In-House Symposium 2012

March 10th 2012, VMCC main auditorium

Department of Chemistry
Indian Institute of Technology Bombay
Mumbai 400 076

In-House Symposium March 10th 2012, Department of Chemistry
Scientific Program

Time **Events**

08.45 – 09. 00 Registration

09.00 – 09.20 Inauguration and Welcome address

Session I

Chairperson: Mr. Narendra Kumar

09.20 – 09.55 Prof. Y.U. Sasidhar
To Direct Or To Be Directed

09.55 – 10.15 Ms. Rama Kanwar
Synthetic Utility of Sugar-Derived Cyclic Nitrones

10.15– 10.35 Mr. Dhirendra Kumar Rai
Reaction of 3-ferrocenylpropynal with iron carbonyl and chalcogenised iron carbonyl clusters: Formation of new ligands; $[Fe(CO)_3\text{-}\eta^4\text{-}(FcC_2CHO)_2]$, $[Fe(CO)_2\{\eta^2{:}\eta^2\text{-}(FcC_2CHO)_2Fe(CO)_3\text{-}\mu\text{-}CO\}]$ ***and 1,2,3-triselenole***

10.35 – 11.05 **Tea break and photo session**

Session II

chairperson: Mr. Palanichamy Kalanidhi

11.05 – 11.25 Mr. E Siva Subramaniam Iyer
Importance of electrostatic interactions in the mobility of cations in Nafion

11.25 – 11.45 Mr. Akhilesh Kumar Sharma
Mechanistic Studies on Proline Catalyzed Reactions: Enamine Carboxylic Acid vs Enamine Carboxylate/Oxazolidinone Transition State Models

11.45 – 12.05 Ms. Hemlata Aggarwala
Correspondence of $Ru^{III}Ru^{II}$ (d^5d^6) ***and*** $Ru^{IV}Ru^{III}$ (d^4d^5) ***Mixed Valent States in a Small Dinuclear Complex***

12.05 – 12.25 Mr. Kalisankar S Bera
Enantioselective Michael Addition of Nitrophosphonates to Activated Olefins for Synthesis of Quaternary α-Aminophosphonates

12.25 – 13.00 Prof. Debabrata Maiti
Palladium Catalyzed Aldehyde Decarbonylation Reaction

13.00 – 15.00 **Lunch and Poster Session**

Session III

chairperson: Mr. Vikram Ashok Sarpe

15.00 – 15.20 Mr. Arghya Dey
Isomer Dependent Fluorescence Quenching in Hydrogen Bonded Complexes of Phenylacetylenes

15.20 – 15.40 Mr. Ajay Singh Tanwar
Structural and Biochemical Studies of Channeling of Unstable Intermediates in Biological Pathways

15.40 – 16.00 Mr. Saurabh K. Singh
New theoretical perspectives on the Magnetic coupling in {3d-4f} Molecular Nano Magnets
16.00 – 16.20 Mr. Pravin Kumar Bhalerao
Inverse Demand Diels-Alder Approach Towards framework of Atisanes: Generation of Molecular Complexity from Simple Aromatics

16.20 – 16.40 **Tea break**

Session IV

Chairperson: Ms. Garima Jindal

16.40 – 17.00 Ms. Susmita Naik
Triazine based tridentate and terpyridine based pentadentate ligands: Synthesis, Transition Metal Chemistry and Photophysical study

17.00 – 17.20 Mr. Sanjay Upadhayay
Temperature dictates the conformational preference of "RGD" in peptide sequence "RIPRGDMP" from kistrin and selects the bio-active conformation: Implications for inhibitor design

17.20 – 17.55 Prof. Anil Kumar
Challenges and Opportunities in Functional Conjugated Polymers and Materials NEMS/MEMS Devices: A Synthetic Chemistry Approach

17.55 – 18.15 Vote of thanks and concluding remarks

18.15 – 18.30 **High Tea**

Poster Session

P1 Subhasree Banerjee, Anjali Dhir, Tuseeta Banerjee, Avinash Kumar Singh, Anindya Datta
Silica Nanodisks as Platforms for Fluorescence Lifetime-based Sensing of pH

P2 Suman De, Arindam Chowdhury
Quantum Confined Stark Effect in Localized Luminescent Centers within (In,Ga)N Quantum Well Based LEDs

P3 Manas Sajjan, Dipanwita De and Anindya Datta
Coumarin in Lamellar Micelles: Diffusion in two dimensions

P4 Arunasish Layek, Abhijit Hazarika, Dipankar Das Sarma, and Arindam Chowdhury
Photoluminescence Imaging and Spectroscopy of Single Nanocrystals: Insight on Mn doping into ZnCdS

P5 Dipanwita De and Anindya Datta
Ground and Excited State Prototropism of 2,2′-bis(2-pyridyl)bibenzimidazole

P6 Sohidul Islam Mondal and G. NareshPatwari
Experimental investigation of hydrogen bonded complexes of metaFluorophenylacetyleneswith water, alcohols and ammines

P7 Ashok Kumar and Anil Kumar
Amplified Fluorescent Poly (phenyleneethynylene)s based on Pentiptycene and its Applications in Sensing

P8 Anita Nehra, V.V. Sreenivasu M. and Chebrolu P. Rao
La^{3+} Sensing by Triazole Linked Picolylimine Derivative of Calix[6]arene and the Complex as Secondary Sensor for F^-

P9 Rekha Singh, Anshu Kumar, Sreelekha P. G. and Anil Kumar
Synthesis of Ultra High Molecular Weight Conjugated Polymers Based on 3, 4 Propylenedioxythiophenes via Solvent Free Chemical Oxidative Polymerization

P10 Tulika Gupta and Gopalan Rajaraman
Magnetic coupling in {4f-radical} systems: A theoretical exploration

P11 Supriya Ghosh, Mayank Kumar Dixit and B. L. Tembe.
An Effective Method for the Calculation of Franck-Condon factors for Diatomics Using the Fourier Grid Hamiltonian Method

P12 Prabha Jayapal and Gopalan Rajaraman
Spectroscopic properties of P-nitrobenzoate N-Oxygenase (AurF) – A Theoretical study

P13 Atanu Sarkar, Anupam Chatterjee, B.L.Tembe
Model Dependence of the Association of Na^+ Cl^- Ion Pair in DMSO – Water Mixed Solvents

P14 ApoorvaUpadhyay and MaheswaranShanmugam
Single-molecule-magnet based on redox active ligand: An effort to increase exchange interaction between lanthanide ions

P15 Nageswar Rao and Prasenjit Ghosh
Synthesis and Characterization of Silver and Gold Complexes of Chiral N-heterocyclic Carbenes

P16 Shefali Vaidya and Maheswaran Shanmugam
Probing the magnetic properties of lanthanide-radical containing ligand complexes

P17 Bimba Choubey and M. S. Balakrishna
Triazole Based phosphinite and phosphonite Ligands: Syntheses, Derivatization and Transition Metal Chemistry

P18 Mohd. Tauqeer, Radhe Shyam ji, Shaikh M. Mobin, Pradeep Mathur, Goutam K. Lahiri
Functionalization of diferrocenylacetylene with diferrocenyl ditelluride: Synthesis and photolytic reaction of (Z) 1-ferrocenyltelluro-1-ferrocenyl-4-ferrocenyl-1-buten-3-yne with $Fe(CO)_5$

P19 Anuj Kumar and Prasenjit Ghosh
Nickel and Gold complexes of Amido-functionalized triazole based N-heterocyclic carbenes –Synthesis, Structure and Characterization

P20 S. M. Mujahuddin and M. S. Balakrishna
Group 11 metal complexes of alkynyl substituted cyclodiphosphazane $[(\mu\text{-}N^tBuP)_2(C\equiv CPh)_2]$

P21 Srimanta Manna, Soham Maity and Debabrata Maiti
Ipso-Nitration of Arylboronic Acids with Bismuth Nitrate and Perdisulfate

P22 Sandeep Kumar Gupta, Subramaniam Kuppuswamy and Ramaswamy Murugavel
Synthesis of Molecular Cobalt Phosphates and Assembling D4R Cobalt Cubanes with NN-donor Ditopic Linker into Porous Framework Solids

P23 Hemanta Kalita and M. Ravikanth
Synthesis and Properties of $B(OR)_2$***-complexes of Smaragdyrin***

P24 Atanu Modak, Arghya Deb and Debabrata Maiti
A General and Efficient Aldehyde Decarbonylation Reaction by Palladium Catalyst

P25 V. Lakshmi and M. Ravikanth
Brominated Boron-Dipyrromethene Building Blocks for the Synthesis of Sterically Crowded Fluorescent Systems

P26 Ritambhara Jangir and Ramaswamy Murugavel
Synthesis and Characterization of Hybrid Polyoxometalates and Schiff-base building blocks of 2,2',6,6'-Tetraisopropylbenzidine

P27 Kalanidhi Palanichamy, Sankar Rao Suravarapu and Krishna P. Kaliappan
A copper-catalyzed multicomponent reaction to the synthesis of 3-C-linked glycosyl iminocoumarins

P28 Vikram A. Sarpe and Suvarn S. Kulkarni
First Synthesis of Maradolipid

P29 Prashant Pavashe, Irishi N. N. Namboothiri
Synthesis of Multi-functional and Bioactive Molecules

P30 Rashid Ali , Arti Tiwari, Sambasivarao Kotha
Diversity Oriented Approach To Novel Spirocyclic compounds via Enyne-Metathesis, Diels-Alder Reaction and [2+2+2] Cycloaddition As Key Steps

P31 Rodney A. Fernandes, Mahesh B. Halle
Diastereoselective synthesis of (+)-nephrosterinic acid and (+)-protolichesterinic acid

P32 Anandaraju Bandaru and Krishna P. Kaliappan
Synthetic Utility of Sugar-Derived Cyclic Nitrones: A Diastereoselective Synthesis of Linear Azatriquinanes

P33 Dipali A. Chaudhari, Rodney A. Fernandes
Development of the first menthane based chiral bis-π-allylpalladium catalysis: Asymmetric allylation of imines

P34 S. Kotha, A. Tiwari, A. K. Chinnam
Synthesis of [4.3.3] Propellane Derivatives Using Weiss-Cook Reaction, Fischer-Indole Cyclization as key steps

P35 Vipul V. Betkekar, Samaresh Panda and Krishna P. Kaliappan
A Tandem Enyne/RCM Approach to 4-Methylene-2-cyclohexenone: An Efficient Entry to Otteliones and Loloanolide

P36 Atul Thawari, Khatija Tabbassum, J.P.Chinta and Chebrolu Pulla Rao
Interaction of Pb^{2+} with Lentil lectin (LL)

P37 Narendra Kumar, Nand Kishore
Interaction of hydrophobic amino acids with sarcosine in presence of denaturant: Volumetric and calorimetric approach

P38 S. Harikrishna, Kiran R. Gore, Pradeepkumar P. I
Molecular Modeling and Dynamics of siRNAs containing 4'-C-Aminomethyl-2-O-Methyl Uridine Nucleotides

Abstracts of Oral Presentations

To Direct Or To Be Directed

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Reverse turns help proteins attain compact globular shape. Very often they play a role in protein function. They also play a role in protein folding. For instance, formation of a turn, in an unfolded protein, can bring together distant regions of the protein and promote folding. However, it is not always clear whether a turn actively played a role in the folding process or remained a mere passive player, played upon by the folding process. In this presentation, I shall talk about a particular turn from staphylococcal nuclease and our efforts to understand what makes it an active turn and what makes it a passive turn through molecular dynamics simulations.

Synthetic Utility of Sugar-Derived Cyclic Nitrones

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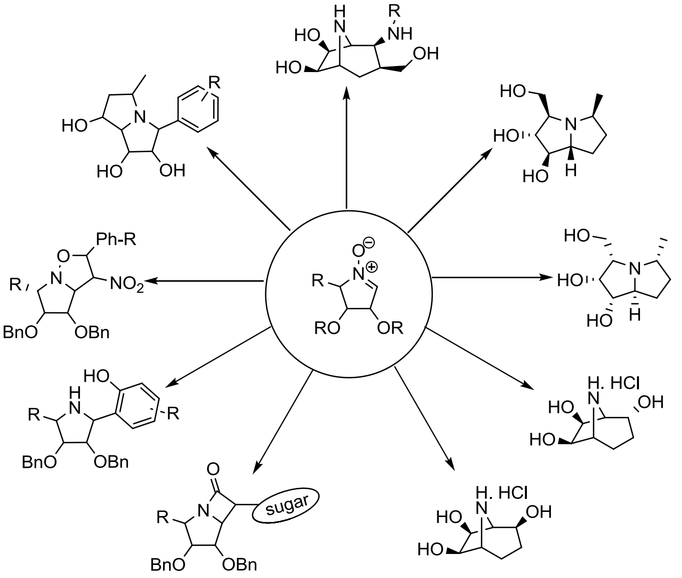
Nitrones have been one of the important building blocks in organic synthesis and they act as an important tool for the synthesis of various complex molecules.[1] Among nitrones, the sugar-derived nitrones have been proved to be versatile substrates as they provide a polyhydroxylated carbon framework with multiple avenues of chirality. Moreover, enantiomerically pure and polyfunctional cyclic nitrones have found applications in the total, asymmetric synthesis of polyhydroxylated pyrrolidine, indolizidine, and pyrrolizidine alkaloids.[2]

Our group has earlier reported the synthesis of calystegine analogues, aza-bridged amino polycyclitols and 5-*epi*-hyacinthacine A3 and 5-*epi*-hyacinthacine A5.[3] In continuance of our interest in nitrone chemistry, we utilized the sugar-derived cyclic nitrones for the synthesis of chiral β-lactam using Kinugasa reaction,[4] aza-C-aryl glycosides using 1,3-dipolar cycloaddition with benzynes followed by reductive cleavage of N-O bond, and nitro-pyrrolo-isoxazole using 1,3-dipolar cycloaddition with aryl nitroalkenes.



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Reaction of 3-ferrocenylpropynal with iron carbonyl and chalcogenised iron carbonyl clusters: Formation of new ligands; $[Fe(CO)_3\text{-}\eta^4\text{-}(FcC_2CHO)_2]$, $[Fe(CO)_2\{\eta^2{:}\eta^2\text{-}(FcC_2CHO)_2Fe(CO)_3\text{-}\mu\text{-}CO\}]$ and 1,2,3-triselenole

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In continuation of our earlier observation on reactivity of mono-substituted acetylenes[1-4] towards mono-nuclear metal carbonyls and chalcogen stabilized metal carbonyl clusters, we now observe that reaction of 3- ferrocenylpropynal and $Fe(CO)_5$ forms $[Fe(CO)_3\text{-}\eta^4\text{-}(FcC_2CHO)_2]$ (**1**) and $[Fe(CO)_2\{\eta^2{:}\eta^2\text{-}FcCC(CHO)C(Fc)C(CHO)Fe(CO)_3\text{-}\mu\text{-}CO\}]$ (**2**), (Fc= $C_{10}H_9Fe$), as a result of [2+2]- cyclization and head to tail C-C coupling of the alkynes. $Fe_3Se_2(CO)_9$ cluster with 3-ferrocenylpropynal yields a novel 5-ferrocenyl-1,2,3-triselenole-4-carbaldehyde ring (**3**) and an intermediate compound, $[(CO)_6Fe_2\{\mu\text{-}SeC(Fc){=}C(CHO)Se\}]$ (**4**), which on decarbonylation by $Me_3NO.2H_2O$ leads to formation of **3**. Contrast in behavior of analogous $Fe_3S_2(CO)_9$ and $Fe_3Te_2(CO)_9$ clusters is observed as they afford only $[(CO)_6Fe_2\{\mu\text{-}SC(Fc){=}C(CHO)S\}]$ (**5**) and $[(CO)_6Fe_2\{\mu\text{-}TeC(Fc){=}C(CHO)Te\}]$ (**6**), respectively.

1 **3**

Figure 1. Molecular structures of **1**, and **3**

References

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Importance of electrostatic interactions in the mobility of cations in Nafion

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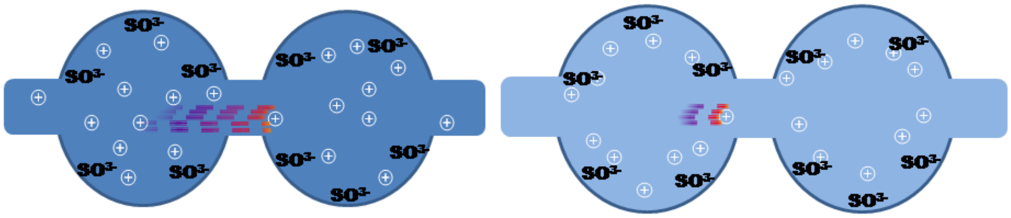
Nafion membranes are polysulfonated teflon membranes and are selective towards cations. It is widely believed that there are water channels present in the membrane that are responsible for conducting cations. The conductivity of Nafion decreases by an order of magnitude upon decreasing the water content. The primary reason has been ascribed to the breaking up of water channels which are of hundreds of nanometers. On the contrary we have observed that proton transfer is hindered in molecular dimensions. We have even observed disruption of this proton transport even through one water molecule.[1,2] We ascribe the reason to enhanced electrostatic interactions upon reducing the water content. We have used Excited State proton transfer (ESPT) in Coumarin 102 (C102), 2-(2′-Pyridyl)-benzimidazole (2PBI) and (2,2′-Bipyridyl)-3,3′-diol to explore proton transfer process in the nafion membrane.



Scheme 1: Effect of drying on mobility of ions in Nafion membrane

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Mechanistic Studies on Proline Catalyzed Reactions: Enamine Carboxylic Acid vs Enamine Carboxylate/Oxazolidinone Transition State Models

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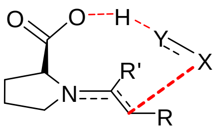
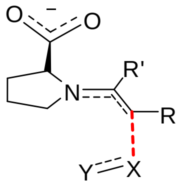
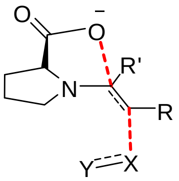
Proline is the one of the earliest known organocatalyst for asymmetric reactions and has seen an unprecedented growth in the last decade. The concept of bifunctional catalysis has been used to develop a variety of proline derivatives. Due to its widespread use in asymmetric synthesis, its mechanism is of utmost importance, and has been explained by combined efforts of experimental and computational studies.[1] The most accepted transition state model for the stereodetermining step is the Houk-List model (**a**). However, this model was questioned by lack of evidence for enamine formation in the reaction. The detection of oxazolindinone in the reaction mixture led Seebach, Eschenmoser and co-workers propose a transition state model in which oxazolindinone (**c**) plays an active role.[2] Due to our continued interest in organocatalysis,[3] we investigated the significance of these intermediates in stereocontrolling step in proline catalyzed reactions. Our results which aid in unraveling the correct TS model (**a**, **b** or **c**) will be the focus of presentation.[4]



Enamine Carboxylic Acid Model (**a**)



Enamine Carboxylate Model (**b**)



Oxazolidinone Model (**c**)

References
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Correspondence of $Ru^{III}Ru^{II}$ (d^5d^6) and $Ru^{IV}Ru^{III}$ (d^4d^5) Mixed Valent States in a Small Dinuclear Complex

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The recent advancement of application potential of mixed valent diruthenium complexes in information transfer, energy-relevant research, and optical devices[1] has initiated the systematic developments of newer molecular frameworks with well defined electrochemical and optical features.[2] In this context structural and electronic properties of the newly designed $\{(\mu\text{-oxa})[Ru(acac)_2]_2\}^n$ ($\mathbf{1}^n$) (n = +, 0, –; oxa^{2-} = oxamidato(2–) and $acac^-$ = 2,4-pentanedionato) has been explored via experimental and theoretical investigations. **1** exhibits an $S = 1$ ground state with intramolecular as well as intermolecular antiferromagnetic spin-spin coupling. The molecular structure of **1** reveals a notable asymmetry within the bridging ligand. The stepwise facile electron-transfer processes lead to the generation of paramagnetic mixed valent intermediates: $Ru^{IV}Ru^{III}$ ($\mathbf{1}^+$) and $Ru^{III}Ru^{II}$ ($\mathbf{1}^-$) of similar thermodynamic stability with K_c = comproportionation constant = $10^{5.9}$ and broad near-infrared absorption bands corresponding to intramolecular metal-to-metal (intervalence) charge transfer (IVCT) transitions. The spin density distributions establish little participation of the ligand bridge in the spin accommodation for all paramagnetic states. Although only one broad NIR band (IVCT) is observed for the $Ru^{III}Ru^{II}$ ($4d^5/4d^6$) system in $\mathbf{1}^-$, the unusual $Ru^{IV}Ru^{III}$ ($4d^4/4d^5$) form in $\mathbf{1}^+$ exhibits extended absorbance over the UV-vis-NIR range due to the presence of multiple holes.

References

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Enantioselective Michael Addition of Nitrophosphonates to Activated Olefins for Synthesis of Quaternary α-Aminophosphonates

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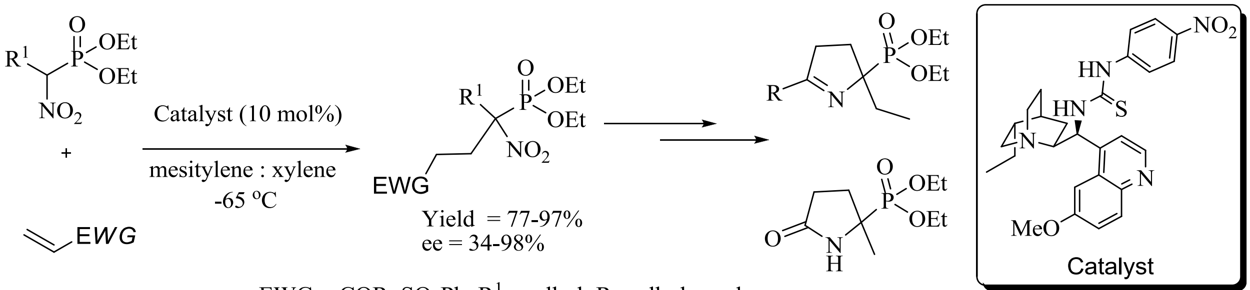
Aminophosphonic acid mimics the tetrahedral transition states of enzyme-mediated peptide bond hydrolysis. Further, the antibacterial, antifungal and anti-HIV properties of α-aminophosphonic acids make them important class of medicinal and pharmaceutical compounds. Their use as organocatalysts and as well as their presence in biologically active natural product K-26 make them attractive synthetic targets.[1] Although various stoichiometric and catalytic methods provide α-aminophosphonic acids with high enantioselectivity, generation of quaternary α-carbon centers via catalytic asymmetric synthesis of α-aminophosphonic acids remains scarcely explored.[2]

Since nitrophosphonates are immediate precursors to aminophophonic acids, our group pursued synthesis of optically active γ-nitrophosphonates and β-nitrophosphonates from nitroalkenes in good yield and enantioselectivity.[3] As a part of our ongoing interest in nitrophosphonate chemistry, we have developed an efficient method for the synthesis of optically active quaternary α-nitrophosphonates by asymmetric Michael addition of dialkyl α-nitrophosphonates to enones[4] and vinyl sulfones. The scope of these asymmetric reactions and transformation of these optically active quaternary α-nitrophosphonates will be discussed.



EWG = COR, SO_2Ph, R^1 = alkyl; R = alkyl, aryl.

References

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Palladium Catalyzed Aldehyde Decarbonylation Reaction

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Existing decarbonylayion catalyst suffers from high cost, limited substrate scope, harsh/impractical reaction conditions. Often, the efficient catalytic (or even stoichiometric) decarbonylation are done under elevated reaction temperatures or with a chemical scavenger to remove the evolved CO. In total synthesis, a stoichiometric (not catalytic) amount of Rh–catalyst is often employed for crucial decarbonylations of aldehyde functionalities. Further, the reported catalysts have limited substrate scope with very few examples involving decarbonylation of heterocyclic aldehydes. It would thus be highly desirable to provide a process that facilitates an efficient catalytic decarbonylation of aldehydes circumventing the aforesaid drawbacks of the prior art processes.

$$\text{R-CHO} \xrightarrow{\text{Pd-cat.}} \text{R-H}$$

We have developed a simple, economical, efficient and easily scalable method for practical decarbonylation reaction with palladium catalyst. Details of our findings will be discussed along with mechanistic insights. Related synthetic transformation(s) along with their bio–relevance will be discussed.

Also, a brief overview of some of the ongoing projects in our group will be presented.

Isomer Dependent Fluorescence Quenching in Hydrogen Bonded Complexes of Phenylacetylenes

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The hydrogen bonded binary complexes of phenylacetylene with methylamine show different fluorescent behavior depending on the structure of the complexes. This signifies that the electronic properties of the complexes vary drastically with change in the geometry of the complexes.Complexes having linear C-H···N hydrogen bonding were found to be non-fluorescent in nature. It is widely known that quenching of fluorescence is facilitated by amines through electron transfer mechanism. However, in the present case electron transfer mechanism is probably not the quenching mechanism. In order to understand the nature of the fluorescence quenching mechanism, investigations on fluorine substituted phenylacetylene were also carried out. In the case of fluorophenylacetylenes, it was found that the fluorescent behavior of the methylamine complexes is dependent on the position of the fluorine substitution. Based on these results, we propose a curve crossing mechanism.

Structural and Biochemical Studies of Channeling of Unstable Intermediates in Biological Pathways

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In this work we use biochemical analysis in conjunction with X-ray crystallography to understand the mechanism of catalysis and channeling in the mulitdomain bi-functional enzyme PurL (StPurL). StPurL, is a 140 kDa four subunit protein in the purine de nova biosynthetic pathway. PurL catalyzes the fourth step in this pathway and is responsible for conversion of formylglycinamide ribonucleotide (FGAR) and glutamine into formylglycinamidine ribonucleotide (FGAM) and glutamate in an ATP assisted fashion. The bifunctional PurL enzyme has a gene duplication in it, one of these gene duplicated subunits contain a potential allosteric adenosine di-phosphate (ADP) regulatory site and the other site is where the ammonia is channeled from the glutaminase domain and FGAR is converted to FGAM. Here in an effort to identify the path traversed by ammonia and to understand the role of structural ADP molecule, we engineered mutants along the proposed ammonia channel using site-directed mutagenesis (overlap PCR method) and subsequently probe the transfer using biochemical assay and X-ray Crystallography. We are also trying to identify the xenon binding residues by passing the xenon into the StPurL which will give an idea to find out ammonia channel. We have solved the StPurL-AMPPNP (analogue of ATP) complex structure at resolution of 3.3Å. This complex shows structural similarity to TmPurL-AMPPCP/TmPurL-ATP complexes and also has some differences in ligand binding site.

New theoretical perspectives on the Magnetic coupling in {3d-4f} Molecular Nano Magnets

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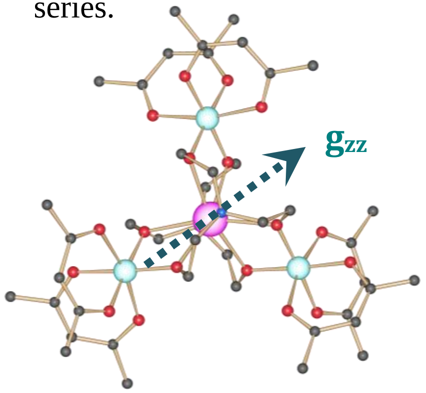
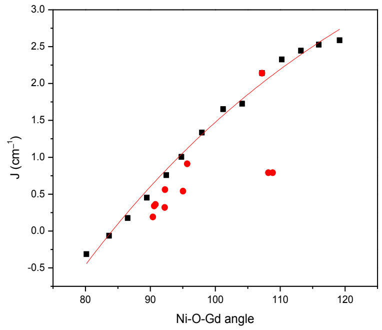
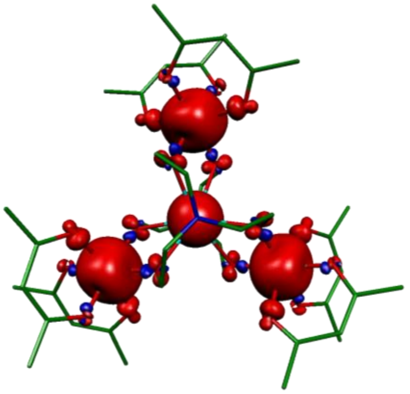
Abstract: Molecular Nano Magnets is a wide area encompassing organic radicals, antiferromagnetic wheels, Single Molecule Magnets (SMMs) to Single chain Magnets (SCMs). Among others, SMMs have been widely studied and these are the molecules which in fact retain magnetization in absence of magnetic field.[1] These SMMs have many potential applications ranging from high-density information storage devices to solid states Q-bits in quantum computing. Despite more than a decade effort, synthesising novel SMMs with the barrier height reaching towards room temperature is still a challenging task. In recent years, an alternative way has been proposed where highly anisotropic 4f ions have been incorporated in cluster aggregation with 3d metals. These {3d-4f} clusters[2] are the appealing candidate for SMMs. Despite extensive experimental reports, theoretical studies are scarce and here we are attempting to study these molecules using density functional methods. We performed density functional calculation and *ab-initio* CASSCF calculations on series of dinuclear complexes of {3d-4f} system[3] and these complexes are the building units of larger polynuclear clusters. We have computed the spin Hamiltonian parameters (magnetic exchange *J*, g tensors, anisotropy etc) to understand the magnetic properties of these clusters and to gain insight in the mechanism of coupling in this series.







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Inverse Demand Diels-Alder Approach Towards framework of Atisanes: Generation of Molecular Complexity from Simple Aromatics

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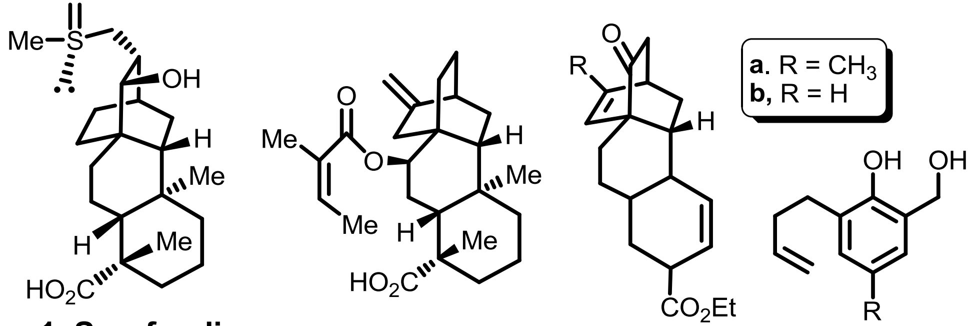
Atisanes are an important class of diterpenoid that has considerable interest in their synthesis by virtue of biological interesting properties and complex molecular architecture.[1] Various natural products of atisane family exhibit important biological properties. For example, serofendic acid A **1,** isolated from calf serum, exhibit neuroprotective activity.[1a] Gumiferolic acid **2** isolated from *Margotia gummifera* by Pinar et al[1b] shows remarkable plant growth activity. These natural products have unique molecular architecture containing a bicyclo[2.2.2]octane system annulated to decalin ring system. In continuation of our studies on generation of molecular complexity from aromatics,[2] we considered devising synthesis of carbocyclic frameworks **3a**,**b** of atisanes from simple aromatic precursor such as **4a**,**b** (**Fig. 1**). Oxidative dearomatization and inverse demand □^{4}s+□^{2}s cycloaddition are the key features of our design.



1, Serofendic acid-A **2, Gummiferolic acid** **3a, b** **4a, b**

Fig. 1

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Triazine based tridentate and terpyridine based pentadentate ligands: Synthesis, Transition Metal Chemistry and Photophysical study

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Triazine based triphos ligand 2,4,6-tris(4-(diphenylphosphino)phenyl)-1,3,5-triazine (**1**) was synthesized by treating 2,4,6-tris(4-bromophenyl)-1,3,5-triazine with $KPPh_2$ in moderate yield. The compound **1** with C_{3v} symmetry is an attractive ligand for producing transition-metal complexes with intriguing geometries.[1] Hence to study its coordinative behavior; it was treated with various transition metal precursors to obtain simple trimetallic complexes to one dimensional polymers or cyclophane type complexes. Terpyridine based ligand systems have also been studied extensively in recent years due to their interesting photophysical aspects.[2] So in order to study the change in the coordination behaviour and its consequences on the photophysical properties, a hybrid diphos/terpyridine ligand 2,4,6-tris(4-(diphenylphosphino) phenyl)-1,3,5-triazine (**2**) was prepared in moderate yield by treating 4′-(*p*-aminophenyl)-2, 2′:6′, 2″-terpyridine with PPh_2Cl in 1:2 molar ratios. Since the ligand contains both the hard and soft coordination centers, the complexation behaviour is governed by the choice of the metal precursor which leads to the formation of varieties of hetero bimetallic complexes. The presence of two different metals affects the photophysical properties of the resulting complexes to a greater extent.

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Temperature dictates the conformational preference of “RGD” in peptide sequence “RIPRGDMP” from kistrin and selects the bio-active conformation: Implications for inhibitor design

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The interactions of peptide ligands with proteins face challenges in recognizing binding surfaces due to availability of a multitude of conformations. Therefore it is essential to constrain the peptide for the recognition of receptors and thus finding the bioactive conformation. The cell surface receptor protein family Integrins recognize “RGD” sequence which is present in different proteins. To determine the bioactive conformation required to bind with receptor αIIbβ3, the peptide sequence “RIPRGDMP” from Kistrin was inserted into CDR 1 loop region of REI protein (REI-RGD34). It helps out in finding the possible bioactive conformation of peptide by restricting the sampling space. The activity of REI-RGD34 was studied and found that as the temperature increased REI-RGD34 showed a higher affinity towards the receptor αIIbβ3. The proposed mechanisms for the increased activity of REI-RGD34 at higher temperature were justified in either of two ways. One, the modified complex forces the restricted peptide to adopt a bioactive conformation or second, it unfolds the peptide in a way that opens its binding surface with high affinity for receptor. In this study we model the conformational preferences of “RGD” sequence in octapeptide alone and in the presentation scaffold at two different temperatures (25^0C and 42^0C). We found that at higher temperature “RGD” sequence from “RIPRGDMP” adopt turn conformation, while a bend conformation was observed at low temperature. The analysis of various pharmacophoric parameters hint that turn conformation of “RGD” sequence adopted at high temperature could be the potential bio-active conformation.

Challenges and Opportunities in Functional Conjugated Polymers and Materials NEMS/MEMS Devices: A Synthetic Chemistry Approach

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Conjugated polymers also known as inherently conducting polymers (ICPs) provide an ideal platform for the design and fabrication of various printable electronic devices because of their ability to respond reversibly to an external physical (temperature, light, electric, magnetic or mechanical) or chemical (pH, chemical agent) stimuli. ICPs exhibit changes in physical (conformation), optical and electrical properties on the applications of these stimuli. Therefore, these polymers have been developed for various applications such as Light Emitting Diodes (LEDs), memory devices, rechargeable batteries, super capacitors, electro optic materials, photovoltaics, thin film transistors, RF tags, biological and chemical sensors, MEMS, actuators, electrochromic materials, displays, electro active fabrics and host of other applications.

One of the major challenges in this area is to integrate the organic semiconductors in various electronic devices. Apart from this, another challenge is the ability to design and synthesize processable and stable organic semiconducting polymers which then enables one to use traditional printing technologies for the fabrication of electronic devices. These not only reduces cost but also increases throughput for production. In this direction, we have been working in the area of design and synthesis of transparent conductors based on 3,4-alkylenedioxythiophenes and graphene and also polymers based on regioregular Poly (3-hexythiophene) to improve mobility and for photovoltaic applications. Recently we have developed a novel synthetic route for the synthesis of ultra high molecular weight polymers based on dialoxythiophenes. Apart from this, we have also developed a novel route for the functionalization of SU-8, a material used extensively for NEMS and MEMS devices. Some of the recent results in these directions will be highlighted in this talk. I will also discuss some of the challenges and possible opportunities where scientists from Physics, Chemistry, Mechanical and Electrical Engineering backgrounds can make significant contributions.

Abstracts of Poster Presentations

Silica Nanodisks as Platforms for Fluorescence Lifetime-based Sensing of pH

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Core-shell nanoconjugates of silica nanodisks and fluorescent dyes have been prepared by surface functionalization of the Silica nanodisks (SNDs). Rhodamine B has been used as the reference dye followed by a layer of silica on the composite nanodisks. Finally, the surface has been functionalized with sensor dye such as Fluorescein in one case and protoporphyrin IX in the other. These dyes exhibit pH-dependent fluorescence properties such as intensity, lifetime and corresponding amplitude. These nanoconjugates are found to sense the pH of the medium by showing the systematic variation in the intensity ratio of the reference dye and the sensor dye. The variation in lifetimes of fluorescein is rather small as compared to protopophyrin IX. For protopophyrin IX the change in amplitudes is prominent in acidic as well as alkaline solutions. The temporal parameters can thus be used to ascertain the pH of the medium, when used in conjunction with each other.

Quantum Confined Stark Effect in Localized Luminescent Centers within (In,Ga)N Quantum Well Based LEDs

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Piezoelectric and spontaneous polarization induced electrostatic field is known to severely affect both the transition energies and radiative recombination efficiencies in group III-nitride heterostructures based light emitting devices by modulating band structure. In this work, using spectrally resolved PL imaging in a high throughput manner, the effect of this built-in electrostatic field known as quantum confined Stark effect (QCSE), on the optoelectronic properties of spontaneously formed individual radiative taps, has been probed within a green emitting InGaN quantum well based light emitting diode. Screening of QCSE in nanoscale domains leads to considerable enhancement of light output efficiencies with synchronized blue-shift of transition energies by up to 400 meV. The extent of QCSE within randomly dispersed individual emission centerss is extremely diverse, magnitude of which is dependent on carrier localization mechanisms. A lack of correlation between the extent of QCSE and local Indium mole-fractions has been found which suggests that size, shape and strain of individual radiative traps centers play a crucial role in modulating the local polarization field.

Coumarin in Lamellar Micelles: Diffusion in two dimensions

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Surface-active agents are known to form micro-heterogeneous molecular aggregates of various morphologies in solvents like water beyond a certain concentration range. Most of the studies are dedicated to the behavioural analysis of spherical micelles, the usually formed candidates. However, some literature on the occurrence of lamellar micelles does exist.[1] In the present investigation, lamellar micelles are prepared from a ternary mixture of AOT/water/-n-heptane using aqueous solutions of three different coumarin dyes to probe the microenvironment of these disc like micelles. It was expected that these probes would show a time-dependant red shift in their TRES due to slow solvatochromatic relaxation of the interfacially bound water molecules. However, no such relaxation occurs, instead the presence of distinct isoemissive point in the TRANES generated for these probes shows the presence of two discrete emissive species where the emission of one progressively decreases with time at the expense of the other species. The cause has been attributed to the slow diffusion of the probe along a potential gradient post excitation from the core of the micellar discs to the interfacial water. The diffusion is most prominent for C-153. We hope our work would throw some light on the solvent structure in the local environment of these nanoaggregates along with elucidating the morphologies and properties of these lamellar micelles.

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Photoluminescence Imaging and Spectroscopy of Single Nanocrystals: Insight on Mn doping into ZnCdS

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Diluted magnetic semiconductor nanocrystals (NCs) have been a major area of research in recent times. Precise control of doping in terms of choosing host crystal, dopant, doping level or doping position provides opportunity to tune the physical properties of these materials. To elucidate deeper insight of these materials, we have performed single particle (SP) photoluminescence microscopy and spectroscopy on undoped and Mn-doped $Zn_xCd_{1-x}S$ alloyed NCs. We have observed that SP photoluminescence of undoped NCs are inherently broad, similar to ensemble solution measurements. However, SP spectra of Mn-doped $Zn_xCd_{1-x}S$ NCs show significantly narrow and discrete Mn-emissions at different energy positions, unlike the broad emission observed in bulk measurements. The different Mn-emission energies arise due to different local environments of the dopant ions in the host NCs. Unlike the previously believed that the Mn-emission is generally broad, we have shown that pure Mn-emission is in fact very narrow with FWHM of around 0.06 eV and the broadening in bulk is entirely due to inhomogeneity Mn doping sites within individual nanocrystals.

Ground and Excited State Prototropism of 2,2′-bis(2-pyridyl)bibenzimidazole

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Bifunctional chromophores showing specific hydrogen bond interactions with indole or pyrrole rings attached to pyridine, pyrimidine or quinoline rings form a class of compounds which is reported to participate in various phototautomerization reactions.[1] Micelles are reported to provide microenvironments that can alter ground and excited state photophysics of various fluorophores.[2] 2-(2′-pyridyl)benzimidazole (2PBI) is one such fluorophore which is reported to undergo solvent assisted excited state proton transfer (ESPT) predominantly in its cationic form at SDS-water interface.[3] Since the photodynamics of 2PBI has been explored in different microheterogeneous environment,[4] attempt is made to further investigate the effect of micelles with different headgroups on ESPT of its dimer, 2,2′-bis(2-pyridyl)bibenzimidazole ($BpbimH_2$). The study of photophysics of $BpbimH_2$ in restricted microenvironment provided by SDS micelles reveals that the cationic form of the fluorophore exhibits different spectral properties as compared to its neutral form. Further, to explore the nature of different cations and neutral forms of $BpbimH_2$ in aqueous solution with varying pH both steady state and time resolved spectroscopic techniques are employed. Different tautomers of $BpbimH_2$ can exist in solution as a distribution of conformers. Quantum chemical calculations are used as a tool to evaluate the structure of most stable conformer of the dimer using density function theory method at the B3LYP level of theory and 6-311+G* as the basis set.

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Experimental investigation of hydrogen bonded complexes of *meta*Fluorophenylacetyleneswith water, alcohols and ammines

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The hydrogen bonded binary complexes of *meta*-fluorophenylacetylene with water, alcohols and ammineshave been investigated using IR-UV double resonance spectroscopy in the acetylenic C–H stretching region. From the comparison of IR spectra of various complexes of *meta*-fluorophenylacetylene complexes, it was observed that the hydrogen bond strength is dependent on the basicity of the interacting molecule. It is seen that the geometry of the water complex of *meta*-fluorophenylacetyleneis different compare to *ortho*- and *para*-fluorophenylacetylenes. This signifies that the position of substitution of fluorine in the ring affects the availability of π electrons in the ring and the acetylenictriple bond and also alters the acidity of the acetylenic CH group.The fluorescent behavior of the *meta*-fluorophenylacetylene complexes with ammines and alcohols is totally different from *ortho*-and *para*-fluorophenylacetylenes. It has been realized that withthe altering the position of the fluorine atom in the ring the fluorescent properties of the fluorophenylacetylene complexes with various moieties can be switched.

Amplified Fluorescent Poly (phenyleneethynylene)s based on Pentiptycene and its Applications in Sensing

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Poly(*p*-phenyleneethynylene)s, containing pentiptycene unit, generally serve as chemo sensors[1,2] for the explosives based on aromatic nitro compounds such as trinitrotoluene (TNT), dinitrotoluene (DNT) and its derivatives. These polymers, because of their fluorescent nature, can be used as an emissive layer in OLEDs. These polymers emit mixed coloured light, generally in blue green region. They have emission at 455 nm (blue) and 490 nm (green). We report here the incorporation of *meta* linkage in polyphenyleneethylene based on pentiptycene polymer to minimize the emission at 490 nm. This polymer is expected to have emission in completely blue region and thus can be useful in blue LEDs. This phenomenon happens due to breaking of the conjugation or introducing defects by incorporation of *meta* linkages in Poly(p-phenyleneethynylene)s backbone.

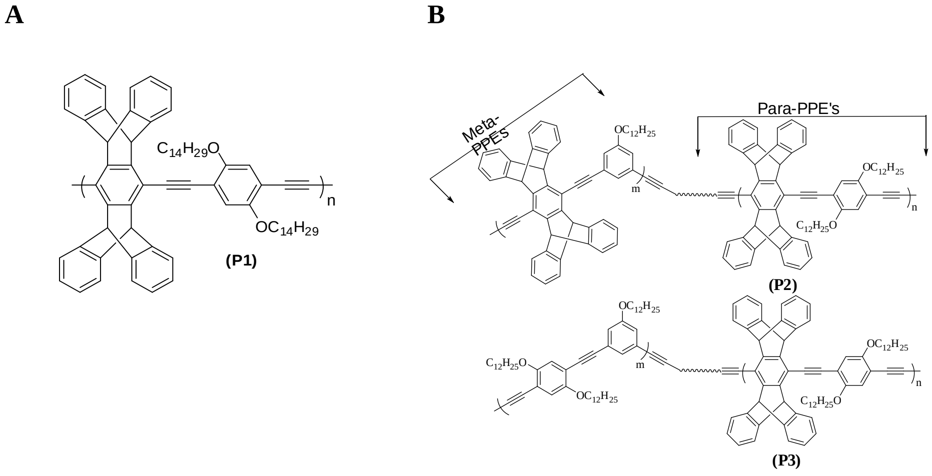

Figure 1. (A) Swager's polymer (*Para*-Polyphenyleneethylenes). (B) Series of *p*- and *m*-polyphenyleneethylenes based on pentiptycene.

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La^{3+} Sensing by Triazole Linked Picolylimine Derivative of Calix[6]arene and the Complex as Secondary Sensor for F^-

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During the past six to seven years, our group has been involved in the development of 1, 3-di-conjugates of calix[4]arene[1] which exhibit sensitivity and selectivity towards biologically relevant metal ions, anions, amino acids and proteins. While such systems are good for mainly the transition metal ions, presence of more number of arms which were well spaced is expected to be suitable for lanthanides. In order to have more than two arms and at the same time these are well separated in space, a calix[6] platform would be ideal. The 1, 3, 5-tri-conjugates of calix[6]arene exhibit large cavity size and can accommodate more binding sites than that of 1,3-di-derivatives of calix[4]arene. Therefore calix[6]arene can be a suitable platform to selectively recognize the rare earth ions which demand higher coordination number. Over the few years coordination and supramolecular chemistry of trivalent lanthanide ions have been noticed and especially applied in biomedical field. Keeping these things in consideration, 1,3,5-tripicolylimine appended calix[6]arene (**R_2**) has been synthesized and well characterized by different spectral and analytical techniques. The **R_2** selectively recognizes La^{3+} ion which is strongly favored by emission and absorption spectroscopy. Further **R_2**La^{3+} complex exhibit quenching in fluorescence in presence of F^- ion. Thus the present poster would deal with the synthesis, characterization, spectral and analytical studies of **R_2** and **R_2**.La^{3+} complex.

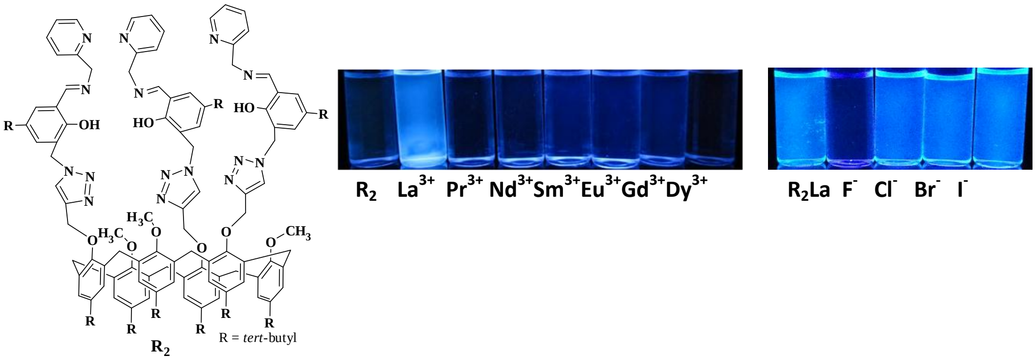

Figure **1**. Structure of 1,3,5-triderivative of calix[6]arene and fluorescent color exhibited by **R_2** in presence of La^{3+} and it is quenched by F^- ion.

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Synthesis of Ultra High Molecular Weight Conjugated Polymers Based on 3, 4-Propylenedioxythiophenes via Solvent Free Chemical Oxidative Polymerization

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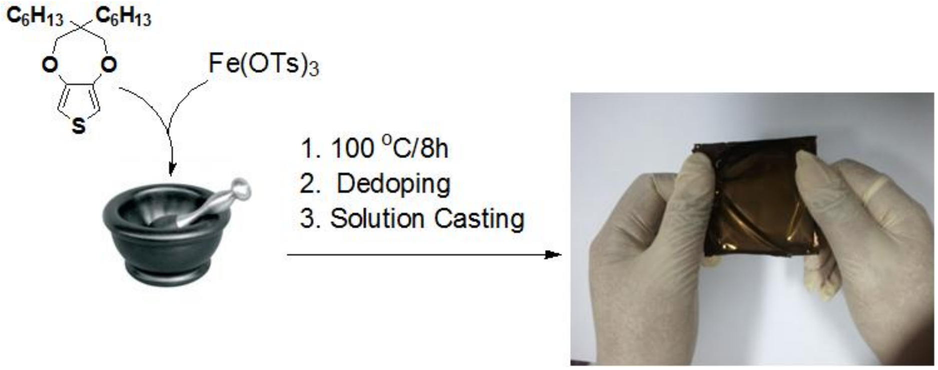
Many stringent reductive polymerization routes, based on transition metal catalyzed coupling of activated organometallic derivatives, are available in order to get high molecular weight organic conjugated polymers. Considering the importance of chemical oxidative polymerization for the syntheses of organic conjugated polymers, we report here on a solvent free chemical oxidative route for the monomer based on 3, 4-propylenedioxythiophenes. It is a completely dry process and applicable to both solid as well as liquid monomers which results in the bulk synthesis of ultra high molecular weight polymers. Interestingly the molecular weights obtained by this method are even much higher than those reported for the reductive polymerization methods.



Magnetic coupling in {4f-radical} systems: A theoretical exploration

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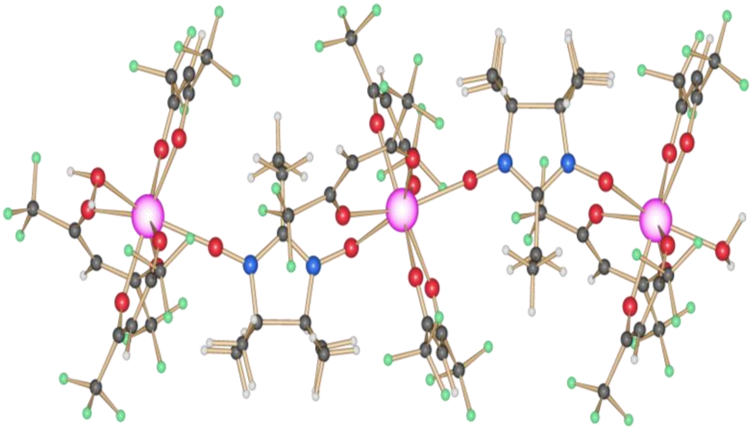
Molecular nanomagnets have many potential applications including high-density information storage devices.[1] Recent developments in this field includes one dimensional materials commonly called single chain magnets (SCM) which have the advantage of possessing higher barrier height for reorientation of magnetization compared to conventional Single Molecule Magnets.[2] Among others, one of the most important discovery in this field is the SCM based on nitronyl nitroxide radicals and Dy(III) ions.[3] These SCMs have peculiar magnetic coupling where the next-nearest-neighbour interactions are stronger than near-neighbour interaction and this has been witnessed in the earlier literature (see Figure).[4] Despite extensive experimental work on these systems, very little have been done to understand the nature of interaction *via* theoretical tools. Here we present a methodology based on density functional theory (DFT) to compute magnetic coupling in Gd(III)-radical complexes. The electronic origin of this peculiar coupling has been probed and the mechanism of coupling will be explained in the poster.



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An Effective Method for the Calculation of Franck-Condon factors for Diatomics Using the Fourier Grid Hamiltonian Method

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In this report, we present an effective and compact method of computing the Franck-Condon factors for electronic transitions for diatomic molecules. We use the Fourier Grid Hamiltonian (FGH) method for computing the vibrational wave functions and the corresponding energy values for the different electronic states of diatomics. For these computations, we need the appropriate functional forms for the potential energy functions for the ground and the excited states of the molecules that we want to study. The Morse potential forms for several diatomics are readily available and we have used these forms for the potential functions for diagonalizing the molecular Hamiltonians. Once the vibrational wave functions for the ground and the excited state are known, one calculates the vibrational overlap integrals (and thereby the Franck-Condon factors for the electronic transitions) by elementary integration. The method is illustrated for the Diatomics N2 and O2.

Spectroscopic properties of P-nitrobenzoate N-Oxygenase (AurF) – A Theoretical study

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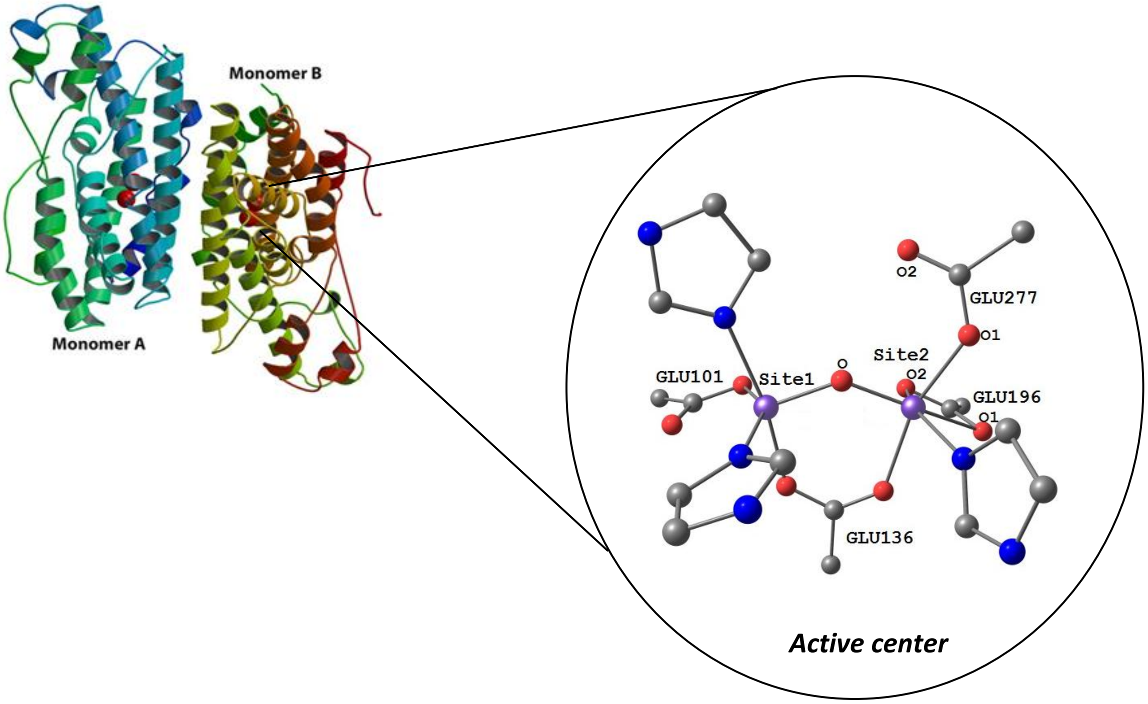
P-nitrobenzoate N-Oxygenase (AurF) [1] is the bimetallic enzyme, which catalyzes the sequential oxidation of aminoarenes to nitroarenes in the biosynthesis of antibiotic-aureothine (Figure). This enzyme gathers the attention of scientific community due to the controversy on the nature of metal ion present in the active centre. We report the first theoretical investigation on the structure-property relationship of this enzyme. Quantum cluster model calculation confirms the active site to be a di-iron center with μ-oxo as the bridging group and protonated terminal glutamate. Our observed spectroscopic parameters are consistent with the experiment.[2]



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Model Dependence of the Association of Na+ Cl- Ion Pair in DMSO – Water Mixed Solvents

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The structure and solvation dynamics of the Na+ Cl- ion-pair has been studied using three different ion-ion direct potential models in DMSO–water mixtures at three different partial mole fractions. In a mixed-solvent medium, the behavior of the contact ion-pair (CIP) and solvent assisted ion-pair (SAIP) is largely dependent on the potential model used. The ion-ion direct potential model defined by Fumi-Tosi (exp-6-8-1 nature) confirms that for Na+Cl- the CIP formed is as stable as the SAIP in all three solvent mixtures (water like behavior) whereas the ion-ion direct potential model defined by Huggins–Meyer (exp-6-1 nature) shows that the CIP formed is much more stable than the SAIP (DMSO like behavior). On the other hand, the ion-ion direct potential model defined by Lennard-Jones (12-6-1 nature) shows a completely different type of behavior which is neither like water nor like DMSO, as the SAIP is completely absent and only the CIP is present. The nature of the CIP and SAIP has been confirmed by following the ion pair trajectories as well as by calculating the residence times. The study has also proved that the stability of the CIP and SAIP varies with the variation of the partial concentration of solvents in the mixed solvent medium with any of the potential model used.

Single-molecule-magnet based on redox active ligand: An effort to increase exchange interaction between lanthanide ions

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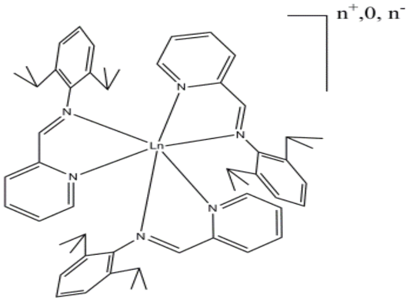
Single-molecule magnets (SMMs) exhibiting slow relaxation of the magnetization have attracted increasing interest because of the prospect of storing and processing magnetic information at a molecular level. For such molecules, the magnetization relaxation depends on the effective energy barrier, which is significantly affected by the anisotropy and ground state possessed by a molecule.[1] Origin of anisotropy in a molecule is due to the presence of spin-orbit coupling and the ground state possessed by a molecule dictated by number of the paramagnetic centres and its effective exchange pathway between them. Interest in studying the lanthanide based SMM is revived after the single-ion-magnet reported (a class of SMM) by Ishikawa et al. in terbium Phthalocyanine complexes.[2]Lanthanides based polynuclear molecular compounds are promising candidate to enhance effective energy barrier however the dominant quantum tunnelling of magnetization triggers multiple relaxation pathways which hampers the observation of SMM property at higher temperature.[3]In order to have control over the Spin Hamiltonian parameters and overcome the issues mentioned above (weak exchange interactions and quantum tunnelling) we are intend to probe lanthanide based SMM fabricated by redox active ligands.[4] The expected structure of complexes and its magnetic properties will be discussed.



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Synthesis and Characterization of Silver and Gold Complexes of Chiral N-heterocyclic Carbenes

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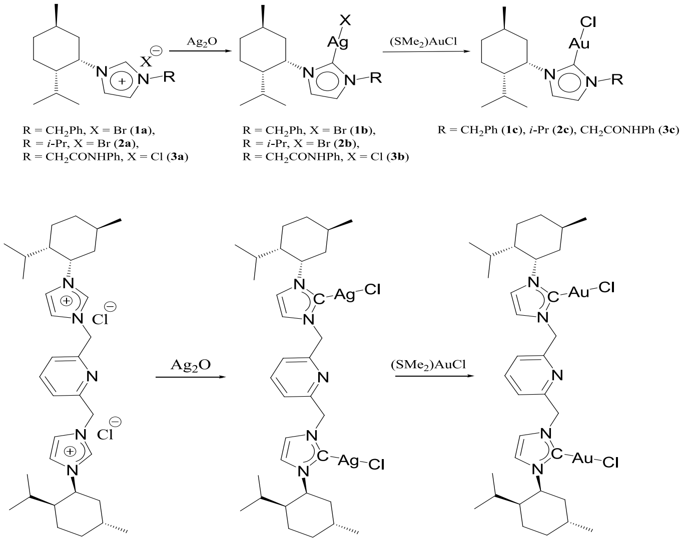
A series of silver and gold complexes supported over chiral N-heterocyclic carbene ligands prepared from readily available enantiopure (−)-menthol (Scheme 1). The gold(I) complexes, [1-(R)-3-((1*S*,2*S*,5*R*)-2-*i*-propyl-5-methylcyclohexyl)-imidazolole-2-ylidene]AuCl, [R = CH_2Ph (**1c**), R = *i*-Pr (**2c**), R = $CH_2CONHPh$ (**3c**)] and [2,6-bis-[{(3-((1*S*,2*S*,5*R*)-2-*i*-propyl-5-methylcyclohexyl)-imidazolium-2-ylidene)AuCl}methyl]pyridine (**4c**)] were synthesized by transmetallation reaction from the silver analogs [1-(R)-3-((1*S*,2*S*,5*R*)-2-*i*-propyl-5-methylcyclohexyl)-imidazolole-2-ylidene]AgX [R = CH_2Ph, X = Br (**1b**), R = *i*-Pr, X = Br (**2b**), R = $CH_2CONHPh$, X = Cl (**3b**)] and [2,6-bis-[{(3-((1*S*,2*S*,5*R*)-2-*i*-propyl-5-methylcyclohexyl)-imidazolium-2-ylidene)AgCl}methyl]pyridine (**4b**)] by treatment with $(SMe_2)AuCl$ in 28-85 % yield. The silver (**1–4**)**b** complexes were successively synthesized from the corresponding imidazolium halide salts (**1–4**)**a** by the reaction with Ag_2O in 78-95 % yield. These enantiopure and sterically demanding silver (**1–4**)**b** and the gold (**1–4**)**c** complexes would be investigated for their catalytic properties in the asymmetric synthesis involving C-C and C-N bond forming reactions.



4a **4b** **4c**

Scheme 1

Probing the magnetic properties of lanthanide-radical containing ligand complexes

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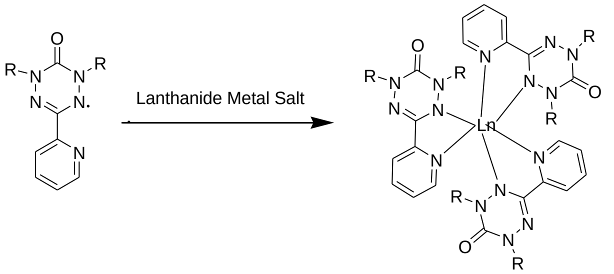
Lanthanide ion plays a crucial role in magnetism, as they possess large magnetic moments and magnetic anisotropy[1]. Lanthanide ions reactivity towards the organic ligand is very sluggish due to the shielding of 4f-orbitals (effective overlap of with ligand orbitals decreases) compare to transition metal ions. However, the recent reports on lanthanide based molecular magnets [2] appears to be a promising candidate to investigate in detail to control the parameters (ground state, anisotropy, Jz, quantum tunnelling etc) to use these molecular magnets for technological application such as data storage, molecular qubits and magnetic refrigeration[3]. It has been speculated that, lanthanide can interact much more strongly with radicals than neutral ligand system[4]. However, isolation of stable radical containing metal complexes is often quite challenging.Another added advantage of working with radical containing ligand is that, it could potentially increase the exchange interaction (whereby the quantum tunnelling will be suppressed to some extent); also the radicals could contribute to the magnetic moment in a constructive way. In this vein, we are interested in testing the coordination capability of verdazyl radical (which is air and moisture stable)[5]with various lanthanide ions and the magnetic properties of these complexes will be investigated in detail to develop magneto-structural correlations.



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Triazole Based phosphinite and phosphonite Ligands: Syntheses, Derivatization and Transition Metal Chemistry

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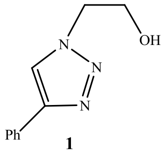
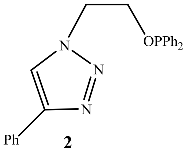
The copper catalyzed azide-alkyne cycloaddition has emerged as a powerful and versatile tool in a variety of research areas, ranging from materials to pharmaceuticals. It connects organic azides and terminal alkynes into 1,4-disubstituted 1,2,3-triazole, referred as click triazole. Further the triazole scaffolds can be combined with phosphorous donors to give a new class of hybrid P-N heterodonor ligands. Reaction between phenylacetylene and azidoethanol in presence of Cu(I), afforded triazole alcohol $[HOCH_2CH_2N_3C(Ph)C(H)]$ (**1**). Treatment of **1** with PPh_2Cl and $PPhCl_2$ gave the corresponding phosphinite $[Ph_2P(OCH_2CH_2N_3C(Ph)C(H)]$ (**2**) and phosphonite $[PhP\{OCH_2CH_2N_3C(Ph)C(H)\}_2]$ (**3**) derivatives in good yield. The reaction of **2** and **3** with $[Ru(\eta^6\text{-Cym})Cl_2]_2$ furnished complexes $[RuCl_2(\eta^6\text{-cymene})\{Ph_2POCH_2CH_2N_3C(Ph)C(H)\}]$ (**4**) and $[RuCl_2(\eta^6\text{-cymene})\ PhP\{OCH_2CH_2N_3C\ (Ph)C(H)\}_2]$ (**5**). The coordination geometry around the ruthenium center in **4** is a typical pseudooctahedral three legged piano stool. The dimeric complex $[RuCl(\eta^6\text{-cymene})\{Ph_2POCH_2CH_2N_3C(Ph)C(H)\}OTf]_2$ (**6**) with N-coordination to ruthenium, was obtained in the reaction of complex **4** with AgOTf. The reaction of **2** and **3** with Pd(II), Pt(II), Au(I) precursors have been studied. The details of synthesis, reactivity and spectroscopic aspects will be presented.



1



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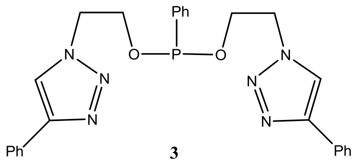

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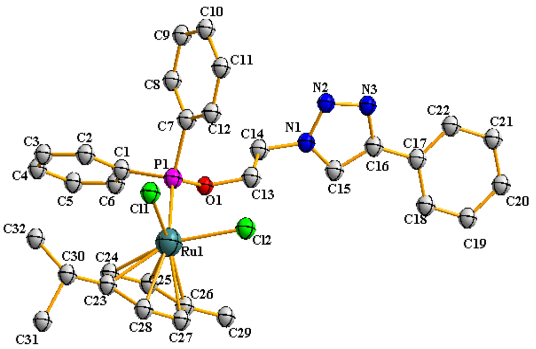

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Functionalization of diferrocenylacetylene with diferrocenyl ditelluride: Synthesis and photolytic reaction of (Z) 1-ferrocenyltelluro-1-ferrocenyl-4-ferrocenyl-1-buten-3-yne with $Fe(CO)_5$

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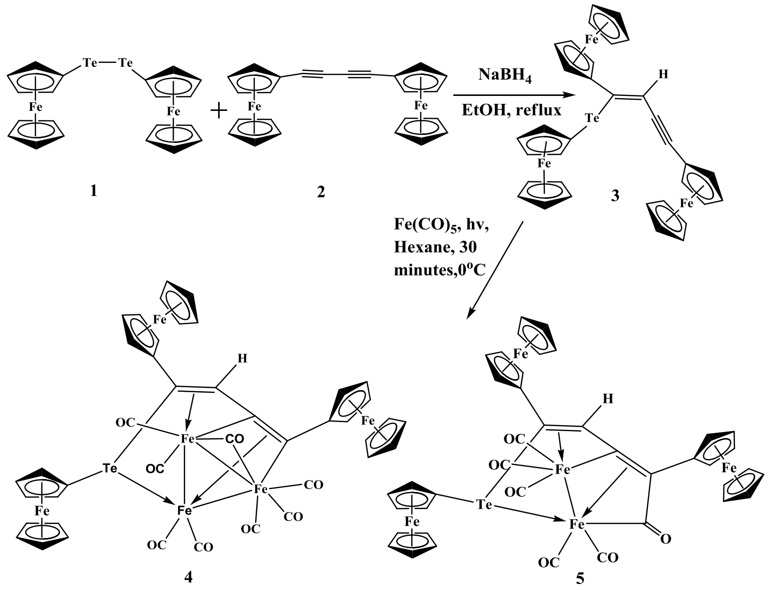
By virtue of the diverse bonding modes exhibited by chalcogen ligands in clusters, they have been recognised as very useful bridging ligands in cluster growth reactions.[1-2]

Synthesis and physical properties of diferrocenyl ditelluride (Fc_2Te_2) (**1**), prompted us to examine the effect of a ferrocenyltellurium moiety on the stability and the reactivity of the corresponding tellurides. Functionalization of diferrocenyldiacetylene (**2**) with diferrocenyl ditelluride leads to the formation of (Z) 1-ferrocenyltelluro-1-ferrocenyl-4-ferrocenyl-1-buten-3-yne (**3**). This Te substituted enyne ligand system provides unique opportunities because of presence of a double and triple bond as well as two coordinate nucleophilic Te centre. Therefore, cluster growth on this unusual ligand system can be explored. Photolysis of (Z) 1-ferrocenyltelluro-1-ferrocenyl-4-ferrocenyl-1-buten-3-yne with ironpentacarbonyl gives different tellurium coordinated enyne ironcarbonyl clusters (**4** & **5**).



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Nickel and Gold complexes of Amido-functionalized triazole based N-heterocyclic carbenes –Synthesis, Structure and Characterization

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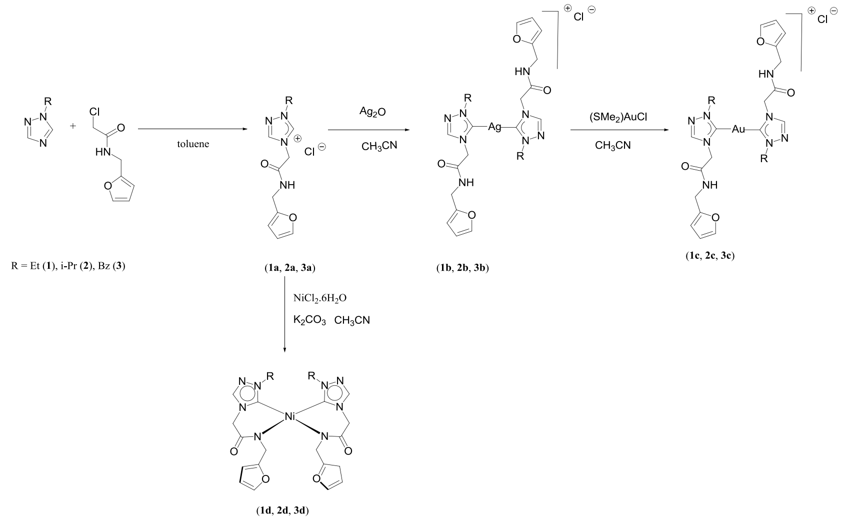
A series of nickel complexes (**1**–**3**)**d** and gold complexes(**1**–**3**)**c** supported over a new chelating N-amido functionalized heterocyclic carbene ligand are reported. The gold complexes {[1-(R)-4-N-(furan-2-ylimethyl)acetamido1,2,4-triazole-5-ylidene]$_2$Au}$^+$Cl$^-$ [R = Et(**1c**), *i*-Pr(**2c**), CH$_2$Ph(**3c**)], were synthesized from the reaction of corresponding silver analogues {[1-(R)-4-N-(furan-2-ylimethyl)acetamido1,2,4-triazole-5-ylidene]$_2$Ag}$^+$Cl- [R = Et(**1b**), *i*-Pr(**2b**), CH$_2$Ph(**3b**)] by treatment with (SMe$_2$)AuCl in 25–30 % yield by following commonly employed transmetallation route (Scheme 1). The silver complexes (**1**–**3**)**b** were synthesized from respective triazolium chloride salt namely, [1-(R)-4N-(furan-2-ylmethyl)acetamido-1,2,4 triazolium chloride [R = Et(**1a**), *i*-Pr(**2a**), CH$_2$Ph(**3a**)] by the direct reaction with Ag$_2$O in 41–81 % yield. The nickel complexes [1-(R)-4-N-(furan-2-ylmethyl)acetamido 1,2,4 triazol-5-ylidene]$_2$Ni [R = Et(**1d**), *i*-Pr(**2d**), CH$_2$Ph(**3d**)], were obtained directly from the corresponding triazolium chloride salts [1-(R)-4N-(furan-2ylmethyl)acetamido-1,2,4 triazolium chloride [R = Et(**1a**), *i*-Pr(**2a**), CH$_2$Ph(3a)], in 13–30% yield. The triazolium chloride salts (**1**–**3**)**a** were synthesized from the respective triazoles by the reaction with 2-chloro-N-(furan-2-yl)-methyl acetamide in 52–66 % yield.



(Scheme 1)

Group 11 metal complexes of alkynyl substituted cyclodiphosphazane $[(\mu\text{-N}^t\text{BuP})_2(\text{C}\equiv\text{CPh})_2]$

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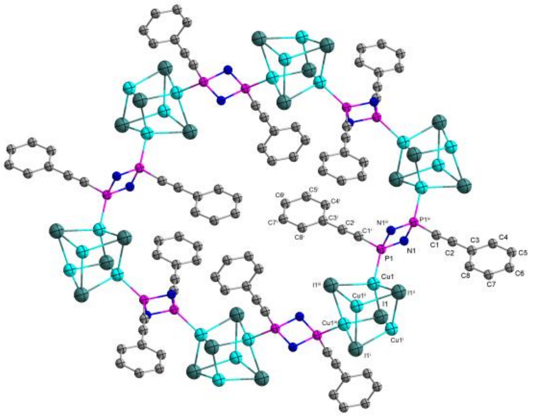
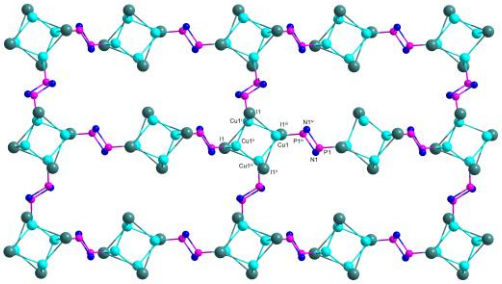
The current interest in the field of cyclophosphazane chemistry is mainly due to its catalytic and biological applications.[1] A review of literature reveals that cyclodiphosphazanes are mainly confined to P-N or P-O functionalized derivatives, because of the difficulties in the synthesis of P-C functionalized cyclodiphosphazanes. Reaction of lithiated phenyl acetylene generated *in situ* with 0.5 equivalents of *cis*-$[^t\text{BuNPCl}]_2$ afforded a mixture of *cis*-$[(\mu\text{-N}^t\text{BuP})_2(\text{C}_8\text{H}_5)_2]$ (**1**) and *trans*-$[(\mu\text{-N}^t\text{BuP})_2(\text{C}_8\text{H}_5)_2]$ (**2**) isomers in 85% and 15% yields respectively. Reaction of **1** and **2** with two equivalents of $\text{AuCl(SMe}_2)$ afforded the corresponding *cis* and *trans* dinuclear complexes *cis*-$[\text{Au}_2\text{Cl}_2\{(\mu\text{-N}^t\text{BuP})_2(\text{C}_8\text{H}_5)_2\}]$ (**3**) and *trans*-$[\text{Au}_2\text{Cl}_2\{(\mu\text{-N}^t\text{BuP})_2(\text{C}_8\text{H}_5)_2\}]$ **(4)**, respectively. Reaction of **2** with two equivalents of CuI yielded a novel 3-dimenisonal cubane polymer $[\text{Cu}_2\text{I}_2\{(\mu\text{-N}^t\text{BuP})_2(\text{C}_8\text{H}_5)_2\}_2]_n$ (**5**), where the vertices of the cubane are occupied by Cu and I atoms. This is the first example of a cubane polymer with a bisphosphine ligand.





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Ipso-Nitration of Arylboronic Acids with Bismuth Nitrate and Perdisulfate[1]

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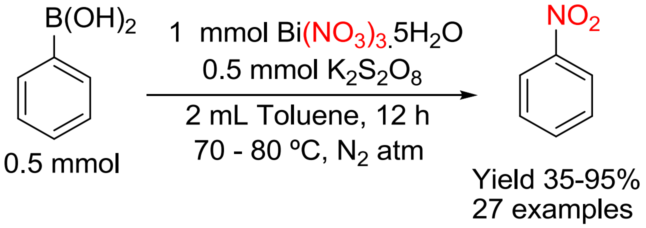
Nitration of aromatic compounds is one of the most widely studied reactions. Commonly nitration is done by strongly oxidizing mixed acid (HNO_3/H_2SO_4) or with dinitrogen pentoxide, and consequently these methods suffer from regioselectivity and functional group compatibility issues. Nitration of arylboronic acids by *ipso*–substitution[2,3] can be considered an efficient method as it circumvents the regioselectivity problem. In this context, an efficient and one pot synthetic method of *ipso*–nitration of arylboronic acids with $Bi(NO_3)_3.5H_2O$ and $K_2S_2O_8$ has been developed.

Scheme : *Ipso*-Nitration of Arylboronic Acids with $Bi(NO_3)_3.5H_2O$ and Perdisulfate



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Synthesis of Molecular Cobalt Phosphates and Assembling D4R Cobalt Cubanes with NN-donor Ditopic Linker into Porous Framework Solids

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Metallaphosphates represent one of the most widely found classes of minerals in nature and are extensively investigated classes of compounds. The diversity in metal phosphates results from variations in their assemblies, the large number of cations to which they coordinate, and the presence of additional anions or molecules. Following the discovery of phosphate analogues of zeolites, AlPOs with porous structures, research on extended metal phosphate and similar framework structures gained momentum in the last three decades. Such materials have been used as ion-exchangers, fast-ion conductors, and catalysts. Further, owing to the fact that phosphate anions do not absorb in the UV-visible region, metal phosphates also find use as optical materials e.g. glasses, phosphors, nonlinear optical, and laser materials. Here we report the synthesis of monomeric, dimeric and tetrameric cobalt phosphates of 2,6-diisopropylphenyl phosphates with a variety of ancillary ligands which are associated through hydrogen bonding of ancillary ligands into 2 and 3 dimensional supramolecular structures. However due to weak secondary interactions and very small pore sizes these systems have very less scope as gas storage materials. Here we are reporting the linking of D4R cubes through ditopic NN-donors into Porous Framework Solids and hence gas absorption properties of these systems.

Synthesis and Properties of $B(OR)_2$-complexes of Smaragdyrin

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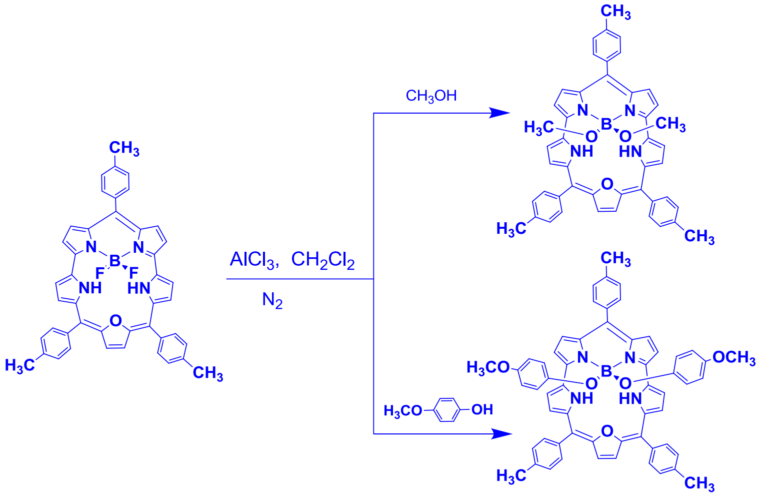
The coordination of boron to a range of polypyrrole containing ligands that includes simple dipyrromethenes to large macrocycles such as porphyrins, corroles and expanded porphyrins has received tremendous attention in recent years. Among these, the most widely utilized class of pyrrole boron complexes are boron difluoride dipyrromethenes (BODIPYs) containing the conjugated, monoanionic dipyrromethene ligand. Porphyrins are tetrapyrrolic macrocycles containing dipyrromethene moieties and have been explored for their complexation behavior toward a BF_2 group in recent years. We recently reported the synthesis of BF_2 complexes of oxasmaragdyrin, the expanded core-modified porphyrin, in decent yields under very simple reaction conditions. The BF_2 complexation of oxasmargdyrin alters the electronic properties of the macrocycle significantly. In due course of time, we realized that the fluoride groups of BF_2 unit in BF_2-smaragdyrin can be replaced with various alkoxy and aryloxy groups under simple reaction conditions and the resulted $B(OR)_2$-smaragdyrin complexes possesses novel photophysical and electrochemical properties. In this poster, we present the synthesis, spectral, and electrochemical properties of series $B(OR)_2$-smaragdyrin complexes and compare their properties with BF_2-smaragdyrin complexes.



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A General and Efficient Aldehyde Decarbonylation Reaction by Palladium Catalyst

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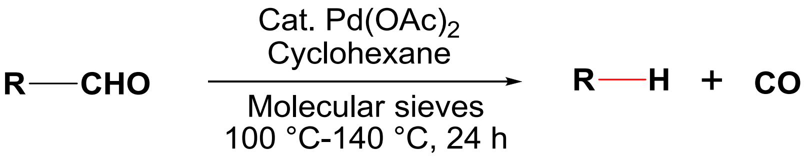
A facile decarbonylation reaction of aldehyde has been developed by employing $Pd(OAc)_2$ as the catalyst. A wide variety of substrates are successfully deformylated under easy to handle reaction condition, without using any exogenous ligand for palladium as well as CO–scavenger. An oxidative addition at the C–H bond of aldehyde, followed by rate determining CO transfer to the palladium center and reductive elimination to form the final deformylated product have been proposed based on the preliminary mechanistic studies. Due to its simplicity, we expect to find its application in synthetic set up, both in industry and in academia.

Scheme:



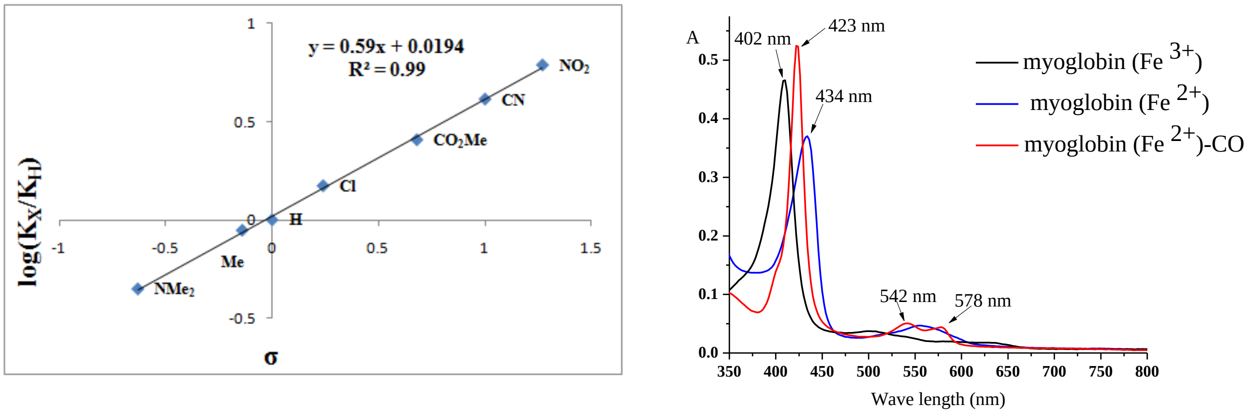


Figure: Hammett plot for decarbonylation of *para*–substituted benzaldehyde [left]. Qualitative determination of carbon monoxide in the reaction mixture using UV/VIS spectroscopy [right].

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Brominated Boron-Dipyrromethene Building Blocks for the Synthesis of Sterically Crowded Fluorescent Systems

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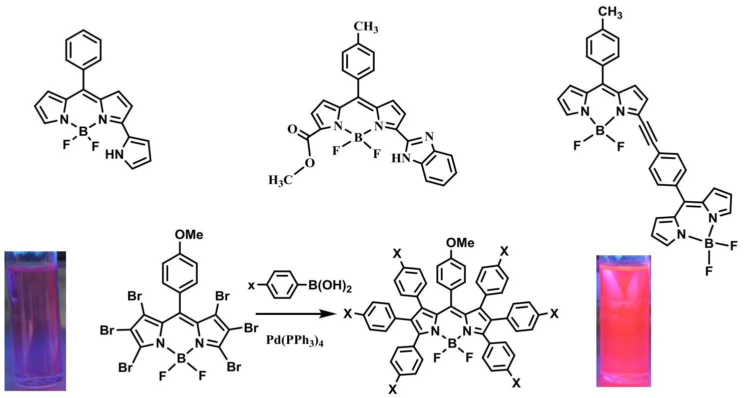
Among the fluorescent dyes available, the boron-dipyrromethene (BODIPY) dyes are becoming increasingly popular because the BODIPY dyes have remarkable characteristics such as high absorption coefficients, high fluorescence yields, long excited state lifetime, good solubility in organic solvents with excellent photostability and amenability toward chromatography. BODIPY dyes have been used extensively as labeling reagents, fluorescent switches, chemosensors and as laser dyes. Porphyrins, anthracenes, pyrenes etc have been used as scaffolds to build multi-BODIPY systems. Various synthetic strategies were developed to tune BODIPYs with absorption and emission in the red-visible or near infrared (NIR) region of the spectrum. Recently, our group is involved in the synthesis[1-7] of various substituted BODIPYs for variety of applications and in this poster, we present our rapid synthetic route for polyarylated boron-dipyrromethenes using hexabromo boron dipyrromethene as key synthon. These compounds are brightly fluorescent in solution and solid state and exhibit red shifted absorption and fluorescence bands with decent quantum yields and reversible oxidation and reduction waves compared to unsubstituted boron-dipyrromethenes. The synthesis and properties of polyarylated boron-dipyrromethene systems will be presented.



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Synthesis and Characterization of Hybrid Polyoxometalates and Schiff-base building blocks of 2,2',6,6'-Tetraisopropylbenzidine

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Hybrid polyoxometalates (POM) 1,2 and Schiff-base 3,4 compounds have been promising research attention because of their diverse structures, nanoscale size of clusters, fascinating electrochemical, catalytic, magnetic, and photophysical properties, which result in their potential applications in various fields including nanomaterials, magnetism, catalysis, photochemistry and medical science. We are exploiting tetraisopropyl substituted benzidine based chemistry for the synthesis of novel MOFs. We have synthesized various Schiff base ligands by varying aldehydes, tetra-carboxylic acid, and hybrid polyoxometalates derived from 2,2',6,6'-tetraisopropylbenzidine. We have also synthesized a hybrid polyoxometalate of 4-bromo-2,6-diisoprylaniline with the existing polyoxometalates. We are working on PNP compounds to exploit their chemistry towards biological purpose. All the compounds were characterized by spectroscopic and analytical techniques.

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A copper-catalyzed multicomponent reaction to the synthesis of 3-*C*-linked glycosyl iminocoumarins

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When the sugar unit is linked to the privileged coumarin[1a] pharmacophore, it leads to a novel class of glycosides, namely coumarin glycosides with interesting biological properties. Further, iminocoumarins, which are derivatives of coumarins, have been shown to be protein tyrosine kinase inhibitors in cancer research.[1b] However, to the best of our knowledge, the chemistry of glycosyl iminocoumarins remains unexplored. Thus, we conceived that linking of the iminocoumarin scaffold to a carbohydrate unit would lead to a new class of glycosides, which may have interesting biological profile. Recently, Wang and co-workers reported copper-catalyzed multicomponent reactions of alkynes and sulfonyl azides with 2-hydroxybenzaldehydes and 2-hydroxyacetophenones to the synthesis of iminocoumarins.[2] In continuation of our interest in exploring the application of sugar-derived alkynes,[3] it occurred to us that the above Cu-catalyzed multicomponent reaction with sugar-derived alkynes, tosyl azide and 2-hydroxy benzaldehyde would lead to the synthesis of *C*-glycosyl iminocoumarins, which could serve as precursors to the synthesis of the corresponding 3-*C*-linked glycosyl coumarins (Fig. 1).

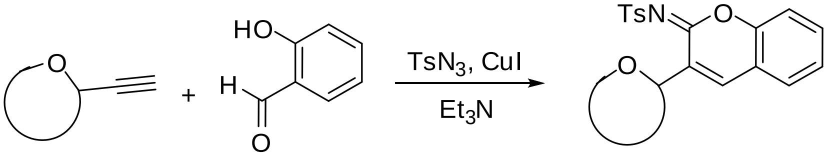

Fig. 1

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First Synthesis of Maradolipid

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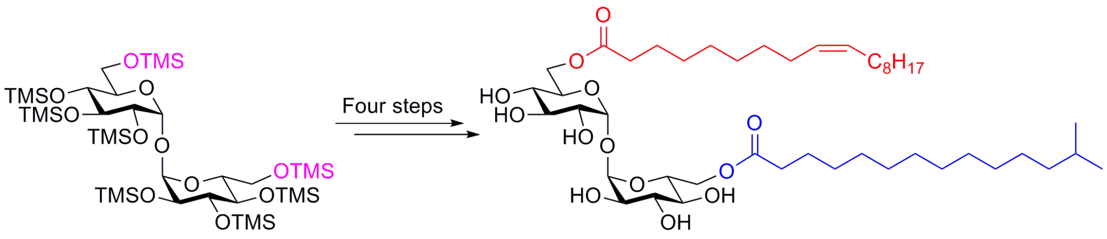
In response to harsh environmental conditions, nematode *caenorhabditis elegans* responds to stress by arresting its reproductive cycle and switching to the highly stress resistant dauer larval stage. During this transition, morphology and metabolism of the worm changes which helps it to live longer. Recently, it was found that in dauer larval stage, the worm synthesizes a novel class of 6,6'-di-*O*-acyltrehaloses, termed maradolipids.[1] In order to study the transition at molecular level and the role of maradolipid, we need maradolipid and its analogs in ample amount and with good purity.

Towards this goal, we completed the first synthesis of the maradolipid in five steps starting from trehalose in 45% overall yield.[2] The short synthesis relies on dissymmetrization of trehalose core, via regioselective acylation of a 2,3,4,2',3',4'-hexa-*O*-TMS trehalose 6,6'-diol derivative, as a key step. Our method allows synthesis of various analogs of maradolipids in a short time and efficient manner.



Per-O-silyl-α,α-trehalose **45% Overall yield** **Maradolipid**

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Synthesis of Multi-functional and Bioactive Molecules

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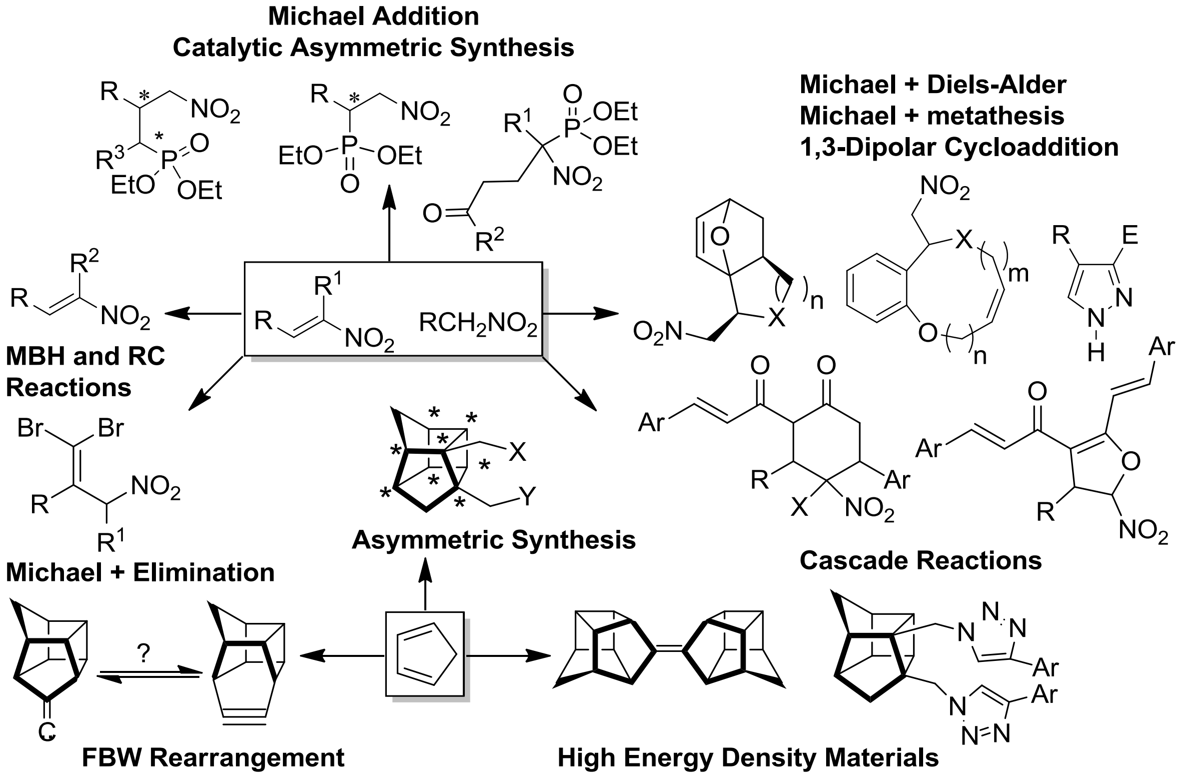
Our research revolves around the chemistry of conjugated nitroalkenes, reactive intermediates and strained polycyclic systems. Our reports on unusual reactivity of nitroalkenes and interesting properties of the products, including anti-cancer, have been highlighted by many journals. For the first time, the reactivity of nitroalkenes as activated alkenes in the MBH and RC reactions, the role of Bestmann-Ohira reagent as a cycloaddition partner, curcumin as a Michael donor/acceptor, functionalized bis-homocubanes as energetic materials and chiral catalysts have been reported by us. Detailed synthetic and mechanistic studies carried out by us have applications in areas as diverse as drug design, materials chemistry and asymmetric synthesis.



Diversity Oriented Approach To Novel Spirocyclic compounds via Enyne-Metathesis, Diels-Alder Reaction and [2+2+2] Cycloaddition As Key Steps

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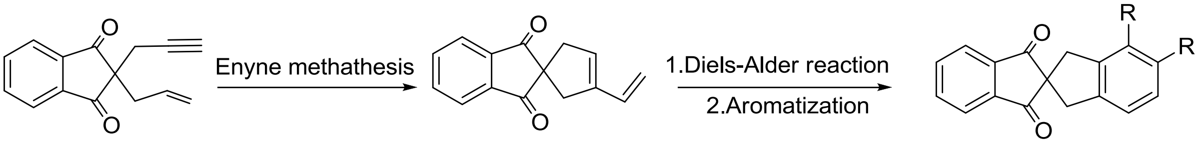
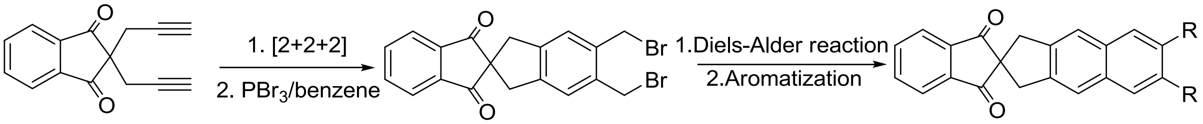
Design and synthesis of spiro cyclic compounds is very difficult task because it involves creation of quaternary center, which is considered to be one of the most challenging tasks in organic transformations [1]. Recently, we have developed a new methodology for spirocycles by using enyne metathesis [2,3], Diels-Alder reaction and [2+2+2] cycloaddition[4] as the key steps. The key precursor required for Diels-Alder reaction (DA) has been generated using rongalite [5], as shown in scheme 1 and scheme 2.



Scheme 1



Scheme 2

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Diastereoselective synthesis of (+)-nephrosterinic acid and (+)-protolichesterinic acid

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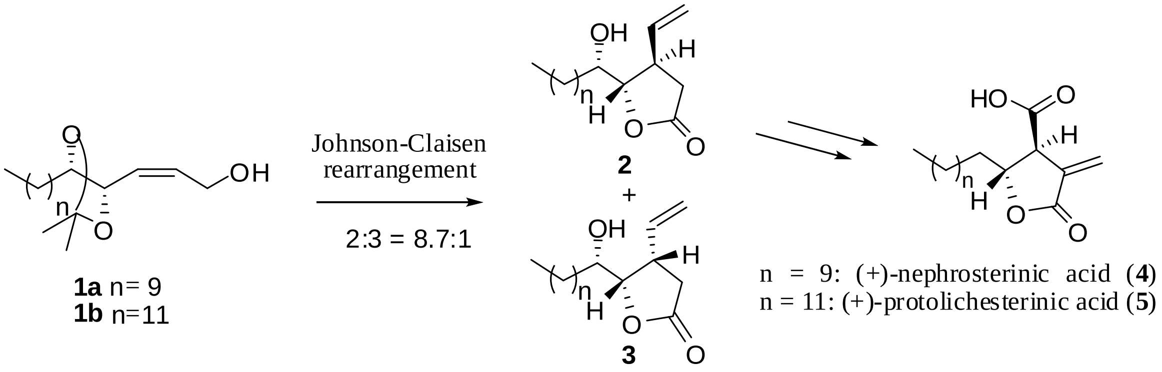
Nephrosterinic acid (**4**),[1] isolated from *Centraria endocrocea* and protolichesterinic acid (**5**),[2] isolated from *Cetraria islandica* and *Parmelia sinodensis* are important members of the family of paraconic acids. The latter are characterized by the presence of a highly substituted *γ*-butyrolactone with a *β*-COOH group and a methyl or methylene group and display varied stereochemical relationships of substituents on adjacent carbon atoms. These compounds are known for their biological activities such as antibacterial, antifungal, antitumor and growth-regulating effects. The synthesis of these paraconic acids is based on a diastereoselective orthoester Johnson–Claisen rearrangement of a (*Z*) allyl alcohol with a vicinal dioxolane moiety (**1a** and **1b**) as key steps[3]. The synthesis is completed in 10 steps and with overall yields of 15.9% for (+)-nephrosterinic acid (**4**) and 16.4% for (+)-protolichesterinic acid (**5**).



Scheme 1: Synthetic strategy for (+)-nephrosterinic acid, and (+)-protolichesterinic acid.

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Synthetic Utility of Sugar-Derived Cyclic Nitrones: A Diastereoselective Synthesis of Linear Azatriquinanes

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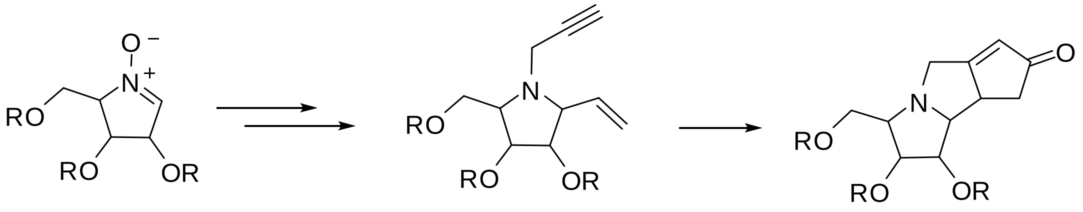
The polyquinane natural products and their analogs have attracted the synthetic community owing to their unique molecular architecture and interesting biological activities.[1] Among the polyquinanes, natural products containing the triquinane framework have elicited much interest due to their potential biological importance. Moreover, the hetero version of triquinanes namely azatriquinanes and oxatriquinanes[2] have been proved to show promising biological activity.

Sugar-derived nitrones that feature polyhydroxylated carbon framework with multiple avenues of chirality, play an important role in the synthesis of some biologically active organic molecules.[3] In continuation of our ongoing projects pertaining to exploring the synthetic potential of nitrones,[3] we became interested in the design and synthesis of azatriquinane frameworks **1** from sugar-derived cyclic nitrones using the Pauson-Khand reaction[4] as the key step. In this poster, we describe our various attempts to synthesize a library of azatriquinanes.



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Development of the first menthane based chiral bis-π-allylpalladium catalysis: Asymmetric allylation of imines

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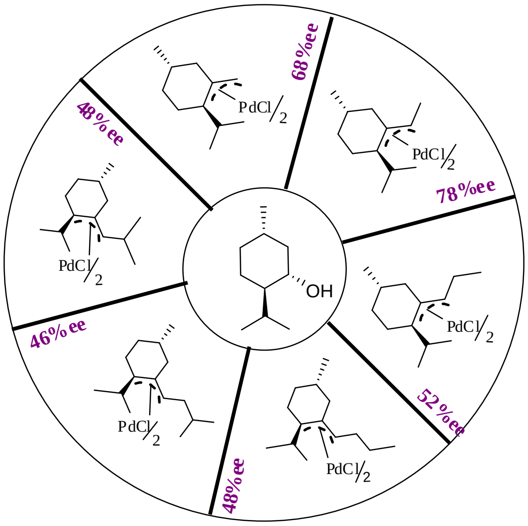
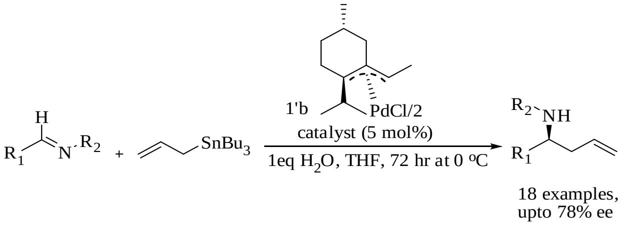
Chiral π-allylpalladium catalysis has proved to possess novelty, investment of small quantity for large amount of asymmetric material generation and new dimensional routes for synthesis of natural products. The present research work was aimed at developing the menthane based π-allylpalladium catalysis for the first time and exploration for asymmetric allylation of varied imines to get the optically active homoallylamines.[2]



Asymmetric allylation of imines with chiral π-allylpalladium catalyst



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Synthesis of [4.3.3] Propellane Derivatives Using Weiss-Cook Reaction, Fischer-Indole Cyclization as key steps

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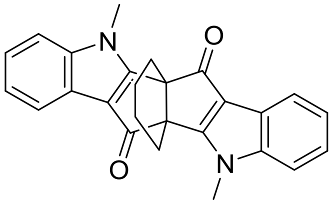
Here we report a simple strategy to [4.3.3] Propallene derivative based on Weiss-Cook reaction, Fischer-indole cyclisation and ring closing metathesis as key steps.



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A Tandem Enyne/RCM Approach to 4-Methylene-2-cyclohexenone: An Efficient Entry to Otteliones and Loloanolide

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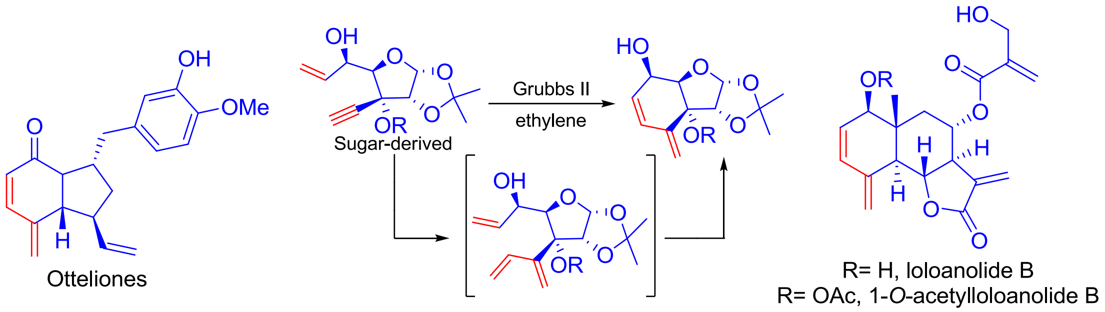
2-Methylene-2-cyclohexenone is an unique substructure present in a few biologically important natural products such as otteliones, loloanolides B and 1-*O*-acetylloloanolide B. Otteliones, isolated from the fresh-water plant *Ottelia alismoides* collected in the Nile Delta,[1] show an impressive biological activity profile, such as antitubercular activity and cytotoxicity at nM-pM levels against a panel of 60 human cancer cell lines. Loloanolides have been isolated[2] from the extract of aerial parts of *Camchaya loloana*, and they exhibit cytotoxicity against the HepG2 cell line, with GI_{50} values at a nanomolar level. It is believed that the biological activity of these molecules is attributed to the presence of a unique 4-methylene-2-cyclohexenone moiety.[3] In continuation of our interest in syntheses of natural products and natural product like molecules using metathesis[4] as key reaction, we felt that it was logical to use a tandem enyne/RCM to synthesize the 4-methylene-2-cyclohexenone/ol moiety present in otteliones and loloanolides. Using this tandem enyne/RCM approach, we have succesfully accomplished[5] the constuction of this sensitive 4-methylene-2-cyclohexenone/ol framework present in these biologically important natural products.



Otteliones

R= H, loloanolide B
R= OAc, 1-*O*-acetylloloanolide B

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Interaction of Pb^{2+} with Lentil lectin (LL)

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Lectin seems to be having several potential metal ion binding cores formed by the presence of one or more of the side chains of Histidine, Aspartate, Glutamate and/or Cysteine. It would be of great interest to explore the potential of such sites for metal ion binding with the transition metal ions. Since such transition ions in the matrix of protein are expected to show unusual reactivity and thereby one can generate artificial metalloenzymes of the corresponding protein. it is of great importance in the field of catalysis, bio-materials such as bio-nanotechnology and bioinorganic structure chemistry.

Heavy metal ions like lead and mercury are major threat to human health. Lead is responsible for the world's most common environmental poisoning by interacting with aspartate and glutamate rich proteins. Lentil lectin (LL) is rich in Asp and Glu and hence that protein can be used to study *in-vitro* binding with heavy metal ions and it helps to understand effect of interaction of heavy metals (Pb^{2+}) on secondary and tertiary structure of proteins.

Interaction of hydrophobic amino acids with sarcosine in presence of denaturant: Volumetric and calorimetric approach

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Densities and speed of sound of homologous serious of five amino acids - glycine, L-alanine, DL-α-amino-n-butyric acid, L-valine, L-leucine were measured in aqueous 1M sarcosine and 1M sarcosine+1M urea solution and corresponding apparent molar volume, apparent molar compressibility were calculated from density and speed of sound data at T = 298.15K. Enthalpy of dilution of amino acids from water to 1M sarcosine and 1M sarcosine+1M urea was also calculated. By linear regression fitting partial molar volume, partial molar compressibility and limiting enthalpy of dilution were calculated. The contribution of zwitterionic and hydrophobic groups of amino acids to partial molar volume was calculated by linear regression fitting. The solvent-solute interactions were interpreted by cosphere overlap model. It was found that as length of alkyl chain of amino acids increased hydrophobic interactions were increased.

Molecular Modeling and Dynamics of siRNAs containing 4'-*C*-Aminomethyl-2-*O*-Methyl Uridine Nucleotides

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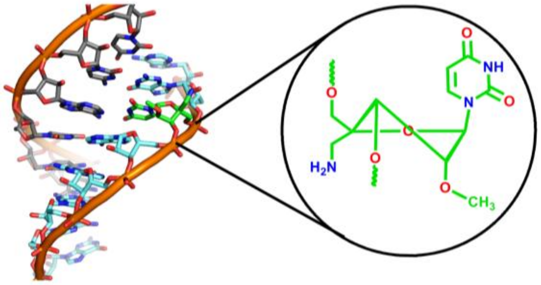
The 4'-*C*-Aminomethyl-2-*O*-Methyl Uridine (4AMU) modified small interfering RNAs (siRNAs) have recently been explored as the candidates for therapeutic applications.[1] The position specific 4AMU modifications in siRNAs were found to have slightly lesser thermal stability than the corresponding unmodified siRNA. In order to rationalize these findings, molecular dynamic simulations (AMBER10) were performed for 20 ns on three isosequential siRNA duplexes bearing modifications at different positions. Overall, the modified siRNA duplexes were found to be structurally similar to the unmodified siRNA duplex, but still they did not resemble the unmodified duplex in number of properties. Importantly, the sugar conformation of 4AMU nucleotides is strongly biased toward the C2'-endo puckering. As this sugar pucker keeps the phosphate and the sugar apart in distance, the expected electrostatic interaction between the 4'-*C*-aminomethyl and phosphate group was not observed. Also, the modified siRNAs were found to have longer inter and intra strand phosphate distances, higher backbone flexibility, fluctuating minor groove width and lesser hydration. The pairing strength and the binding affinity at the modified nucleotide regions were evaluated using DFT calculations.



Reference
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