective synthesis of functionalized pyrazolylanilines 3. IBX-mediated synthesis of pyrazoloquinolines via oxidative aromatization of pyrazolines followed by cyclization 4. Synthesis of aryl and heteroaryl-annulated [α] carbazoles via sigmatropic hydrogen and methyl shift. Summary of the work and copies of the publications.

10. DHILLON (Shweta)

**Spatially Resolved Electrochemical Impedance Spectroscopy and Chronoamperometry on Disordered Electrodes: Theory, Experiment and CV-SEM Method.**

Supervisor: Prof. Rama Kant

Th 23025

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1. Introduction 2. 3D reconstruction of electrode roughness using cyclic voltammetry and SEM images 3. Theory for local electrochemical impedance spectroscopy at corrugated electrode under reversible charge transfer 4. Theory for spatially resolved electrochemical impedance on realistic rough electrode under reversible charge transfer 5. Simulation of local electrochemical impedance spectroscopy using SEM micrographs 6. Theory for electrochemical impedance in presence of charge transfer heterogeneity at electrode 7. Theory for double potential step and square wave Chronoamperometry at rough electrodes: Reversible redox reaction and ohmic effects 8. Experimental validation of the theory of chronoamperometry nonuniformly deposited gold nanoparticles electrodes.

11. GUPTA (Akanksha)
**Novel Mixed Metal Oxides of Lithium and Bismuth: Synthesis, Structural Investigation and potential Applications.**
Supervisor: Prof. S. Uma
<u>Th 22998</u>

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1. Introduction. 2. Synthesis and characterization of oxides, $Li_2Mn_{1-x}Ti_xO_3$ (0.0 ≤ x ≤1.0) belonging to the rocksalt superstructure family. 3. Formation of layered oxides $Li_3$ ($LI_{1.5x}Fe_{3-(x+1.5x)}$ $Te_x$) O6, (0.1 ≤ x ≤1.0)by cationic ($Li^+/Fe^{3+}/Te^{6+}$) variations and exploration of extending the series for other M (III) + Cr,Mn,A1, Ga ions. 4. Synthesis and characterization of ordered and disordered polymorphs of $Li_2Ni_2TeO_6$. 5. Synthesis and crystal Structure of $Bi_6$ ($Bi_{0.5}Cu_{0.5}$) $V2O15_{+Y}$. 6. Investigation on the extent of stabilization of $Bi^{3+}$ in apatites: Synthesis and characterization of $Ca_7Bi_3$ $(PO_4)_5$ $(SiO_4)$ O2, $Ca_6Bi_4$ $(PO_4)_3(SiO_4)_3OFCa_8Bi_2$ $(PO_4)_4(SiO_4)_2F_2$ and $Cd_4Bi$ $(PO_4)_3O$. Appendices.

12. GUPTA (Rakesh)
**Synthesis, Characterization and Physical Properties of Lanthanoid Containing $[PW_{11}O_{39}]^{7-}$, $[PW_{10}O_{36}]^{7-}$ And $GeW_{11}O_{39}]^{8-}$ Units**
Supervisor: Dr. Firasat Hussain
<u>Th 22994</u>

*Contents*

1. General introducation of POMs 2. Experimental and characterization of POM precursors 3. Syntheses and characterization of sandwich-type rareearth substituted monovacant Keggin-type phosphotungstates by using $K_{14}$ $[P_2W_{19}O_{69}$ $(H_2O)]\cdot 24H_2O$ 4. Syntheses and characterization of lanthanoid containing tetrameric tungstophosphates by using dilacunary $K_{14}$ $[P_2W_{19}O_{69}$ $(H_2O)]\cdot 24H_2O$ 5. Syntheses and characterization of early lanthanoid substituted sandwich- and dimeric-type germanotungstates by using Na10 $[GeW_9O_{34}]\cdot 18H_2O$. Conclusion of thesis and appendix.

13. INDRANI
**Deciphering the Role of Ionic Liquids in the Structure and Stability of Proteins.**
Supervisor: Dr. P. Venkatesu
<u>Th 23007</u>

*Abstract*
*(Not Verified)*

Research in the field of protein-IL interactions has remained a prospective avenue of investigation for years. More details describing the role of ILs in protein folding/unfolding studies have emerged from a range of both experimental and theoretical studies. These studies suggest that modification of the cation and anion structure of ILs have vast impact on the structure, stability and activity of protein/enzymes, however, the need is to assess the behaviour of different enzymes and proteins when they are exposed to different family of ILs. Chapter 1 delineates the general introduction of proteins and their interaction with the ionic liquids (ILs). The chapter explains the role of ILs (particularly ammonium and imidazolium-based ILs) on the structure and stability of proteins. Chapter 2 describes the materials and methods used throughout the research for carrying various studies related to protein stability in the presence of ILs. In chapter 3, we report structural stability of heme proteins such as Mb and Hb in a series of ammonium-based ILs such as TMAH, TEAH, TPAH and TBAH by fluorescence and circular dichroism (CD) spectroscopic studies. Chapter 4 delineates spectroscopic and molecular docking investigations carried out to characterize the effect of imidazolium-based ILs with varying chain length of the cation on the thermal as well as spectroscopic behaviour of heme protein hemoglobin (Hb). Chapter 5 describes the perturbations in the structure, stability and activity of stem bromelain (BM) as a result of its interaction with imidazolium-based ILs using different techniques. Chapter 6 explains the counteraction effects of ChCl to offset pH-induced denaturation of Lyz along with the corresponding activity in various solution systems. Chapter 7 basically provides the crux of all the experiments performed on the structure and stability of different proteins in the presence of ammonium- and imidazolium-based ILs.

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14. KANSAL (Kirti)
**Study of Anti-corrosive Properties of Some Quinoxalines for Mild Steel Corrosion in Sulphuric Acid**
Supervisor: Prof. Gurmeet Singh
Th 23009

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15. M. RAJESWARI
**Synthesis of Novel Heterocycles Containing Spirooxindoles, Phenazines and Pyrimidines, and Functional Group Oxidations Using $NaBrO_3$-[bmim] HSO4.**
Supervisor: Prof. J.M.Khurana
Th 23015

*Contents*

condensation using PEG-400. 2. Efficient and mild one-pot synthesis of functionalized benzo [a] chromeno phenazine fused ring systems using $H_2SO_4$ and phosphotungstic acid. 3. One-pot four component domino strategy for the synthesis of novel spirooxindole-pyrrolizine linked 1, 2, 3,-triazoles via 1, 3,-dipolar cycloaddition in Acidic Medium. 4. A facile and green approach for the synthesis of spiro [naphthalene-2, 5'-pyrimidine]-4-carbonitrile by one-pot three component condensation using DBU as catalyst. 5. Functional group oxidations using $NaBrO_3$ in presence of [bmim] $HSO_4{:}H_2O$. 6. Summary and conclusions. List of publications.

16. MANGAWA (Shrawan Kumar)
**Design, Synthesis and Applications of Asymmetric Organocatalysts and Synthesis of Newer Fluorescent Peptide Nucleic Acid Monomer.**
Supervisor: Prof. Satish Kumar Awasthi
Th 23022

*Abstract*
*(Not Verified)*

The thesis entitled "Design, Synthesis and Application of Asymmetric Organocatalysts and Synthesis of Newer Fluorescent Peptide Nucleic Acid Monomer" describes synthesis of asymmetric organocatalysts and their characterization and its application as chiral catalysts in some organic transformation reactions. Organocatalysis is an emerging area of research in chemistry. Earlier, Cinchona alkaloids, spirocyclic, binapthol and pentacyclic guanidine type chiral organocatalysts were used for organic transformation reactions. The synopsis of thesis consists of five chapters. Chapter I, deals with introduction of asymmetric organocatalysts, its historical background, variety of asymmetric organocatalysis, synthesis and applications. Chapter II includes synthesis of s-triazene based asymmetric organocatalysts, their characterization and its application in natural and unnatural α-amino acids synthesis in higher yield and better enantioselectivity. Chapter III deals synthesis of L-proline and s-triazene based asymmetric organocatalyst, their characterization and application. Optically bioactive quinazolinones were synthesized using newer asymmetric organocatalysts. Chapter IV describes synthesis of metal free fluorinated reagent and its characterization by $^{1}H$ NMR, $^{13}C$ NMR, $^{19}F$ NMR and mass spectrometry. Fluorinated alkylation of alcohols and phenols is done in acetonitrile using p-toluenesulphonic acid as an oxidant by metal free reagent TriTFET. Moreover, TRiTFET has been also utilized for amide synthesis . Chapter V includes design and synthesis of fluorescent nucleobase, their photophysical studies and synthesis of PNA oligomer. Pre and post modification of PNA oligomer using click chemistry has been discussed.

*Contents*

1. Asymmetric Organocatalysts, an overview, historical background, synthesis and applications 2. Design and synthesis of s-triazene based asymmetric Organocatalysts and its application in asymmetric alkylation 3. Design and synthesis of s-triazene and L-proline based asymmetric organocatalysts and their application in chiral quinazolinone synthesis 4. Part A: synthesis of fluorinated ethers using metal free reagent (TriTFET). 4. Part B: amide bond formation using a flourous coupling reagent 5. Synthesis of fluorescent peptide nucleic acids via post and pre synthetic methods. List of publications.

17. MANISH KUMAR
**Chemo-Enzymatic Synthesis of Conformationally Restricted Nucleosides**
Supervisor: Prof. Ashok K. Prasad
Th 22995

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1. Chemo-enzymatic synthesis of 3'-azido/-amino-ribo-LNA monomers 2. Chemo-enzymatic synthesis of 3'-azido/-amino-C-4'-spiro-oxetano-ribonucleosides 3.

Chemo-enzymatic synthesis of 3'-azido/-amino-C-4'-spiro-oxetano-xylonucleosides 4. Chemo-enzymatic synthesis of 3'-azido/-aminoxylo-LNA monomers. Summary and list of publications.

18. MATTA (Akanksha)

**Total Synthesis of Simplified Analogues of Peloruside & Synthesis of Coumarin Based Oxadiazoles, Dihydropyrimidones and their Fluorescent Spectral Studies.**

Supervisor : Dr. B.K.Singh

Th 23012

*Abstract*

*(Not Verified)*

The work presented in Chapter I entitled "Total synthesis of simplified analogues of peloruside" describes an efficient and convergent synthesis of 2 simplified analogues of peloruside. Peloruside is a cytotoxic polyketide, which was first isolated from the New Zealand marine sponge. Peloruside functions as an antitumor agent by promoting tubulin polymerization and interfering with microtubule dynamics. So, new peloruside analogs by replacing the pyranose ring with a phenyl ring have been designed and termed as "phenyl peloruside". The total synthesis of two analogues of phenyl peloruside have been described. In order to obtain an efficient and convergent synthesis for the simplified phenyl analogues of pelorusides, the synthesis was initiated from commercially available 3-bromophenylacetonitrile. With this molecule we have constructed a 16-membered macrolactone ring structure in a series of 17 steps. Microtubule inhibiting activity of the synthesised analogues is under investigation. The work presented in Chapter II entitled "Synthesis of oxadiazolyl coumarin and their fluorescent spectral studies" describes the synthesis of thirty novel 4-oxadiazole substituted coumarin and their photophysical studies. The synthetic route to novel oxadiazolyl coumarin has been discussed. 7-hydroxy-4-methylcoumarin. The oxadiazolyl coumarin were obtained in moderate yields (35-59%) by the reaction of the variously substituted 2H-chromene-4-carboxylic acid with the appropriately substituted arylamidoximes in presence of potassium carbonate and ethyl chloroformate. The work presented in Chapter III entitled "One-pot synthesis of coumarin based triazolyl-dihydropyrimidone (DHPM) and their fluorescent spectral studies" describes a one-pot synthetic methodology for its synthesis and their fluorescence studies. The synthetic route to novel coumarin based triazolyl-DHPM have been discussed. The synthetic strategy mainly involve three steps. Mild reaction conditions and easy processing are among few advantages offered by this new synthetic methodology. The structures of all the synthesized compounds were established by analysis of their spectral data (IR, $^1$H NMR, $^{13}$C NMR and HRMS spectra).

*Contents*

19. MOGHA (Navin Kumar)

**Graphene Oxide Based Nanohybrids for Applications in Biosensors and Catalysis.**

Supervisor: Dr. Dhanraj T. Masram

Th 22999

*Abstract*

*(Not Verified)*

I have successfully demonstrated Lanthanum Oxide/Reduced graphene oxide electrode for Ascorbic Acid (AA) electrochemical sensing. High catalytic activity of Lanthanum Oxide/Reduced graphene oxide toward the oxidation of AA is main reasons of the successfully detection of Ascorbic Acid. Moreover, the proposed method was applied to the determination of AA in real samples with satisfactory results. Furthermore, Nanostructured RGO supported $ZrO_2$ nanocomposite ($ZrO_2$/RGO) was synthesized as the electrode matrix form enzyme immobilization, presents high performance for AChE based biosensor applications. Our results demonstrate the detection as low as $10^{-13}$M concentration of the Chlorpyrifos with 29% enzyme inhibition. Additionally, Gold nanoparticles Immobilized over the surface of Graphene oxide Nano Ribbons (Au/GONR) is used as the platform for the immobilization of single stranded DNA of specific gene for Mycobacterium Tuberculosis. Results showed that Au/GONR based DNA biosensor is able to detect DNA from trace amount of 0.1fM to $10^{-6}$M. Synthesis of $La_2O_3$@PTHF/GO nanohybrids having uniform distribution of 20 – 30 nm sized $La_2O_3$ nanoparticles on polymeric brushes PTHF modified GO surface is reported in this chapter. $La_2O_3$@PTHF/GO nanohybrids have been employed as the catalyst for the degradation studies of RhB, MO and ESY in water in the presence of $NaBH_4$, giving excellent catalytic performance as evident by the apparent Rate constant ($k_{app}$), which is found to be 26.8, 28.6, and 20.5 ($X10^{-3}$ $s^{-1}$). In continuation to this work gold nanoparticles (AuNPs) on poly (dimethylaminoethyl methacrylate) (PDMAEMA) brushes immobilized reduced graphene oxide (Au/PDMAEMA/RGO) is synthesized and used as catalyst for degradation kinetic studies of Rhodamine B (RB), Methyl Orange (MO) and Eosine Y (EY) dyes, having an excellent catalytic activity, as evident by the apparent Rate constant ($k_{app}$), which is found to be 21.8, 26.2, and 8.7 (x $10^{-3}$ $s^{-1}$), for RB, MO and EY respectively.

*Contents*

1. Introduction to Graphene Oxide Nanohybrids synthesis and Applications in biosensing and Catalysis 2. Sensitive and reliable ascorbic acid sensing by lanthanum oxide-reduced graphene oxide nanocomposite 3. Biocampatible ZRI2-reduced graphene oxide immobilized ACHE biosensor for chlorpyrifos detection 4. Redox indicator free detection of mycobacterium tuberculosis using specific electrochemical DNA Biosensor based on the graphene oxide nanoribbon immobilized gold nanoparticles 5. Synthesis of lanthanum oxide nanoparticles immobilized graphene oxide polymer brush nanohybrid for the catalytic degradation of organic dyes 6. Gold nanoworms immobilized graphene oxide polymer brudh nanohybrid for catalytic degradation studies of organic dyes 7. Conclusion and future aspects. List of publications.

20. MOHAN KUMAR
**Unusual DNA Structures and their Interaction with Phenothiazinium Analogues.**
Supervisor: Prof. Shrikant Kukreti
Th 23089

*Abstract*
*(Not Verified)*

With the advancement in the investigation tools and techniques, DNA has quite extensively been explored for its varied structures and functions. Certain guanine-rich sequences were studied for the possibility of cruciform structures, using biophysical and biochemical techniques. Further, their interaction with phenothiazine dyes along with Calf-Thymus DNA had also been done. The truncated sequences of human telomere differing at 5'-end were studied in this work. It was observed that GM9 oligomer adopt an antiparallel tetramer in $Na^+$ whereas in $K^+$ a mixed species of hybrid G-triplex / tri-G-quadruplex and tetramer G-quadruplex was obtained. The GM10 and GM11 oligomers form bimolecular G-quadruplexes in $Na^+$ while GM11 oligomer adopts antiparallel/ parallel bimolecular G-quadruplex and G-triplex or tri-G-quad in $K^+$. The structural status of designed DNA sequences (CR & CRC) prone to form cruciform in 1:1 ratio was also determined. By correlating CD spectra, melting profiles and gel electrophoresis, it was concluded that the CR could form a bulge duplex structure with flanking ends, while CRC formed a hairpin structure with flanking ends. The CR+CRC duplex was proposed to form a cruciform junction type structure. The interaction studies with methylene blue (MB) analogues i.e. the new methylene blue (NMB) and calf thymus DNA (ctDNA) were undertaken. The binding constants were calculated. The calculated thermodynamic properties like the change in enthalpy ($\Delta H°$) and entropy ($\Delta S°$) were calculated. It suggested that the binding mode is intercalation. Also, the comparative studies of phenothiazine dyes with calf-thymus DNA (ctDNA) have been performed. These results are indicative of the intercalation binding mode. The binding affinity of the dyes to DNA is found to be in order as thionine acetate> azure A> azure B. This work might further facilitate our basic understanding about the DNA-drug interactions for utilizing them for medicinal purposes and nanochemistry.

*Contents*

1. Introduction 2. Materials and Methods 3. G-triplex/Tri-quadruplex formation 4. Cruciform DNA formation at physiological pH 5. Biophysical aspects of DNA-new Methylene blue interactions 6. Conclusions. Bibliography.

21. PANDEY (Alka)
**Synthesis and Crystallographic Studies of Cu-Ni Complexes and Characterization of Curcumin Nanoparticle.**
Supervisor: Prof. Satish Kumar Awasthi
Th 23090

*Abstract*
*(Not Verified)*

The thesis entitled “Synthesis and Crystallographic Studies of Cu-Ni Complexes and Characterization of Curcumin Nanoparticle” is a summary of the research carried out in the Department of Chemistry, University of Delhi under the supervision of Prof. Satish Kumar Awasthi.The thesis deals with the synthesis and characterisation of Schiff base ligands and their corresponding transition metal complexes derived from o-hydroxyaldehyde. The present work also enlightens improved aqueous solubility of natural polyphenol, curcumin in the form of curcumin nanoemulsion.Recently, inorganic chemistry witnessed a great outflow of coordination compounds, with unique structural properties and diverse applications. The structural diversity exhibited by the coordination complexes have led to their usage as sensors, models for enzyme mimetic centres, medicines etc. Schiff base complexes of transitional metal ions have played a major role in the coordination chemistry. The convenient route of synthesis and stability of Schiff base complexes has contributed significantly to their varied applications. Hence there is a persisting interest in the synthesis of new Schiff base complexes.

*Contents*

1. Complexation Behaviour of Schiff Base Ligands with CU and Ni 2. Section A: Study of Intramolecular Hydrogen Bonding and Tautomerism in N-ALKYL-2-Hydroxy Shiff Bases 2. Section B: Direct in situ transmination reaction promoted by ammonia in the formation of bisbidentate shiff base metal (II) complexes 3. Preparation and antioxidant activity of water soluble curcumin nanoemulsion 4. Plant derived anticancer coumarins. Summary and list of publication.

22. PARVEEN
**Theories of Pulse Voltammetries on Rough Electrodes:**
Supervisor: Prof. Rama Kant
Th 23018

*Contents*

1. Introduction 2. Theory of pulse voltammetries on rough electrodes: single step reversible charge transfer mechanism 3. Theory of pulse voltammetries on rough electrodes: two step reversible charge transfer mechanism 4. Theory of pulse voltammetries on rough electrodes: multistep reversible charge transfer mechanism 5. Theory of pulse voltammetries on rough electrodes: reversible charge transfer coupled to homogeneous catalytic step 6 Summary and prospects.

23. PATEL (Monika)

**Base Assisted Chemo-and Regioselective C-N, C-S and C-O Bond Formation with Isotopic Labelling Studies.**

Supervisor: Prof. Akhilesh K. Verma

Th 23167

*Abstract*

*(Not Verified)*

We have demonstrated the broad scope of superbasic KOH/DMSO system for various chemo- and stereoselective addition of 5-aminoindole, tryptamine and histamine onto broad range of alkynes to synthesize a variety of indolyl/imidazolyl enamines without affecting the primary amino groups (aromatic and aliphatic) present in the substrates. We observed that 5-aminoindole was more reactive than tryptamine, and histamine was found to be least reactive as validated by the control experiments. Then, we have described an efficient approach for the stereoselective addition of imidazoles onto alkynes to provide a broad range of synthetically and biologically important (Z)- and (E)-imidazolyl enamines selectively in good yields. The stereselectivity was found to be time-dependent. This transition-metal and ligand-free methodology utilizes a superbasic system of KOH/DMSO for the addition of imidazoles onto alkynes. The competitive experiments clearly demonstrates that imidazole is less reactive than pyrrole and more reactive than aniline. Later an operationally simple and base-mediated approach for the preferential chemo-, regio- and stereoselective addition of thiophenols onto bromo-substituted arylalkynes over S-arylation of aryl halides has been described. The study also represents a new insight into the role of super-base (KOH/DMSO) mediated regio-, stereo-, and chemoselective nucleophilic addition of phenols onto substituted alkynes in anti-Markovnikov fashion. Further the deuterium-labeling experiments uncover that the source of styryl protons in hydrophenoxylation products from the DMSO/DMSO-$d_6$ and not from the substrate. After successful accomplishment of above goal we studied, additional insight the mechanistic studies using isotopic labeling strategy. The chemistry involves an environmentally benign catalyst-free approach for deuteration using superbasic system. The protocol has a wide application in the field of hydroamination, hydrothiolation, hydrophenoxylation and tandem synthesis.

*Contents*

1. Base-mediated chemo- and stereoselective addition of 5-aminoindole/tryptamine and histamines onto alkynes 2. Base –catalysed stereoselective intermolecular addition of imidazoles onto alkynes: an easy access to imidazolyl enamines 3A. Nu-addition vs $S_NAr$ study: chemo-region- and stereoselective preferential hydrothiolation of haloarylalkynes over S-arylation of aryl halides 3B. Metal-free intermolecular hydrophenoxylation of aryl alkynes 4. Mechanistic investigation via deuterium labelling studies. Summary of the work and copies of the publications.

24. POOJA RANI

**In-Silico Study of Globular and Disordered Proteins through Sequence Analysis and Hydration Properties**

Supervisor: Prof. Parbati Biswas

Th 23014

*Contents*

1. Introduction 2. Does lack of secondary structure imply intrinsic disorder in proteins: A sequence analyses 3. Shape dependence of the radial distribution function of hydration water around proteins 4. Local structure and dynamics of hydration water in intrinsically disordered proteins 5. Diffusion of hydration water around intrinsically disordered proteins 6. Characterizing the structure of hydration water through reference interaction site model 7. Capturing molten globule state of – lactalbumin through constant pH molecular dynamics simulations. Bibliography.

25. PRABHAKAR (Swati)
**Synthesis of Organic-Inorganic Hybrid Polyoxometalates and their Structural Characterization by Various Analytical Techniques.**
Supervisor: Dr. Firasat Hussain
Th 23091

*Abstract*
*(Not Verified)*

The thesis entitled "Synthesis of organic - inorganic hybrid polyoxometalates and their structural characterization by various analytical techniques" incorporates the synthetic approach to isolate new branch of organic – inorganic hybrid polyoxometalates and their various analytical characterization. Chapter I, deals with introduction of polyoxometalate compounds along with brief eye to history, structural versatility of POMs compounds. It's also explicitly describes the chemical composition, classification, synthetic and structural properties of POMs. The solution behavior of lacunary POMs are also included in this chapter and a layout of a new branch of organic – inorganic hybrid POMs. Chapter II includes the reagents, various characterization techniques and initial precursors used for the preparation of new class organic – inorganic hybrid POMs. Chapter III includes sandwich type organic - inorganic hybrid of silicotungstates $[\{Cu_2(1,10\text{-phen})_2(\mu\text{-}CH_3COO)_2\}Ln(\alpha\text{-}SiW_{11}O_{39})_2]^{11-}$ {Ln = Pr$^{III}$(1a), Nd$^{III}$(2a), Sm$^{III}$(3a), Eu$^{III}$(4a), Gd$^{III}$(5a) and Dy$^{III}$(6a)}. All these compounds were isolated as alkali salts using conventional one pot synthesis and characterized by Single crystal X-ray diffraction, Powder X-ray diffraction, FTIR, ICP - AES, liquid UV/vis, solid state photoluminescence spectroscopy, thermogravimetric analysis and magnetic studies only for Gd$^{III}$(5a). Chapter IV includes the sandwich type organic - inorganic hybrid of germanotungstates $[\{Cu_2(1,10\text{-phen})_2(\mu\text{-}CH_3COO)_2\}Ln(\alpha\text{-}GeW_{11}O_{39})_2]^{11-}$ {Ln = Pr$^{III}$(1a), Nd$^{III}$(2a), Sm$^{III}$(3a), Eu$^{III}$(4a) and Gd$^{III}$(5a)}. All compounds were isolated from solution and used for further structural characterization by Single crystal X-ray diffraction, Powder X-ray diffraction, FTIR, liquid UV/vis, photoluminescence spectroscopy, thermogravimetric analysis and magnetic studies of Gd$^{III}$(5a). Chapter V includes the self assembled organic - inorganic hybrid arsenotungstates. The organic – inorganic hybrid acetate bridged arsenotungstates were isolated using one pot synthetic procedure using copper, lanthanoids, trilacunary arsenotungstates and 1,10-phenanthroline (1,10-phen): $\{[Cu_2(1,10phen)_2(\mu\text{-}CH_3COO)_2]_4[Ln_2(H_2O)_2(\mu\text{-}CH_3COO)_2(\alpha\text{-}AsW_{11}O_{39})_2]\}^{2-}$ [Ln$^{III}$ = Pr(1a), Nd(2a), Sm(3a), Eu(4a), Gd(5a), Tb(6a), Dy(7a), Ho(8a), Er(9a), Tm(10a), Yb(11a) and Lu(12a)]. The compounds are characterized using various analytical techniques like FTIR, Single crystal X-ray diffraction, liquid UV/Vis spectroscopy and thermogravimetric analysis.

*Contents*

1. Polyoxometalates: An introduction 2. Materials and methods. 3. Sandwich type organic-inorganic hybrid of silicotungstates $[\{Cu_2\ (1,\ 10\text{-phen})_2(\mu\text{-}CH_3COO)2\}Ln(\alpha SiW_{11}O_{39})_2]^{11-}$: Syntheses, crystal structures, photoluminescence and magnetic properties. 4. Sandwich type organic-inorganic hybrid of germanotungstates $[\{Cu_2\ (1,\ 10\text{-phen})_2(\mu\text{-}CH_3COO)2\}Ln(\alpha GeW_{11}O_{39})_2]^{11-}$: Syntheses, crystal structures, magnetic and photoluminescence properties. 5. Self-assembled organic-inorganic hybrid arsenotungstates: synthesis, structure and characterization. Conclusion and list of publications.

26. PRASAD (Suchita)
**Non-Ionic Amphiphilic Architectures & Benzopyranone Derivatives: Study of Physico-Chemical Properties and Biological Applications.**
Supervisor : Prof. Sunil K. Sharma
Th 23092

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27. RAJESH KUMAR

**Chemo-Enzymatic Route to Novel Oxetano/Spiro-Oxetanonucleosides and Synthesis & Anti-Tubercular Activity of Triazolonucleosides.**

Supervisor: Prof. Ashok K. Prasad

Th 23023

*Abstract*

*(Not Verified)*

Abstract of the thesis entitled: “Chemo-enzymatic route to novel oxetano / spiro-oxetanonucleosides and synthesis & anti-tubercular activity of triazolonucleosides” The thesis is divided into four chapters, i.e. Chapter I, Chapter II, Chapter III and Chapter IV. A brief description of each chapter is given below: The work presented in Chapter I entitled “Chemo-enzymatic synthesis of 3'-O,4'-C-methylene-arabinonucleosides” describes the biocatalytic strategy to manipulate one of the hydroxyl groups present in 4'-C-hydroxymethyl-β-D-xylofuranosylnucleosides to synthesize the bicyclonucleosides. In the present work, we have studied the selective chemo-enzymatic acetylation on 4′-C-hydroxymethyl-β-D-xylofuranosylnucleosides with an aim to develop an efficient and simple route for the synthesis of 3'-O,4'-C-methylene-arabinonucleoside monomers. The work presented in Chapter II entitled “Chemo-enzymatic synthesis of C-4'-spiro-oxetanolyxonucleosides” describes the biocatalytic strategy to manipulate the different acetoxy groups present in 4'-C-acetoxymethyl-2',3',5'-tri-O-acetyl-β-D-xylofuranosylnucleosides. In the present work, we performed chemo and regio-selective deacetylation studies on 4′-C-acetoxymethyl-2',3',5'-tri-O-acetyl-β-D-xylofuranosylnucleosides with an aim to develop an efficient and effective route for the synthesis of C-4'-spirooxetanolyxonucleosides. The work presented in Chapter III entitled “Synthesis and anti-tubercular activity of triazole linked coumarinylbicyclonucleosides” describes the synthesis as well as antitubercular activity profile of 1-(3'-deoxy-2'-O,4'-C-methylenenucleoside-3'-yl)-4-(coumarin-4'''-yl)-1,2,3-triazole by Cu(I) catalyzed azide-alkyne cycloaddition (CuAAC) reaction. Our key precursors for these reactions are different azides, i.e. 3'-azido-3'-deoxy-2'-O,4'-C-methylene-β-D-ribofuranosylthymidine/uridine/cytidine/6-N-benzoyladenosine and four different alkynes, i.e. 4-ethynylcoumarin, 4-ethynyl-6-methoxycoumarin, 4-ethynyl-7-methoxycoumarin and 4-ethynyl-7,8-dimethoxycoumarin and total sixteen novel triazole linked coumarinylbicyclonucleosides have been synthesized and were further evaluated for their anti-tubercular activity. The work presented in chapter IV entitled “Synthesis and anti-tubercular activity of 4-aroyl-5-aryl-1-(thymin-5'-yl)triazole” describes the synthesis as well as antitubercular activity of 1,4,5-trisubstituted triazole containing thymidine nucleosides. we have designed and synthesized novel 4-aroyl-5-aryl-1-(thymin-5'-yl)triazoles using tetrabutylammoniumhydrogen sulphate (TBAHS) as catalyst in dimethylformamide (DMF) at 100 °C employing azide-olefine cycloaddition reaction and further investigated their anti-tubercular activity. The key precursor for this reactions were 5'-azido-5'-deoxythymidine and various substituted chalcones and total fifteen compounds have been synthesised.

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28. R. SANDHYA

**Multimodal Probes for Brain and Integrin Receptor Imaging: Design, Synthesis and Biological Evaluation.**

Supervisors: Dr. Sandeep Kaur and Dr. Raunak

Th 23029

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29. RAMAN KUMAR

**Investigation of Some New Schiff Bases as Corrosion Inhibitor for Mild Steel in Acidic Media.**

Supervisor: Prof. Gurmeet Singh

Th 23000

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30. REDDICHERLA (Umapathi)

**Influence of Ionic Liquids on Thermoresponsive Polymers in Aqueous Media.**

Supervisor: Dr. P. Venkatesu

Th 23168

*Abstract*
*(Not Verified)*

In this thesis we have explored the influence of ionic liquids (ILs) such as 1-ethyl-3-methylimidazolium chloride ($[Emim]^+[Cl]^-$), 1-allyl-3-methylimidazolium chloride ($[Amim]^+[Cl]^-$), 1-butyl-3-methylimidazolium chloride ($[Bmim]^+[Cl]^-$), 1-hexyl-3-methylimidazolium chloride ($[Hmim]^+[Cl]^-$), 1-benzyl-3-methylimidazolium chloride ($[Bzmim]^+[Cl]^-$), 1-decyl-3-methylimidazolium chloride ($[Dmim]^+[Cl]^-$), 1-butyl-3-methylimidazolium thiocyante ($[Bmim]^+[SCN]^-$), 1-butyl-3-methylimidazolium iodide ($[Bmim]^+[I]^-$), 1-butyl-3-methylimidazolium bromide ($[Bmim]^+[Br]^-$), 1-butyl-3-methylimidazolium acetate ($[Bmim]^+[CH_3COO]^-$) and 1-butyl-3-methylimidazolium hydrogen sulafte ($[Bmim]^+[HSO_4]^-$) on the phase transition behaviour of thermo-responsive polymers (TRPs) such as poly(ethylene glycol)-block-poly(propylene glycol)-block-poly-(ethylene glycol) (PEG-PPG-PEG), Poly(N-isopropylacrylamide) (PNIPAM) and poly(N-vinylcaprolactam) (PVCL). To accomplish our study of TRPs and ILs interaction studies, we have used biophysical techniques such as UV-visible spectroscopy, fluorescence spectroscopy, dynamic light scattering (DLS), viscosity ($\eta$), and Fourier transform infrared spectroscopy (FTIR) studies. Field emission scanning electron microscopy (FESEM) has been performed to depict the morphological changes of TRPs in the presence of imidazolium-based ILs. Chapter 1 delineates the general introduction of TRPs and ILs. Chapter 2 describes the materials and methods of sample preparation and information of the instrumentation used for experiments. Chapter 3 characterizes the effect of imidazolium-based ILs possessing fixed $Cl^-$ anion and a set of cation [C$_n$mim]$^+$ with increasing alkyl chain length of cation on the micellization behaviour of PEG-PPG-PEG. Chapter 4 uncovers the effect of ILs possessing fixed Cl$^-$anion and a set of cations [C$_n$mim]$^+$with increasing alkyl chain length such as on the aggregation behavior, and variation in phase transition temperature of PNIPAM aqueous solution. Chapter 5 highlights the conformational changes of PVCL aqueous solution in ILs of different cations with varying alkyl chain length such as fixed Cl$^-$ anion. Chapter 6 dictates the changes in the LCST of the PVCL in the presence of ILs with fixed cation [Bmim$^+$], and commonly used anions. Chapter 7 provides the crux of all the experiments performed on the phase transition temperature of TRPs in the presence of imidazolium-based ILs.

*Contents*

1. Introduction and review of the literature 2. Materials and experimental techniques 3 (a). Influence of imidazolium –based ionic liquids on the CMT of PEG-PPG-PEG: role of the alkyl chain length of cations 3 (b). Influence of imidazolium-based ionic liquids on the CMT of PEG-PPG-PEG: a comparative study of two ionic liquids possessing different cations with same anion 4. Influence of imidazolium-based ionic liquids on the phase transition temperature of PNIPAM: role of the alkyl chain length of cations 5. Influence of imidazolium-based ionic liquids on the phase transition temperature of PVCL: role of the alkyl chain length of cations 6. Influence of imidazolium-based ionic liquids on the phase transition temperature of PVCL: a comparable study of the role of various anions 7. Conclusions.

31. ROBIN KUMAR
**Half Sandwich Ruthenium (II) and Rhodium (III) Electron Deficient N, N', N"-Triarylguanidinato Complexes and their Applications in Transfer Hydrogenation and Azide-Alkyne Cycloaddition Reactions**
Supervisor: Prof. N Thirupathi
Th 22996

*Abstract*
*(Not Verified)*

Sym N,N′,N″-triarylguanidines, (ArNH)$_2$C=NAr (Ar = 2-ClC$_6$H$_4$ (L7), 2-FC$_6$H$_4$ (L8), 3-ClC$_6$H$_4$ (L9), 4-ClC$_6$H$_4$ (L10), 2-(CF$_3$)C$_6$H$_4$ (L11), 4-(CF$_3$)C$_6$H$_4$(L12), and 3,5-(CF$_3$)$_2$C$_6$H$_3$ (L13)), ionic complex [(ArNH)$_3$C][($\eta^6$-C$_{10}$H$_{14}$)RuCl$_3$] (Ar = 2-ClC$_6$H$_4$ (2.1.1)) and neutral half sandwich complexes [($\eta^6$-p-cymene)RuCl{k$^2$(N,N′)((ArN)$_2$C-N(H)Ar)}] (Ar = 2-ClC$_6$H$_4$ (2.1.2), 2-FC$_6$H$_4$ (2.1.3), 4-ClC$_6$H$_4$ (2.1.4), 2-(CF$_3$)C$_6$H$_4$ (2.2.1), 4-(CF$_3$)C$_6$H$_4$ (2.2.2) and 3,5-(CF$_3$)$_2$C$_6$H$_3$ (2.2.3) were isolated in good yields. The nucleophilic substitution of the chloride in 2.2.3 by OAc, N$_3$, and SCN/NCS enabled us to isolate [($\eta^6$-p-cymene)RuX{k$^2$(N,N')((ArN)$_2$C-N(H)Ar)}] (X = OAc (2.2.4), N$_3$ (2.2.5), and SCN/NCS (2.2.6/2.2.7)) in good yields. On the other hand, metathesis reaction of 2.2.3 with AgSbF$_6$ in the presence of MeCN afforded [($\eta^6$-p-cymene)Ru(NCMe){k$^2$(N,N')((ArN)$_2$C-N(H)Ar)}][SbF$_6$] (2.2.8) in good yield. Complex 2.2.5 upon treatment with diethylacetylenedicarboxylate in CH$_2$Cl$_2$ at RT for 24 h afforded [($\eta^6$-p-cymene)Ru(N$_3$C$_2$(C(O)OEt)$_2$){k$^2$(N,N')((ArN)$_2$C-N(H)Ar)}] (2.2.9) in good yield. Half sandwich neutral complexes [($\eta^5$-Cp*)MCl{k$^2$(N,N')((ArN)$_2$C-N(H)Ar)}] (M = Rh, Ar = 2-(CF$_3$)C$_6$H$_4$ (2.3.1), 4-(CF$_3$)C$_6$H$_4$ (2.3.2), 3,5-(CF$_3$)$_2$C$_6$H$_3$ (2.3.3), 2-ClC$_6$H$_4$ (2.3.4), 4-ClC$_6$H$_4$ (2.3.5), 2-FC$_6$H$_4$ (2.3.6); M = Ir, Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$(2.3.7) and a cationic complex [($\eta^5$-Cp*)Rh(MeCN){k$^2$(N,N')((ArN)$_2$C-N(H)Ar)}] (Ar = 2-ClC$_6$H$_4$ (2.3.8)) were synthesized in good yields. Complexes 2.3.1–2.3.8 besides six related complexes were screened as catalysts for transfer hydrogenation (TH) of acetophenone under basic and base free conditions. The utility of 2.3.3 as catalyst in TH of several distinct carbonyl/nitro compounds were explored. The reactions of 2.3.4 and 2.3.6 with excess of NaN$_3$ in ethanol at RT afforded the respective azido complexes [($\eta^5$-Cp*)RhN$_3${k$^2$(N,N')((ArN)$_2$C-N(H)Ar)}] (2.4.1 and 2.4.2) in 86% and 88% yields respectively. [3+2] Cycloaddition reactions of 2.4.1 and 2.4.2 with RO(O)C-C≡C-C(O)OR in CH$_2$Cl$_2$ at RT for 24 h afforded the respective triazolato complexes, [($\eta^5$-Cp*)Rh(N$_3$C$_2$(C(O)OR)$_2$){k$^2$(N,N')((ArN)$_2$C-N(H)Ar)}] (Ar = 2-XC$_6$H$_4$, X = Cl, R = Me (2.4.3); X = F; R = Et (2.4.4)) in 75% and 68% yields respectively. All new compounds were characterized by analytical and spectroscopic techniques and representative compounds were characterized by X-ray diffracion.

*Contents*

1. Introduction 2. Results and discussion 3. Supporting information. Abstract, List of new compounds synthesized in the present investigation and publication.

32. SANDEEP KUMAR

**Core/Shell Heterostructures: Synthesis, Characterization and Applications in Photocatalytic & Photoelectrochemical Water Splitting.**

Supervisors: Dr. M. Thirumal and Dr. Ashok Kumar Ganguli

Th 23093

*Abstract*
*(Not Verified)*

Owing to the persistent depletion of fossil fuels (natural gas, oil and coal) and elevation of environmental pollution, the quest for reliable potential alternatives has intensified. In this regard, semiconductor photocatalysis has gained immense attention by the scientific world because of the great potential as one of clean, low cost, and environmentally friendly strategies to solve the energy crisis and environmental issues toward sustainable processes. In the context of renewable energy source, photoelectrochemical (PEC) water splitting is considered as the propitious approach for the generation of hydrogen as clean burning fuel using sunlight. Solar stimulated photocatalytic degradation has become a promising strategy to alleviate the contamination in water via mineralization of virulent organic pollutants. However, recent researches on sodium niobate wide band gap semiconductor have shown that it has the potential to be an alternative material for the photoelectrochemical cells and photocatalytic decomposition of organic pollutants. Because $NaNbO_3$ an intriguing material with a typical perovskite structure and rich pool of useful properties. In the current study, have been synthesized anisotropic $NaNbO_3$ and $TiO_2$ core/shell heterostructures using a facile surface functionalization method. These core/shell heterostructures were synthesized using mercaptopropionic acid (MPA) as the surface functionalizing agent. The fabricated core/shell heterostructures exhibited efficient light harvesting with high photoelectrochemical water splitting and photocatalytic dye degradation efficiency due to their wide range of light absorption and type-II band alignment. Here, investigated the mechanism of photoelectrochemical water splitting and photodegradation of methylene blue (MB) and Rhodamine b (RhB) dye to elucidate the efficiency enhancement of the $NaNbO_3$ and $TiO_2$ based core/shell nanostructures. The thesis deals with the synthesis, characterization and band gap engineering of type-II band alignment in $NaNbO_3$ and $TiO_2$ based core/shell heterostructures for photoelectrochemical water splitting and photocatalytic dye degradation.

*Contents*

1. Introduction. 2. Enhanced Photocatalytic activity using type-II $NANbo_3$/CdS core/shell heterostructures in visible region. 3. Dominant {100} facet selectivity for enhanced photoelectrochemical water splittingand Photocatalytic dye degradation by $NANbo_3$/CdS core/shell heterostructures. 4. Visible-light-driven photoelectrochemical and photocatalytic performance of $NANbo_3$/CdS core/shell heterostructures. 5. Fabrication of $TiO_2$/CdS/$Ag_2S$ nano -heterostructured photoanode for enhancing the photoelectrochemical and photocatalytic activity under visible light. 6. Synthesis and characterization of NaNbO3/$CuInS_2$/$In_2$S3 core/shell with mechanistic insights into the z-scheme system and photocatalytic applications. 7. Conclusions and future prospects.

33. SHARMA (Chiranjeev)

**Synthetic, Spectroscopic, Crystallographic and Thermal Studies of Antimalarial Peroxides.**

Supervisor: Prof. Satish Kumar Awasthi

Th 23010

*Abstract*
*(Not Verified)*

The thesis entitled “Synthetic, Spectroscopic, Crystallographic and Thermal Studies of Antimalarial Peroxides” is an endeavor to develop new molecules to transform them into an appropriate clinical candidate against malaria, which continues to be a persistent menace wreaking havoc especially in tropical and sub-tropical regions despite tremendous efforts towards its control and eradication. Artemisinin, a naturally occurring sesquiterpene endoperoxide has established the cyclic peroxides as potential antimalarial. The discovery of peroxide based antimalarials has intrigued scientists to explore structurally diverse cyclic peroxides. Synthetic cyclic peroxides especially tetraoxanes have shown great promise. In view of the developments in the recent past, it can be stated that tetraoxane holds great promise. First an exhaustive literature survey on the development of organic peroxides as newer antimalarial drugs was done. From the comprehensive overview, it was speculated that by incorporating nitrogen within the cyclohexyl ring of cyclic peroxides will improve antimalarial activity. The reactions began with 4-piperidone as a substrate for the synthesis of N-substituted piperidine tetraoxanes. Despite several attempts, the desired compound could not be isolated in workable amounts. However, the by-products formed in the attempted tetraoxane synthesis have been isolated, characterized and crystallized. Further, the mechanistic insights were gained in the hydrogen peroxide assisted oxidation reaction. The use of molecular iodine and hydrogen peroxide as heterogenous catalytic system for the oxidation of adamantan-2-one with 30% $H_2O_2$ in $CH_3CN$ revealed the mechanistic perspective. Finally success in the synthesis of non-symmetric N-sulfonylpiperidine tetraoxanes was achieved. They were evaluated for antimalarial and anticancer activity. Some of the compounds showed very good antimalarial and anticancer potency. The tetraoxanes were also crystallized and their conformational features were studied.

*Contents*

1. An overview on the development of organic peroxides as newer antimalarial drugs. 2. Piperidine based tatraoxane synthesis: spectroscopic and crystallographic investigation of symmetrical cyclic organic peroxides. 3. Reinvestigating the mechanistic studies of the hydrogen peroxide assisted peroxidation reactions. 4. Synthesis of unsymmetric dispiro N-sulfonylpiperiding tetraoxane for antimalarial and anticancer activities. 5. Structural investigation of crystalline tetraoxane and future outlook. References and list of publications.

34. SHARMA (Shivani)
**Design, Synthesis and Application of Silica Nanospheres Based Organic-Inorganic Hybrid Materials as Sensor for Copper Ions and Catalysts for Oxidative Amination and Coupling Reactions.**
Supervisor: Prof. R.K.Sharma
Th 23003

*Abstract*
*(Not Verified)*

Nanotechnology is one of the most rapidly growing research fields in the realm of technoscience which is involved in the production, characterization and application of materials with the nanoscale dimensions. In fact, the last decade has witnessed considerable attention in the design and development of nanomaterials owing to their outstanding physical and chemical properties which include controllable chemical compositions, large surface-to-volume ratios and many more. In particular, organic–inorganic hybrid nanocomposites employing several types of solid support materials have recently captivated the interests of chemists and material engineers worldwide as they synergistically combine functional organic moieties and inorganic building blocks into unique nanostructures. In this context, silica nanospheres have emerged as an excellent and promising solid support material due to their unique and adjustable physiochemical properties such as large surface area, high mass exchange characteristics, cost effectiveness, excellent thermal and mechanical stability and the presence of surface silanol groups which allow the incorporation of a wide variety of functionalities. Further, the properties of these hybrid silica nanospheres based materials can be tailored from the atomic scale to the nanoscale through incorporation of different functional organic and inorganic components which greatly expand their applications in a wide variety of multidisciplinary fields including catalysis, fuel cells, electronics, membranes, protective coatings, actuators, optics, electrochemical sensing, and medical therapy. We have developed novel, highly efficient and recyclable silica nanospheres based organic-inorganic hybrid catalytic systems and investigated their activity in various industrially significant organic transformations namely oxidative amination of aldehydes, one pot synthesis of propargylamines and oxidative amidation of methyl ketones. In addition, a novel nano-structured carbon paste electrochemical sensor has also been fabricated for the determination of copper ion concentration in some real samples. The present work has been divided into six chapters.

*Contents*

35. SINHA (Devapriya)
**Mechanism of Action of Bisbenzimidazoles with DNA Topoisomerases and its Antibacterial Activity.**
Supervisor: Prof. Vibha Tandon
Th 23001

*Abstract*
*(Not Verified)*

Scientific community is constantly involved in developing and identification of new and effective antibacterial agents to overcome bacterial resistance. Bacterial topoisomerase IA is a novel antibacterial drug target and drugs leading to accumulation of cleavable complex would be bactericidal. Reports from our laboratory shows DMA (5-(4-methylpiperazin-1-yl)-2-[2'-(3,4-dimethoxyphenyl)-5'-benzimidazolyl]benzimidazole) targets bacterial topoisomerase IA specifically. In the present study 24 bisbenzimidazoles were studied for their antibacterial activity and topoisomerase inhibition. The results suggest that, these compounds were active against both Gram-positive and Gram-negative bacteria. Out of the 24 compounds; PPEF was observed to be the most potent. All the 24 compounds were also evaluated for the inhibition of topoisomerase activity. Compounds PPEF, EPEF, NNEF, PYRVF, PYMVF and PPVF were observed to inhibit E. coli topoisomerase IA significantly. Result shows these molecules target E. coli topoisomerase IA specifically over E. coli gyrase, human topoisomerase IB and human topoisomerase II. Biochemical assays suggest PPEF chelates $Mg^{2+}$ required for religation of the DNA and thus probably acts as E. coli topoisomerase IA poison inhibitor. To further decipher the mechanism of inhibition alanine substituted mutants of the acidic triad D111A, D113A and E115A were generated. PPEF interaction leads to reduction in the % α helix and increase in % random coils at the secondary structural level. Analysis of ITC thermogram further shows half fold reduction in the binding association of mutants as compared to the wild-type topoisomerases. Results of DSC study suggest with EcTopoIA PPEF forms a more stable complex whereas with the mutants PPEF does not affect the stability. Present study shows, PPEF does not lead to target specific topoisomerase IA mutation. However, PPEF is subjected to efflux pumps. The synergistic composition of efflux pump inhibitor CCCP and PPEF killed the persistent population both in vivo and in vitro and also shows anti-biofilm activity.

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the mechanism of inhibition of EcTopoIA by PPEF 5. Investigation of effect of PPEF on E. coli topoisomerase IA gene and activation of the efflux pumps. Appendices.

36. SONU KUMAR

**Tandem Approaches for the Synthesis of Fused N-Heterocycles via 6-Endo-Dig Ring Closure of Alkynes.**

Supervisor: Prof. Akhilesh K.Verma

Th 23094

*Abstract*

*(Not Verified)*

We have developed a versatile and environmentally benign tandem protocol which provided a broad range of functionalized benzothienopyridines and benzofuropyridines in good to excellent yield from easily accessible starting substrates with excellent regioselectivity. This developed chemistry has been successfully extended for the selective synthesis of C-4 deuterated benzothienopyridines and benzofuropyridines. which further supports the proposed mechanism as well as the role of alcohol (solvent) in the reaction. Alkynes bearing electron-releasing, electron-withdrawing, alkyl, acyl and thienyl groups successfully provided the desired products in good yields. Then, we have designed a one-pot three-component tandem approach for the synthesis of naphthyridine, isoquinoline, pyrido indole, benzothienopyridines and benzofuropyridines derivatives from corresponding o-haloaldehyde, alkyne and tert-butyl amine via electrophilic cyclization. This developed tandem approach employed dual role of tert-butyl amine and CuI. Later, we have described an intramolecular alkyne-hydroarylation reaction in the presence of Pd-catalyst under strong acidic condition. The reaction was well tolerated with electron-rich and electron-neutral groups and provided the intriguing benzophenazines and quinoxalines in good yields, while new enolic compounds were obtained with electron–withdrawing substitutents. Various preliminary studies involving deuterium-labeling experiments were performed to support the mechanistic pathway via electrophilic metalation on aromatic C-H bond over alkyne activation. After successful accomplishment of above goal we have developed the facile route for the synthesis of iodo benzophenazine derivatives via the ($I_2$) induced electrophilic intramolecular regioselective cyclization of 2-aryl-3-(aryl/alkylethynyl) quinoxaline under mild reaction conditions. This methodology accommodates a wide range of 6-iodo-5-aryl/alkylbenzo[a]phenazine derivatives in good to excellent yields. The structures of the cyclic products were confirmed by the X-ray crystallography studies. Finally, the cyclized products 6-iodo-5-phenylbenzo[a]phenazine having iodo group could be further elaborate for using organopalladium chemistry.

*Contents*

1. Domino approach for the synthesis of benzothieno-and benzofuropyridines from o-alkynyl aldehydes via silver-catalyzed 6-endo-dig cyclization 2. Metal-catalyzed: one-pot tandem synthesis of pyrido fused heterocycle via sonogashira conjoined electrophilic cyclization 3. Palladium-catalyzed intramolecular fujiwara hydroarylation: synthesis of benzo [α] phenazines derivatives. 4. Iodine-mediated electrophilic synthesis of iodo substituted alkyl/arylbenzo [α] phenazine. Summary of the work and copies of the publications.

37. SRIVASTAVA (Sumit)

**Metalloligands Appended with Pyridine or Arylcarboxylic Acid Groups: Discrete Complexes, Hydrogen Bonded Assemblies and Coordination Networks**

Supervisor: Prof. Rajeev Gupta

Th 23006

*Contents*

1. Introduction of coordination complexes as the metalloligands: Designed architectures and self-assemblies. 2. Synthesis and characterization of trinuclear

{Co$^{2+}$-M$^{3+}$-Co$^{2+}$} (M=Co Fe) complexes and their catalytic applications in the reduction of nitro compounds. 3. Synthesis, crystal structures and heterogeneous catalytic applications of two – dimensional {Co$^{3+}$-Cd$^{2+}$} and {Fe$^{3+}$-Co$^{2+}$} networks. 4. Cobalt complexes appended with arylcarboxylic acid groups: Hydrogen bonded self-assemblies. 5. Three-dimensional {Co$^{3+}$-Zn$^{2+}$} and {Co$^{3+}$-Co$^{2+}$} Heteromatallic coordination networks originated from tris-chelated Co3+ complexes: Syntheses, Crystal Structures, topologies and heterogeneous catalysis. 6. Synthesis, crystal structures, and heterogeneous catalysis of {Co$^{3+}$ - M$^{2+}$} (M = Zn, Cd and Mn) Heterometallic) coordination networks. List of publications.

38. SUDESH KUMARI
**Synthesis of Oxindole, Pyrrolidine, Chromenopyridine and Triazole Tethered Heterocycles using Green Approaches.**
Supervisor: Prof. J.M. Khurana
Th 23169

*Abstract*
*(Not Verified)*

ABSTRACT The thesis entitled “Synthesis of oxindole, pyrrolidine, chromenopyridine and triazole tethered heterocycles using green approaches” presents applications for developing a variety of novel heterocycles. The chapter wise brief account is given below. Chapter I describes an efficient synthesis of novel triazolyl spirocyclic oxindole derivatives via one-pot five component condensation of acetylacetone, aryl azides, aromatic aldehydes, isatin and L-proline in presence of DBU as catalyst in PEG-400 at 80°C. The synthesis of novel triazole containing dispirooxindole pyrrolidine heterocycles by condensation of isatin, 2-(2-oxo-1-(prop-2-ynyl)indolin-3-ylidene)malononitrile, sarcosine and aryl azides using Cu(I) as catalyst in PEG-400 at 100°C is described in chapter II and a green synthesis of novel 7,11-dihydro-6H-chromeno[3,4-e]isoxazolo[5,4-b]pyridin-6-one conjugates through one-pot three component reactions of 4-hydroxycoumarin, aromatic aldehydes and 5-amino-3-methylisoxazole in [bmim]HSO$_4$ at 80°C has been described in chapter III. Chapter IV describes a catalyst free synthesis of novel 7,12-diaryl-10,10-dimethyl-9,10,11,12-tetrahydro-6H-chromeno[4,3-b]quinoline-6,8(7H)-dione derivatives through domino protocol of dimedone, aromatic amines, 4-hydroxycoumarin and aromatic aldehydes in ethylene glycol at 60°C. Chapter V has described the synthesis of spiro[indolo-3,10’-indeno[1,2-b]quinolin]-2,4,11’-trione derivatives via one-pot three component condensation of 1,3-indandione, isatins and enaminones using La(OTf)$_3$ as catalyst in PEG-400 at 40°C under conventional heating and ultrasonic irradiation. The applications of [NMP]H$_2$PO$_4$ for the synthesis of a variety of heterocycles has been reported in chapter VI which is subdivided in three parts. Part A describes an environmentally benign protocol for one-pot synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[a]xanthene-11-one conjugates by condensation of 2,7-dihydroxynaphthalene/2-naphthol/2,6-dihydroxynaphthalene, aromatic aldehydes and dimedone/cyclohexan-1,3-dione in task specific acidic ionic liquid [NMP]H$_2$PO$_4$ at 80°C. Part B describes one-pot three component condensation of isatin, 5-amino-3-methyl-1-phenylpyrazole and 1,3-dicarbonyls for the synthesis of spirooxindole derivatives in presence of [NMP]H$_2$PO$_4$ as catalyst in H$_2$O:EtOH (4:1, v/v) at 80°C. Part C describes the synthesis of benzo[b]xanthenes, pyrimido[4,5-b]quinolines, chromeno[2,3-d]pyrimidines and pyrazolo[3,4-b]quinolin-5(6H)-ones using 20 mol% of [NMP]H$_2$PO$_4$as both catalyst and reaction medium at 80°C.

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1.An efficient green approach for the synthesis of novel triazolyl spirocyclic oxindole derivatives via one-pot five component protocol using DBU as catalyst in PEG-400 2. One-pot four component condensation for the synthesis of novel dispirooxindole pyrrolidine linked 1, 2, 3-triazoles via stereo-and regioselective [3+2] cycloaddition reaction in PEG-400 3. An efficient approach for the synthesis of novel 7,11-dihydro-6H-chromeno[3,4-e] isoxazolo [5,4-b] pyridine-6-one derivatives using acidic ionic liquid [bmim]HSO$_4$ 4.an efficient catalyst free synthesis of novel chromeno [4-,3-b] quinolines through Michael initiated ring closure 9MIRC) reaction with in situ generated 3-(arylmethylene) chroman-2,4-diones 5. La $(OTf)_3$ - catalyzed, three-component synthesis of spiro [indolo-3,10'-indeno [1,2,-b] quinolin] -2,4,11'-triones in PEG-400 under conventional beating and ultrasonic irradiation 6. $[NMP]H_2PO_4$: an efficient task specific acidic ionic liquid for the synthesis of various heterocycles 7. Summary and conclusions. List of publications.

39. TIWARI (Vinod)

**Radioprotective Effects of DMA: A Bisbenzimidazole and Elucidation of its Mechanism of Action.**

Supervisor: Prof. Vibha Tandon

Th 23005

*Abstract*

*(Not Verified)*

Radiation therapy is widely used treatment for cancer treatment. Indiscriminate killing of normal cells along with cancerous cells reduces the therapeutic index of radiation therapy. There is need to develop radioprotectors as an adjuvant for radiation therapy which would increase therapeutic index of it by imparting protection to normal cells against the radiation induced damage. DMA (5-(4-methylpiperazin-1-yl)-2-[2'-(3,4-dimethoxyphenyl)-5'-benzimidazolyl] benzimidazole), a 3,4-dimethoxy derivative of Hoechst33342 is a small minor groove binding ligand with better radioprotective properties than its parents compound. It was less toxic to cells and reached to its maximum concentration within 2h in cells. It did not affect the viability of cells up to 72h once inside the cells. There was protection of balb/c mice against the lethal whole body irradiation by DMA when administered by oral, i.v., i.p and s.c. DMA delivered better radioprotective effect at 9 Gy through systemic administration at 50mg/kg bw. Histopathology results demonstrated that DMA ameliorated radiation induced damage of hematopoietic and gastrointestinal system. DMA is pharmacologically active in Balb/c mice.It reached to Cmax in systemic circulation at 6h whereas reached highest concentration in intestine within 2h of administration. DMA reached at nearly 12 fold higher concentration in intestine when delivered through i.v.Transcriptional modulation study showed that DMA upregulated Gadd45α, and Akt whereas level of p21got lowered down when prior treatment of DMA was subjected to irradiated mice. Similarly there was elevated level of Akt in response to DMA in irradiated mice.Study of molecular mechanism releaved Akt mediated NFκB activation by DMA was pivotal pathway which responded to protect the cells from lethal damages from radiation in both in vivo and in vitro. These pathways were not activated in tumor tissues when subjected to DMA treatment prior to radiation indicated either no or less uptake of DMA or different biochemical fate in tumor tissues.

*Contents*

1. Review of literature. 2. To study the cytotoxicity, uptake, efflux, radioprotective and dose modification factor of DMA on MRC5, A549, HEK293, A549 and U87 cell lines. 3. To elucidate the molecular mechanism of DMA as a radioprotector 4. Pharmacokinetics and biodistribution of DMA in Balb/c mice through oral and intravenous mode of administrations. To study the radioprotecive effect of DMA against sublethal and lethal total body irradiation (TBI) in normal and tumor bearing balb/c Mice. Appendix.

40. TOMAR (Vartika)

**Noscapine: A Promising Therapeutic Agent for Cancer**

Supervisor: Prof. Shrikant Kukreti

Th 23011

### *Abstract*
### *(Not Verified)*

Noscapine is an oral, well-tolerated tubulin-binding agent its micromolar binding affinity to tubulin requires high doses for anti-cancer activity. Therefore, to enhance binding affinity whilst preserving low toxicity, we synthesized 21 noscapinoids analogues that were characterized by NMR, IR and mass spectroscopy. Their yields were in the range of 60-90%. The halo derivatives of noscapine gave good yield. We have attempted to develop a viable nanoformulation of noscapine and 9-bromo-noscapine to augment drug delivery and cytotoxicity in cancer cells. 9-Bromo-noscapine (9-Br-Nos), a brominated derivative of noscapine reflects its superiority over Nos by showing significant tubulin binding activity as it influences tubulin polymerization in a different way from Nos. Despite favourable therapeutic index, 9-Br-Nos has limited clinical applications due to its poor solubility in aqueous solution ($0.35\times10^{-3}$g/ml) and high lipophilicity (log P~3.03±0.61) which ultimately results in suboptimal therapeutic efficacy at the site of action. Therefore, to raise the concentration of 9-Br-Nos at the tumor site, we have encapsulated 9-Br-Nos into particulate drug nanocarriers composed of human serum albumin (HSA). The aim of the current study was to design HSA nanoparticles for 9-Br-Nos delivery and establish a standard protocol for their synthesis. In summary, the synthesized inhalable drug loaded nanoparticles exhibited increased cytotoxicity, apoptosis and cellular uptake in-vitro in non-small cell lung cancer cells. The prepared niosomes were characterized for particle size, entrapment efficiency, in vitro release and storage stability profile. In conclusion, our novel analogues of noscapine as well as developed nanoformulation like 9-bromo-noscapine loaded human serum albumin nanoparticles, noscapine bearing rapid release solid lipid nanoparticles, noscapine and 9-bromo-noscapine loaded optimized liposomes and noisome have shown promising consequences in in-vitro and in-vivo setup. Further, in depth in vivo investigations are needed on these optimized nanoformulations of noscapine and 9-bromo-noscapine, for translating in to the clinical viable anticancer products.

### *Contents*

41. TRIPATHI (Mohit)
**Rational Strategies for Facile Synthesis of Medicinally Relevant Molecules and their Biological Activity Evaluation.**
Supervisor: Prof. Diwan S. Rawat
Th 23170

### *Abstract*
### *(Not Verified)*

Molecular hybridization which combines two or more pharmacophores into a single ‘hybrid’ entity anticipated to act simultaneously on two or more targets is a rational strategy to develop medicinally relevant molecules. This strategy having humble beginnings in the past decade has seen a recent spate of reports on the development of hybrid antimalarials and has been reviewed in Chapter 1 of this thesis. Chapter 2 describes the synthesis of 4-aminoquinoline−pyrimidine hybrids incorporating terminal aminoalkanol chains or modified anilines as part of SAR studies. Results of the antimalarial activity evaluation against CQ-sensitive (D6) and CQ-resistant (W2) strains of P. falciparum and anticancer activity

evaluation of representative compounds on NCI-60 cancer cell panel are included, along with the results of antimalarial mechanistic studies. Chapter 3 describes the synthesis of FAQ-pyrimidines wherein the –OH group in amodiaquine (AQ) was substituted with a –F atom and the resulting moiety (FAQ) was hybridized with pyrimidine scaffold substituted with cyclic amines. These molecules displayed high antimalarial activity against the CQ-sensitive (NF54) and CQ-resistant (Dd2) strains of P. falciparum and the results are presented in this chapter. Another analogous series of molecules was synthesized wherein a 1,3-cyclohexyl diamine linker was introduced in place of benzyl linker in AQ. These molecules also displayed submicromolar anticancer activities and potent Nurr1 (target for Parkinson disease) activation. Chapter 4 presents an overview of M. tb. BioA enzyme and recent reports on BioA inhibitors as potential anti-TB agents. Thiazolyl ureas were identified as weak inhibitors of BioA enzyme through a computational approach, followed by their synthesis and biological evaluation. Based on these results and computational studies, a new series of BioA inhibitors was proposed. Chapter 5 describes improved protocols for reductive cyclization of 2-nitrobiphenyls/2-nitrostyrenes to medicinally relevant carbazoles/indoles and IPA-mediated transfer hydrogenation of nitro-aromatics, catalyzed by CoPc and FePc, respectively.

*Contents*

1. An Overview of hybridization strategy in medicinal chemistry and development of 4-aminoquinoline based molecular hybrids as antimalarials 2. Synthesis, antimalarial and anticancer activity evaluation of 4-aminoquinoline-pyrimidine hybrids 3. Synthesis of amodiaquine-pyrimidine hybrids as multifunctional agents 4. Design of m.tuberculosis bioA inhibitors as novel anti tuberculosis agents 5. Metal phthalocyanines as novel catalysts for reductive cyclization and IPA-mediated transfer hydrogenation of nitro-aromatics. Summary. List of publications and patent.

42. SAUNTHWAL (Rakesh Kumar)
**Novel Approaches for the Synthesis of N-Heterocycles via C-H Activation/ {4+2} Cycloaddition and Michael Addition.**
Supervisor: Prof. Akhilesh K. Verma
Th 23016

*Contents*

1. Pd (II)- Catalyzed C-H activation of styrylindoles: Short, efficient and regioselective synthesis of functionalized carbazoles 2. Metal-free [4+2] cycloadditions of alkynes with ortho-substituted anilines: An efficient assembly of highly functionalized quinolines 3. Cu (II)-catalyzed tandem synthesis of 2-imino [1, 3] benzothiazines from 2-aminoarylacrylates via thioamidaton and concomitant chemoselective thia-michael addition 4. An efficient synthesis of highly functionalized tetrahydroquinazolines from o-substituted anilines via chemosselective aza-michael addition. Summary of the work and copies of the publications.

43. VARDHINENI (Satyapavan)
**Facile and Green Synthesis of Biologically Relevant Heterocycles.**
Supervisor: Prof. Diwan S. Rawat
Th 23024

*Abstract*
*(Not Verified)*

Abstract Thesis Title: Facile and Green Synthesis of Biologically Relevant Heterocycles Submitted by Mr. Satyapavan Vardhineni Supervisor: Prof. Diwan S. Rawat Department of Chemistry, University of Delhi, Delhi-110007, India. This thesis has been divided into four chapters. Each of the chapter 1 to 3 has again divided into part A and B. Chapter 1A deals with the synthesis of $BaCO_3$ NPs as efficient, recyclable and transition metal free solid base catalyst for the synthesis of propargylamine via A3 coupling for the first time. Chapter 1B deals with the GO/MC nanocomposite as novel, efficient and green protocol for the synthesis of indolizines by A3 coupling strategy in the presence of EG. Chapter 2A describes the synthesis 3-substituted indoles using L-Ser@Cellulose as a heterogeneous catalyst. Chapter 2B deals with the green and sustainable pathway for one pot synthesis of 1,2,3,6-tetrahydropyrimidine-4,5-dicarboxylate at room temperature using RGO/$Fe_3O_4$ catalyst. Chapter 3A describes the synthesis of 3-amino-alkylated indole via one-pot three-component Mannich type reaction. Chapter 3B deals with the synthesis of dihydroquinazolinones and pyrrolo[1,2 a]quinoxaline via one-pot reaction. It is easy and safe to handle along with short reaction time. Further, the purification process does not involve column chromatography making the process easy and less time consuming. Chapter 4 describes the synthesis of 4 aminoquinoline-pyrimidine hybrids. The synthesized compounds were evaluated for their antimalarial activity against CQ-sensitive (NF54) and CQ-resistant (Dd2) strains of P. falciparum in an in-vitro assay. One of the synthesized hybrids exhibited 74-fold better potency than chloroquine and 4-fold better potency than artesunate against drug-resistant strain of P. falciparum.

*Contents*

1. Barium carbonates rods as efficient recyclable heterogeneous catalyst for the synthesis of propargylamines. 1 B. Go/malachite nanocomposite as a recyclable catalyst for one pot synthesis of indolizines via A3 coupling 2A. Amino acid grafted on cellulose as efficient heterogeneous organocatalyst for yonemitsu type reactions 2 B. RGO/$Fe_3O_4$ nanocomposite: Magnetically recoverable catalyst for synthesis of tetrahydropyrimidines 3A. Ethylene clycol promoted one-pot three component synthesis of 3-amino alkylated indoles via mannich-type reaction. 3B. CSA-catalyzed one-pot synthesis of 1, 2,-dihydroquinazolines and pyrrolo [1, 2,-α] quninoxalines. 4. Design and development of 4-aminoquinoline pyrimidine based molecular hybrids as next generation antimalarial agents. Summary and list of publications and patent.

44. VINOD
**Synthesis and Study of Supramolecular Assemblies of 2,6-Anhydro-Heptitols, Sugar-Based Polymers and Macrocycles.**
Supervisor : Prof. Ashok K. Prasad
Th 22993

*Contents*

1. Design and synthesis of chiral sugar-Aza-crown-8 derivatives and [2] pseudorotaxanes involving them 2. Greener biocatalytic synthesis of sugar-PEG based polymers for nanoformulation of indocyanine green 3. Synthesis of β-C-glycopyranosyl aldehydes and2, 6-annnhydro-heptitols 4. Pegylation of 2, 6-anhydro-heptitols and encapsulation studies of non-polar drugs in micelles derived from them. Summary.

45. YADAV (Geeta Devi)
**Synthesis and Characterization of (L)-Prolinamides and their Application as Organocatalysts for Direct Asymmetric Aldol Reaction.**
Supervisor: Dr. Surendra Singh
Th 23013

*Contents*

1. Introduction 2. Direct asymmetric aldol reaction catalyzed by trans-4-hydroxy-(S)-prolinamide in solvent-free condition 3. (L)-Prolinamideimidazolium hexafluorophosphate ionic liquid as an efficient reusable organocatalyst for direct asymmetric aldol reaction in solvent-free condition 4. N-Arylprolinamie as an organocatalyst for the direct asymmetric aldol reaction of acetone with isatin 5. Trans-

4-Hydroxy-(L)-prolinamide as an efficient catalyst for direct asymmetric aldol reaction of acetone with isatins. Summary and list of publications.

46. YADAV (Kumar Karitkey)

**Synthesis of Selected Metallophthalocyanines and their Applications in Organic Transformations.**

Supervisor: Prof. S.M.S. Chauhan

Th 23020

*Contents*

1. Efficient method for the synthesis of metallophthalocyanines and their applications in narylation of heterocycles. 2. Synthesis of selected Cu (II) phthalocyanines and their applications in click reactions. 3. Synthesis of Co (II) phthalocyanines and their applications in conversion of sugars to HMF, DFF and EMF. 4. Synthesis and photophysical progperties of Zn (II) phthalocyanines and their applications in singlet oxygen generation. 5. Synthesis of phenanthroline-substituted phthalocyanines and their application in organic synthesis.

47. YADAV (Manavi)

**Design, Synthesis, and Application of Nano Magnetic Silica Supported Transitions Metal Catalysts for Cross-Coupling and Oxidation Reactions.**

Supervisor: Prof. R. K. Sharma

Th 23004

*Contents*

1. Introduction 2. Instrumentation and theory of the characterization techniques used 3. Silica based magnetic palladium nano-catalyst for direct coupling of acyl chlorides with alkynes 4. Magnetically retrievable silica based nickel nano-catalyst for suzuki-miyaura cross-coupling reaction 5. Silica coated magnetic copper nano catalyst for the decarboxylative cross-coupling of aryl halides with alkynyl carboxylic acids 6. Silica based magnetic manganese nano-catalyst for the oxidation of organic halides and alcohols. Summary, spectral data and list of publications.

48. YADAV (Neha)

**Microwave Assisted Synthesis and Biological Activity Evaluation of 4-Pyranopyrazolyl/Aryl-1,4-Dihydropyridines and 1-Triazolypyranopyrazoles.**

Supervisor: Dr. Rakesh Kumar

Th 23002

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1. Microwave assisted synthesis of a novel class of 1, 4,-dihydropyridines having pyranopyrazole ring at 4-position as potent positive inotropes and CytP450/Androgen inhibitors. Section A. Microwave assisted synthesis of a novel class of 1, 4,-dihydropyridines having pyranopyrazole ring at 4- position. Section B. In Silico, in vitro and in vivo characterization of the Pyranopyrazolyl1, 4, -dihydropyridines as potent positive inotropes and CytP450/Androgen inhibitors. 2. Design & microwave assisted synthesis of biologically active 4-aryl-1, 4,-dihydropyridines having N-heterocyclic ringhsystem at 4’-position of the aryl group. 3. Microwave assisted synthesis of 1-triazolylpyranopyrazole derivatives and evaluation of their antimicrobial activity. Summary.

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**Frame Work Aluminophosphate Materials Derived from Microporous Precursor: Potential Catalysts for Various Transformation.**
Supervisor: Dr. A. Sakthivel
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1. Introduction 2. Experimental methods 3. Mesoporous SAPO-37 (MESO-SAPO-37) molecular sieves synthesis, characterization and its catalytic application for hydroisomerization 4. Mesoporous SAPO-37 ((MESO-SAPO-37): Vapor phase hydroisomerization of 1-octene 5. Catalytic study on MESO-SAPO-37 for alkylation of 2-naphthol and effect of bond dissociation energy for product distribution 6. Titanium containing mesoporous SAPO-37 (MESO-TSAPO-37) molecular sieves and study its catalytic activity for cyclohexene oxidation 7. Synthesis of mesoporous SAPO-37 using neutral surfactants, its characterization and catalytic application for trans-alkylation of naphthalene 8. Diamine functinalized SAPO-37: synthesis, characterization and catalytic application for ring opening of epoxide. List of publications.