In-House Symposium 2013

2nd March 2013

VMCC main auditorium

Department of Chemistry
Indian Institute of Technology Bombay
Mumbai 400 076
# Program Schedule

**Venue:** Main auditorium, Victor Menezes Convention Centre (VMCC).

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<td>09.50 - 10.20</td>
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<td>10.20 - 10.40</td>
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<td>&quot;1,3,5-Tris(4'-aminophenyl)benzene as a supramolecular sensor for polynitroaromatics; solid and solution phase studies&quot;</td>
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10.40 - 11.10 **Tea and Group Photo Session**

**SESSION 2**  
**Chairperson:** Mr. Parthasarathi S.

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<td>11.40 - 12.00</td>
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<td>12.00 - 12.20</td>
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<td>&quot;Establishing Structure-Activity Relationship of an Enzyme with Unknown Function&quot;</td>
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<td>12.20 - 12.40</td>
<td>Ms. Yogita Pareek</td>
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<td>12.40 - 13.00</td>
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13.00 - 15.00 **Lunch and Poster Session**
SESSION 3  
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15.00 - 15.30  Prof. Rodney Fernandes :  
"From Chiral Catalysis to Asymmetric Total Synthesis"

15.30 - 15.50  Mr. Vijaykant Khorwal :  
"The formation of inclusion complex with cucurbit[n]uril family: A host-guest interaction with [CB]n and 2-(4’-Pyridyl)benzimidazole"

15.50 - 16.10  Mr. Nageswar Rao :  
"Synthesis of Chiral N-heterocyclic Carbene complexes and their Utility in Asymmetric Catalysis"

16.10 - 16.30  Tea Break

SESSION 4  
Chairperson : Ms. Varsha Tuteja

16.30 - 17.00  Prof. Rajarshi Chakrabarti :  
"Transport through nuclear pore complex: Theory and simulation"

17.00 - 17.20  Mr. Gopalkrushna Waghule :  
"Diversity Oriented Approach to Normuscopyridine and its Higher Analogues by Ring-Closing Metathesis"

17.20 - 17.30  Vote of Thanks and concluding remarks
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L1  Dr. Nagesh Palepu  
"Drug Development Big Pharma, Generic, Specialty"

L2  D.K. Sharma and A. Chowdhury  
Morphological evolution of Nafion thin films with changing moisture content: An insight using single molecule rotational dynamics

L3  Pratap Vishnoi and Ramaswamy Murugavel  
1,3,5-Tris(4′-aminophenyl)benzene as a supramolecular sensor for polynitroaromatics; solid and solution phase studies

L4  Maheswaran Shanmugam  
Molecular Nano Magnets: Transition from transition metal to inner-transition metal complexes

L5  Gore, K. R., Nair, D. T., Pradeepkumar, P. I.  
Synthesis of N²-furfuryl-dG adduct bearing DNAs and X-ray structure with E. coli translesion polymerase DinB

L6  Aruna Birra, Ruchi Anand  
Establishing Structure-Activity Relationship of an Enzyme with Unknown Function

L7  Yogita Pareek and M. Ravikanth  
1D & 2D NMR spectroscopy to deduce the molecular structure of multi-porphyrin arrays

L8  Vikram A. Sarpe, Suvarn S. Kulkani  
Synthesis of Trehalose Based Cell Surface Glycolipids

L9  Rodney A. Fernandes  
From Chiral Catalysis to Asymmetric Total Synthesis

L10  Vijaykant Khorwal, Uma Nudurupati, Sohidul Islam Mondal and Anindya Datta  
The formation of inclusion complex with cucurbit[n]uril family: A guest-host interaction with [CB]n and 2-(4′-Pyridyl)benzimidazole

L11  Mitta Nageswar Rao  
Synthesis of Chiral N-heterocyclic Carbene complexes and their Utility in Asymmetric Catalysis

L12  Rajarshi Chakrabarti  
Transport through nuclear pore complex: Theory and simulation

L13  Sambasivara Rao Kotha, Gopalkrishna T. Waghule, Mukesh E. Shirbhatne  
Diversity Oriented Approach to Normuscopridine and its Higher Analogues by Ring-Closing Metathesis
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P5  Subrata Tewary and Gopalan Rajaraman
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P8  D. G. Vanga and K. P. Kaliappan
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Fluorescence modulation and electron transfer reactions in hydrogen bonded complexes of substituted phenylacetylenes

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Matti Spectroscopy of Fluorophenylacetylenes
Oral Presentation
“Drug Development Big Pharma, Generic, Specialty”

Dr. Nagesh Palepu
Ph.D | SciDose LLC | Co-founder & CSO|
E-mail-npalepu@scidoseusa.com

The drug development process is an ever-evolving one, with the time and cost to develop a novel compound increasing in recent times. Generic drug development, while accelerating the timeline and lowering the development costs, does not offer a patient or payer-benefit, other than price. Improved reformulations of existing products share the same development benefits as generic products but offer therapeutic advantages to the patients, the medical professionals, and the payers. This presentation will examine the development of these three types of products and discuss the future of them in today's pharmaceutical climate.
Morphological evolution of Nafion thin films with changing moisture content: An insight using single molecule rotational dynamics

D.K. Sharma and A. Chowdhury*

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai -400076
E-mail: arindam@chem.iitb.ac.in

Nafion is a perfluorinated ionomer and has potential applications in electrochemistry, sensors and sol-gel techniques for various applications because it allows H⁺ or ion transport. The Gierke’s model of network of spherical cluster connected by 1-nm-diameter channels is most popular for Nafion membranes, however in thin films it is yet to be established. It is becoming apparent that the control of film architecture and surface study is needed to fully exploit and understand the Nafion’s physical property at molecular level. Single-molecule fluorescence polarization and defocused imaging has been used to understand the morphological changes and heterogeneity of the local environments in Nafion thin films. The rotational mobility of fluorescent probes such as Rhodamine 6G and Heptylhexylperylenediimide dye incorporated in Nafion has been studied at the single-molecule levels in order to understand the morphological changes in the Nafion thin films upon exposure to water vapor. The dynamic behaviors of individual molecules were examined under dry and in various moisture containing environments. Observation of single molecule dynamics in Nafion thin films allows us to directly probe the changing environment experienced by probe molecule in its local domains.
1,3,5-Tris(4'-aminophenyl)benzene as a supramolecular sensor for polynitroaromatics; solid and solution phase studies

Pratap Vishnoi and Ramaswamy Murugavel*

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai-400076, India
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Designing of sensing materials for chemically inert and low vapor pressure polynitroaromatics (PNACs) such as TNT, PA and DNT is a challenging task within the area of chemical sensors. Owing to the unique electron-deficient property of PNACs, these analytes can form π-stacks and produce optically readable signal upon binding with electron rich fluorophores. Using single crystal X-ray diffraction studies, we have investigated the binding of TNT, PA, DNT and m-DNB with a supramolecular fluorophore, 1,3,5-tris(4'-aminophenyl)benzene (TAPB). The crystal structures show that the nitro compounds intercalate TAPB sheets through strong π-π stacking, whereas the NO₂ groups form hydrogen bonds (N-H···O) with the NH₂ groups. The strong binding affinity also enhances markedly the sensing efficiency which is further confirmed by the steady state Stern-Volmer quenching studies where the fluorescence intensity of TAPB quenched increasingly upon systematically titrating with the nitro analytes. Furthermore, vapor phase detection of DNT demonstrates the utility of TAPB as selective and discriminatory real time sensor for nitroaromatic explosives.
Molecular Nano Magnets: Transition from transition metal to inner-transition metal complexes

Maheswaran Shanmugam

Department of Chemistry, IIT Bombay, Powai, Mumbai 400076

Molecules retain magnetization below their blocking temperature ($T_B$) in the absence of magnetic field called Single-Molecule-Magnets (SMMs). Blocking temperature of the molecule is depends on the effective energy barrier ($U_{\text{eff}}$) which is directly proportional to the ground state and anisotropy associated with it. In this respect magnetic properties of structurally related $[\text{Mn}^{\text{III}}_{20-X} \text{Mn}^{\text{II}}_X]^{n-}$ (where $X = 2$ or $4$ or $6$) clusters will be discussed, followed by magnetic properties of lanthanide based molecular magnets. In addition, other potential applications such (molecular coolants and molecular Qubits) of these molecular nanomagnets will be presented.
Synthesis of $N^2$-furfuryl-dG adduct bearing DNAs and X-ray structure with *E. coli* translesion polymerase DinB

Gore, K. R.,§ Nair, D. T.,§ Pradeepkumar, P. I.†

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§National Centre for Biological Sciences, Bangalore
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DNA replication takes place in cells employing replicative polymerase enzymes. DNA contains multiple reactive sites, which are vulnerable for attack by various external agents to form adducts or damages in DNA. These DNA damages creates block in replication process since replicative polymerases stalls at the damaged site. Translesional polymerases (Y-family) are low fidelity polymerases, which can incorporate the correct nucleotide against damaged nucleotide and then bypass the damaged site. Our aim was to get the clear perspective about conformational changes induced by the $N^2$-furfuryl-dG (fdG) modification, a naturally occurring damage, in *E. coli* translesion polymerase DinB. We have synthesized of fdG phosphoramidite and successfully incorporated into oligo DNAs by solid phase synthesis. Primer extension studies showed that DinB selectively incorporates the dCTP against the fdG adduct. We have obtained the X-ray crystal structures (2.18 - 2.7Å resolution) of three modified DNA-DinB complexes with incoming nucleotide. It was evident that the active site of DinB polymerase was preconfigured to accommodate the fdG adduct and incorporate the correct dCTP without affecting the base pairing.

DNA containing $N^2$-furfuryl-dG modification (fdG)  

X-ray snapshot of complex of DinB-fdG DNA with incoming dCTP in the incorporation mode

Reference
(2) Sharma, A.; Kottur, J.; Narayanan, N.; Nair, D. T. *Nucleic Acids Res.* **2013**, (Manuscript accepted)
Establishing Structure-Activity Relationship of an Enzyme with Unknown Function
Aruna Bitra, Ruchi Anand

Department of Chemistry, IIT Bombay, Mumbai, 400076, India.

One of the most important challenges in biology is to identify the function of a protein that a gene encodes. As a result of structural genomics project a large number of protein structures are deposited in protein data bank (PDB) with no functional information. Deciphering the exact function of the protein is still a daunting task. Some of the challenges faced in the field are that many enzymes may either catalyze many types of reactions with varying catalytic efficiency or may possess several potential substrates if more than one analogue with same functional group can be accommodated in the active site. In this study we identified the function of NE0047 from Nitrosomonas Europaea an enzyme with known structure but unknown function. A combination of bioinformatics, biochemical and X-ray crystallographic studies were employed to determine the function. Sequence similarity network and structural complementarily studies gave a clue that NE0047 is a probable base deaminase. Subsequent experimental studies revealed that the enzyme under study is a guanine deaminase with a catalytic efficiency of $1.2 \times 10^5 \text{ M}^{-1}\text{ sec}^{-1}$, which is comparable with other guanine deaminases reported in literature. Along with guanine this enzyme can also accept 8-azaguanine, atrazine as substrates. In order to understand the structural basis of substrate specificity, we have solved the crystal structure of the enzyme with various substrates and substrate analogs. In addition, a systematic mutational study of the active site was performed to decipher the role of individual residues in catalysis and to decipher the mechanism of deamination. We have successfully identified the function of NE0047 and conclude that it primarily serves as a guanine deaminase. Additionally, it also exhibits a moonlighting activity towards ammeline deamination, which is an intermediate involved in the melamine pathway. A structural analysis of the member belonging to this superfamily reveals that although the core fold is conserved among all family members, the substrate binding site is diverse and each deaminase has evolved to accommodate its specific ligand. In addition, X-ray crystallographic and mutational studies show that optimal positioning of the deaminating amine group of the substrate is vital in conferring activity. Furthermore, we also demonstrate that along with zinc, two glutamic acid residues in the active site are involved in proton transfer reactions for the removal of ammonia.
1D & 2D NMR spectroscopy to deduce the molecular structure of multiporphyrin arrays

Yogita Pareek and M. Ravikanth

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Covalent and noncovalent approaches have been widely applied for the construction of multiporphyrin arrays which are used as models for understanding the energy and electron transfer processes and also for variety of applications including opto-electronic devices. In general, multiporphyrin arrays have been synthesized by covalent strategies which involve sequential steps, separation of statistical mixtures, extensive chromatographic purifications and low product yields. Here, we present, multiporphyrin arrays constructed on cyclophosphazene and Sn(IV) porphyrin scaffolds (Chart) which were synthesized in high yields (80-90%) by adopting very simple reaction conditions. We have made an attempt to deduce the molecular structures of these multiporphyrin arrays using 1D and 2D NMR techniques.

Chart

References:
Synthesis of Trehalose Based Cell Surface Glycolipids

Vikram A. Sarpe, Suvarn S. Kulkani*

Department of Chemistry, Indian Institute of Technology Bombay, Mumbai-400076, India.
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Trehalose glycolipids are attractive synthetic targets due to their complex structures and interesting biological activities.¹ Their synthesis needs differentiation of C2-symmetric trehalose core which can be achieved by stereoselective glycosylation or regioselective differentiation of commercially available trehalose. Stereoselective glycosylation provides lower selectivity and involves lengthy synthesis of monomeric building blocks.² Regioselective differentiation of hydroxyl groups on trehalose have been long studied, but till date there is no common solution for the differentiation of the 8 hydroxyl groups on trehalose. We have successfully explored differentiation at 6 and 6’ position by regioselective differentiation of primary hydroxyls making use of TMS protecting group and regioselective ring opening of benzylidene acetal. The methodologies were used for synthesis of 6,6’-diacylated maradolipid,³ and 4-monoacylated analog of recently isolated glycolipid fusaroside.⁴ We applied this strategy for the synthesis of 4-deoxy-4-amino-galacto-gluco derivative of trehalose.

References:
From Chiral Catalysis to Asymmetric Total Synthesis

Rodney A. Fernandes

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The development of a new pinane based π-allylpalladium catalyst 1 and its use in asymmetric allylation\(^1\) will be discussed. Our recent endeavor in the total synthesis of (+)-cardiobutanolide\(^2\) 2 and (−)-asteriscunolide C\(^3\) 3 will be presented.

References
The formation of inclusion complex with cucurbit[n]uril family: A host-guest interaction with [CB]n and 2-(4'-Pyridyl)benzimidazole

Vijaykant Khorwal, Uma Nudurupati, Sohidul Islam Mondal and Anindya Datta*

Department of Chemistry, Indian Institute of Technology Bombay
E-mail- vijaykant@chem.iitb.ac.in

In the present study, we report the modulation of the ground- and excited state proton transfer processes of 2-(4'-pyridyl)benzimidazole (4PBI) in aqueous solutions by CB5, CB6, CB7 and CB8 in acidic and alkaline media and in order to examine if the protonation-deprotonation equilibria involving different forms of 4PBI are affected by inclusion in macrocyclic hosts of this class. Given a choice between a cation, anion and a neutral it is known that CB would selectively stabilize the cation, but the question we have addressed here concerns the choice between two monocations of the same molecule. 2-(4'-Pyridyl)benzimidazole (4PBI) guest comprising two binding sites, one benzimidazole group and one pyridyl group, proved could form inclusion complexes with cucurbit[n]uril (CB[n]) in aqueous solution. The binding in the cavity and at the portals of cucurbit[n]uril, absorption and fluorescent response of a guest could be dramatically changed, so by the steady state and time resolved fluorescence spectroscopy, it very easy to demonstrate that the 2-(4'-Pyridyl)benzimidazole could be interact with both cavity and portal. $^1$H NMR spectroscopy is also proving the formation of inclusion complexes. $^1$H NMR of both the guest and the host indicates that guests might enter in CB[n] from the benzimidazole side with in hydrophobic cavity.

![Different forms of 2-(4'-Pyridyl)benzimidazole and the glycouril unit of Cucurbit[n]uril.](image_url)
Synthesis of Chiral N-heterocyclic Carbene complexes and their Utility in Asymmetric Catalysis

Mitta Nageswar Rao

Department of Chemistry, Indian Institute of Technology, Bombay, Powai, Mumbai 400 076, E-mail: nageswar@chem.iitb.ac.in

A series of new silver, gold, nickel and palladium complexes supported over chiral N-heterocyclic carbene ligands prepared from readily available enantiopure (+)-pinene, (+)-camphor and (−)-menthol. Designing the chiral catalyst plays a crucial role in the asymmetric synthesis. We have developed a new class of N-heterocyclic carbene (NHC) complexes of 6-membered and 12-membered bifunctional catalysts and CNC type cationic pincer architecture (Fig. 1). These NHC complexes have been characterized by NMR, elemental analysis and the structures are unambiguously determined by X-ray crystallography. The catalytic applications of some of these catalysts in asymmetric synthesis will be discussed.

![Chiral NHC complexes diagram](image.png)

**Figure 1:** Design of new chiral NHC complexes

M = Ag (or) Au (or) Ni (or) Pd; X = Cl (or) BF₄
Transport through nuclear pore complex: Theory and simulation

Rajarshi Chakrabarti

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The nuclear pore complex (NPC) is most probably the nature’s finest analytical chemist [1]. Seated at the gateway between the cytoplasm and nucleus in eukaryotic cells it distinguishes proteins by their chemical affinity. In the earlier part of the talk I will present a simple theoretical model [2] that addresses this issue of “selectivity” and the transport mechanism of proteins. Our model also suggests that the central plug of NPC is most likely to be a gel than a brush. In the later part of the talk, I will show how a simple coarse-grained molecular dynamics simulation on a NPC like model system [3] can shed light on the issue of normal versus anomalous mode of transport of tracers.

References:
**Diversity Oriented Approach to Normuscopyridine and its Higher Analogues by Ring-Closing Metathesis**

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Macrocycles are important molecules for drug discovery, and binding of different metal ions. Various methods have been developed to prepare these molecules. Macrocycles containing pyridine rings are abundant in nature and of great importance in pharmaceutical industry. Various pyridines containing compound possesses properties like, antidiabetic, antiviral, anticancer, antioxidant, antibacterial, antifungal, and analgesic Ring closing metathesis reaction (RCM) is a prominent reaction to prepare macrocycles. Normuscopyridine is one of the pyridinophane, derivative of muscopyridine. Since muscopyridine is widely used in perfumery industry, normuscopyridine was synthesized to study the effect of having diversity in chain length. Normuscopyridine and its corresponding benzene derivatives were synthesized by using lutidine, and m-xylene dibromide as a starting material. Diversity oriented approach was applied to synthesize higher homologue of normuscopyridine. Also, the corresponding dimers were formed during RCM reaction.

![Diagram](image.png)

*Figure 1. Various derivatives of normuscopyridine prepared*
Poster Presentation
Computational Studies on Dioxygen Activation and Autocatalytic O₂ Cleavage by a Trianionic Pincer Cr(III) Complex

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Air or molecular oxygen are ideal oxidants due to its natural, benign, inexpensive and environmentally friendly characteristics, and it will be of great value, if chemists can use oxygen in synthesis under ambient conditions in the same way as enzymes do in nature. Considering the propensity of Cr⁵⁺ to be reduced to Cr³⁺ by biological reductants, Cr⁵⁺O is a reasonable fragment as an oxygen-atom-transfer catalyst. One advantage of the trianionic pincer ligand is the presence of a strong metal-carbon bond, which is fixed relative to the other anionic pendant donors. So substrate or other ligand opposite the M-C bond experiences a strong trans influence, which is exploited to enhance reactivity. We have done theoretical studies on the first catalytic event for a complex supported by a trianionic pincer ligand. We are trying to characterize reactive Cr⁴⁺-O-Cr⁴⁺ intermediate in Cr³⁺/⁵⁺ catalytic cycle and conclusively demonstrate that trianionic OCO pincer ligand enables remarkably swift O₂ activation by creating an open coordination site. We have performed DFT calculations to understand the electronic structure and spectroscopic properties of the intermediates involved and to get an insight of overall reaction mechanism. All these results along with the energetics of formation, structure and bonding aspects of various possible high valent metal superoxo and peroxo intermediates will be presented.

References:
Chemical synthesis of damaged DNAs to study structure and function of Y-family polymerases

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DNA damage is a constant threat caused by endogenous and exogenous sources; presence of these damages block the progress of DNA replication process by replicative polymerases. An important mechanism to overcome this problem entails the use of specialized DNA polymerases (Y family) to carry out Translesion Synthesis (TLS). TLS is defined as the bypass of damaged sites by incorporation of a nucleotide across the damage, which can be error-free or error-prone. Compared to the replicative polymerases, additional little finger domain of the TLS polymerases enhances the binding with template DNA and influences fidelity and activity. Among the Y-family polymerases, the structure of DinB polymerase (DNA polymerase IV from *E. Coli*) is yet to be determined. A Recent study suggests that DinB polymerase and its orthologs can efficiently bypass the different $N^2$-dG potential lesions. To understand the structural and functional requirement of DinB polymerase, we carried out synthesis of oligonucleotides containing site-specific $N^2$-modified-dGs. The clear perspective of lesion induced conformational changes in DinB polymerase with $N^2$-modified-dG oligonucleotides is currently being studied by primer extension and X-ray crystallography.

References:
Glucopyranosyl conjugate of anthraquinone linked through thiourea in the recognition of $\text{Hg}^{2+}$ and $\text{F}^-$ by turn on the fluorescence

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Small molecular receptors are highly valuable tools for selective recognition of chemical and biological species. Their value further increases if these were water soluble and biologically benign. In this regard, synthetically modified glyco-moieties resulting in glycoconjugates would be of great relevance and important owing to their water solubility and biological compatibility in the selective recognition of ions and molecules of importance in biology and environment. Our research group has been using this as basic factor in developing receptors suitable for different ions and molecules.\(^1\)\(^-\)\(^5\) In the present work, a glucopyranosyl conjugate of anthraquinone linked through thiourea (L) has been synthesized and studied for its anion and cation (metal ion) recognition by spectroscopy and electrochemistry. L has been shown to act as selective turn-on fluorescence sensor for $\text{F}^-$ with 12 fold enhancement and its minimum detection limit is 450 ppb. In addition, L has also been shown to be selective for $\text{Hg}^{2+}$ and responds through fluorescence enhancement down to a concentration of 25 ppb. In both the cases, the complex formation was addressed by spectroscopy ($^1\text{H}$, $^19\text{F}$, $^{13}\text{C}$ NMR, ESI-MS) and electrochemistry (cyclic voltammetry) techniques. The results of all these and related studies I will be present in that conference.

References:
Brightly Fluorescent Boron Dipyrrromethene Dyes

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Abstract

The synthetic chemistry on boron-dipyrrromethenes (BODIPYs) is rapidly growing in recent years owing to their numerous applications. Our research group is interested in making novel functionalized BODIPY-derivatives that will be useful for diverse applications. We recently reported the facile synthesis of 3,5-diformyl BODIPYs 1 under simple reaction conditions and demonstrated their use as pH based optical sensors. However, aldehyde functional groups on BODIPY core are very useful to synthesize several new types of BODIPYs and we synthesized novel 3,5-bis(dipyrrromethanyl) BODIPYs 2 based chemosensors and demonstrated their selectivity for fluoride ion detection. The two carbonyl groups at 3- and 5-positions of BODIPY dye are reactive sites where anion can attack via nucleophilic addition by altering the electronic properties of the dye and our spectral and electrochemical studies showed that 3,5-diformyl BODIPY can acts as an exclusive chemodosimetric and colorimetric sensor for CN⁻ ion. These systems will be presented in our poster.

Chart: Structures of some selected BODIPY derivatives

References:
Theoretical Perspectives on Redox “Non-innocent” Oxazolidine-N-oxide Iron and Cobalt Nitrooxide Complexes

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Abstract:

One electron redox processes in ligands exhibiting non-innocent behaviour invariably leads to the generation of radical species which when coupled with redox-active metal centres can lead to strong magnetic exchange, ambiguous electronic structures and even spin-crossover (SCO).¹ We have chosen two radical complexes (1) [Fe”(L’)]2(BF₄)₂ and (A) [Co”(L’)]2(NO₃)₂ along with their two electron reduce species (2) [Fe”’(L’)]2(BPh₄) (B) [Co”’(L’)]2(BPh₄) (L’ = 4-dimethyl-2,2-di(2-pyridyl) oxazolidine N-oxide) to undertake an extensive theoretical study to underpin the influence and interplay of the strong magnetic exchange, the redox non-innocent behaviour and any possible spin transitions.²³ A series of calculations establishes the low-spin character of both the metal ion as well it gives us a valuable insight into the electronic structure.

References:

Conformational Dynamics Study of the Free Antigenic Peptide from Influenza Hemagglutinin and its Bound-Form with Antibody using Molecular Dynamics Simulations: Implications for the Role of Turns in Protein Folding and Peptide Immunogenicity

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Immunological experiments on a synthetic 36 residue peptide (75-110) from Influenza hemagglutinin, produced anti-peptide antibodies which could cross-react with the parent protein [1]. The shorter 13mer peptide 98YPYDVPDYASLRS110 forms a β-turn involving sequence 104DYAS107 which is crucial for antigen-antibody interactions [2]. To understand the conformational preferences of the 13mer antigenic peptide in its free and antibody-bound forms, we performed MD simulations on free 13mer peptide Ac-2YPYDVPDYASLRS14-NMe (free An), on Fab fragment of antibody (free Ab) and on the complex of 13mer peptide with Fab fragment (bound An-Ab) separately using GROMACS 4.0.4 and OPLS-AA force field. Our simulation results show that free 13mer peptide samples a native-like conformation at its C-terminus, along with transient sampling of the β-turn involving sequence 8DYAS11. This turn is also seen to initiate formation of the other native turns in the free 13mer peptide. Further, 8DYAS11 β-turn is sampled persistently by the 13mer peptide in the antibody-bound form. The residues in 13mer peptide and the CDRs of the Fab fragment involved in antigen-antibody interactions show lower flexibility in the bound form in comparison to the free form. Thus, a difference in conformational preferences observed for the 13mer peptide in the free and antibody-bound simulations suggest the role of β-turns in both protein folding and peptide immunogenicity.

References
Towards a Protecting-Group-Free Synthesis of
(+)-Cardiobutanolide and Hagen’s Gland Lactones

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The concept of protecting group free and aiming ideal synthesis is practical and highly demanding.¹ In this context, We have developed a step-economic protecting group free synthesis of (+)-cardiobutanolide in three steps with 22.4% overall yield from cheap material, D-glucono-δ-lactone. The strategy is based on one-pot conversion of D-glucono-δ-lactone to β-hydroxy-γ-vinyl-γ-lactone, hydroxyl groups compatible cross metathesis and substrate controlled Upjohn dihydroxylation reactions.² Using the key building block β-hydroxy-γ-vinyl-γ-lactone, a practical protecting group free synthesis of Hagen’s gland lactones are achieved in four steps with high overall yields. The strategy relies on one-pot conversion of D-glucono-δ-lactone to β-hydroxy-γ-vinyl-γ-lactone, cross-metathesis and iodocyclization-deiodinization as key steps.³ Our journey towards developing a protecting-group-free strategies for (+)-cardiobutanolide and Hagen’s gland lactones will be presented in the poster.

References:
**Synthesis of Angucycline Antibiotics**

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Angucycline\(^1\) is one of the relatively new and large groups of novel antibiotic natural products featuring a carbocyclic skeleton which is assembled in an angular manner. These natural products are isolated from the culture broth of different microorganisms. Besides their interesting structural features they also exhibit widespread biological activities including antitumor, antifungal and antiviral properties.\(^2\) To date, several synthetic strategies have been reported to construct the benz[a]anthraquinone skeleton of angucycline employing Diels–Alder and Friedel–Crafts reactions, nucleophilic additions, free radical annihilations, rearrangements of cyclobutanes and cobalt-mediated [2+2+2] cycloadditions. Among all these strategies, the Diels-Alder approach has been widely used to frame the benz[a]anthraquinone skeleton by using chiral catalyst, enantiopure diene or chiral dienophile.

Owing to their promising biological activities and interesting structural framework, we became interested in the synthesis of angucycline and their analogues. In continuation of our earlier work on enantioselective total syntheses of YM-181741, (+)-oehromycinone, (+)-rubiginone B\(_2\), (−)-tetrangomycin and MM-47755,\(^3\)\(^a\) herein we describe the total syntheses of anhydrolandomycinone, tetrangulol, X-14881-E, kanglemycin M,\(^3\)\(^b\) the enantioselective synthesis of (−)-zenkequinone B\(^3\)\(^c\) and rubiginones by utilizing a sequential enyne metathesis and Diels-Alder reaction sequence.

**References:**


Sn(IV) Porphyrin based Multiporphyrin Architectures: One pot synthesis using complimentary bonding approach and studies

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Since porphyrins and metalloporphyrins reveal enormous versatility in their electron transfer, redox and photoactive properties, incorporation of these species into multicomponent arrays has proved to be an attractive strategies for the construction of functional arrays. In this regard, our group recently reported two novel tetrads containing Sn(IV) porphyrin and expanded porphyrin such as thiasapphyrin and thiarubyrin and Ru(II) porphyrin by adopting complimentary binding approach\textsuperscript{2,3}. This methodology has been now extended to prepare a series of Sn(IV) porphyrin based multiporphyrin arrays ranging from tetrad to heptad. In this poster we present the synthesis and detail characterization of Sn(IV) porphyrin based multiporphyrin architectures from tetrad to heptad using 1D ans 2D NMR spectroscopic technique\textsuperscript{4}. The spectral and electrochemical properties of these Sn(IV) porphyrin based multiporphyrin architectures also have been discussed.

References:
Theoretical Investigation of Stilbene as Photochromic Spin Coupler

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We performed Density Functional Theory based investigation of the magnetic behavior, spectroscopic transitions and possible photomagnetic properties of stilbene derivatives. Nitronylnitroxide (NN), iminonitroxide (IN), tetrathiafulvalene-cation (TTF) and verdazyl (VER) are used as radical centers at p, p' positions. To obtain reliable estimates of the intramolecular exchange coupling constants (J), we used the hybrid B3LYP functional, adopt the broken symmetry approach, and rely on large basis set. We find that with stilbene as spacer, the coupling of TTF with NN, IN and VER is always antiferromagnetic with J generally large and negative. Absorption wavelengths are estimated for both substituted and unsubstituted species from TDDFT using the same functional. Similarity in the calculated absorption wavelengths and oscillator strengths (f) between the unsubstituted and substituted stilbenes indicate that the diradical isomers would have good photoswitching properties. Finally, we show that when these diradicals are placed in a matrix, photochromicity would be accompanied by a significant change in paramagnetic susceptibility.

References:
Four-Center Oxidation State Combinations and Near-Infrared Absorption in [Ru(pap)(Q)_2]^n, Q = 3,5-Di-tert-butyl-N-aryl-1,2-benzoquinonemonoimine and pap = 2-Phenylazopyridine

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The delicate electronic structures of the complex series [Ru(pap)(Q)_2]^n ([1]^n-[4]^n) (n = 2+, 1+, 0, 1−, 2−) having two redox non-innocent ligands, 2-phenylazopyridine (pap) and 3,5-di-tert-butyl-N-aryl-1,2-benzoquinonemonoimine (Q; aryl = C_6H_5 (1^+); m-(Cl)C_6H_5 (2^+); m-(OCH_3)C_6H_5 (3^+); m-(tBu)C_6H_5 (4^+)), have been established via experimental and DFT calculations. Crystal structure of the representative [1]ClO_4 establishes the selective stabilization of the ctt isomer, with respect to the mutual orientations of O and N donors of two Q, and the azo N atom of pap. The three-spin configuration of [Ru^{III}(pap^0)(Q^•−)]^2+ has been established as the electronic structural form for 1^+-4^+ where the resultant unpaired spin resides on Q^•−. [1]ClO_4-[4]ClO_4 undergo one oxidation and three reductions corresponding to [Ru^{III}(pap^0)(Q^•−)(Q^0)]^{2+} (1^2+-4^2+) (S=0) ⇄ [Ru^{III}(pap^0)(Q^•−)]^+ (1^+-4^+) (S=1/2) ⇄ [Ru^{II}(pap^0)(Q^•−)] (1-4) (S=1) ⇄ [Ru^{II}(pap^•−)(Q^•−)]^- (1^−-4^−) (S=1/2) ⇄ [Ru^{III}(pap^•−)(Q^•−)]^{2−} (1^2−-4^2−) / [Ru^{I}(pap^•−)(Q^•−)]^{2−} (S=1).

**Experimental and DFT Evidence for Fractional Non-innocence of a β-Diketonate Ligand**

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Electronic structural aspects of the newly designed [Ru(pap)₂(L)](ClO₄) [1]ClO₄, [Ru(pap)(L)]₂, 2 and [Ru(acac)₂(L)] 3 (pap = 2-phenylazopyridine, L⁻ = 9-oxidophenalenone, acac⁻ = 2,4-pentanedionato) have been investigated via experimental and DFT calculations. The oxidation of L⁻ to L’ could be deduced from [Ru^{III}(pap)(L')(L⁻)]²⁺, which exhibits a near-IR absorption due to ligand/metal to metal/ligand charge transfer transition. A ligand-to-ligand intervalence charge transfer (LLIVCT) band is observed at about 2000 nm corresponds to pap•− → pap in the electrogenerated complex [Ru^{II}(pap⁻)(pap₀)(L⁻)]. Other intense long-wavelength transitions including LMCT (L⁻→Ru^{III}) and LL'I CT (pap•−→L') processes were confirmed by TD-DFT results. DFT calculated spin densities and EPR data for paramagnetic intermediates allowed to establish two resonating forms involving L-based radical center i.e. [Ru^{III}(pap₀)₂(L⁻)]²⁺ ↔ [Ru^{II}(pap₀)₂(L')]²⁺ and [Ru^{III}(pap₀)(L⁻)]⁺ ↔ [Ru^{II}(pap₀)(L')(L⁻)]⁺. The strong π-acceptor effect of the pap ligand on the metal leads to full or fractional oxidation of potentially redox-active β-diketonate derived L⁻ to L’.

Metal Carbonyl Mediated Transformation of Tellurium Based Ligands

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Reactivity of ferrocenylacetylene towards mononuclear metal carbonyls and chalcogen stabilized metalcarbonyl clusters has been investigated earlier in our group.\textsuperscript{1-3c}

Formation and Interconversion of coordinated products, formed from diferrocenyl ditelluride with different mononuclear metal carbonyl have been observed (Figure 1). Also, a new ligand, (Z)-1-ferrocenyltelluro-1-ferrocenyl-4-ferrocenyl-1-buten-3-yne have been reacted with ironpentacarbonyl to give novel tellurium coordinated complexes. These complexes are important in cluster growth purposes as not only the alkyne group but also the double bond and tellurium are involved in coordination.

![Diagram](image)

**Figure 1** Transformation of dferrocenyl ditelluride complexes of group VI metal carbonyls

**References:**
Reaction of Ruthenium phenyl acetylide with Iron-chalcogen clusters and Iron pentacarbonyl

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At 0 °C, photolysis of a THF solution containing ruthenium acetylide \[\text{[(η}^5\text{-C}_5\text{H}_5]\text{Ru}(\text{PPh}_3)_2(\text{η}^1\text{-C≡CPh})]\] with \[\text{[Fe}_3(\text{CO})_9(\text{µ}_3\text{-Se})_2]\] cluster affords an adduct \[\{\text{µ-}\text{SeC(C}_5\text{H}_5\text{Ru}(\text{PPh}_3)(\text{CO}))=\text{C(Ph)Se}(\text{CO})_6\text{Fe}_2\}\], 1, while under similar reaction condition with \[\text{[Fe}_3(\text{CO})_9(\text{µ}_3\text{-Te})_2]\] cluster a Ru-inserted product \[\text{[(η}^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{η}^1\text{-C≡CPh})\text{RuFe}_2(\text{µ}_3\text{-Te})_2(\text{CO})_6]\], 2 was obtained. Under thermal condition \[\text{[(η}^5\text{-C}_5\text{H}_5]\text{Ru}(\text{PPh}_3)_2(\text{η}^1\text{-C≡CPh})]\] react with Fe(CO)_5 to give an acetylide stabilised Fe₂Ru mixed metallic cluster 3.

**Figure:** Molecular structures of compound 1, 2 and 3
Designing of sensing materials for chemically inert and low vapor pressure polynitroaromatics (PNACs) such as TNT, PA and DNT is a challenging task within the area of chemical sensors. Owing to the unique electron-deficient property of PNACs, these analytes can form π-stacks and produce optically readable signal upon binding with electron rich fluorophores. Using single crystal X-ray diffraction studies, we have investigated the binding of TNT, PA, DNT and m-DNB with a supramolecular fluorophore, 1,3,5-tris(4′-aminophenyl)benzene (TAPB). The crystal structures show that the nitro compounds intercalate TAPB sheets through strong π-π stacking, whereas the NO₂ groups form hydrogen bonds (N-H···O) with the NH₂ groups. The strong binding affinity also enhances markedly the sensing efficiency which is further confirmed by the steady state Stern-Volmer quenching studies where the fluorescence intensity of TAPB quenched increasingly upon systematically titrating with the nitro analytes. Furthermore, vapor phase detection of DNT demonstrates the utility of TAPB as selective and discriminatory real time sensor for nitroaromatic explosives.
Study of electrochemically tuned transport through a polyaniline membrane at two different pH levels

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Conducting polymers have very high conductivity which is applied to develop functional electronic devices, biosensors, actuators, batteries. Among these conducting polymers polyaniline possess good environmental stability, electro chromic behavior and it can be easily synthesized also. Polyaniline exists in three different states which are reduced, leucoemeraldine and half-oxidized, emeraldine states and it can be reversibly interconvertable in between these states.\(^1\) Since switching properties of polyaniline can be controlled after its synthesis, it opens up a new route for chemical separation.\(^2\) Therefore to understand this phenomenon, composite membranes consisting of a porous polycarbonate support was coated with a thin gold layer and then an electrochemically synthesized Polyaniline film was deposited on its top. These membranes were characterised by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM) to study the extent of the deposition of polyaniline on the pore mouths. The present study will support in understanding these processes in a better way.

References:
Diversity Oriented Synthesis of Benzoepines, Isochromenes and Naphthalenes from Chlorovinylogous Carbonates

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Diversity oriented synthesis (DOS) aims to synthesize a collection of small molecules having skeletal and stereochemical diversity. DOS is not obvious and remains challenge to synthetic chemists.1 We have developed reagent based approach (differentiating process) for diversity oriented synthesis of benzoxapane, isochromene and naphthalene using common intermediate chlorovinylogous carbonate (1).2 Because of their widespread presence in natural products, drugs, and materials new protocols for the synthesis of substituted benzoxapane, isochromene and naphthalene are of value, especially if they can be conducted inexpensively and conveniently.3,4,5 The chlorovinylogous carbonate (1) when treated with active methylene compounds, underwent tandem alkylation-Michael reaction to give substituted benzoxapane derivatives in stereoselective manner. Isochromene derivatives were also accessed from the same intermediate by intramolecular Heck reaction. Phosphine salt of chlorovinylogous carbonate on heating under basic conditions, gave substituted naphthalene derivatives. Scope of this diversity oriented approach for synthesis of benzoxapanes, isochromenes and naphthalenes will be presented.

References:
Morphological evolution of Nafion thin films with changing moisture content: 
An insight using single molecule rotational dynamics

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Nafion is a perfluorinated ionomer and has potential applications in electrochemistry, sensors and sol-gel techniques for various applications because it allows H\(^+\) or ion transport. The Gierke’s model of network of spherical cluster connected by 1-nm-diameter channels is most popular for Nafion membranes, however in thin films it is yet to be established. It is becoming apparent that the control of film architecture and surface study is needed to fully exploit and understand the Nafion’s physical property at molecular level. Single-molecule fluorescence polarization and defocused imaging has been used to understand the morphological changes and heterogeneity of the local environments in Nafion thin films. The rotational mobility of fluorescent probes such as Rhodamine 6G and Heptylhexylperylene diimide dye incorporated in Nafion has been studied at the single-molecule levels in order to understand the morphological changes in the Nafion thin films upon exposure to water vapor. The dynamic behaviors of individual molecules were examined under dry and in various moisture containing environments. Observation of single molecule dynamics in Nafion thin films allows us to directly probe the changing environment experienced by probe molecule in its local domains.
Aqueous Dispersible Powder of Poly(3,4-Ethylene dioxythiophene)

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Poly(3,4-ethylenedioxythiophene), PEDOT, has emerged as one of the most successful conducting polymer due to its widespread applications in organic electronic devices as antistatic coatings, hole transport layer, electrochromic coatings and transparent conductor coatings etc. Due to the insolubility of PEDOT, it has been processed from the aqueous dispersion in presence of anionic polyelectrolyte sodium salt of poly(styrene sulfonate), PSS-Na, and is available under the trade name of "Clevios-P". The tedious purification processes and the stability of the final dispersion (shelf life) are the major drawbacks in this process. Therefore, it will be advantageous if one can synthesize PEDOT powders which can be dispersed in water in presence of stabilizers as when needed. This will increase the ease of purification, improve shelf life as well and one can control the surface charge of the colloidal particles based on the added stabilizer. Control of the surface charge becomes crucial in multilayer electronic devices. We have been working in this direction to synthesize aqueous dispersible PEDOT powder and have now developed a route for this. This method allows us the synthesis of PEDOT powder which then can be dispersed in water in presence of various stabilizers resulting in the syntheses of stable dispersions with particle size ranging from 200-1200 nm wherein surface charge can be controlled from highly negative to positive. In this presentation, we will highlight the recent results from our laboratory.
Studies Towards Total Synthesis of Oligosaccharide OSE-1 of *Mycobacterium gordonae* (Strain 990)

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OSE-1 is highly antigenic glycan isolated in 1993 by Besra from the cell surface of *Mycobacterium gordonae* (strain 990).¹ *Mycobacterium gordonae* also known as “tap-water bacillus” is a slow-growing scotochromogenic acid-fast bacillus with characteristic cultural and biochemical properties. In AIDS patients this strain causes pulmonary infections similar to Tb but it is resistant to anti-Tb drugs like isoniazid, pyrazinamide, ethambutol and cycloserine.² It is observed mainly in patients with prosthetic devices, compromised immunity, chronic pulmonary disease or history of trauma.³ It is considered as a potential opportunistic respiratory tract pathogen in patients with advanced HIV-1 infection. Also a number of infections involving skin, soft tissues, liver, respiratory tract and underlying immunosuppression have been reported.² Synthesis of OSE-1 would enable speedy serodiagnosis and vaccine development. The key step involved in the synthesis of OSE-1 is Intramolecular Aglycone Delivery method to obtain the right hand terminal desymmetrized trehalose unit. Remaining part of the molecule is assembled in a convergent fashion via stereoselective glycosidation reactions using trichloroacetimidate and thiol donors.

References:
Density Functional Investigation of Electronic and Magnetic Structures of MnAs, MnSb and MnBi

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Magnetic alloys have attracted the attention due to their potential applications in the spintronics. In this context, manganese pnictides, a group of ferromagnetic alloys, are of great interest due to their possible half-metallic and magneto-optic characteristics. In this work, we investigate the electronic and magnetic structures of ferromagnetic MnX (X=As, Sb, Bi) systems using unrestricted hybrid DFT methodology with B3LYP, B3PW and PBE0 hybrid functional. CRYSTAL09 code is used for all computations. Single point energy calculations are performed on the crystallographic unit cell in both ferromagnetic and antiferromagnetic phases. The Ising model magnetic exchange coupling constants ($J$) are calculated. The calculated $J$ values are close to those determined from experimental Curie temperature and mean field theory. The calculated $J$ values for MnAs (24–28.3 cm$^{-1}$) are almost within the range of the estimated $J$ (27.6 cm$^{-1}$). Coupling constants for MnSb and MnBi are almost 70% of the estimated ones. Among the three hybrids, UB3LYP shows a greater degree of consistency.

References:
Total Synthesis of (+)-Murolic Acid

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Thousands of plant glycosides have been isolated in nature, but a few numbers have been identified in lichens. In 2001, two new glycosides\(^1\) (1 and 2), were isolated from an extract of central Asian lichens, consisting of (+)-murolic acid\(^2\) (3) as the aglycone part and an oligosaccharide moiety linked at C-18 made up of two or three glucose units (Scheme 1). To the best of our knowledge, there are no reports on the total synthesis of these molecules as well as on their biological significance. Here we will present the synthesis of the aglycone part of these glycosides. Sharpless asymmetric dihydroxylation, Johnson-Claisen rearrangement and decarboxylative methylenation were used as key steps.

![Scheme 1](image-url)

References:
Stereoselective Synthesis of Morpholines and 1,4-Oxathianes using Reductive Etherification Reaction

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Substituted Morpholines and 1,4-oxathianes have attracted considerable attention over the years due to their presence in a variety of biologically active compounds and natural products.\textsuperscript{1} Morpholines and 1,4-oxathianes possess fungicidal and pesticidal activities. 1,4-oxathianes have also been shown as glycosyl donors for highly selective 1,2-\textit{cis}-glycosylation,\textsuperscript{2} and act as important precursors for the synthesis of biologically significant oxathillins. Recently, some of the chiral oxathianes have been synthesized and successfully used for the asymmetric sulphur ylide mediated epoxidation.\textsuperscript{3} Even though some progress has been made for the synthesis of morpholines,\textsuperscript{4} there are very few methods reported for the stereoselective synthesis of 1,4-oxathianes. A general, efficient method for the stereoselective synthesis of both, morpholines and 1,4-oxathianes, has been developed using reductive etherification reaction starting from the diketones (Scheme 1).\textsuperscript{5} The method was used in the stereoselective synthesis of morpholine based natural product chelonin C.

\textbf{Scheme 1}

\begin{align*}
\text{R, R'} &= \text{Alkyl, Aryl, Heteroaryl} \\
X &= \text{NP, S}
\end{align*}

\textbf{References:}

Biphosphines with heterodonor ligands based on bis(imidazol-1-yl) and bis(pyrazol-1-yl)methane backbone: Synthesis and transition metal chemistry

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The curiosity in designing phosphorus based ligands is essentially due to their interesting coordination chemistry and their potential application in various homogeneous catalytic processes. Although bisphosphine ligands with a variety of frameworks are known, the chemistry of bisphosphine ligands based on bis(imidazolyl)methane and bis(pyrazolyl)methane frameworks is not much explored. In the present investigation, the ligands of type $C_7H_6N_4(PPh_2)_2$ [bpizm] (1) and $C_7H_6N_4(PPh_2)_2$ [bppzm] (2) were synthesized in good yield. The reaction of [bpizm] with [M(COD)Cl$_2$] (M = Pd, Pt) in 1:1 ratio afforded mononuclear complexes $[C_7H_6N_4(PPh_2)_2MCl_2]$ (5, M=Pd; 6, M=Pt). The reaction of 1 with AuCl(SMe$_2$) in 1:1 and 1:2 molar ratios afforded colorless mononuclear complex, $[C_7H_6N_4(PPh_2)_2AuCl]$ (7) and a binuclear complex, $[C_7H_6N_4(PPh_2)_2\{AuCl\}_2]$ (8). The reaction between 1 and [Ru($\eta^5$-$p$-cym)(\mu-Cl)Cl]$_2$ in 1:1 ratio yielded a binuclear complex $[C_7H_6N_4(PPh_2)_2\{Ru(\eta^5$-$p$-cymene)Cl$_2\}_2]$ (9), whereas the reaction with [Ru($\eta^5$-$C_5H_5$)(PPh$_3$)$_2$Cl] in 1:1 ratio afforded $[\{C_7H_6N_4(PPh_2)_2\}Ru(C_5H_5)Cl]$ (10). The reaction of 1 with CuBr and CuI in 1:1 ratio yielded 8-membered chelate complexes of type $[(CuX)(CH_3CN)\{C_7H_6N_4(PPh_2)_2\}]$ (12, X = I; 13, X=Br ) and with CuCl in 1:1 ratio a bridged binuclear complex $[Cu_2(\mu-Cl)_2\{C_7H_6N_4(PPh_2)_2\}_2]$ (11). The reaction between 1 and [Rh(COD)Cl]$_2$ or [($\eta^3$-$C_3H_5$)PdCl]$_2$ in the presence of AgOTf in dichloromethane afforded cationic chelate complexes, $[\{C_7H_6N_4(PPh_2)_2\}Rh(COD)]$ OTf (14) and $[\{C_7H_6N_4(PPh_2)_2Pd(\eta^3$-$C_3H_5)\}]OTf (15)$ respectively.
Total Synthesis of the L-Aspargine linked Hexasaccharide from *Methanothermus fervidus*

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Chronic periodontitis is an oral disease, arising from polymicrobial infection. It may cause loss of teeth and has been involved in endocarditis, atherosclerosis, stroke, and preterm delivery of low birth weight infants.\(^1\)\(^2\) There is a little information about the relationship between methanogenic archaea and chronic periodontitis.\(^3\) Although there is a rapid accumulation of information about the archaeal biochemistry, phylogenitic diversity and genetics, little is known about the interactions of archaea with human immune system.\(^4\) Methanogens seem to participate in pathogenicity indirectly through syntrophic relationship. It is plausible that they are secondary colonizers of infection process.\(^5\) Methanogens may play a key role in the mucosal diseases by favouring the growth of certain bacterial groups.

We report herein the first total synthesis of the aspargine linked hexasaccharide through a convergent [3+3] glycosylation approach. Galactosamine derivative was accessed from the glucosamine building block via the Lattrell–Dax inversion of 4-OH and aspargylation was carried out in later stage. Synthesis of 3,3’-di-O-methylated mannose disaccharide and construction of other glycosidic linkages through thioglycoside building blocks.

![Chemical structure of the hexasaccharide](image)

References:
A series of novel N–heterocyclic carbene complexes of iron have been synthesized which includes both achiral and chiral variants. To accomplish the achiral Fe–NHC complexes (1c – 3d) the respective N–benzyl substituted imidazolium salts (1a – 3b) were deprotonated either with LiHMDS or KHMD and the formed carbenes were further metalated with the Fe(II) precursor, cyclopentadienyliron dicarbonyl iodide (I). On the other hand, for the chiral family of Fe–NHC complexes, N–menthyl substituted chiral imidazolium salts (4a – 7b) were prepared from the enantiopure (−)–menthol. And the carbenes were made by deprotonating the chiral ligands and subsequent complexation with the Fe(II) precursor, cyclopentadienyliron dicarbonyl iodide (I) yielded the final chiral Fe–NHC complexes (4c – 7d) in 40 – 78 % yield. All these Fe–NHC complexes were well characterized by the spectroscopic methods viz. $^1$H, $^{13}$C, $^{19}$F, IR and HRMS, elemental analyses and by XRD as well. A brief description about the synthetic protocols, characterization methods and structural aspects of these Fe–NHC complexes would be presented in the poster.

References:
(1) Laszlo Mercs, Organometallics, 2006, 25, 5648-5656
(2) Daniel Serra, Organometallics, 2011, 30, 5568-5577
Synthesis of small molecule analogues of metalloenzymes

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The structural models for the active site of purple acid phosphatase and phosphoesterases, enzymes that degrade organophosphate neurotoxins, has been synthesised. The symmetrical ligands 2,6-\textit{bis}[(2-hydroxybenzyl)(2-pyridylmethyl)aminomethyl]-4-\textit{t}-butylphenol and 2,6-\textit{bis}[(\textit{bis}(2-pyridylmethyl)amino)methyl]-4-\textit{t}-butylphenol and the corresponding unsymmetrical ligands 2-(\textit{N},\textit{N}-\textit{bis}(2-(1-methylimidazol-2-ylmethyl)aminomethyl)-6-(\textit{N}-(2-hydroxybenzyl)-\textit{N}-(2-pyridylmethyl)aminomethyl)-4-\textit{t}-butylphenol , 2-(\textit{N}-(1-methylimidazol-2-ylmethyl)-\textit{N}-(2-pyridylmethyl)-6-(\textit{N}-(2-hydroxyphenyl)-\textit{N}-(2-pyridylmethyl)aminomethyl)-4-\textit{t}-butylphenol and 2-(\textit{N},\textit{N}-\textit{Bis}(2-methylpyridyl)aminomethyl)-6-(\textit{N}-(1-methylimidazol-2-ylmethyl)-\textit{N}-(2-pyridylmethyl)aminomethyl)-4-\textit{t}-butylphenol have been synthesized. The symmetrical ligands have been used to prepare a series of bimetallic complexes to provide models for binuclear metal-oxo centres in proteins, viz. [\textit{Fe}_2(2,6-\textit{bis}[(2-hydroxybenzyl)(2-pyridylmethyl)aminomethyl]-4-\textit{t}-butylphenol)(\textit{\mu}-\textit{OAc})_2]\textit{ClO}_4\cdot\textit{H}_2\textit{O} (1), [\textit{Zn}_2(2,6-\textit{bis}[(2-hydroxybenzyl)(2-pyridylmethyl)aminomethyl]-4-\textit{t}-butylphenol)(\textit{\mu}-\textit{OAc})].\textit{H}_2\textit{O} (2), [\textit{Zn}_2(2,6-\textit{bis}[(\textit{bis}(2-pyridylmethyl)amino)methyl]-4-\textit{t}-butylphenol)(\textit{\mu}-\textit{OAc})_2]\textit{BPh}_4 (3), and [\textit{FeM}(2,6-\textit{bis}[(\textit{bis}(2-pyridylmethyl)amino)methyl]-4-\textit{t}-butylphenol)(\textit{\mu}-\textit{OAc})_2]2\textit{BPh}_4 (where \textit{M} = \textit{Zn}, \textit{Mn} and \textit{Fe}) (4). These complexes would be investigated for their catalytic activity as phosphodiesterase and monoesterase to understand the enzymatic activities of the corresponding metalloenzymes.
Reactivity of Dihaloselenones: Synthesis of Cationic Diselenides and Metal Halide Adducts

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The reactions of various substituted benzimidazolin-2-dihaloselenones with elemental iron and zinc lead to the formation of dicationic diselenides supported with metal halide complexes as counter anion. In these reactions dihaloselenones act as oxidizing agents. The reaction with iron afforded dicaticionic diselenide as a single product while the reaction with zinc gave a mixture of dicationic diselenide and the selenone coordinated metal halide adduct as the products. The structures of the dicationic diselenides have been confirmed by common spectroscopic techniques and single crystal X-ray analysis. The dicationic diselenides have skewed geometry similar to that of H$_2$O$_2$ molecule and the counter anions show tetrahedral geometry.
Magnetic refrigeration is a cooling technology based on magneto-caloric effect (MCE). The change in temperature of the metal complexes in the presence of external magnetic field is due to the change in magnetic entropy during the adiabatic demagnetization. This energy-efficient technique is particularly promising for refrigeration in the ultra-low-temperature region, providing a valid alternative to use of helium-3(3He) which is quickly becoming rare and expensive.\(^1\) To achieve such molecules, the molecule should be possess relatively large ground state \((S = \text{Rln}(2S+1))\) for ferromagnets or ferrimagnets with weak super exchange interaction preferable with zero or negligible anisotropy. Gd\(^{3+}\) is excellent candidate for making 3d-Gd complexes, as Gd\(^{3+}\) is isotropic hence we expect negligible anisotropy where 4f orbitals are buried inside which leads to the weak exchange interactions. To isolate large paramagnetic clusters we have employed the ligand shown in the left. Using this we have isolated single crystals of \([\text{Gd}_4(\mu_4-O)(L)_4(CH_3OH)_4]\text{Br}_2\). The electronic and magnetic properties along with MCE properties of Gd\(_4\) complexes will be discussed.

**Fig 1.** The crystal structure of \([\text{Gd}_4(\mu_4-O)(L)_4(CH_3OH)_4]\text{Br}_2\)

**Reference:**
A Chiral Pool Based Synthesis of (+)- and (−)-Disparlure

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Abstract: A key chiral template, silyl protected vinyl lactone (1), derived from gluconic acid-δ-lactone, was used for the synthesis of sex pheromone of Gypsy moth, (+)-disparlure (2a) and its enantiomer1,2 (2b, Scheme 1). Their syntheses were achieved by successful utilization of cross-metathesis, Wittig olefinations and hetero atom directed reverse Wacker oxidation as key steps.

Scheme 1

References:
Structure Based Virtual Screening for the Discovery of Selective G-quadruplex Binding Fragments

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G-quadruplex nucleic acids are four-stranded Hoogsteen-paired structures formed by regions of guanine rich residues that are stabilized by monovalent cations. G-quadruplex forming sites in the genome include the telomeric region\(^1\), promoter regions of proto-oncogenes and 5’-UTR of mRNAs. Stabilizing such G-quadruplex structures specifically, offers a platform to develop anti-cancer drugs.\(^2\) G-quadruplex structures formed by telomeric and promoter regions exhibit unique structural features such as loops and grooves. We have attempted to find selective groove binding fragments, which can discriminate various quadruplex topologies. Atomic resolution structural data of human telomeric, \textit{C-MYC}, and \textit{C-KIT} G-quadruplex were chosen for virtual screening. ZINC fragment library containing \(~500,000\) fragment-like molecules was screened using Autodock Vina. The ligands found to have good binding affinity for human telomeric (< -6 kcal/mol: \(~46,900\)), \textit{C-MYC} (\(~17,300\)) and \textit{C-KIT} (\(~17,400\)) promoter quadruplexes were segregated. Ligands from each library were docked with other two quadruplexes yielding the final library of \(~100\) potential hits that can discriminate between G-quadruplex topologies. Potential hits are currently being individually evaluated using Autodock 4.2.

References:
Photoluminescence Dynamics of Eu(III) Complex with 9-Oxidophenalenone Near Single Molecule Levels

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The luminescent europium complexes have been thoroughly investigated at ensemble level; however, very scarce literature is available about their PL behavior at single molecule levels. In this work, we have attempted to look at the PL behavior of a luminescent europium complex near single molecule levels. A visible light excitable luminescent Eu(III) complex, Eu(OPH)$_3$.2H$_2$O {where OPH = 9-oxidophenalenone} has been synthesized and characterized. The PL spectrum of the complex at ensemble level displays both broad band (short lifetime) ligand fluorescence and sharp (long lifetime) Eu(III) emission. The spectrally resolved PL imaging was performed near single molecule levels by exciting the energy states of the ligand using 405 nm laser. The PL spectra near single molecule levels display very high degree of heterogeneity. The local environment around the Eu(III) centre near single molecule levels is highly asymmetric as compared to the local Eu(III) environment at ensemble level. The results of the work will be discussed.
Novel Selenium and Tellurium Derivatives of NCN-Pincer Ligand

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Synthesis of new air-stable organoselenium and -tellurium compounds based on the NCN-pincer ligand, arylamine, [2,6-(CH2-NMe2)2C6H3]− described. The compounds include: [2,6-(CH2-NMe2)2C6H3Se]−.Br− (1), [2,6-(CH2-NMe2)2C6H3]2Te (2), [2,6-(CH2-NMe2)2C6H3-Te-n-Bu] (3), [2,6-(CH2-NMe2)2C6H3]2TePdCl2 (4), [2,6-(CH2-NMe2)2C6H3TeO]+.2X− where X = Br (5) and Hg2Cl6 (6). All the compounds were characterized by various analytical techniques including single crystal X-ray analysis (except 3). Compounds 5 and 6 are the novel examples in the class of cationic organotelluroxanes. The detailed synthesis and characterization will be presented in the poster.

Molecular structure of 6
Probing the molecular mechanism of catalytic coupling and ammonia channeling in the PurL protein using statistical coupling analysis

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PurL protein catalyzes the fourth step in purine biosynthesis. It has two active sites about 35 Å away from each other. It is known that ammonia produced in one active site is consumed at the other. Even though the crystal structure of the protein is solved, it is not known how ammonia travels from one active site to the other and how the different domains communicate with each other to carry out the complete reaction. We are using statistical coupling analysis, a method that takes advantage of conservation and correlation patterns in multiple sequence alignments of proteins to find coevolving groups of amino acids called sectors that highlight the functionally and structurally important amino acids so that we can focus the research in those areas. Upon carrying out the analysis on PurL protein we have found sectors that span the length and breadth of the protein and connect the two active sites via sparse yet mostly contiguous routes. These amino acids could be important for catalytic coupling and ammonia channeling. These results are being validated with experiments like Xenon trapping and site directed mutagenesis.
Insights into Channeling of Unstable Intermediates in Purine Biosynthetic Pathway

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In enzymes, substrate channeling is the process by which a reaction intermediate is transported from one active site to another via an intra- or inter-molecular tunnel. These passages have evolved to protect the unstable intermediate from degradation by the cellular environment. In this work using a combination of biochemical analysis and X-ray crystallography we have investigated the mechanism of catalytic coupling and ammonia channeling in the purine biosynthetic enzyme PurL also known as formylglycinamidine ribonucleotide amidotransferase. PurL catalyzes the conversion of FGAR (formylglycinamidine ribonucleotide) to FGAM (formylglycinamidine ribonucleotide) in an ATP assisted fashion.

Two paths for ammonia channelling were proposed by spatial analysis of the protein. Mutational and crystallographic studies along one of the proposed ammonia channel show that, disturbing residues lining the path have varied effect on channel efficiency. Mutation of channel blocking residues at the mouth of the proposed channel results in a slight increase in channelling efficiency. Whereas, constricting the centre of the channel by placing bulkier amino acids results in drastic reduction in activity. Additionally, to understand the mechanism of catalytic coupling we have solved the structure of PurL in various states of ligand occupancy, that is; in the absence and presence of ammonia producer, glutamine, and also solved the structure of PurL complexed with analogue of ATP at a resolution of 3.3 Å.

In this work we have identified one of the channels as the preferred path traversed by ammonia and conclude that tweaking the path followed by ammonia has varied affect on enzyme activity. Additionally, by process of elimination we propose that binding of FGAR is the most likely mechanism for induction of catalytic coupling.
Mixed valence class of transition metal complexes are of great interest since they play a vital role in the biological systems. In recent years they gain wide interest in the field of the material chemistry because of their emerging potential application in quantum computing. There are several experimental and theoretical reports dealing with these classes of systems. These mixed valence complexes have been classified in the three categories which can be found elsewhere. There are several occasion when density functional calculations probes the robustness in understanding of the properties of these complexes. The major issues with theoretical characterizations, no direct methodology yet avail to deal with the excited states which are very essential in studying mixed valence complexes. In this regard we are using time dependent density functional calculations (TD-DFT) to estimate these subtle parameters e.g. vibronic coupling, double exchange along with spin Hamiltonian parameters.

Here we have studied a mixed valence dinuclear complex of (V\textsuperscript{III}-V\textsuperscript{II}) bridged via imidazole moiety reported by Long et al. The antiferromagnetic interaction has been found with a significant delocalization in the ground state. Here we have estimated electron localization, delocalization parameters (double exchange) for all the possible different spin states. All these results including solvent effect on IVCT band for this compound will be presented here.

References:
Regiospecific Synthesis of Arenofurans via Cascade Reactions of Arenols with Morita-Baylis-Hillman Acetates of Nitroalkenes and Total synthesis of Isoparvifuran

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Naphthofuran and benzofuran nuclei are important structural components present in various natural products, drugs and synthetic products and possess broad range of biological activities. Arenofurans are also utilized as fluorescent dyes and probes. Numerous furan containing compounds exhibit anti-cancer, anti-fungal, anti-viral and anti-bacterial activities. Because of their wide range of applications in medicinal chemistry they have been the subject of extensive studies and numerous methods have been developed for their synthesis. Recently, we have reported the possible application of acetates of Morita-Baylis-Hillman adducts of nitroalkenes as bi-electrophiles in the formation of furans, pyrans and imidazopyridines. The strategy involves a cascade Michael-S2'-intramolecular Michael sequence that took place under simple and mild conditions. To further establish the application of MBH acetates of nitroalkenes we have synthesized a variety of arenofurans by the reaction of arenols as bi-nucleophiles with MBH acetates of nitroalkenes. Our methodology is also suitable for the total synthesis of Isoparvifuran (an antifungal agent), which was isolated from the heartwood of Dalbergia parviflora.

![Chemical Reaction Diagram]

References:
Applications of Rauhut-Currier adducts of nitroalkenes for the synthesis of highly substituted furans and decalins

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Furans are the core structure of numerous types of natural products, drugs, biologically active molecules and new synthetic products that are useful in normal life.¹ Numerous furan containing compounds exhibit anti-tuberculosis, anti-psoriatic, anti-tumour, anti-cancer, anti-inflammatory and anti-HIV activities. Decalins are precursors of various natural products, in particular polysterpenoids and steroids.² For example, 1,3-Diaxially substituted trans-decalin compound RU-486 is a potential non-steroidal human progesterone receptor inhibitor. Since furans and decalins are important building blocks of various natural products and biologically active molecules, our group is actively involved in the synthesis of furans from MBH acetate of nitroalkenes.⁴ As a part of our ongoing interest in Rauhut-Currier adducts of nitroalkenes and MVK,⁵ we have developed an efficient method for the synthesis of furan and decalin from dimedone and cyclohexanone, respectively.

References:
The potential of silica nanostructures as scaffolds for construction of light harvesting nanoantennae

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Abstract

Silica nanoparticles have been used as scaffold to establish FRET among organic fluorophores where Fluorescein and Rhodamine B were used as donor - acceptor pair, respectively. The dyes were covalently attached to bi-functional silane coupling agent, 3-aminopropyltriethoxy silane (APTES) forming dye-conjugates. Different donor to acceptor conjugate ratios was co-condensed with silica precursor, tetraethoxysilane (TEOS) by sol-gel method. The steady state spectroscopic measurements of the silica-dye nanoconjugates reveal the possibility of energy transfer. The time-resolved study shows faster fluorescence decay of donor which further supports the presence of resonance energy transfer to the acceptor.
Synthesis and Spectrally Resolved Single Particle Photoluminescence Imaging of CdS Quantum Dots

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Abstract:
ZnO is a wide band-gap (3.37 eV) semiconductor with large exciton binding energy (60 meV). Steady state Photoluminescence spectra (λ_{ex} 320 nm) give two emission bands-weak transition in the UV (~360 nm) region and a broad red-shifted band covering the entire visible region. The broad visible emission is composed of multiple closely lying defect states situated in between valence band and conduction band. The inhomogeneous broadening effect due to different factors can be known only if the nanocrystals can be probed at the single particle level. Excitation using 488nm laser enabled direct population of defect states. The spectral line width associated with each single particle spectrum of ZnO nanocrystal was found to be inherently broad which establishes the presence of multiple closely spaced defect energy levels associated with each ZnO nanocrystal. CdS is a direct band-gap (~2.42 eV) semiconductor. 405 nm laser enables the study of both band-edge and defect emission simultaneously which was impossible in the case of ZnO.

References:
Layek, A; De,S; Thorat,R; Chowdhury,A; J.Phys.Chem.Lett. 2011,2,1241-1247
Influence of geometry on the anisotropy of lanthanide metal complexes

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Single-molecule magnets (SMMs) exhibiting slow paramagnetic relaxation of the magnetization have attracted increasing interest because of its potential applications in storage devices, refrigerants, spintronics, spin valves etc. at a molecular level. For such molecules, the magnetization relaxation depends on the effective energy barrier, which is significantly altered by the anisotropic parameter and spin ground state.\[1\] 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. 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 molecular magnets are promising candidate to enhance effective energy barrier however the dominant quantum tunnelling of magnetization causes multiple relaxation pathways which hinders energy barrier to be large.\[3\] 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 Schiff base ligands. The preliminary magnetic properties of the isolated complexes will be discussed.

\[A\] \[B\]

Figure 1: a) Crystal structure of \(A) [La(L)_3(NO_3)_3] (1) B) [Ln(L)_2(NO_3)_3] \) where \(Ln = Gd^{3+} (2) \) or \(Ho(3) Tb^{3+} (4), Pr^{3+} (5) \)

References:
A General and Efficient Defromylation and Dehydroxymethylation Reaction using Pd(OAc)\textsubscript{2} as Precatalyst

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A facile decarbonylation reaction of aldehyde has been developed by employing Pd(OAc)\textsubscript{2} as the catalyst. In mechanistic interest, it is observed that an oxidative addition at the C–H bond of aldehyde, followed by rate determining CO transfer to the palladium centre and reductive elimination to form the final deformylated product have been proposed based on the mechanistic studies. We have also discovered that Pd(OAc)\textsubscript{2} with Na\textsubscript{2}CO\textsubscript{3} is capable for one pot dehydroxymethylation of primary alcohol. It has been observed that dehydroxymethylation is going through two successive steps (1) oxidation of R–CH\textsubscript{2}OH to R–CHO (2) and subsequent decarbonylation of R–CHO to R–H. Due to its simplicity, we expect to find its application in synthetic set up, both in industry and in academia.

References:
Iron-Catalyzed Direct C–H Arylation of Heterocycles and Quinones with Arylboronic Acid

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Biaryl compounds (Ar’–Ar) are conventionally synthesized by Suzuki coupling reaction involving arylboronic acids and aryl halides. Synthesis of related heteroaryl-aryl (Het–Ar) and arylatedquinones (Quin–Ar), which are ubiquitous in bioactive and pharmaceutical compounds, are somewhat problematic possibly due to the coordination of heteroatom(s) with the metal catalyst. Arylation of C–H bond to generate these Het–Ar and Quin–Ar compounds have received great attentions to achieve sustainable goals in synthetic chemistry. Despite significant advances, arylation of a broad range of Het–Ar and Quin–Ar remain a challenging task.

Herein, we report direct C–H arylation of various heterocycles and quinones with arylboronic acid by using an inexpensive iron catalyst, Fe(NO₃)₃ and an co-oxidant, persulphate. This protocol enables rapid synthesis of a variety of Het–Ar and Quin–Ar compounds which is otherwise difficult to synthesize by conventional methods. The reaction is also applicable for large-scale synthesis and is expected to find application due to its operational simplicity.

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\text{Het} \overset{H}{\longrightarrow} \text{Ar} + \text{Quin} \overset{H}{\longrightarrow} \text{B(OH)}_2 \xrightarrow{\text{K}_2\text{S}_2\text{O}_8, \text{air}, 1:1 \text{ TFT: water}} \xrightarrow{\text{TFA, RT-70} ^\circ\text{C}, 12-24 \text{ h}} \text{Het} \overset{Ar}{\longrightarrow} \text{Quin} \overset{Ar}{\longrightarrow}
\]

References:
Synthesis of organoimidido derivatives of polyoxometalates

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Organoimidido derivatives of polyoxometalates with a remote, active functional group may be exploited to prepare covalently-linked nano-dumbbells, polymeric chains and even networks of polyoxometalates in more controllable manners. In this regard, we have prudently introduced the alkyl unit in the ortho position of the aryl ring of the arylimido ligand to provide enough steric hindrance to strengthen and effectively protect the Mo-N bonds. Herein, we report organic-inorganic polyoxometalate derivatives of 2,2’,6,6’-tetraisopropylbenzidine and 4-bromo-2,6-diisopropylaniline. Compounds have been characterized by analytical and spectroscopic methods and further confirmed by single crystal X-ray diffraction technique.
Calix[6]arene conjugate as sensor for La$^{3+}$ and its complex for F$^-$

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Both cations and anions play important role in biology and environment, wherein the lanthanides and halides are not exceptions. Lanthanides are being used as structural and functional substitutes for different ions in biology. La$^{3+}$ accelerates the phosphodiester hydrolysis and its complexes are found to be useful in the diagnosis of hyper phosphatemia. Concentration dependent effect of LaCl$_3$ on lipid peroxidation and ATPase activity has been shown in the plasma membranes of rice seedling roots. Fluoride is one of the most significant anion in the biological systems due to its role in dental care and in the treatment of osteoporosis. Excess fluoride exposure may cause collagen breakdown, bone disorders and immune system disruption. Thus the development of synthetic receptors for the selective recognition of lanthanum as well as fluoride continues to intrigue the researchers. A newly synthesized 1,3,5-tris-triazole linked picolylimine conjugate of calix[6]arene (L) has been shown to be selective towards La$^{3+}$ by turn on fluorescence with ~70 fold enhancement and emits blue fluorescence and can sense this ion up to 65 ± 5 ppb (0.49 µM). The in situ complex of L with La$^{3+}$ senses fluoride ion. The species of recognition of La$^{3+}$ by L is modeled by HF computations to have a mono capped twisted square antiprismatic geometry with N$_6$O$_3$ core. Thus L is a potential sensor for La$^{3+}$ followed by F$^-$ in a sequential manner and perhaps finds application in biological and ecological systems.

References:
Solvation Structures and Dynamics of Magnesium Chloride (Mg2+-Cl-) Ion-Pair in Water-Ethanol Mixtures

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Magnesium dication as well as hydrated magnesium dication play very important role in the unfolding process of macromolecules such as proteins, DNA, RNA etc. Many Chemical as well as biological reactions are studied in water-ethanol mixtures. Therefore, the study of solvation structure of magnesium chloride in water-ethanol mixtures is very important for understanding of biological reactions. We have performed constrained molecular dynamics simulations of magnesium chloride in water-ethanol mixtures. During this study, we notice that, as the mole fraction of ethanol increases, the depths of the minima of the contact ion pair (CIP) and solvent shared ion pair (SAIP) increase, but the depth of the CIP minimum increases more in comparison to the SAIP minimum. This shows that ion pairing becomes more favorable with an increase in the mole fraction of ethanol. There is sharp decrease in the depth of the CIP minimum as compared to the SAIP minimum in the mole fraction range of water between 0 to 0.40, which shows that adding even a slight amount of water in pure ethanol tends to decrease the relative stability of the Mg2+-Cl- CIP in comparison to the SAIP. This result is also confirmed by data from the running coordination numbers (RCNs), which shows a water molecule in the coordination shells (RCN>=1) even when the mole fraction of water in the bulk mixture is only 0.2. The local percentage of water molecules in the first solvation shell of ions is significantly greater than in the bulk. The diffusional behavior of the solvent molecules in the solvation shells of the ion-pair indicates that the ion as well as the first solvation shell of the ions diffuses at a rate which is about 1/3rd of the rate of the bulk solvent value. Also, the diffusion constant of bulk water in the mixtures is greatly reduced compared to the bulk pure solvent value.
Fluorescence modulation and electron transfer reactions in hydrogen bonded complexes of substituted phenylacetylenes

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The fluorescence behavior of fluorophenylacetylene complexes changes with their intermolecular potentials as well as their geometries with bonded ligands. In case of 2, 6-difluorophenylacetylene all C-H_{ac}···O bonded complexes are non-fluorescent whereas C-H_{ac}···N are fluorescent. In 3-fluorophenylacetylene all C-H_{ac}···N complexes are fluorescent but the fluorescence behavior of C-H_{ac}···O bonded complexes changes with the strength of the ligand. The red shift of the acetylenic C-H stretch with respect to proton affinity of the central atom of the bonded ligand correlates the fluorescence properties of the fluorophenylacetylenes.

The electron transfer from the bonded amine ligand to parent complex of fluorophenylacetylene happens in the excited (ionic) state for the amine complexes. This is because the ionization potential of amines is lower compare to the parent fluorophenylacetylene molecules.
MATI Spectroscopy of Fluorophenylacetylenes

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MATI (Mass Analysed Threshold Ionization) spectroscopy is a two colour R2PI process to probe ro-vibronic states of ions and the exact ionization energy (IE) of molecules with an accuracy of ±3-5 cm⁻¹. MATI of 2-Fluorophenylacetylene (2FPHA) molecule has been studied extensively. Introduction of Fluorine in Phenylacetylene band origin transition red shifts to 289 cm⁻¹ and IE blue shifts to 215 cm⁻¹. Theoretical calculation has been done to assign the bands obtained in the spectra for ground state, first excited state and cationic state. It is seen that breathing mode (1¹₀) for this molecule has considerable amount of blue shift in cationic state. This accounts for the fact that in 2FPHA bonds are more rigid in cationic state than ground state. Red shift in IE also accounts for this fact. These experimental finding may be attributed to gain more insights about the nature of substitution in aromatic molecules.