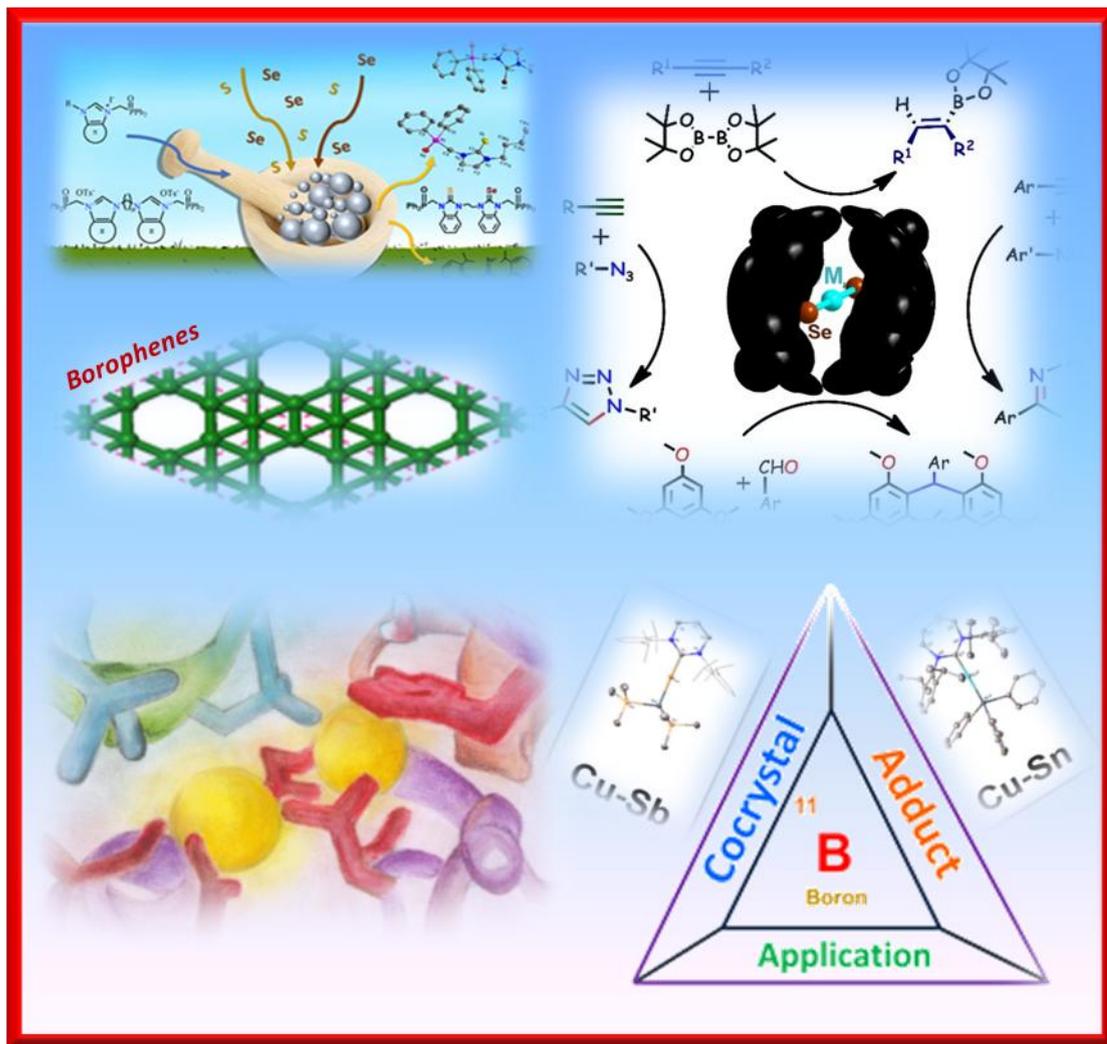


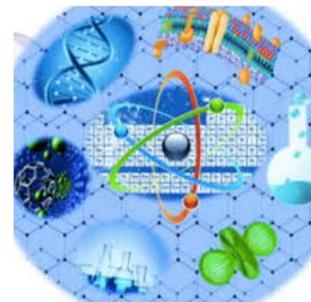
Main-group Molecules to Materials-4

9-12th February, 2025

Abstract Booklet



Department of Chemistry
Indian Institute of Technology Bombay
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Preface

On behalf of the Organizing Committee, we are delighted to welcome you to the 4th edition of the International Conference on Main-Group Molecules to Materials-4 (MMM-4) being organized at the Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai, scheduled on February 9-12th, 2025. As a part of the conference proceedings, we are thrilled to present this abstract book showcasing innovative research and groundbreaking discoveries in the field of the main group chemistry. The main group chemistry has seen a resurrection, from the shadows of the long dominated transition metal chemistry, over the last decade in the fields of materials, energy, catalysis, and to some extent in medicine, claiming the spotlight of the research in the near future. This conference brings together leading scientists, researchers, postdoctoral fellows, doctoral students, and industry experts from India and worldwide to share the latest knowledge, discoveries, and developments, that would inspire future advancements. This collection of abstracts is the finest exposition of the latest state-of-the-art discoveries in the main group chemistry and the related domains, thus providing valuable insights and future directions to this rejuvenating area of main group chemistry.

Thank you for being a part of this exciting international conference!

Professor Prasenjit Ghosh, Convener

Professor Gopalan Rajaraman, Co-convener.

Professor Deepti Kalsi, Co-convener

Schedule

MMM4 Conference

9th to 12th February 2025

| Time | 10 th Feb | 11 th Feb | 12 th Feb |
|--------------------------------------|--|---|---|
| Session 1 09:00-09:40 AM | B. Nag Auditorium Chair: M. Ravikanth PL3: Balsji R. Jagirdar | B. Nag Auditorium Chair: Venkateswaru Yalagadda PL5: K. C. Kumara Swamy | B. Nag Auditorium Chair: Krishna P. Kollappan PL7: R. Boomi Shankar |
| Session 2 (9:45-11:00) AM | B. Nag Auditorium Chair: Nandita Madhavan | 2A B. Nag Auditorium Chair: Rajarshi Chakrabarti | 2A B. Nag Auditorium Chair: Srinivasan Ramakrishnan |
| 09:45-10:10 AM | IL1 Gilles Alcaraz | IL28 Srinivasan Natarajan | IL55 Sanjog S. Nagarkar |
| 10:10-10:35 AM | IL4 Azal Ansari | IL31 Vadapalli Chandrasekhar | IL58 Moumita Majumdar |
| 10:35-11:00 AM | IL7 Adinarayana Doddi | IL34 Jitendra K. Bera | IL61 Selvakumar Karubhapanandi |
| Tea Break (11:00-11:20 AM) | | | |
| Session 3 (11:20-13:05) AM | 3A B. Nag Auditorium Chair: Sanjog S. Nagarkar | 3A B. Nag Auditorium Chair: Vadapalli Chandrasekhar | 3C Room 22 Chair: Santosh J. Gharpure |
| 11:20-11:45 AM | IL10 Freder Jakle | IL37 Kyle G. Pearce | IL39 Viswanathan Baskar |
| 11:45-12:10 AM-PM | IL13 Stephen Hill | IL40 K. Geetharani | IL42 Gouriprasanna Roy |
| 12:10-12:35 PM | IL16 Krishnamurthi Muralidharan | IL18 Senthikumara Muthalah | IL45 Sangit Kumar |
| 12:35-01:05 PM | ERL (1-3) | ERL (7-9) | ERL (16-18) |
| 01:05-01:15 PM | ERL (4-6) | ERL (10-12) | ERL (13-15) |
| Sponsors Presentation | | | |
| Lunch break (01:15-02:00 PM) | | | |
| Session 4 | Photo Session (02:00-02:15 PM) Poster Presentation (02:15-03:40 PM) Chair: Freder Jakle, Krishnamurthi Muralidharan, Prabusankar G. K. Geetharani, Anukul Jana and Shabana Khan | Poster Presentation (02:00-03:40 PM) Tea Break (03:40-03:55 PM) | Poster Presentation (02:00-03:40 PM) Tea Break (03:40-03:55 PM) |
| Session 5 (03:55-05:10) PM | 5A B. Nag Auditorium Chair: Achintya Kumar Dutt | 5A B. Nag Auditorium Chair: Anil Kumar | 5C Room 22 Chair: Amber Jain |
| 03:55-04:20 PM | IL19 Sanjay Singh | IL46 Malalichamy Sathiyendran | IL48 Nalassamy Palanisami |
| 04:20-04:45 PM | IL22 David Liprot | IL24 Samir Kumar Sarkar | IL51 Venkateswara Rao Pedireddi |
| Session 3 (4:30-05:50) PM | IL25 Prabusankar G. | IL26 M. Mujahuddin Siddiqui | IL54 Sharanappa Nembenna |
| 04:30-05:10 PM | PL1: Marwanji S. Balakrishna | B. Nag Auditorium Chair: R. Muregavel PL2: Michael L. Klein | B. Nag Auditorium Chair: Irithi N. Namboothiri PL6: Mairfred Scheer |
| 05:10-05:50 PM | PL2: E. D. Jenmis | B. Nag Auditorium Chair: R. Muregavel Conducted by R. Muregavel | B. Nag Auditorium Chair: R. Muregavel |
| Dinner (07:30-09:00 PM) | Dinner (07:30-09:00 PM) | Dinner (07:30-09:00 PM) | Dinner (07:30-09:00 PM) |

PL = Plenary Lectures (7)
IL = Invited lectures (63)
ERL = Early Research Career Lectures (27) (8min + 2min)



Cyclodiphosphazanes: Versatile Inorganic Ring System

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Cyclodiphosphazanes, also known as diazadiphosphetidines, are saturated inorganic ring systems containing alternating trivalent phosphorus and nitrogen atoms. With a rigid planar structure and moderately stable P–N bonds, cyclodiphosphazanes have shown versatility not only in coordination chemistry as both neutral and anionic ligands but also as useful scaffolds in supramolecular chemistry, resulting in a plethora of molecules with interesting structural features. The fundamental feature that distinguishes cyclodiphosphazanes from other classes of compounds is their ability to form stable, neutral cyclic structures, where the nitrogen and phosphorus atoms are held together by strong covalent bonds. This unique bonding environment leads to distinct electronic properties and reactivity profiles that set cyclodiphosphazanes apart from other organophosphorus and organonitrogen compounds. Their utility in generating several 3D-coordination polymers including those with sodalite and diamondoid structures, cyclodiphosphazane based N-heterocyclic carbenes and stable biradicaloids, highlight the versatility of these novel phosphorus–nitrogen cyclic compounds. The key points on the empirical model proposed to highlight the coordinating ability of cyclodiphosphazanes to build soft–soft MOFs and an analysis of pertinent structural features will be presented.

B_3H_5 and $B_3H_6^+$, Isoelectronic to Cyclopropenyl Cation, form the basis for Structural Chemistry of Boron

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A large part of the chemistry of boron, (eg with one, two or three boron-atom-containing molecules) can be understood using the analogy to carbon chemistry. The polyhedral boranes and related molecules call for a different model of bonding. Wade's Rules, Rudolf diagram and the mno Rule relate these polyhedral boranes to 3D allotropes of boron.¹ We propose here that B_3H_5 and $B_3H_6^+$ are the starting point in the structural analysis of boron chemistry.² Sequential replacements of the bridging hydrogens by BH units in the C_{3v} $B_3H_6^+$ could generate all structures of the Rudolf diagram. For example, replacement of bridging hydrogens of $B_3H_6^+$ by BH and bringing them to bonding distances lead to the octahedral $B_6H_6^{2-}$. On the other hand if we start from the flat B_3H_5 and replace the H by BH groups we end up in borophenes. If the same process is followed with the flat $B_3H_6^+$, we get borophenes with no holes. We use Orbital Engineering to explore infinite variety of 2D-

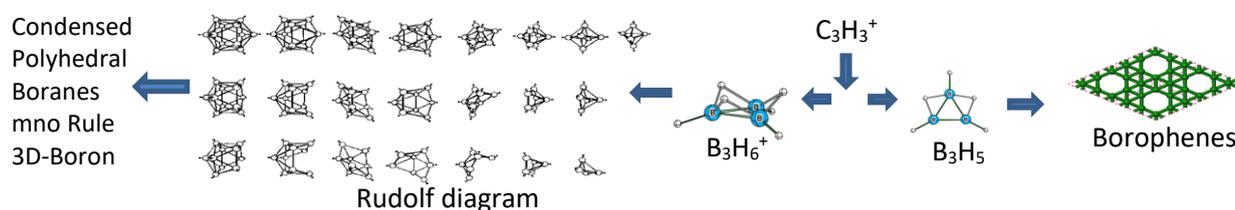


Figure 1 $B_3H_6^+$ and B_3H_5 form the structural link between 3D and 2D boron chemistry.

allotropes of boron; variations are plenty within the combination of interlayer bonds, and hole density.³⁻⁷ Traditional van der Waals interactions and localized 2c-2e bonds between stacks of borophenes allow potentially infinite variety of "borophites".⁷⁻⁹

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Activation of the H–H bond in molecular hydrogen: dihydrogen versus dihydride equilibrium

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Studies towards binding and activation of the H–H bond in molecular hydrogen is vital to energy storage and catalytic hydrogenation of organic substrates.¹ Hydrogenation is perhaps one of the massive 'human-made' chemical reactions in the world. Splitting a dihydrogen molecule apart in a controlled fashion has deep implications in the field of homogeneous hydrogenation catalysis. In this context, a fundamental question that has remained unanswered for several decades is: "at what stage in the reaction coordinate for the oxidative addition of H₂ to a metal center could the H–H bond be considered to be broken?" This fundamental question has been under focus of study for several research groups around the world. If the point at which the H–H bond is found to be cleaved, it is a major breakthrough and could prove to be extremely useful from the standpoint of catalysis leading to the most efficient hydrogenation catalysts. We recently discovered a unique H₂ pressure dependence on the dihydrogen \rightleftharpoons dihydride equilibrium which is hitherto unknown. Systematic variation (raising) of the H₂ pressure on a system wherein the H–H bond is intact could drive the equilibrium towards the oxidative addition product, the dihydride. The results of these experiments will be discussed in the context of the implications in hydrogenation catalysis.

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Computation as a Route to Understanding & Discovery in Chemistry.

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Mathematics and Physics have had a long and synergistic relationship, going back even further than Isaac Newton's contributions to mechanics, three centuries ago. Chemists have not been shy about adopting contributions from Mathematical Physics. The kinetic theory of gases, advanced by Daniel Bernoulli, James Clerk Maxwell, and Ludwig Boltzmann is an early example. The seminal works of J. Willard Gibbs on Thermodynamics, which transformed Physical Chemistry into a "rigorous deductive science," have stood the test of time. Cross fertilization has not been in one direction. Michael Faraday's experiments inspired Maxwell to give birth to the Theory of The Electromagnetic Field. Statistical Mechanics and Statistical Thermodynamics, which originated from Mathematical Physics, were adopted by Physical Chemists, almost immediately. Notably, Chemists were quick to embrace the ideas of Quantum Mechanics. The marriage of Physical Chemistry and Physics was arguably consummated in 1933 with the creation of The Journal of Chemical Physics. Indeed, it is instructive, almost one century later, to read some of the wonderful publications from the first volume of this journal. Five of the authors in Volume-1, subsequently won Nobel Prizes: Harold Urey 1934; Peter Debye 1936; Linus Pauling 1954; Robert Mulliken 1966; and John Van Vleck 1977. Since its inception, the Chemistry Nobel Prize has been awarded about once every decade for "Theory". Recognition of Computational Chemistry obviously had to wait for the birth (1940's) and subsequent proliferation (1970's) of computers. The first explicit recognition of "Computation" by the Nobel-Chemistry-Committee was in 1998, with the Nobel Chemistry Prize being awarded jointly to physicist, Walter Kohn for "Density Functional Theory" and chemist, John Pople for "Computational Methods in Quantum Chemistry". Fifteen years later, the Chemistry Nobel Prize in 2013, recognized the contributions of computation to Chemical Biology. Specifically, this award was given to Martin Karplus, Michael Levitt, and Arieh Warshel for "Multiscale Models for Complex Chemical Systems." The 2024 Chemistry Nobel Prize was awarded to David Baker, for "Computational Protein Design" plus Demis Hassabis and John Jumper for "Protein Structure Prediction." My talk will use selected examples to illustrate the impact of computational methodologies have had on Chemistry. Examples will be shamelessly biased by my own interests.



Phosphorus/Sulfur Containing Allenes/Alkynes/Alkenes as Reacting Partners in Annulation Reactions

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Allenes and alkynes, tethered by phosphoryl or sulfonyl group, are prone to exhibit reactivity that could often be different from normal allenes/alkynes. Examples of the type of reactions that will be discussed in this talk are depicted in Figure 1.¹⁻⁴

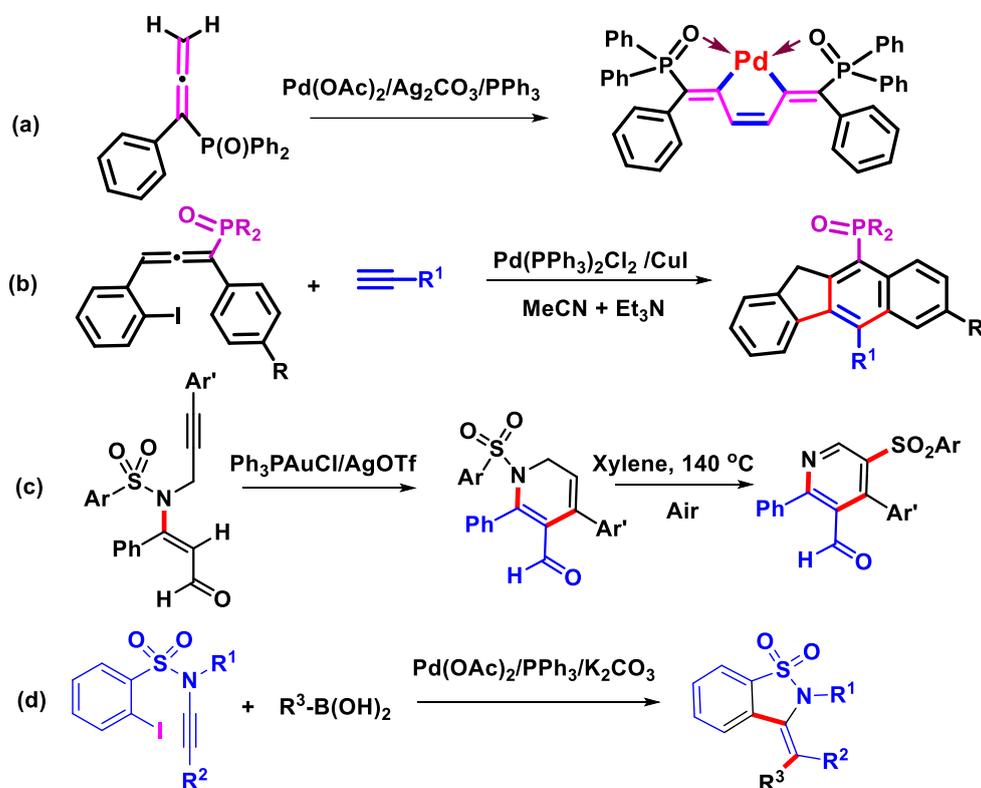


Figure 1. Selected reactions of allenes/alkynes tethered with phosphoryl/sulfonyl scaffolds

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Highly reactive Monomers – Building Blocks for novel Polymers and Materials

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Parent compounds of pentels and triels (13/15-compounds) that are only hydrogen-substituted are direct congeners of hydrocarbons that possess both similar and, due to their differences in reactivity, different properties in relation to hydrocarbons and are of interest as regards e.g. the build-up of inorganic polymers and for semiconductor technology. The talk will focus on the synthesis and characterization of first parent chain compounds of the pentelyltriellanes (13/15-compounds) with heavier pentels and triels as well,¹ and the directed insertion of group 14 parent units (EH₂-units) in order to access unprecedented compounds of this class with group 13/14/15 sequences.² A potential use to generate polymers will be discussed. (cf. Figure 1).³

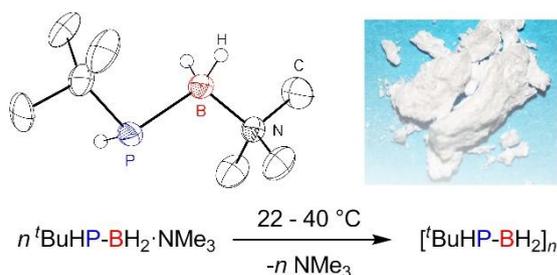


Figure 1 Head-to-tail polymerisation of a phosphanylborane monomer

Moreover, polyphosphorus ligand complexes, like $[\{\text{Cp}^*\text{Mo}(\text{CO})_2\}_2(\mu, \eta^2\text{-E}_2)]$ ($\text{E} = \text{P}, \text{As}, \text{Sb}$), can be used as starting materials for the synthesis of unprecedented organometallic-organic hybrid materials.^{4,5} The perspectives of this research area will be discussed.

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Molecular Ferroelectrics Based on Neutral Boron Compounds

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Materials that display ferro- and piezoelectric are attractive for technology applications in non-volatile memory devices, electronic sensors, electro-optical systems and as piezoelectric energy harvesters, which are popularly denoted as piezoelectric nanogenerators. Small molecules with organic and hybrid organic-inorganic backbones exhibiting ferroelectric and piezoelectric properties are of major attention as alternatives for ceramic materials for their ease of synthesis and in the preparation of flexible devices based on them.¹ We have been interested in the development of novel molecular ferroelectrics with single, two-component and multi-component assemblies derived from main group scaffolds. We have synthesized several high-performance ferroelectric materials based on phosphorus-centered motifs, such as organo- and amino-phosphonium cations supported by borates and organo-phosphate as anions. Owing to the renowned interest in obtaining single-component and neutral ferroelectrics, we turned our attention towards boron-centred compounds such as Lewis acid-based adducts and boronic acids and its co-crystals as stable platforms for obtaining ferroelectric materials for piezoelectric energy harvesting applications (Figure 1). Some recent significant results from our group in this regard are covered in this presentation.²

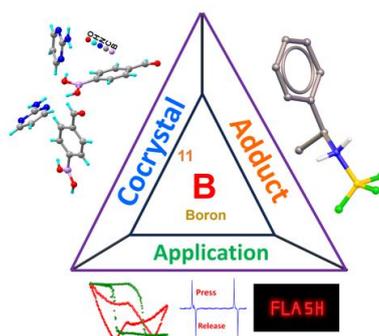


Figure 1 Schematic showing the use of neutral boron-compounds as ferro- and piezoelectric materials.

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Monosubstituted Boranes and Aminoboranes in Hydroboration and Boron-containing Polymers

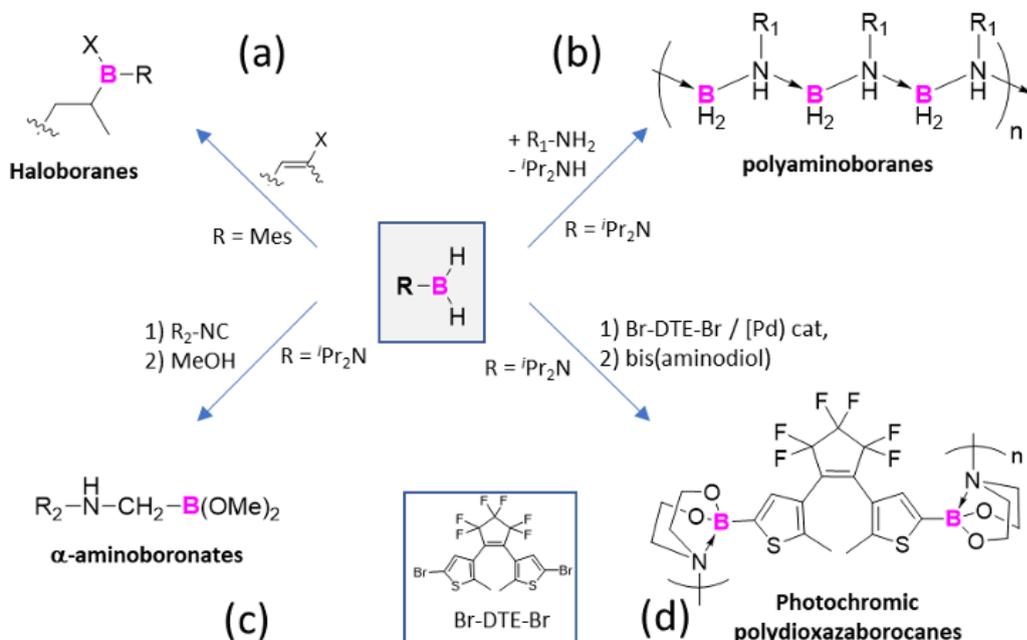
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Monosubstituted boranes have received relatively little attention, despite the many advantages they offer as synthetic tools and as building blocks for new materials development. We are constantly working to understand the mechanisms involved in the use of this family of compounds, in order to optimize their use and the properties of the molecules and materials obtained.

Through 4 examples of reactivities and by tuning their intrinsic Lewis acidity, we will illustrate the synthesis and formation mechanism of mesityl(haloboranes)¹ (a) and polyaminoboranes²⁻³ (b). The easy synthesis and behavior of α -aminoboronates⁴ (c) will also be discussed, as will that of photochromic polymers based on dithienyethene units incorporating dioxazaborocane type connectors⁵ (d).



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Main-group Complex Catalyzed Small Molecule Activations: Computational Mechanistic Studies

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Recently, there has been a surge of interest in employing main group species in activating small molecules including H₂, CO₂, N₂, N₂O and other greenhouse gases.¹ It is evident from the gradually increasing realization that the chemistry of the heavier main group species resembles closely to that of transition-metal complexes.² The constant increase of greenhouse gases, particularly CO₂, in the atmosphere has resulted in adverse environmental effects worldwide in the form of global warming.³ Scientists from diverse disciplines have engaged themselves in devising efficient protocols to sequester CO₂ and subsequently convert them to value-added chemicals. Since 2011, our group is committed to unravel the mechanistic understanding of small molecule activation using computational methodologies in presence of some unique main group complexes. In today's presentation, I will discuss one of our recent examples on the use of NHC stabilized germa-acylium ion and gerymiumylidene species in catalytic activation of CO₂ and other small molecules leading to chemical feedstocks.⁴ The polarized Ge=O bond in the germa-acylium ion was used to activate CO₂ and silane, thus mimicking the behavior of transition metal oxides. If time permits, we will additionally showcase the efficacy of alkaline earth metal complexes in catalytic alkene and alkyne hydroboration reaction.⁵

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Maximizing the Magnetic Anisotropy in Four-Coordinate Cobalt(II) Single-Ion Magnets

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A comprehensive understanding of the ligand field and its influence on the degeneracy and population of d-orbitals in a specific coordination environment are crucial for the rational design and enhancement of magnetic bistability.¹⁻² Research on 3d-single-ion magnets (SIMs) has revealed that a large negative zero-field splitting (D) besides a high-spin ground state (S) is the essential requirement to realize a high anisotropic energy barrier (U_{eff}) for slow magnetization reversal. To add further understanding of the underlying factors that affect magnetic anisotropy, we have investigated a family of four-coordinate dianionic mononuclear Co(II) complexes with the general formula $[\text{L}_2\text{Co}][\text{X}]_2$ (where L is a diamido ligand and X are counter-cations). These complexes exhibit a pronounced variation in the magnetic anisotropy which can be directly correlated to the local dihedral angle (δ) (Figure 1). The study further shows that slow magnetic relaxation can be switched “on” and “off” by carefully manipulating the dihedral angle.³ A combination of single-crystal synchrotron X-ray diffraction for the determination of experimental electron density (EED) and polarized neutron diffraction (PND) that quantifies the magnetic anisotropy provides key information about d-orbital populations and the magnetic anisotropy tensor.⁴ We will also present a strategy to enhance the SIM properties of 3d metal complexes with hard O-donors by modulating the ligand field character via the coordination of diamagnetic ions and the benefit of robust metalloligands in that regard.⁵

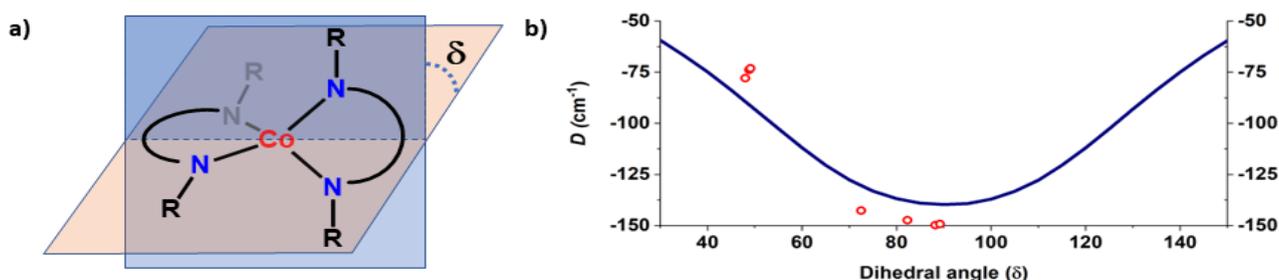


Figure 1. (a) Schematic representation of $[\text{L}_2\text{Co}][\text{X}]_2$ core elucidating the dihedral angle (δ). (b) D plotted as a function of the dihedral angle. The blue line shows the CASSCF calculations with rotated geometries starting from an idealized D_{2d} geometry.

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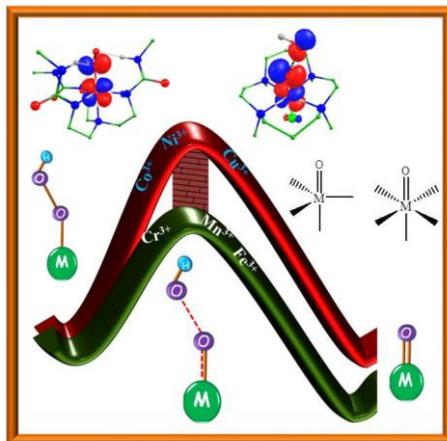
Understanding the Formation of High Valent Metal-oxo Species by using DFT Approach

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Heme and non-heme metal-oxo/hydroxo metalloenzymes are leading intermediates to involve in participation of catalytic transformation such as hydroxylation, epoxidation and C-H activation of aliphatic/aromatic hydrocarbons.¹⁻⁴ In the past decades, these bio-mimetic complexes have been synthesized and several high-valent metal-oxo/hydroxo complexes are spectroscopically detected and for some even X-ray structures are available, their catalytic selectivity, efficiency and robustness is diverse.²⁻⁴ In this presentation, we will describe our research efforts to underpin the formation of high-valent metal-oxo oxidants by the O-O bond cleavage of metal hydroperoxo species and our theoretical findings also illustrate the concept “oxo wall”.³⁻⁵



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Mixed Donor Pincer Manganese(I) Catalyst for the Chemoselective Hydrogenation

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Developing transition metal catalysts based on earth-abundant metals is important to attain sustainable and environmentally benign chemical transformation. In this direction, transition metal catalysts based on manganese have given considerable attention, particularly for the chemoselective hydrogenation at mild conditions. To this end, our research activities have been focused on the design and development of suitably ligated manganese catalysts for the chemoselective hydrogenation of various unsaturated bonds (Figure 1).^{1,2} In this presentation, design and synthesis of various manganese-based catalysts and their application towards chemoselective hydrogenation of α,β -unsaturated ketones, amides and epoxides will be discussed. The applicability of the method for the synthesis of biologically active compounds will be highlighted. In addition, the focus will be paid to the mechanistic aspects of these reactions. Overall, a comprehensive catalyst development, catalytic scope, and reaction mechanism of the manganese-catalyzed hydrogenation under mild conditions will be discussed.

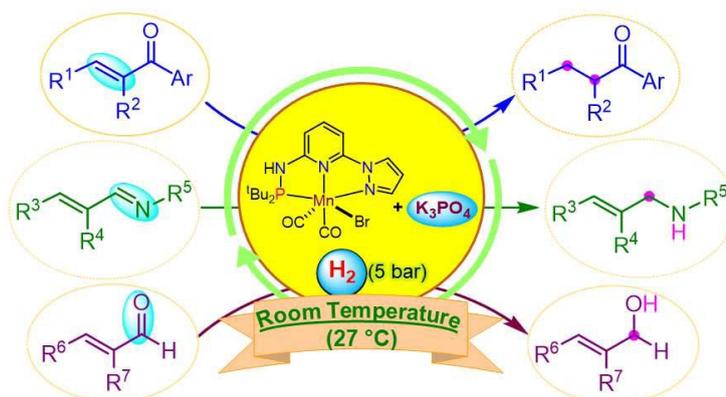


Figure 1 Manganese(I)-catalyzed chemoselective hydrogenation.

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Design and Synthesis of Pyridinamine Scaffold of Diselenides and their Biological Activity

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A facile method for synthesizing biologically active pyridinamine-based organoselenium derivatives i.e. 2-amino pyridine diselenide derived from the 2-halopyridinamines followed by the hydrazine reduction method. The method involves treating 2-halopyridinamines with Se^{2-} which was generated in situ from selenium and a reducing agent in the presence of the base alkaline hydroxide. The synthesis became much more straightforward when we optimized the reaction conditions. Furthermore, the product was obtained with a yield of about 74% in pure form without the need for column chromatography. Using this methodology, we have successfully synthesized hitherto unknown compounds 6,6'-diselanediybis(pyridin-2-amine) and 6,6'-ditellanediybis(pyridin-2-amine). Moreover, the synthetic methodology worked well for the compound 2,2'-diselanediy bis(pyridine-3-amine) which was known previously with a low yield and laborious methodologies. Also, the synthesized 2,2'-ditellanediy bis(pyridin-6-amine), which was unachievable by conventional methods was successfully synthesized using this procedure. Synthesized compounds were studied for their glutathione peroxidase (GPx)-like antioxidant activities using coupled reductase assay. It was observed that all compounds exhibited greater GPx-like antioxidant activity than diphenyl diselenide which was used as a reference. To understand the mechanism and find out the intermediates involved during the reaction was further analyzed by ^{77}Se NMR spectroscopy. Cytotoxicity assessments of antioxidants have also been carried out using MTT assay. They also evaluated for anticancer activity. Compounds were further authenticated by single-crystal X-ray crystallography.

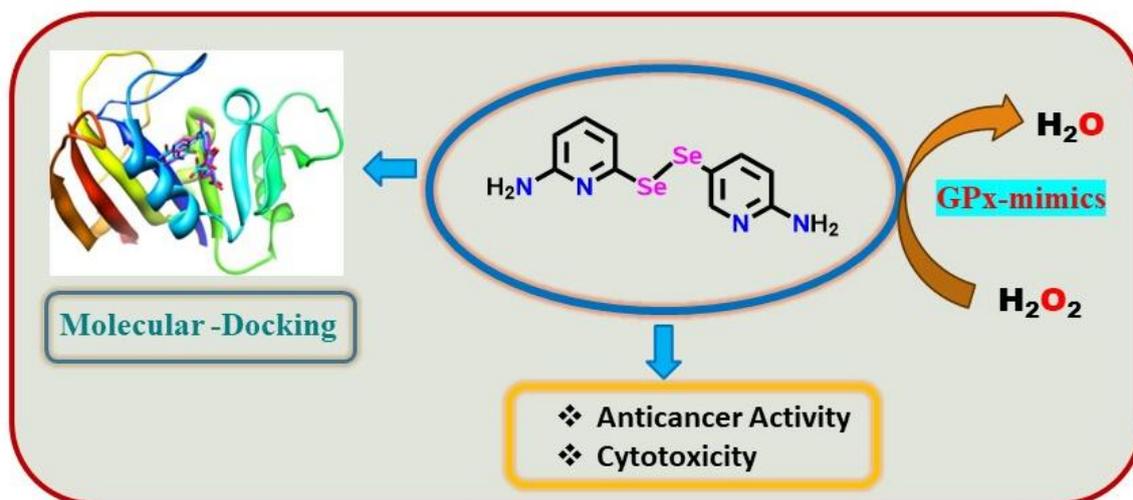


Figure 1. Synthesis and biological activity of 2-aminopyridine diselenide

Keywords: Organoselenium derivatives, Pyridine diselenide, GPx-mimics, Docking, anticancer activity.

References: *New J. Chem.*, 2022, 46, 18447–18457

Novel P(III) Species Bearing Reactive Silyl Groups and NHOs; Utility in Metal-Free and Metal Based Catalytic Reactions

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In recent times, widespread attention has been devoted towards the isolation of main group element consisting species such as silyl phosphines and NHO supported P(III) compounds. [1-3] Stereo-electronically tuned ligands play crucial role not only for the isolation of various novel, and unusual main-group, organometallic fragments, but also find widespread utility as ancillary ligands in homogeneous catalytic transformations. Phosphine ligands featuring group 13/14 elements supported pincer type ligands have been explored [1-3] but their mono-dentate counterparts have not been studied in organometallic synthesis and also in homogeneous catalysis. Among this class of species, the silyl (SiR₃) groups functionalized phosphines would offer new reactivity aspects as these are sterically, and electronically tuned reactive species. As shown in the Scheme, silylphosphines with Si-H bonds were treated with various Ru and Pd metal precursors and isolated the corresponding Ru(II) and Pd(II) complexes. In the latter case, Pd(II) insertions into the Si-H bonds were observed to give palladium-silicon bonded species, however, the corresponding reactions with R₂PSiMe₃ afforded Pcoordinated complexes, indicating the superior use of Si-H species over Si-R (R = aryl, phenyl) species in organometallic synthesis. Additionally, the cationic ruthenium complex (see Scheme) was employed as a potential catalyst in the hydroboration of a series of carbonyl compounds, which were achieved in very low catalyst loadings (as low as 0.05 mol%). [5,6] Furthermore, we have isolated a series of electronic rich neutral, and cationic phosphorus (III) species featuring N-heterocyclic olefins, and subsequently used for the isolation of a series of half-sandwich ruthenium-complexes. [4] The details of isolation, structural and catalytic studies will be discussed in this presentation.

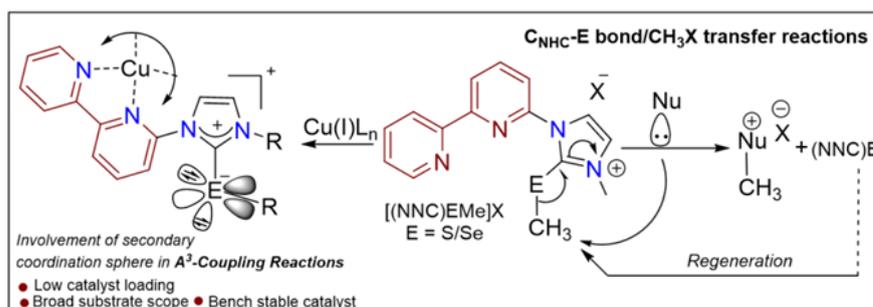


Figure. Pincer carbene supported group 16 cationic species.

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Main Group Catalysts for Biodegradable Polymer Synthesis

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In recent years, substantial amount of research has resulted in the genesis of new sustainable technologies towards the manufacture of polymers derived from renewable sources. The major reason for such a heuristic approach stems from the pollution problems associated with conventional plastics.¹ One such biodegradable material that has attracted increasing attention is poly(lactic acid) (PLA) which is commercially produced using the ring-opening polymerization (ROP) of lactide (LA). This methodology allows better control over molecular parameters (polydispersity index, molecular weight) under mild reaction conditions.¹ A study by Tolman et al. found that the stereoselectivity present in PLA is a result of thermodynamic preference of the initiating monomer molecule from a racemic mixture of LA enantiomers.² It is now beginning to unravel that an unsymmetrical transition state produced from LA and the catalyst during the initiation step plays a key role in deciding the stereospecificity of the propagation step, ultimately governing the final stereochemistry of the PLA, in addition to the thermodynamic preference for its molecular parameters. Jones et al. reported a Zr-*meso* salan complex, which is capable of producing an isotactic enriched PLA.³ Recently, Kol et al. prepared an enantiopure salan magnesium complex which produces isotactic enriched PLA.⁴ Earlier, we had reported iminophenoxide compounds of Group 13 which are capable of producing highly isotactic PLA.⁵ However, the existing literature pays little attention towards the study of the symmetry of the transition state during initiation in LA polymerization. Thus, one of our objectives is an understanding towards the control of the molecular parameter as well as the tacticity of the PLA which is anticipated to depend on symmetry of the transition state. This was surmised to be solved either by using non-centrosymmetric ligand frameworks in the catalyst, or by using an enantiopure ligand. In addition, this lecture shall cover the important aspects of our research towards the synthesis of sustainable polymers and copolymers using main group compounds.



Figure 1 Biodegradable implant

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Defect Engineering in Hybrid Porous Materials for Enhanced Energy Technologies

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Metal-organic frameworks (MOFs) are materials made of metal centers linked by organic ligands to form two-dimensional (2D) or 3D structures, offering unique properties for sorption and electrochemical applications. However, their chemical instability, poor conductivity, and inaccessible pores limit their performance. Hybrid two-dimensional porous materials (H2DPMs), combining MOFs with robust 2D materials, address these issues, enhancing their electrochemical and physicochemical properties and expanding their application potential, although technical challenges remain. However, defect engineering in MOFs and two-dimensional porous materials involves the intentional introduction of defects to modify their properties, creating new active sites, increasing surface area, and enhancing overall performance. In my presentation, I will discuss recent advances in defect engineering of MOFs and two-dimensional materials, focusing on synthesis strategies, precise manipulation, and enhanced functionalities for heterogeneous catalysis and noble gas separation, while also addressing challenges and future application perspectives¹⁻⁵.

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Enriching the Properties of Polycyclic Aromatic Hydrocarbons by B-N Lewis Pair Functionalization

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The incorporation of main group elements into π -conjugated materials distinctly affect their electronic structure, allowing for judicious fine-tuning of the properties and enabling new applications.¹ More specifically, the ability of tricoordinate boron to participate in π -delocalization tends to selectively lower the LUMO orbital levels, leading to interesting optical and electronic properties.² The electron-deficient character of boron also enables the reversible formation of Lewis pairs (LPs) by interaction of Lewis acids with Lewis bases. Aspects of our recent work will be discussed where we explore the functionalization of polycyclic aromatic hydrocarbons (PAHs) via B-N Lewis pair formation. The boron-fused products exhibit desirable properties such as low-lying LUMOs, strong absorption and emission in the visible and/or near-infrared region, fast intersystem-crossing into the triplet manifold, electrochromic behavior, and high charge carrier mobilities; they are of interest in organic electronics, sensing, molecular switches, singlet oxygen generation, photocatalysis, bioimaging and biomedical applications.³⁻⁸

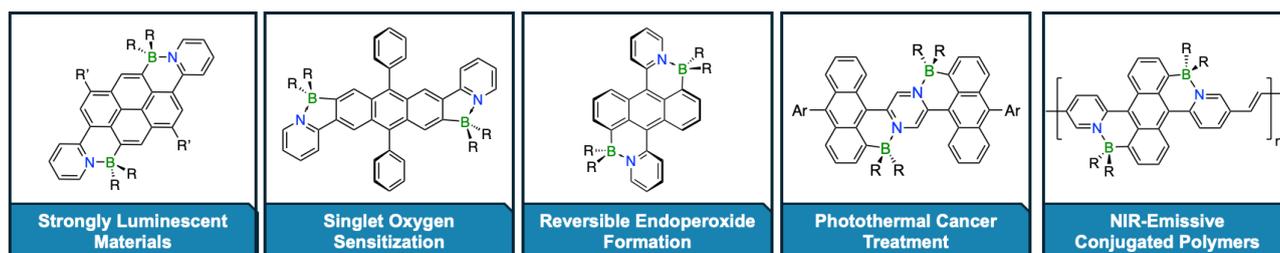


Figure 1. Selected B-N Lewis Pair Functionalized PAHs and Their Applications

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Magnesium as an alternative to hydrophosphinylation of Alkynes and alkenes: Evidence for Ligand Dependency

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The pursuit of practical, straightforward, and sustainable methods for forming carbon-phosphorus bonds is crucial in both academia and industry. Traditional synthetic methods often rely on hazardous, halogenated precursors through salt-metathesis routes. While several transition-metal-free methods for hydrophosphination of unsaturated species exist,¹ the hydrophosphinylation reaction is a less significantly investigated topic.² Given the involvement of s-block metals as hydrophosphinylation catalysts, they are even rare.³ To the best of our knowledge, the hydrophosphinylation of alkynes catalysed by a neutral Mg metal complex alone has yet not been reported to date. In this study, we have synthesized and characterized magnesium complexes $[L(Mg-nBu)_2]$ which effectively catalyses the hydrophosphinylation of alkynes alkenes. This transformation showcases an excellent atom economy, broad functional group tolerance and gram scale synthesis for organophosphorus compounds.

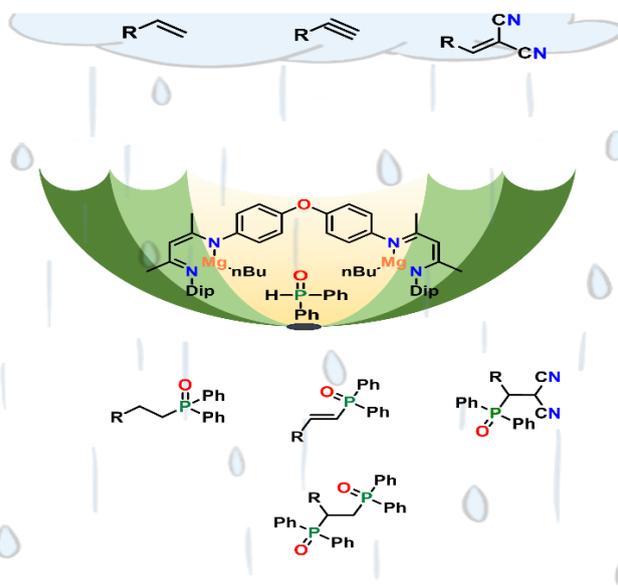


Figure 1

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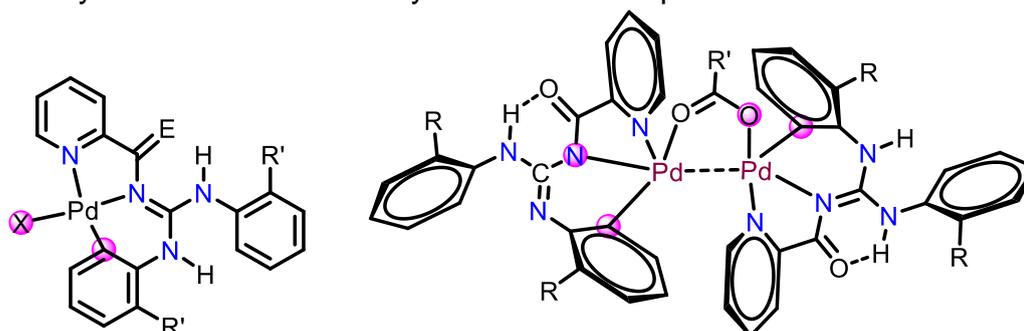
CNN Palladium(II) Pincer Complexes of Directing Group Tethered *N*-Arylguanidines

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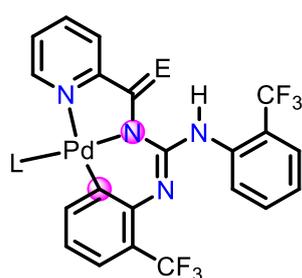
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In the past, we reported two types of cyclopalladated *N*-arylguanidines, namely $[Pd\{\kappa^2(C,N)(\mu-X)\}]_2$ ($X = OC(O)R$ ($R = Me, CF_3$ and tBu) and Br) and $[Pd\{\kappa^2(C,N)(X)L\}]$ ($L =$ Lewis Base) and their organometallic reactivity studies including bridge-splitting reaction,¹ alkyne insertion² and depalladation of alkyne inserted cyclopalladated *N*-arylguanidines.³ Recently, we began to explore coordination chemistry of directing group, DG ($DG = -C(O)Py-2$ and $-CH_2Py-2$) tethered *N*-arylguanidines towards Pd(II) salts which resulted the formation of pincer complexes **A** and **B** or **C** depending upon the guanidines and carboxylate moieties in the Pd(II) source.^{4,5} The reaction of **C** with L such as $C\equiv N-Xyl$ afforded a neutral complex **D** while such reactions of **B** with L afforded cationic complexes of the type **F**. Further, the reaction of **F** with $tBuOK$ in the presence of air afforded complexes of the type **D**. The mechanism of **E** to **D** transformation was investigated by DFT calculations. The catalytic utilities of CNN Pd(II) complexes in Suzuki-Miyaura coupling reactions and cycloisomerization of alkynoic acid will be presented.

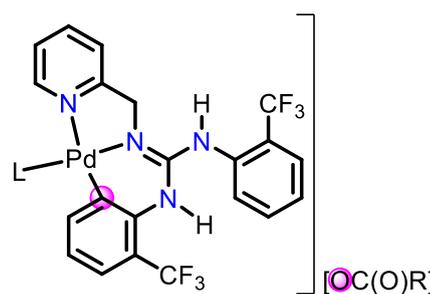


$X = OC(O)R$; $R = Me, CF_3$ and tBu
 $R' = Me$ & CF_3 ; $E = O$ (**A**) & none (**B**)

$R = Me$ and CF_3 ; $R' = Me$ and tBu (**C**)



$L = C\equiv N-Xyl$; $E = O$ (**D**) and None (**E**)



$L = C\equiv N-Xyl$ (**F**)

\Rightarrow Location of a formal negative charge

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Substituent Effects on Exchange Anisotropy in Single- and Multi-Orbital Organic Radical Magnets

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The contribution of heavy atom substituents to the overall spin-orbit interaction in two classes of organic radical molecular magnets is discussed. In “single-orbital” radicals, spin-orbit coupling (SOC) effects are well described with reference to pairwise anisotropic exchange interactions between singly-occupied spin-bearing orbitals on neighboring molecules; anisotropy requires the presence of spin density on heavy atom sites with principal quantum number $n > 3$. In “multi-orbital” radicals, SOC involving virtual orbitals also contributes to anisotropic exchange and, as a result, the presence of heavy ($n > 3$) atoms in formally non-spin-bearing sites can enhance pseudo-dipolar ferromagnetic interaction terms. To demonstrate these effects, ferromagnetic and antiferromagnetic resonance spectroscopies have been used to probe the exchange anisotropy in two organic magnets, one a “single-orbital” ferromagnet, the other a “multi-orbital” spin-canted antiferromagnet, both of which contain a heavy-atom iodine ($n = 5$) substituent [1]. While the symmetry of the singly-occupied molecular orbital in both radicals precludes spin-orbit contributions from iodine to the overall exchange anisotropy, the symmetry and energetically low-lying nature of the lowest unoccupied molecular orbital in the latter allows for appreciable spin density at the site of iodine substitution and, hence, a large exchange anisotropy.

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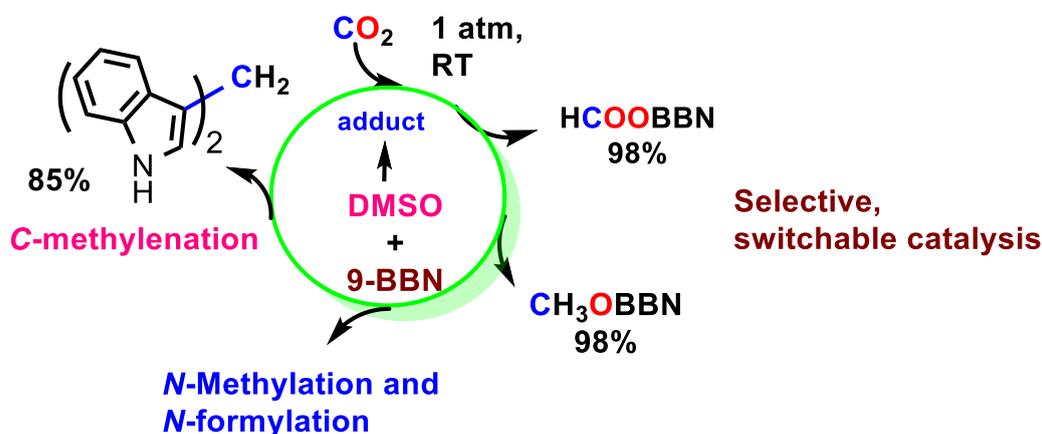
DMSO Catalyzed CO₂ Reduction and Functionalization of Organic Molecules

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The amount of CO₂ in the earth's atmosphere is gradually increasing every year and mainly responsible for the unfavorable weather conditions we experience. One of the ways to mitigate these problems is to valorize CO₂ as a C₁ building block for producing fuels and useful organic compounds. Our investigation in this area led to the development of a switchable catalytic system and offered to make new C-N and C-C bonds under mild conditions. DMSO as a Lewis base catalyzes the reduction of CO₂ (1 atm) with 9-BBN to selectively give either formoxy- or methoxyborane in excellent yields at room temperature, which upon hydrolysis offer formic acid and methanol, respectively. This selectivity is achieved by varying the amount of DMSO. The reduction of CO₂ with other bases - sulfoxide, sulfone, sulfide or pyridine showed that not all adducts are able to reduce CO₂ but only those Lewis bases which enhance the hydricity of 9-BBN. Mechanistic studies showed stepwise formation MeOBBN from HCOOBBN via acetal product. The methylene group of the acetal product was transferred to *N*-methyl- and *N*-unsubstituted indoles to produce bis(indolyl)methane derivatives in good isolated yields under relatively milder conditions with detailed mechanistic studies. In addition, *N*-methylation and *N*-formylation were carried out under milder conditions to give a series of products in excellent yields and their mechanisms were studied.



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From Waste to Value: CO₂-Based Aliphatic Polycarbonates and Their Functionalization for Advanced Applications

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The catalytic coupling of CO₂ and epoxides makes effective use of CO₂ as C1 feedstock to achieve polycarbonate polymers. This process plays a vital role in carbon capture, utilization, and storage (CCUS), providing a solution to address CO₂-related environmental challenges. Since its inception, the field of CO₂-epoxide copolymerization has seen exponential growth, driven by its economic and ecological importance. Over the past two decades, interest in this area has been rejuvenated as it offers a sustainable means to utilize CO₂ as a C1 feedstock, simultaneously contributing to the reduction of plastic pollution. In this talk, I will discuss our advancements in synthesizing polycarbonates through this process. I will highlight how we have introduced functionalization using chain-transfer & click chemistry to expand the applicability of these polymers. Additionally, I will explain how this chemistry has been extended to achieve metallopolymers, presenting new opportunities in material science. These innovations provide a promising outlook on addressing global environmental challenges through the integration of CO₂ into functional and sustainable polymers.

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Molecules and Materials of Phosphorus and Sulphur

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Many materials derived from main-group elements find applications in diverse fields, including environmental remediation, energy harvesting devices, catalysis, and advanced propellant science and technology. The properties of these materials are largely determined by their structural design and the synthetic procedures employed in their production. We have identified several limitations in material properties and have sought to address these challenges by implementing new synthetic protocols. Enhancing the safety of lithium-ion batteries regarding fire hazards poses a substantial challenge, particularly for large-scale applications in electric vehicles. A key design strategy to prevent thermal runaway—potentially leading to fire or explosion at elevated temperatures—is incorporating flame-retardant properties into the batteries without compromising ion conductivity. The randomized trials in our lab have indicated the tunability of microstructure-assisted lithium-ion conductivity in phosphorus-containing polymers. This lecture will provide an overview of our lab's design and synthesis strategies for producing metal sulfide and phosphate materials with improved properties tailored for specific applications.

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Stable Radicals of Main-Group Element as Ligands in Enzyme Cofactor, Organic Catalysis and Molecular magnetism

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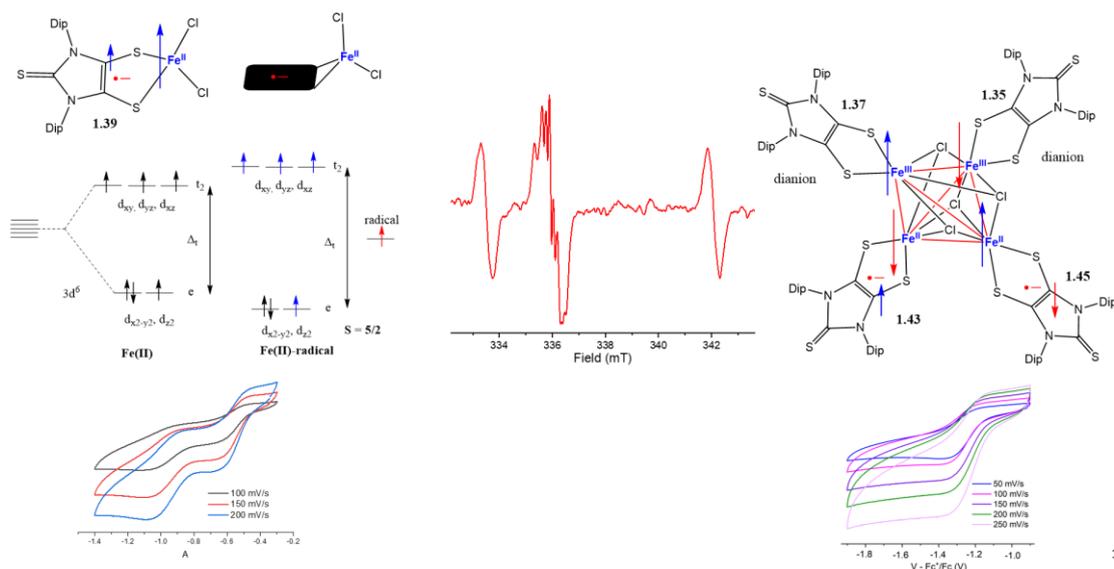
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There have been several reports of synthesis, isolation and characterization of stable radicals of main group elements. However, utilization of those radicals as ligands for the isolation of stable metal-radical complexes, is limited due to their ready access, sensitivity to air and moisture and synthetic infrastructure available around the world. N-hetero cyclic carbene (NHC) was functionalized with S-atoms and converted as a stable radical anion.

Dithiolene is a class of two sulfur -donor ligands, which is a redox non-innocent in nature ranging in charge from zero to di-negative (neutral singlet, anionic doublet and di-anionic singlet). Dithiolene unit is often commonly observed as a part of Mo/W-containing proteins (such as pyranopterin cofactor) where the metal can switch in between different oxidation states with the electronic buffering effect of dithiolene ligand. In addition, many cofactors of enzymes possess M-S bonds. Very recently air and moisture sensitive redox non-innocent N-heterocyclic carbene (NHC) functionalized (C2, C4, C5) tri-sulfur compound which behaves as a dithiolene ligand $[(SS-NHC=S)^0 \rightarrow (SS-NHC=S)^{\bullet-} \rightarrow (SS-NHC=S)^{2-}]$ isolated by Robinson et al in radical anion and non-radical dianionic form.¹ Herein, I will present synthesis, isolation, characterization, catalysis, slow relaxation of magnetization of metal-radical complexes of two sulfur donor radical anion ligand $[(SS-NHC=S)^{\bullet-}]$. Some of these complexes are closely relevant to enzyme cofactors. In addition, the physical and chemical properties of dithiolene based metal-radical complexes will be discussed.

Electronic Structures of Fe-Radical Complexes



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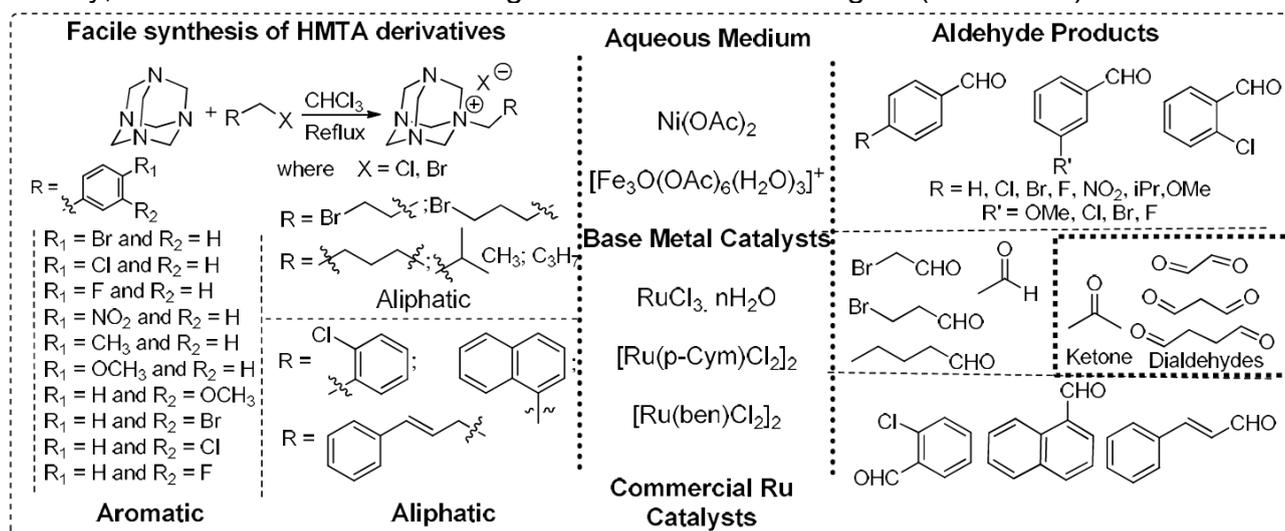
Role of Hexamethylenetetramine in Organic Synthesis

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Hexamethylenetetramine (HMTA) is one of the most versatile and most utilised nitrogen containing heterocyclic compounds in both academia and industries. Most of the reactions involving HMTA employ stoichiometric or excess amount of acid, which hampers the sustainability of the reactions. Currently, the scientific community is focusing on improving the sustainability of the reactions involving HMTA. This lecture will focus on various applications of HMTA and more emphasis will be given on the acid/metal induced decomposition of HMTA and utilising it as a tool to improve the sustainability of the reaction namely, Sommelet reaction involving HMTA as reactant/reagent (Scheme 1).



Scheme 1. Metal mediated conversion of methyl halides into aldehydes

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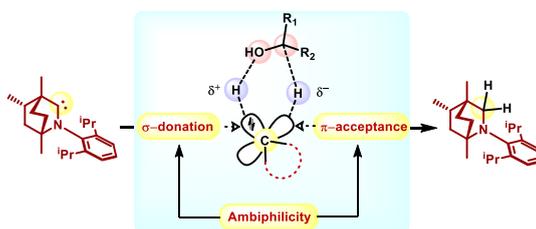
Taming Exceptional Ambiphilicity of Bicyclic (Alkyl)(Amino) Carbene Towards Alcohol Dehydrogenation Reaction

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Introduction:

Herein we utilized the exceptional ambiphilicity of BICAAC,^[1] to emulate transition metals in Borrowing Hydrogenation (BH) Reaction. The first step of the BH cycle, i.e. alcohol dehydrogenation step, has been successfully achieved by the simultaneous capture of a proton and a hydride from the alcohol molecule, forming BICAAC-H₂ (Figure below, **1^{H,H}**) as an active intermediate, which was isolated and characterized using various spectroscopic methods.^[2] The energy barrier for the dehydrogenation step leading to the formation of **1^{H,H}** was computed by DFT calculations. Along with this, computational calculations were also performed for the oxidative addition of alcohol over the carbene centre which was apparent from the *in-situ* NMR studies. This hydrogenated BICAAC was further used to reduce *in-situ* generated olefin leading to the C-alkylation of 9H-fluorene molecule.^[2,3] Further, the species **1^{H,H}** has also been able to hydrogenate imine bonds thereby achieving N-alkylation reaction. Careful control experiments prove radical intermediacy for the latter half of the reaction and the indispensability of light for the 1e⁻ reduction to the imine backbone.



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Making of the Multi-Cavity Discrete Coordination Cages

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A self-assembled coordination cage usually possesses one well-defined three-dimensional (3D) cavity whereas infinite number of 3D-cavities are crafted in a designer metal-organic framework (or coordination polymer). Construction of a discrete coordination architecture possessing multiple but finite number of 3D-cavities is a challenging task. Complexation of Pd(II) with a nonchelating bi- or poly-dentate ligand is a known strategy for the construction of one-cavity containing 3D-cages of various shapes and sizes. We introduced a Pd(II)-based double-cavity discrete coordination cage having a Pd₃L₄-type architecture, that was prepared by combining Pd(II) with a designer “E-shaped” tridentate neutral ligand. Subsequently, we prepared a variety of Pd(II)-based double, triple and quadruple-cavity containing discrete coordination cages. We are involved in making of single cavity-based cages using known strategies, multi-cavity conjoined-cages using new strategies, and exploiting functional aspects of the isolated nano-space present in the coordination architectures.¹⁻⁵ Some of the coordination architectures are represented using cartoon form as shown in Figure 1. We are in the process of establishing a concept that we call as Neighbouring Cage Participation (NCP) in the realm of our Multi-Cavity Discrete Coordination Cages (MCDCCs).

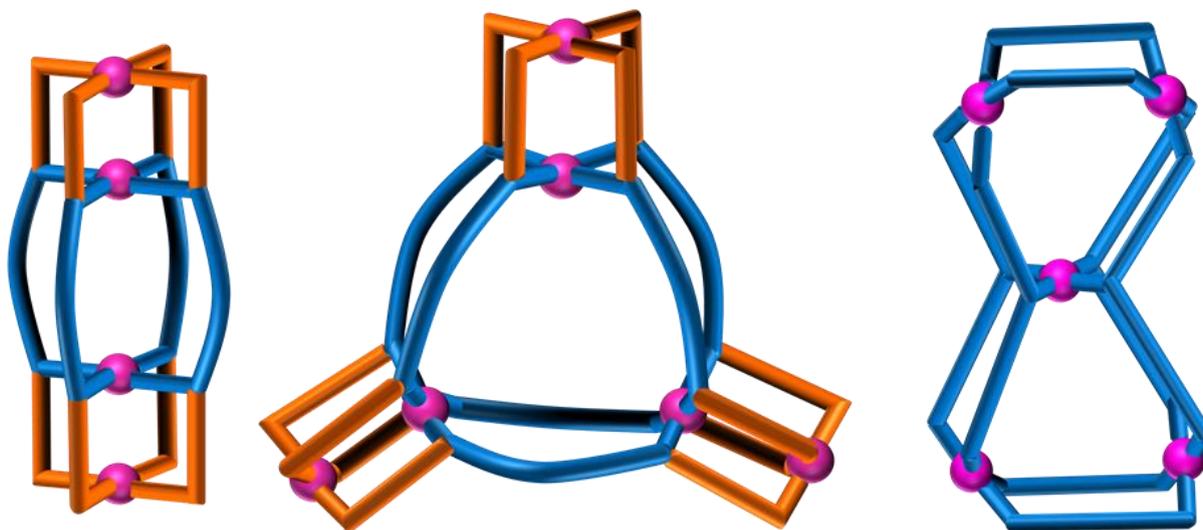


Figure 1 Cartoon representation of a few Multi-Cavity Discrete Coordination Cages.

References:

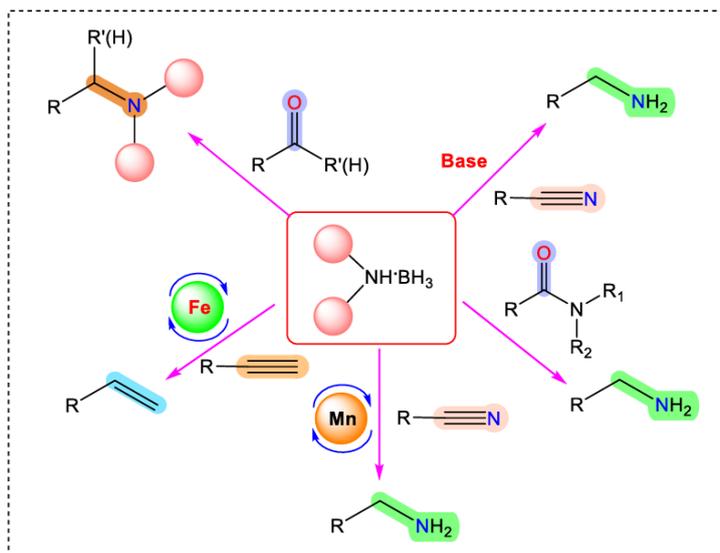
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Unlocking the Diverse Reactivity of Ammonia-Borane Derivatives

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Ammonia-borane and its derivatives have been employed as an attractive molecular scaffold in various organic transformations owing to their high hydrogen content, low molecular weight, and ease of handling.¹ They are relatively air-stable, water-soluble, non-toxic, and can be produced directly from low-cost raw materials, making them economically attractive. In this presentation, I will give an overview of our recent efforts in developing the reactivity of various ammonia-borane derivatives as a functional group transfer agent to carbonyl compounds,² reducing agent of amides³, and hydride transfer agent to various unsaturated C–X (X = C and N) multiple bonds in the presence/absence of catalyst (Scheme 1).⁴⁻⁶



Scheme 1. An overview of the reactivity of ammonia-borane derivatives.

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Transmuting Copper into a Main Group Element

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A vast number of chemical reactions rely on the near-inevitable preference of copper for positive oxidation states to make useful compounds. Over the last 5 years the Liptrot lab has sought to complete a “p-block” of catalytically relevant copper-element bonds and applied these moieties in catalytic and stoichiometric transformations. These species allow exquisite control in the introduction of main group fragments into molecules.

Recently, we have isolated a stable compound with a copper-magnesium bond, which conforms to the formal oxidation state of Cu(-I). Quantum chemical calculations further support the assignment of a sub-zero oxidation state at copper, and a $3d^{10} 4s^2$ electronic configuration at copper, an electronic transmutation of copper away from the d-block and into the main group. The CuMg bond acts as a source of the cupride anion, transferring the NHC-copper fragment to electrophilic s-, p-, and d-block atoms to make known and new copper-containing compounds, such as a complex with an unsupported CuZn bond. We can now access copper-element bonds a much wider swathe of the periodic table.

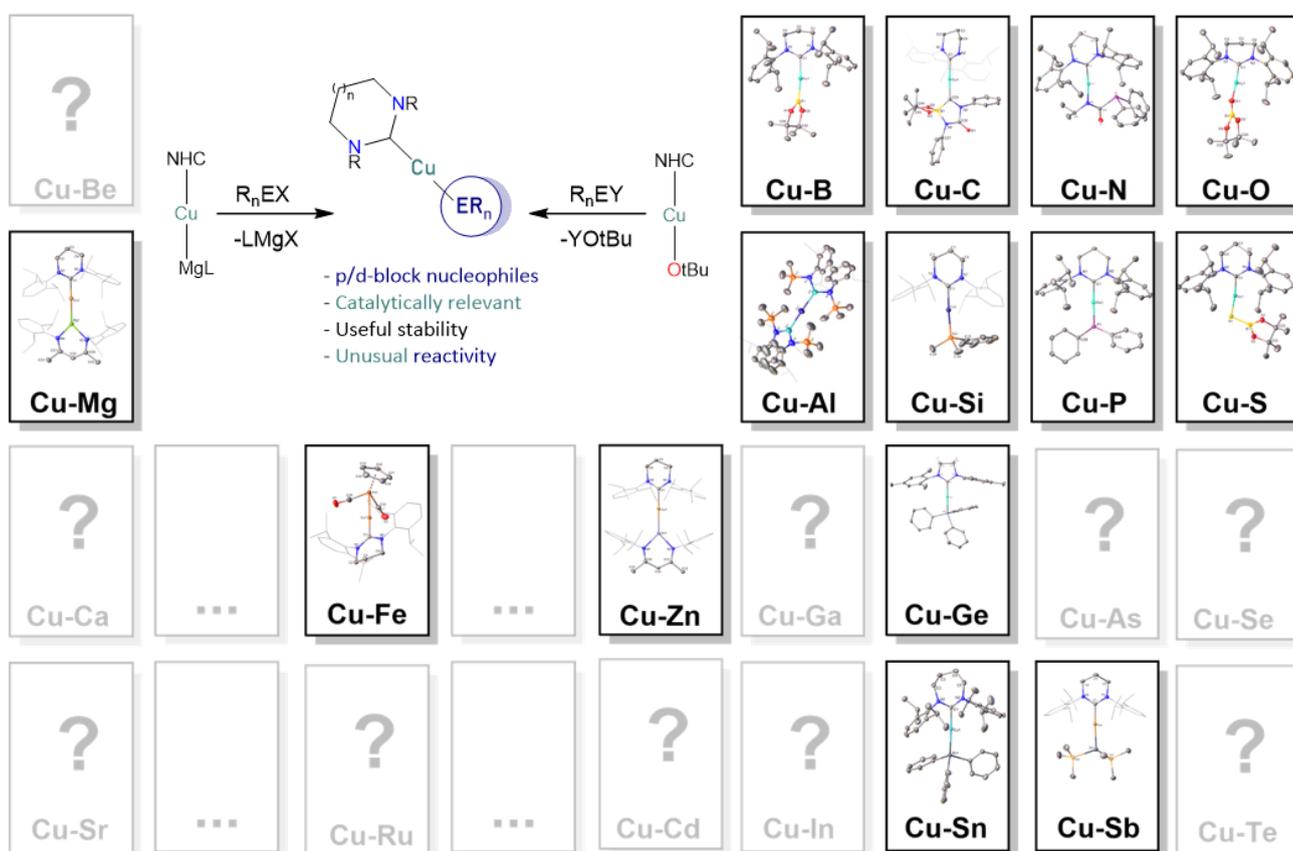


Figure 1 A summary of our exploration into copper-element bonds.

Functionalized N-Heterocyclic Carbene (NHC) Supported Metal Complexes in Catalysis

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Ancillary ligands are known to play crucial roles in the activity of any metal complexes and their stereoelectronic parameters are normally considered as important factors to modulate their properties thus, essentially their reactivity. Over the past few decades, N-Heterocyclic carbene (NHC) ligands have established themselves as an elite class of ligands in various fields such as organometallic chemistry, homogeneous catalysis, material chemistry, metallopharmaceuticals.¹ In this context, detailed understanding of the combined steric and electronic influence of the ancillary NHC ligands, especially the functionalized ones, towards structural diversity in metal complexes and their activity in catalytic transformations would provide important information for the development of future efficient catalyst systems.² To study such effects, we have synthesized a range of metal complexes (Figure 1) and to understand the influence of the functionalized NHC ligand variations, all these complexes were tested in different catalytic transformations which uncovered that substantial tailoring of activity is indeed possible *via* subtle alteration of their stereoelectronic profiles.³ Further, structural chemistry involving these NHC ligand systems will also be discussed.

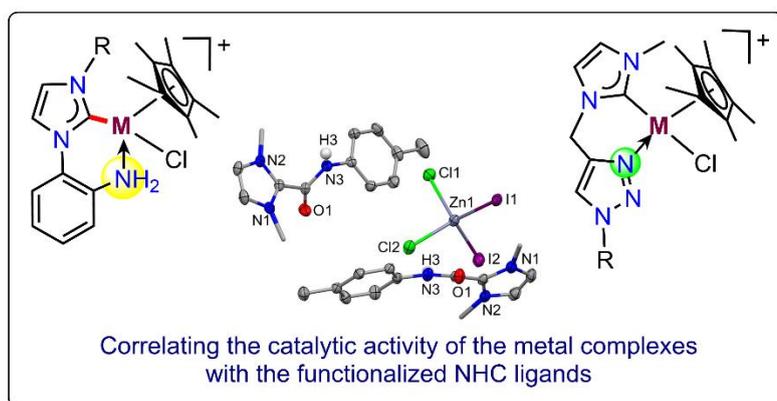


Figure 1 Different types of metal-NHC complexes used in this study

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Boron-Phosphorus Heterocyclic Ring Expansion via Small Molecule Activation, Chemical Reduction, and Halide Abstraction

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Since the first report in 2006, FLPs have been used to activate various small molecules, including H₂, CO₂, and NO.¹⁻⁵ In typical FLPs, sterically bulky functional groups on the Lewis base (LB) and Lewis acid (LA) preclude the formation of the typical acid-base adduct, resulting in a formal lone pair on the Lewis base and an empty orbital on the Lewis acid. This results in the FLP acting as both an electron donor and acceptor, similar to the frontier d orbitals of transition metals. This has led to FLPs being a key component of the main group “metallomimetic” reactivity and catalysis for various hydrogenation, reduction, and small molecule capture reactions.⁶⁻⁸ Traditionally, FLPs consist of distinct acid and base fragments. However, reports have also shown that cyclic FLPs with highly strained membered LB–LA rings can react similarly to traditional FLPs.⁹ Although the reactivity of phosphorus–boron FLPs has been well-documented in the literature, the resulting products are often not the subject of redox chemistry.¹⁰ In this talk, I will present the synthesis of a boronine-based Frustrated Lewis Pair (FLP) that has been shown to activate chalcogen containing small molecules, resulting in main group cyclopentene derivatives, as well as the reactivity of these species towards either potassium graphite or silver (I) trifluoromethanesulfonamide resulting in ring expansion.¹¹⁻¹² I will also discuss the reaction mechanism, electronic properties, photo-physical properties, and bonding interactions of the synthesized heterocycles.

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Discrete Metal Chalcogenones and their Catalytic Applications

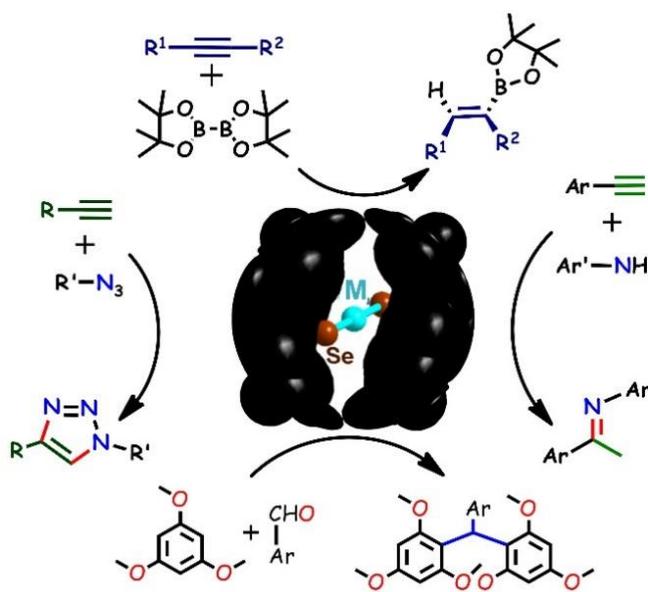
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Remarkable progress has been made since 1991 in the area of metal-NHC (NHC = N-heterocyclic carbene) based catalysis due to (i) a better catalyst lifetime, (ii) a consistent reactivity and (iii) well-balanced steric and electronic nature of NHC towards the metal Centre. However, most of these known metal-NHC molecules are mononuclear, dinuclear or trinuclear, and the NHC-metal clusters are limited. Unlike phosphine or carbonyl based metal clusters, the polynuclear metal-NHC derivatives and their catalytic applications are limited due to a strong σ donor and poor π accepting nature of NHC along with steric hindrance. Therefore, the search for suitable NHC or analogues of NHC-type ligands to isolate the polynuclear or nano-size metal clusters or cages is in great demand. Recently, imidazoline chalcogenones have been employed as a potential ligand to replace NHC-type ligands. Surprisingly, the catalytic efficiency of metal-imidazoline-2-chalcogenone complexes is better than metal-NHC complexes due to the tunable σ -donor and π -accepting nature of imidazoline-2-

chalcogenone
significant impact of
chalcogenone
catalysis will be



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Synthetic Versatility of Cyclic (Alkyl)(Amino)Carbenes: Isolation of Cationic, Radical & Anionic Main Group Compounds

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Past two decades have seen considerable interest in the synthesis of compounds with low-valent main-group elements due to their interesting structure and bonding properties, electronic features and unusual reactivity patterns.¹ Some of these low-valent systems exhibit transition metals like behavior in redox catalysis and for activation of small molecules (H₂, NH₃, CO₂, etc.).² Carbene ligands have played a pivotal role in the development of low-valent main group chemistry. Strong σ -donor and π -acceptor properties of cyclic (Alkyl)(Amino)Carbene (cAACs) have been judiciously exploited for the stabilization of various radicals, radical cations, radical anions, and several other low-valent species of p-block elements.³

In this talk, versatile synthetic utility of cyclic (Alkyl)(Amino)Carbene (cAAC) ligands for the isolation of the following different compounds will be discussed

- i) Two-coordinate acyclic Sb(I) and Bi(I) cations – Isoelectronic analogues of carbones⁴
- ii) Acyclic neutral two-coordinate Germanium radicals⁵
- iii) Silanylidene and Germanylidene anions – Isoelectronic analogues of phosphinidenes⁶

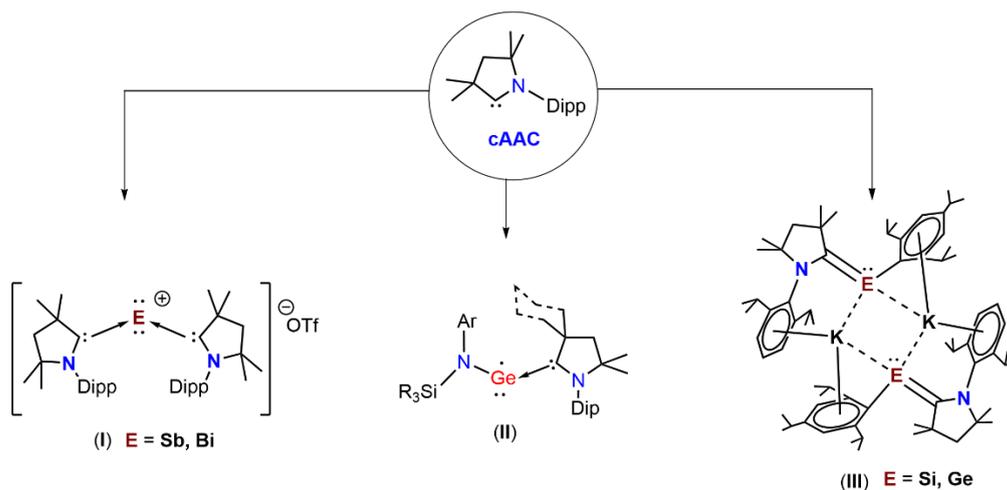


Figure 1: Cationic, radical & anionic compounds stabilized by cAACs

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Combining Diazoalkane with Low-Valent Group 14 Species

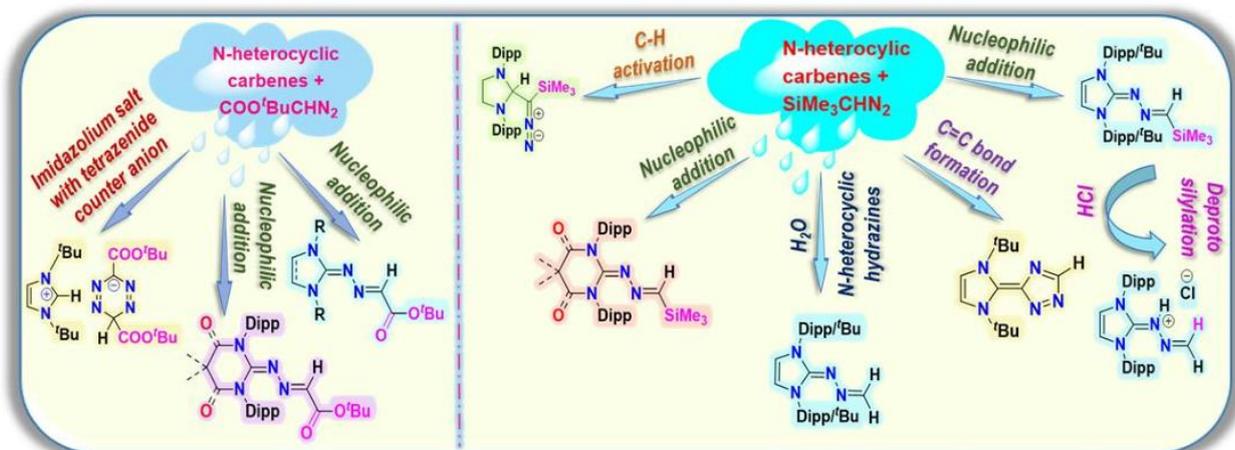
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N-heterocyclic carbenes (NHCs) have attracted significant attention due to their strong σ donating capabilities, as well as their transition-metal-like reactivity towards small molecules. However, their interaction with diazoalkanes remains understudied. In this talk, the reactivity of a series of stable carbenes, encompassing a wide range of electronic properties, with $\text{Me}_3\text{SiCHN}_2$ will be described.¹ Further into the talk the analogous chemistry with germanium² and magnesium will be demonstrated.



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New white light emitting materials

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In recent years, much effort has been expended to develop new hosts for solid-state devices. Two approaches have been adopted towards the development of white LEDs. In the first approach, blue-emitting LEDs such as InGaN, (450–480 nm) in combination with near UV-emitting LEDs and a suitable phosphor can be attempted. In the second approach, the use of UV-LED with tricolor (Red, Green, Blue; RGB) phosphors.[1] Controlling the photoluminescence behavior in the material would require the following considerations: (i) crystal structure needs to be flexible (adaptable) to accommodate different substitutions and (ii) good coupling of activators to host lattice along with efficient energy transfer. Single-phase white-light-emitting phosphors have attracted much attention recently to develop white LEDs. The advantages of this approach are many: (i) good luminescence efficiency and color rendering index; (ii) reproducibility of the luminescence and (iii) easier synthesis, which reduces the manufacturing costs. It may be noted that it is important to realize good energy transfer between the sensitizer and activator in a single-phase phosphor. Over the years, we have explored many mineral structures towards developing new and interesting compounds. Our studies also indicate that we could successfully develop white-light emission using minimal use of rare-earth ions. We have also been successful in creating white light emission by combining Bi³⁺ ions and rare earths.[2]

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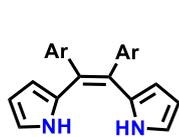
5,6-Diaryl Dipyrroethenes: Novel Precursors for the Synthesis of Porphyrinoids

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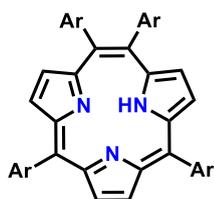
E-mail: ravikanth@chem.iitb.ac.in

Dipyrroethenes **1** (DPEs) containing two pyrroles connected by two *meso* sp^2 carbons are very useful precursors for the synthesis of very novel porphyrinoids. Synthesis of DPEs require few skilled synthetic steps to obtain in good quantities. In last decade, the DPEs have been used as key precursors¹⁻⁵ to synthesize contracted porphyrins such as triphyrins(2.1.1) **2**, porphyrin isomers such as porphycene(2.0.2.0) **3** and several expanded porphyrins such as **4**.



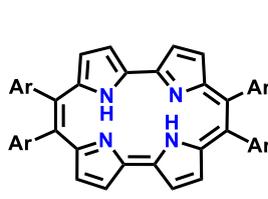
Dipyrroethene

1



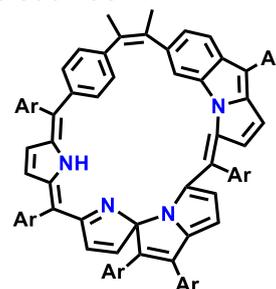
Triphyrin(2.1.1)

2



Porphycene 2.0.2.0

3



Calixdicarbahexaphyrins

4

In my talk, I will present simple synthesis of 5,6-diaryl dipyrroethenes and their use as precursors in the synthesis of different porphyrinoids ranging from contracted porphyrinoids to expanded porphyrinoids.

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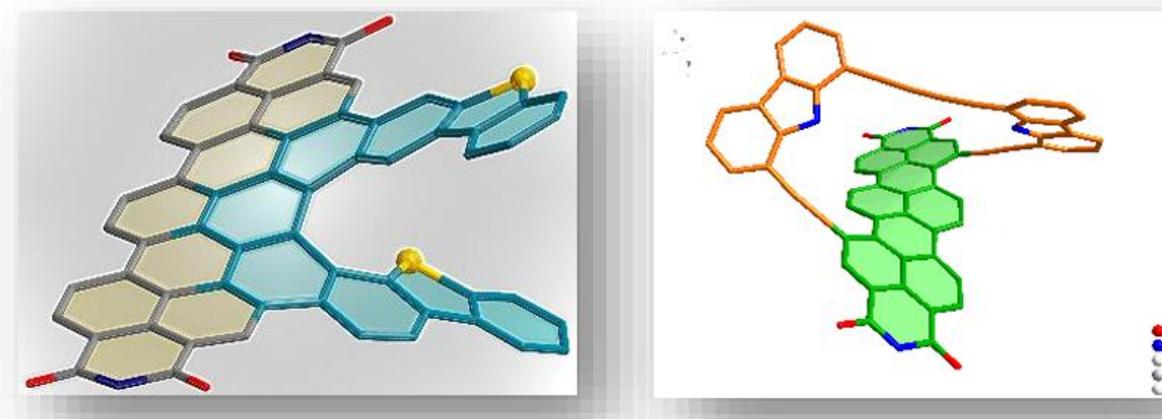
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Terrylene Bisimides Exhibiting Circularly Polarized Luminescence

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π -conjugated molecules having intense emission in the longer wavelengths have multiple utilities in optoelectronic devices to bioimaging. Herein, we demonstrate that precise functionalization and modulation of the frontier molecular orbital energies of terrylene diimides, a class of larger rylene diimides, can exhibit intense emission. Their emission maxima can be tuned from red to range under various external stimuli. Further structural modifications can lead to chiral derivatives that show interesting circularly polarized delayed emission. This talk will highlight the strategies employed to obtain delayed emission in solution from a single component, along with structure-property correlation.



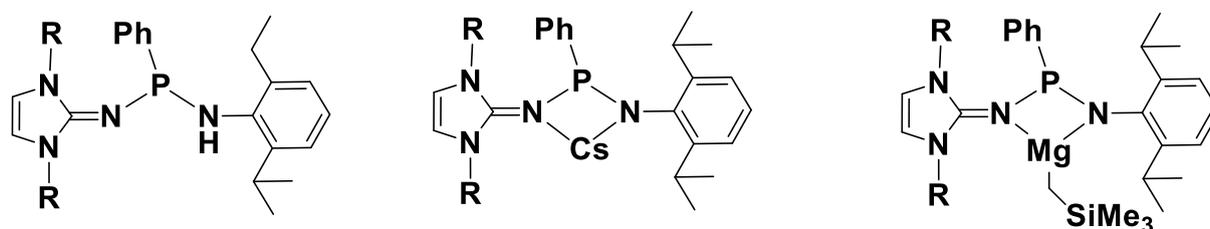
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Alkali- and Alkaline Earth Metal Complexes as Catalysts for Sustainable Polymers

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Efficient polymerization methods for the preparation of sustainable polymers such as poly (lactic acid) or poly (ϵ -caprolactone) and the corresponding co-polymers are important targets of research. In this context, unsymmetrical imino–phosphanamidinate, N-P-N ligands (Figure) were designed and synthesized, and their reactivity with various metal precursors was studied. In general, such reactions proceed to afford a monoanionic chelating N-P-N motif that can bind to metal centres affording four-membered rings¹⁻⁴ (Figure). Utilizing this strategy we prepared a Cs(I) complex² and a Mg(II) complex⁴ which were studied by NMR and crystallography. Further, these complexes were shown to be highly efficient catalysts for the homopolymerization of lactide and ϵ -caprolactone as well for the block co-polymerization of lactide with caprolactone.^{2,4} These results will be presented.



Figure

References

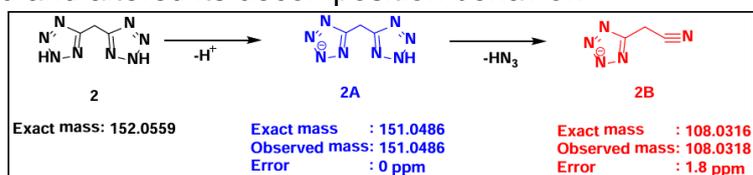
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High-Resolution Mass Spectrometry for Designing Nitrogen-Rich Energetic Molecules and Assessing Their Stability

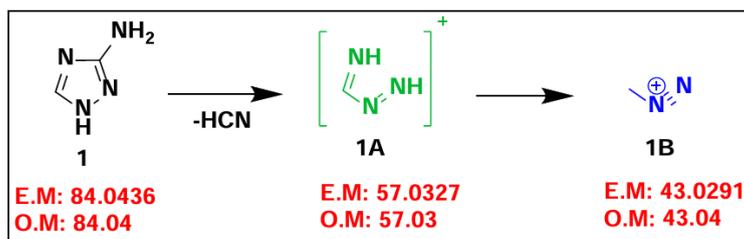
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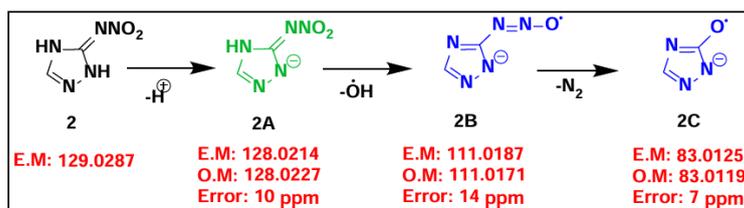
High-resolution mass spectrometry (HRMS) is an invaluable analytical tool for the design and characterization of high-nitrogen-containing molecules, which are often used in areas such as energetic materials. This is particularly useful for the design of energetic materials, where the nitrogen content directly correlates with performance. Precise mass measurements can ensure compliance with the desired oxygen balance and energy density requirements. In energetic materials, the decomposition pathway directly affects the performance. Investigations into the influence of introducing an alkylidene bridge between the energetic nitrogen heterocycles on the decomposition mechanism and pathways of different bridged tetrazoles, namely 5,5'-Bis-1H-tetrazole, 1,2-Bis(5 tetrazolo)methane, and 1,2-Bis(5-tetrazolo)ethane, indicated that the initial rupture occurred in the tetrazole ring, where the positive phase was localized according to electrostatic potential calculations. Consequently, the stability order varied as 5,5'-Bis 1H-tetrazole < 1,2-Bis-(5-tetrazolo)ethane. Furthermore, the introduction of amino and nitramino groups into 1,2,4-triazole was investigated, and these functional groups enhanced the thermal stability of the compound and altered its decomposition behavior.



Scheme. 1 Possible fragmentation pathway of 3-amino-1,2,4-triazole



Scheme. 2 Possible fragmentation pathway of 3-amino-1,2,4-triazole



Scheme. 3 Possible fragmentation pathway of 2,4-Dihydro-3H-1,2,4-triazol-3-ylidene-nitramide

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Design, development and optical features of Boronic acid derived tris(salicylidene)triaminoguanidine conjugates

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Multifunctional organic molecules have emerged as a pivotal focus in material science research, owing to their vast applications in various fields. A particularly fascinating subset of these compounds comprises AIE-active luminescent organic molecules, distinguished by their unique ability to exhibit aggregation-induced emission (AIE). Within the realm of multifunctional materials, multi-stimuli responsive materials have garnered significant attention.

Our research endeavours have led to the development of several multifunctional materials based on hydrazone and acylhydrazone motifs, with a thorough investigation into their responsive behaviours. Recently, organoboron complexes have garnered significant attention due to their remarkable optical properties and diverse applications. However, synthesizing stable fused five-, six- and seven-membered organoboron complexes poses significant challenges. In this presentation, we present design and development of novel mono-nuclear and di-nuclear organoboron complexes supported by tris(salicylidene)triaminoguanidine based C_3 -symmetric Schiff base ligands and its aggregation induced emission and mechano-responsive features.

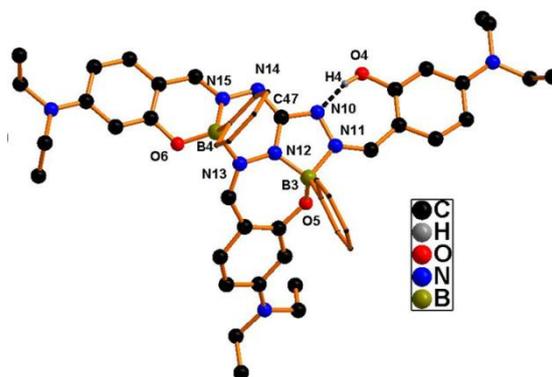


Fig: Molecular structure of diorganoboron derivatives

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Asking Ligands to Lend a Hand: Heteroatom on Ligand Scaffold for Cooperative and Supramolecular Catalysis

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The lack of well-defined metal-precursors, kinetic lability, metal redox and achieving selectivity are the key challenges in the development of 3d metal based catalytic systems. Ligand design can play an important role in overcoming these difficulties. In this talk, I will discuss the use of secondary coordination sphere interactions for the development of Fe based oxidation catalyst for the Wacker process. Judicious installation of O center on the ligand scaffold to achieve hydroboration reactions on Mn center will be discussed. Further, new ligand scaffolds that display metal-ligand cooperation will be disclosed.

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Mixed Pnictogen and Tetrel Containing Chalcogenides with Intrinsically Low Thermal Conductivities

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The combination of electropositive alkali/alkaline earth metals and main group metalloids with chalcogens produced unique chalcogenide structure types in the past that have been extensively studied for their semiconducting applications such as thermoelectrics (TE), data storage, photovoltaics, charge density wave, etc. Heavier main group elements are the key constituents of many state-of-the-art TE chalcogenide materials such as SnSe , Bi_2Te_3 , and PbTe [1]. In the last decade, complex telluride structures made up of metals and metalloids have been extensively studied for their promising TE properties, mainly due to their low thermal conductivity values. Thus, our group has been actively working on synthesizing new mixed main-group metalloid-based tellurides with intrinsically low thermal conductivity values for thermal coatings and TE applications.

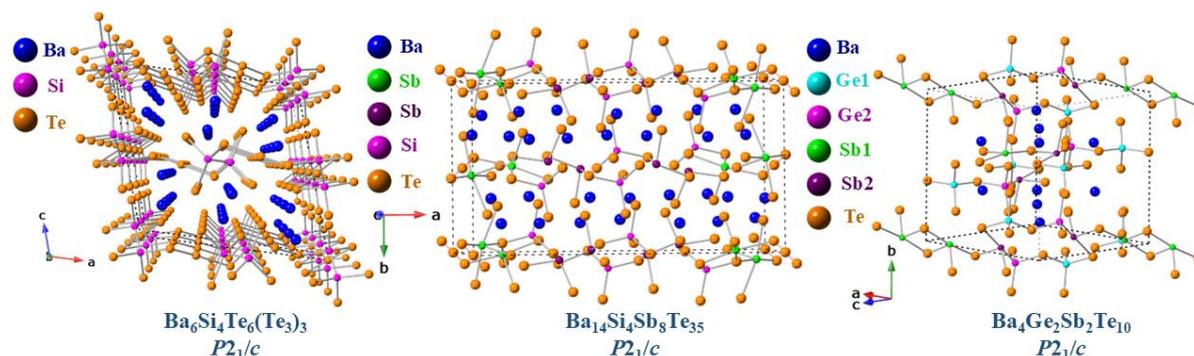


Fig. 1: The unit cell structures of $\text{Ba}_6\text{Si}_4\text{Te}_6(\text{Te}_3)_3$, $\text{Ba}_{14}\text{Si}_4\text{Sb}_8\text{Te}_{32}(\text{Te}_3)$, and $\text{Ba}_4\text{Ge}_2\text{Sb}_2\text{Te}_{10}$.

Our efforts have led to the identification of several new multinary chalcogenides with unprecedented structure types such as $\text{Ba}_{16}\text{Si}_8\text{Te}_{44+\delta}$, $\text{Ba}_6\text{Si}_4\text{Te}_6(\text{Te}_3)_3$, $\text{Ba}_{14}\text{Si}_4\text{Sb}_8\text{Te}_{32}(\text{Te}_3)$, $\text{Ba}_3\text{GeTeS}_4$, $\text{Ba}_{3.14(4)}\text{Sn}_{0.61(1)}\text{Bi}_{2.39(1)}\text{S}_8$, $\text{Ba}_4\text{Ge}_2\text{Sb}_2\text{Te}_{10}$, $\text{In}_{1-x}\text{M}_{1+y}\text{Si}_2\text{Te}_6$ ($M = \text{Mn}$ and Mg) etc. Single-crystal X-ray diffraction studies show that all these phases have complex anisotropic structures (Fig. 1) [2-5]. Some of these structures also show complex hypervalent Te–Te interactions. This presentation will focus on the structural aspects and physical properties of some of these complex compounds that are primarily narrow bandgap semiconductors or semimetals with low thermal conductivity values, promising for TE applications.

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Tetrylene Stabilized Gold Nanoparticles and their Catalytic Application

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Recent years have witnessed tremendous growth in the field of N-heterocyclic carbene (NHC) capped metal nanoparticles due to their interesting σ -donating properties. The NHC functionalized AuNPs is a milestone discovery from the main group chemistry perspectives. It has already been established that NHC-capped metal nanoparticles (MNPs) can be utilized as heterogeneous catalysts for the electrochemical reduction of CO_2 to CO , CH_4 , and HCOO^- , and the activity of the catalysts is controlled by the electronic properties of NHCs on the surface. Seeing the vast development of imidazoline-based NHCs on gold surfaces, we envisioned using unexplored cyclic(alkyl)(amino)carbene (CAAC) and N-heterocyclic silylene (NHSi) ligands on the surface of the AuNPs, which possess completely different σ -donation and π -acceptor properties. Herein, I will discuss the synthesis of extremely electron-rich CAAC stabilized gold nanoparticles (AuNPs) and their utilization for the selective electrochemical reduction of CO_2 , followed by NHSi ligated AuNPs and their catalytic application in CO_2 functionalization.

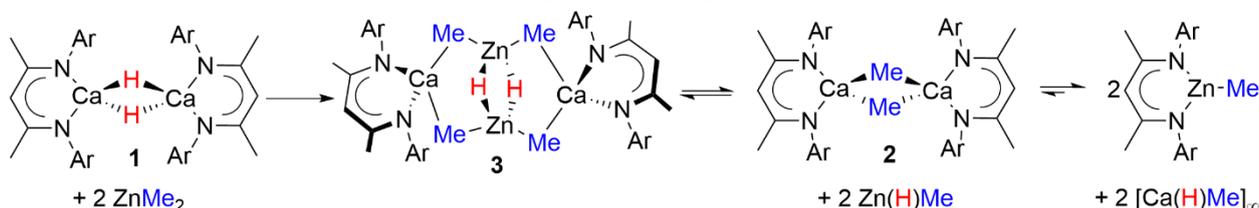
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Zinc-Mediated Divergent Transmetalation from a β -diketiminato Calcium Hydride

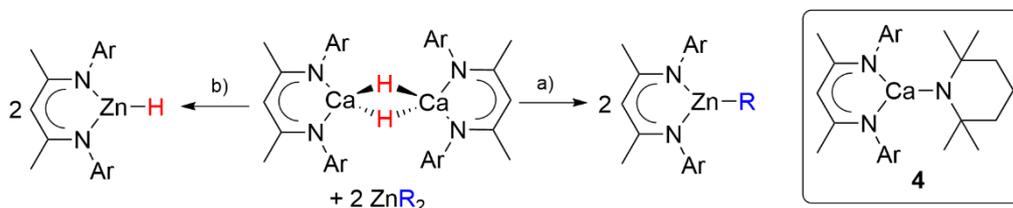
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Transmetalation, the process by which ligands are transferred from one metal to another, is a key reaction step in most catalytic cycles and thus extensively studied. In stark contrast, pre-transmetalation intermediates are less explored, though provide useful insight into the reaction mechanism, which could be exploited for reaction optimisation. With this in mind, the dimeric β -diketiminato calcium hydride (**1**) reacts with dimethyl zinc to ultimately afford a β -diketiminato zinc methyl complex *via* methyl-for-hydride transmetalation (**Scheme 1**).¹ Under appropriate conditions, the calcium methyl complex (**2**) can be prepared, and the intermediate on this reaction pathway (**3**) can be isolated exclusively, yielding insight into the reaction mechanism, which would typically only be observed *in-silico*.



Scheme 1 Reaction pathway between ZnMe_2 and $[(\text{BDI})\text{CaH}]_2$.

In an extension of this work (*unpublished*), divergent reactivity has been observed, in which the identity of the zinc reagent dictates the transmetalation product. For example, zinc diamides undergo not only amide-for-hydride exchange but also transmetalation of the β -diketiminato ligand scaffold (**Scheme 2**), thus ligating and functionalising the zinc centre in a one-pot reaction. Furthermore, the reaction intermediates can be isolated, allowing for the preparation of previously inaccessible organocalcium complexes such as **4**. This work is currently being extended to more exotic zinc reagents, whilst also exploring the reactivity and potential of the isolated intermediates.



Scheme 2 Reaction between ZnR_2 (a = R = alkyl, b = R = amide) and $[(\text{BDI})\text{CaH}]_2$.

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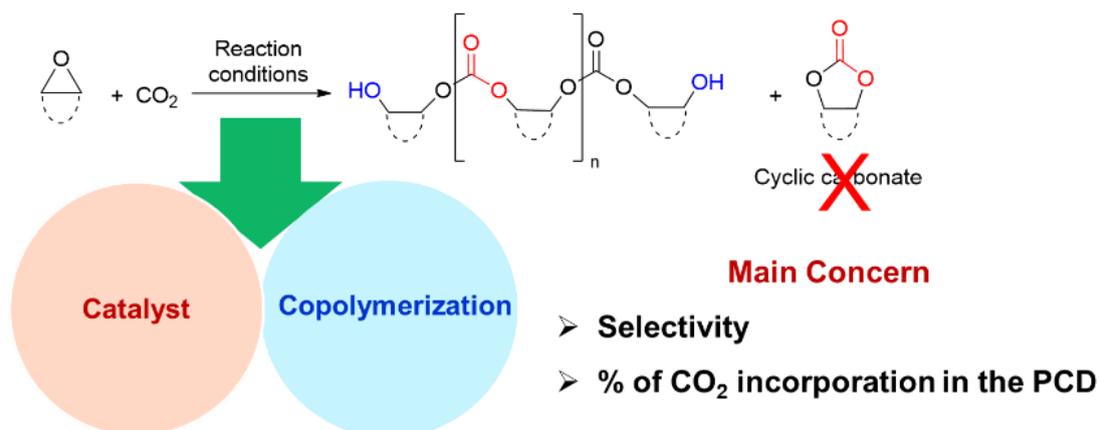
CO₂ to Value-Added Polycarbonate Diol

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Carbon dioxide (CO₂) as an abundant, non-flammable, economical, and renewable C1 feedstock is of strategic importance for our dependence on depleting non-renewable fossil derivatives. One of the most attractive areas of CO₂ utilization is its direct application as a renewable raw material for polymer synthesis, as large amounts of CO₂ can be utilized to make value-added polymeric products.¹ Polycarbonate has a terminal hydroxyl group (polycarbonate diol; PCD) plays a role in its excellent adhesive properties. The primary application of low-molecular-weight polycarbonate diol is widely used as an intermediate in the production of polyurethane (PU) foams. PCD-derived polyurethane has both financial and environmental benefits. The present work mainly involves the development of efficient, scalable catalysts for the production of PCD with excellent selectivity as well as tunable molecular weights and enhanced CO₂ incorporation.² The production of polycarbonate diol will be achieved at ambient temperature and low pressure of CO₂. This process may open varied opportunities and emerge as a game-changer technology for engineering polyurethane foams.



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Functionalized Organotelluroxane Macrocycles to Hybrid Material and their Electrocatalytic Applications

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Organotelluroxanes have been used to assemble fascinating molecular architecture in the recent past. We have been actively involved in this research area and recently a discrete lipophilic organotelluroxane macrocycle has been synthesized which has been found to catalyze the hydrogen evolution reaction (HER) by proton reduction efficiently.¹ The compound $[(p\text{-OMeC}_6\text{H}_4)_2\text{Te}]_2(\mu\text{-O})(\mu\text{-BF}_4)(\mu\text{-BF}_4)]_2$ is the first reported organotellurium electrocatalyst for electrochemical hydrogen evolution reaction. Meanwhile, the reaction of these systems with octahedral anion has led to the isolation of organotelluroxane macrocycle $[(p\text{-OMeC}_6\text{H}_4)_2\text{Te}]_2(\mu\text{-O})(p\text{-OMeC}_6\text{H}_4\text{Te})(\mu\text{-PF}_4)(\mu\text{-PF}_4)]_2$ stabilized by rare PF_4^- anion. Further, we synthesized a 12-membered macrocycle on a diorganotellurium backbone with functionalized phosphinates. These macrocycles, acting as building blocks were interlinked to form 1D architectures by using silver- π interaction. This hybrid material has been utilized as an electrocatalyst for the reduction of NO_3^- to NH_3 .² A detailed DFT study showed cooperative catalysis occurring between two Ag centers.

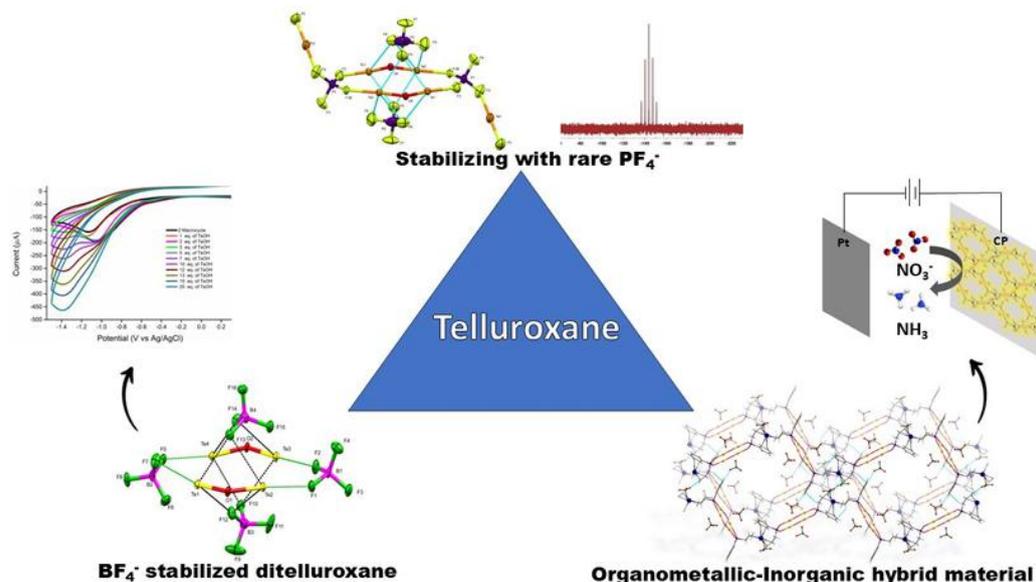


Figure 1 Graphical abstract

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Activation of Diboron Reagent by Main Group Compounds

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The application of organoborane compounds is of considerable significance across chemical, medicinal, and materials sciences due to their stability and the diverse functionalization they enable via various transformation protocols.¹ The synthesis of organoboron compounds commonly proceeds through hydroboration or borylation, utilizing metal-catalyzed or metal-free strategies that activate diboron reagents.² Traditional approaches typically employ organometallic reagents and precious metal catalysts, including transition metals such as Pt, Rh, Re, Ru, and notably Ir, which have been extensively developed over past decades. However, the high cost and limited availability of these metals underscore the need for more sustainable catalytic systems based on main-group elements. Strong bases like t-BuOK, Cs₂CO₃, or NHCs (N-heterocyclic carbenes) are required to activate diborons owing to the high BDE of B-B bond.³

A notable advancement in diboron activation has been achieved recently, where two nucleophilic species can coordinate with both the boron atoms of the diboron reagent, facilitating B-B bond cleavage. In this context, we have developed a protocol for the homolytic cleavage of B-B bonds in diboron compounds utilizing simple diazabutadiene.⁴ We have also developed a protocol for direct diborylation of azoarenes using its photo switchable nature without the use of any catalyst. The thorough mechanistic studies proposed a sequential coordination mechanism for the transformation and ruled out the involvement of a radical pathway. These methodologies expand the synthetic methodology for organoboron chemistry, offering new pathways to functionalized boronic esters.

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Reticular Synthesis and Design of New Materials for Diverse Applications

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The time-honored challenge of designing and building new crystalline solid-state materials from molecular building blocks is just beginning to be addressed with success. A conceptual tactic that requires the use of secondary building units to direct the gathering of well-ordered frameworks symbolizes this process. This methodology is titled as reticular synthesis. Such chemistry has yielded materials designed to have predetermined structures, compositions and astonishing properties. In precise, highly porous frameworks held together by robust M–O–C bonds and with exceptionally large surface area and capacity for gas storage have been prepared and their pore metrics systematically varied and functionalized. Current widespread research into the design and synthesis of metal-organic frameworks (MOFs) and Covalent Organic Frameworks (COFs) has led to numerous practical and conceptual developments in that course. Explicitly, the chemistry of MOFs and COFs has provided an extensive class of crystalline materials with high stability, tunable metrics, organic functionality, and porosity. Here we present some of the important improvements that have shaped this rapidly growing field by designing MOFs and their composites for various applications like catalysis, dye adsorbents, Multi-Phase Iodine Sequestration and COFs as adsorbents of organic pollutants, catalysts and energy storage materials. Precursors for synthesis of new materials have been strategically designed to tune the properties. Thus, designing structural skeleton is coupled with the ability to control chemical functionalization and adjustment of metric dimensions of MOFs and COFs to present the exciting prospects.

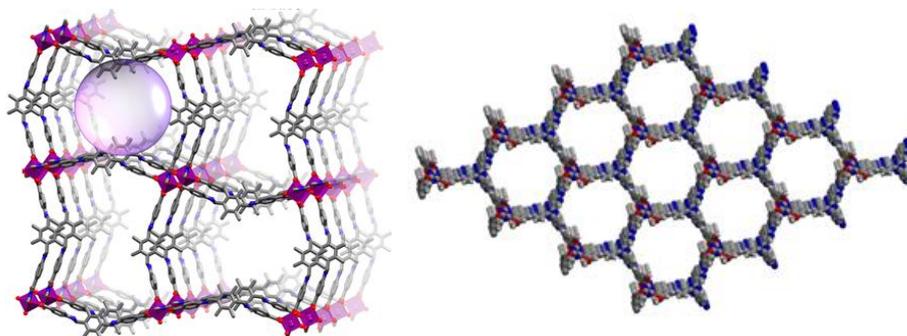


Figure 1 Presentation of Left: $\{[Zn_2(PMBADH_2)_4(DMF)_2] \cdot 4DMF\}_n$ (SVNIT-1); Right: TMPTTPA-COF with (4x4x4) supercells.

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Modulation of Arsenic Methylation by Functional Model of Arsenite S-Adenosylmethionine Methyltransferase

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Arsenic (As) is one of the most ubiquitous toxic environmental contaminants that poses a serious threat to human health. It consistently ranks first on the Agency for Toxic Substances and Disease Registry's (ATSDR 2022) substance priority list. According to the WHO, an estimated ~ 200 million people worldwide are at risk of exposure to elevated As concentrations, mainly in the form of inorganic As (iAs), including arsenite (iAs^{III}) and arsenate (iAs^V) in groundwater and food.^{1,2}

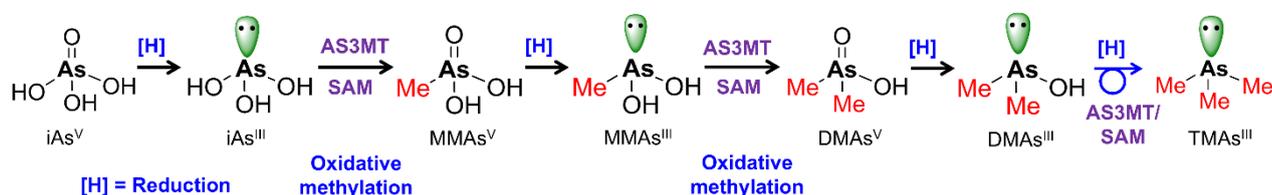


Figure 1. The plausible arsenic detoxification mechanism in microorganisms.

Biomethylation of iAs^{III}, catalyzed by arsenite S-adenosylmethionine methyltransferase (referred to as ArsM in microbes or AS3MT in animals), is a major arsenic detoxification pathway in organisms, resulting in the formation of dimethylated metabolite DMAs, which has less retention time in the body.³⁻⁶ However, ArsM orthologs from different organisms show different arsenic methylation efficiencies. For instance, mice have very fast urinary arsenic elimination, excrete a higher fraction of DMAs in urine than human. Nevertheless, the molecular basis for the variation in arsenic methylation efficiency among ArsMs remains obscure. In this conference, we will present our recent work on developing various synthetic methylating agents, which demonstrate different arsenic methylation efficiencies under mild conditions.

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Synthesis of Open-Shell Compounds Involving 5th and 6th Elements

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Exploratory research serves as the cornerstone of synthetic chemistry, with today's curiosity paving the way for tomorrow's innovations. Over the last ten years, our group has focused on the rational design and synthesis of various closed- and open-shell compounds involving fifth and sixth elements of the periodic table that is boron and carbon, respectively. At the same time, we have developed the modular redox mediated synthetic routes for the synthesis of various unprecedented compounds.

I will present the effort of our research group in designing and developing convenient modular routes for synthesizing compounds that contain mono-/bis-alkenes as electron-donor motifs¹ and mono-/bis-cyclic/acyclic carbocations/iminium cations along with boranes/boryl-cations as electron-acceptor motifs,² subsequently its utilization as synthons for isolating various open-shell compounds: radicals, radical-cations, (cationic)-diradicals, radical-trications, and (cationic/heteronuclear)-diradicaloids under redox (reduction/oxidation) reaction conditions will be elaborated.³ Moreover, I shall discuss the pivotal role of the spin-carriers and spin-couplers in the resulting electronic situation of the open-shell molecules.

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Pincer-Metal Catalysis for Generation of Hydrogen, Fuel & Specialty Chemicals

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Abstract

Current global research is greatly focused on the development of greener, sustainable and atom-economical methods for the formation of C-C bonds leading to versatile fuels and value-added chemicals.¹ This greatly negates the typical disadvantages of classical coupling of alkyl halides that generally are accompanied by the formation of hazardous waste. Well explored approaches towards greener and sustainable C-C bond forming reactions involve catalytic C-X (X = H, Cl, Br, I) activation and subsequent cross coupling either involving radical mechanisms² or purely organometallic mechanisms.³ Transition metal catalyzed coupling of alcohols is a promising route to new C-C bonds as they are greener and atom-economical with water as the sole by-product.

For efficient catalysis, it would be desirable to have a subtle balance between catalyst stability and reactivity.⁴ For nearly five decades now, it has been more often found, that pincer-metal complexes perform exceedingly well in striking this balance.⁵ With a particular emphasis on base metals, the current talk would provide a glimpse on the pincer chemistry that is being investigated in our lab, while shedding light on their role in catalyzing C-H activation/functionalization mediated C-C bond formation of alcohols via radical/organometallic pathways that ultimately lead to synthesis of hydrogen, high value fuels and specialty chemicals starting from waste.⁶

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The 8-Aminoquinoline Ligand in Organochalcogen Chemistry

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Abstract: The quinoline ligand has widely been used as a directing group for TM-catalyzed C-H bond functionalization exclusively.¹ However, it has not been well explored in the field of organochalcogen (C-E, E = Se, Te). A quinoline-derived, intramolecular Se...N chalcogen bonded spiro-selenuranes Se(IV) has been synthesized and explored for the disproportionation of H₂O₂ for the first time in organochalcogen chemistry, along with the catalytic organic transformation.² Recently, we have studied the maverick role of quinoline ligand in stabilizing synthetically challenging Te-N heterocycle and tetravalent spiro-telluranes, which exhibited unique catalytic activities.³⁻⁶ We have also synthesized and isolated a new class of hexavalent selenium(VI) benzoselenonates using 8-aminoquinolinyl directing ligand and further explored for metal-free, electrochemical hydrogen evolution reactions (HER).⁷

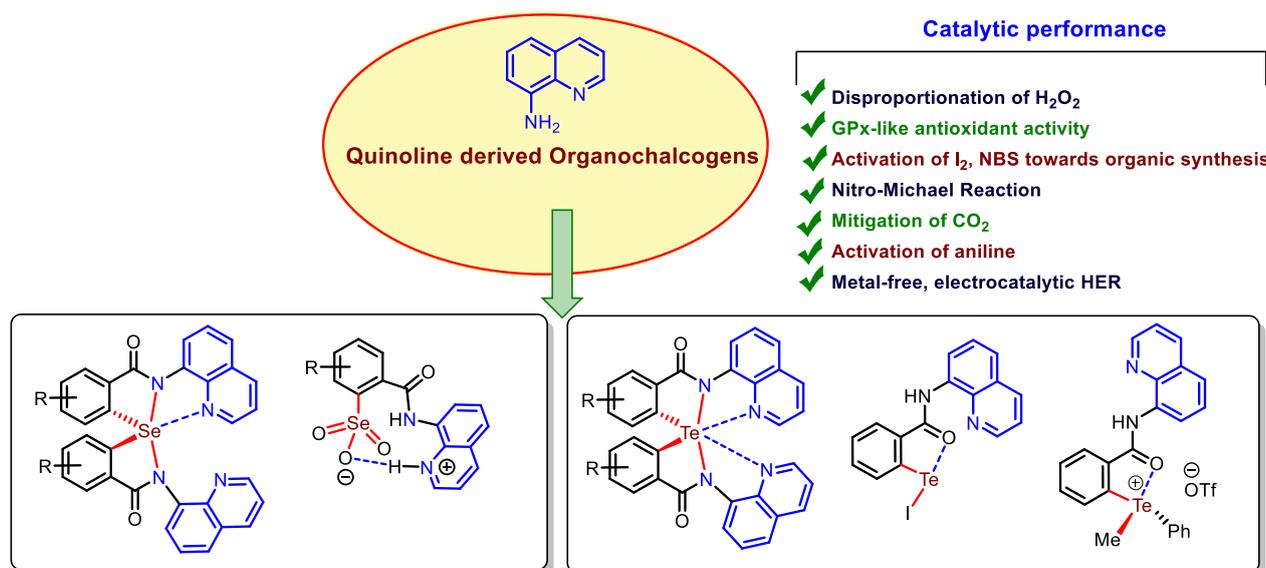


Figure 1. Quinoline-embedded synthesis of organochalcogens and their catalytic activities

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Self-Assembly of Small Supramolecules

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Small inorganic complexes such as cisplatin, carboplatin, and oxaliplatin are well-known frontline chemotherapeutic drugs used against various types of cancer cells. Because of the poor selectivity and severe side effects linked to these compounds, intense research has been going on for the design and synthesis of alternative metallodrugs. Diverse metal ions including gallium, titanium, rhenium, ruthenium, palladium, platinum, silver, and gold have been used in the preparation of potential anticancer agents. Among the metal complexes, rhenium complexes, particularly *fac*-[Re(CO)₃]-based complexes are emerging as one of the promising class of anticancer agents with the potential to overcome the drawbacks of the Pt-based drugs. Considerable research on acyclic *fac*-[Re(CO)₃]-core-based complexes as anticancer agents have been explored, leading to initiation of clinical trials for fourteen Re complexes. Therefore, the design and synthesis of new cyclic rhenium complexes and their biological studies are of utmost importance in search of new class of anticancer metallodrugs. This talk presents a new type of small multi-component rhenium metallocycles which are self-assembled using via multicomponent coordination driven self-assembly approach and their biological studies.

Multifunctional MOFs for Gas Adsorption, Sensor, and Catalysis

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A class of microporous inorganic-organic materials known as metal-organic frameworks (MOFs) has enchanted a colossal amount of research interests due to their extensive applications in gas adsorption, separation of small molecules, renewable catalysis, sensing, drug delivery, nonlinear optics, proton conductivity, imaging, and biomedical applications over the past two decades. Due to their robustness, thermal stability, crystalline nature, larger pores, and Lewis acid, they are on the vacant side of the metal center. MOFs are immensely used as heterogeneous catalysts in some of the challenging and sustainable chemical synthesis such as chemical fixation of carbon dioxide (CO₂) with an epoxide and multicomponent Strecker synthesis gives α -aminonitriles, which are versatile building blocks in the synthesis of α -amino acids. Moreover, luminescent MOFs are found to be efficient sensors in the detection of explosive material (TNP). In this talk, an overview of our efforts in utilizing various imidazole di(tri)benzoic acid MOFs as multifunctional materials for catalysis, adsorption of dyes, and nitroaromatics sensors will be discussed.

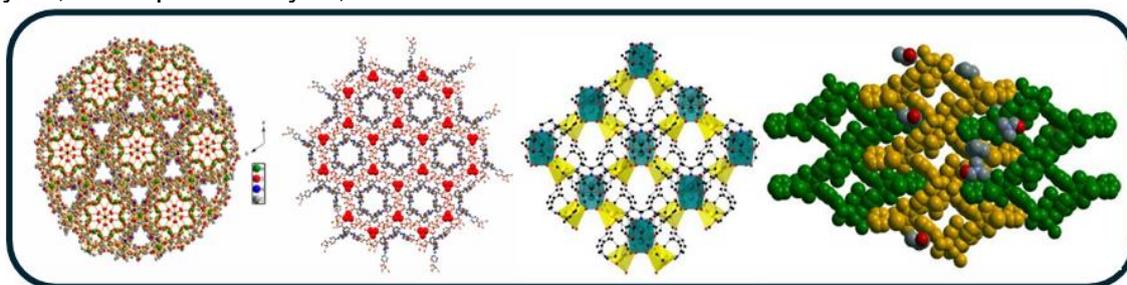


Figure 1: Representative examples of MOFs synthesized from our group

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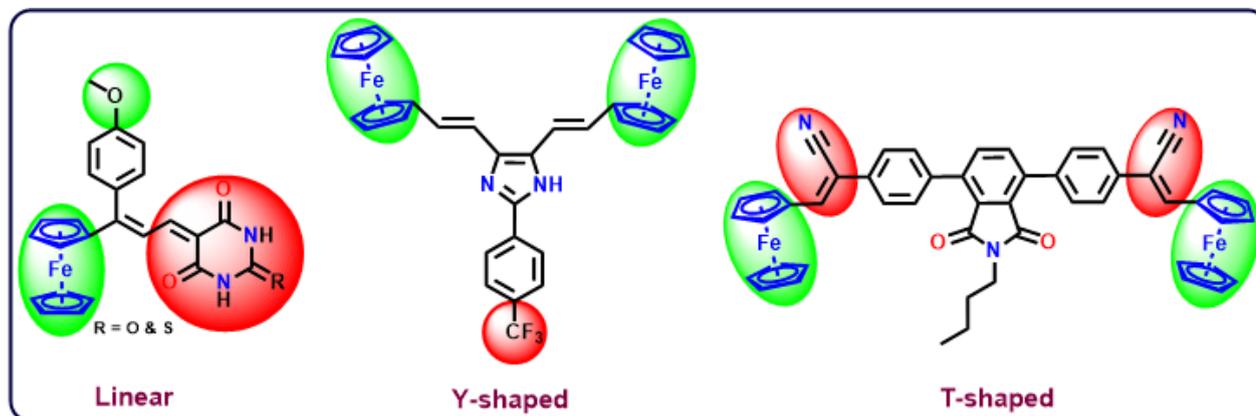
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Linear and Multidimensional Push–Pull Ferrocenyl Chromophores for Second Order Non-Linear Optics

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Materials with second-order nonlinear optical (NLO) properties are of great interest since they can be used for various important applications such as optical communication, optical data processing and storage, and electro-optical devices. Ferrocene (Fc) is an ideal donor in Donor-Acceptor (D-A) or D- π -A motif due to the stability of neutral Fe^{2+} and cationic Fe^{3+} species, and the possibility of convenient interconversion between the two oxidation states. In addition, ferrocene-based X-, Y-, V- and T-shaped heteroaromatic chromophores show enhanced non-linear optical properties compared to linear molecules due to the extended π -conjugation and steric effect. In this context, we have synthesized and structurally characterized a series of linear, X-, Y-, V- and T-shaped ferrocenyl heteroaromatic chromophores (Figure 1). The solid state SHG efficiencies in bulk was measured using Kurtz and Perry powder technique, and the solution state molecular hyperpolarizability (β) was carried out by either Hyper-Rayleigh Scattering (HRS) or Electric Field-Induced Second Harmonic (EFISH) generation techniques. We have observed that the enhanced second order nonlinear optical properties in multidimensional ferrocenyl chromophores and the results will be presented.¹⁻²



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Thiophene-based fused conjugated systems as organic semiconductors

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π -Conjugated systems that include conjugated small molecules and polymers have been an integral part of organic electronic devices such as organic photovoltaics (OPVs), organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs), and organic thermoelectric (OTE). The main prerequisites for using organic semiconductors in printed, flexible electronic devices are (i) high chemical and thermal stability, (ii) high charge-carrier mobility, (iii) solution processability, and (iv) simple synthetic pathways. In addition to molecular design and synthesis, understanding molecular orbital engineering and crystal engineering are crucial for creating the next-generation organic semiconductor. In this context, thiophene-containing conjugated systems are fascinating candidates and are at the forefront of research. In this talk, synthetic approaches to intriguing thiophene-containing conjugated systems, their structure-property connection, and their response in organic electronic and photonic devices will be discussed.

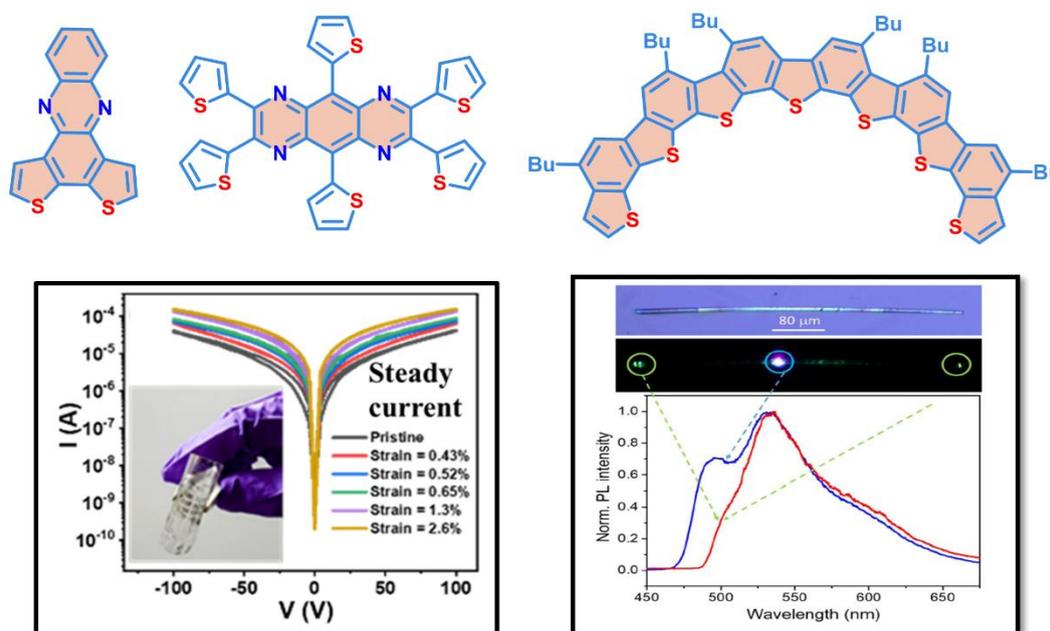


Figure 1 Structures of compounds, device and response of electronic and optical devices.

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Multifunctional Palladium(II) Pincer Complexes of Thiozoline Derivatives

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Pincer ligands are an exciting class of tridentate ligands bonded to a metal center meridionally *via* sigma and/or coordinate covalent bonds. The new generation neutral or monoanionic pincer ligands, P^oC^oP, P^oN^oP, N^oC^oN, S^oC^oS, N^oN^oS, S^oN^oS and N^oN^oN, has been shown to provide stability to the metal centers under drastic conditions. Recently, the late transition metals stabilized through amido pincer ligands are less explored due to the nature of metal repulsive filled p_π-d_π electronic repulsions which make the M-N bond weaker. However, the intrinsic structure of the pincer ligands allows the development of late transition metal amido complexes and to explore their potential applications.

In this regard, we developed a new class of monoanionic amido pincer ligands from thiozoline derivatives (N^{Thio}NH^{Nmp/mor/pip}) and explored their palladium chemistry. The (κ³-N^oN^oN^{Nmp/mor/pip})PdX, palladium complexes have successfully employed in organic transformations (synthesis of quinazolin-4(3H) ones through acceptorless dehydrogenation process), as electrocatalyst (hydrogen evolution reaction) and in biological applications (disrupting the biofilms in urinary catheters).

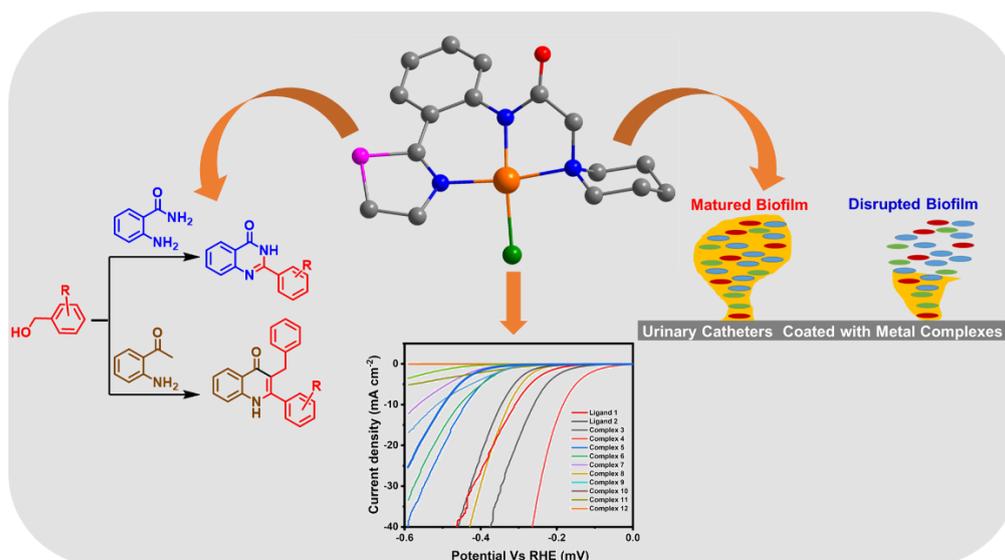


Figure 1: Multifunctional Palladium(II) Pincer Complexes

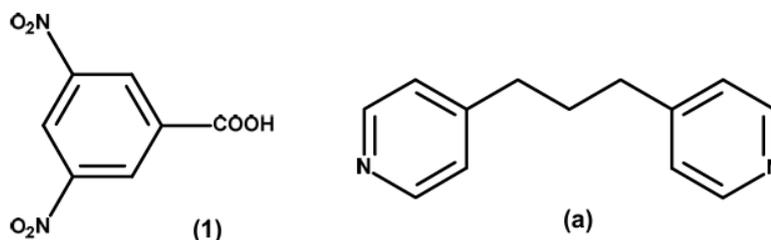
A Landscape of an Organic Composite 3,5-dinitrobenzoic acid and 1,3-bis(4-pyridyl)propane

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In the contemporary supramolecular chemistry, co-crystallization is one of the popular methods to develop organic composite materials, often referred as co-crystals, of varied properties than the co-formers. However, because of the labile nature of intermolecular interactions, for example, hydrogen bonds, prediction of the ultimate ensemble is still an elusive feature in several instances. Herein, such an example is presented considering the co-crystallization studies carried out employing 3,5-dinitrobenzoic acid (1) and 1,3-bis(4-pyridyl)propane (a) as co-formers.



Depending upon the choice of solvent and crystallization conditions, co-formers (1) and (a) form varied types of co-crystals. Thus, at room temperature, a CH₃OH solution yields monohydrated 2:1 crystals, while an anhydrous form in a 2:1 ratio is obtained from a desiccator. Remarkably, changing the solvent from CH₃OH to water, while crystallization at room temperature yields the same as obtained from CH₃OH, interestingly from the desiccator, a sesquihydrated 2:1 composition co-crystals are obtained. Furthermore, by thermal process (heating the co-formers below the m.p.), the co-formers surprisingly form an anhydrous 2:1 ratio co-crystals with three symmetry independent molecules (three) in the asymmetric unit. In addition, the forms obtained from solution growth ultimately undergo transformation at higher temperature to the same as obtained by thermal process.

Polyhedral Oligomeric Silsesquioxane Nanocage Driven Synthesis of Robust and Hydrophobic-Oleophilic Metal-Organic Frameworks for Oil-Water Separation

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The degradation of aquatic ecosystems due to organic pollutants, primarily from industrial wastewater discharge, underscores the need for advanced materials, such as hydrophobic/oleophilic substances, to enhance water remediation efforts. However, the widespread use of hydrophobic materials is hindered by the incorporation of low-surface-energy fluorinated compounds during their synthesis, which raises significant environmental concerns due to their potential toxicity. In contrast, silicon-based compounds offer an eco-friendly, non-toxic alternative and can effectively address these limitations. In response to this challenge, we present a novel, fluorine-free approach for developing hydrophobic Metal-Organic Framework (MOF)-Polyhedral Oligomeric Silsesquioxane (POSS) hybrid materials through both covalent and non-covalent strategies. The successful integration of POSS into MOFs is confirmed using various analytical techniques, including PXRD, TG analysis, FT-IR, ^{29}Si NMR, and X-ray photoelectron spectroscopy. The resulting MOF-POSS materials exhibit an exceptional water contact angle greater than 140° , demonstrating superior sorption selectivity and efficient absorption of organic solvents from water. Moreover, the MOF-POSS@PDA@Sponge composites effectively remove a wide range of organic solvents from water mixtures, achieving separation efficiencies exceeding 90% over 25 cycles. Notably, these materials maintain excellent stability and durability under harsh chemical conditions, owing to the mechanically and chemically resilient nature of the POSS nanocage. Overall, our findings highlight the potential of POSS-supported MOFs as non-toxic, hydrophobic materials, offering significant promise for the efficient separation of organic solvents from aqueous solutions.

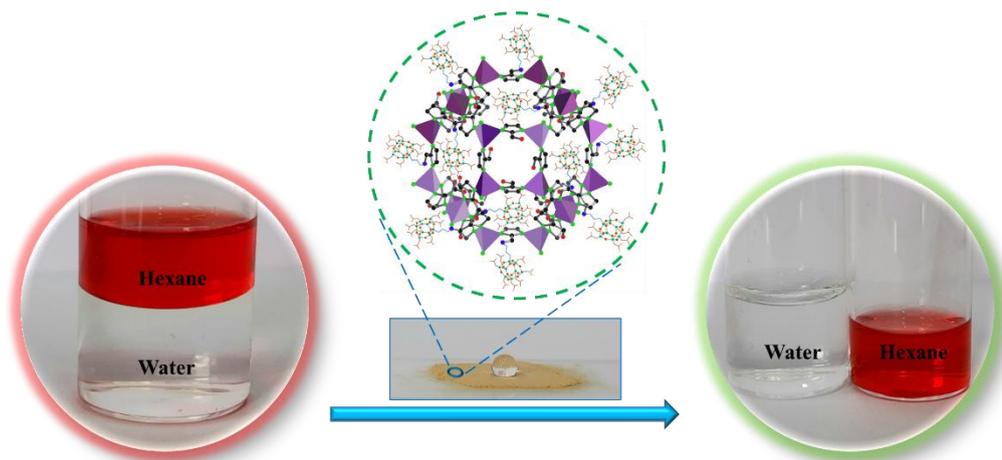


Fig. 1 Schematic representation of Oil-Water Separation by MOF-POSS materials

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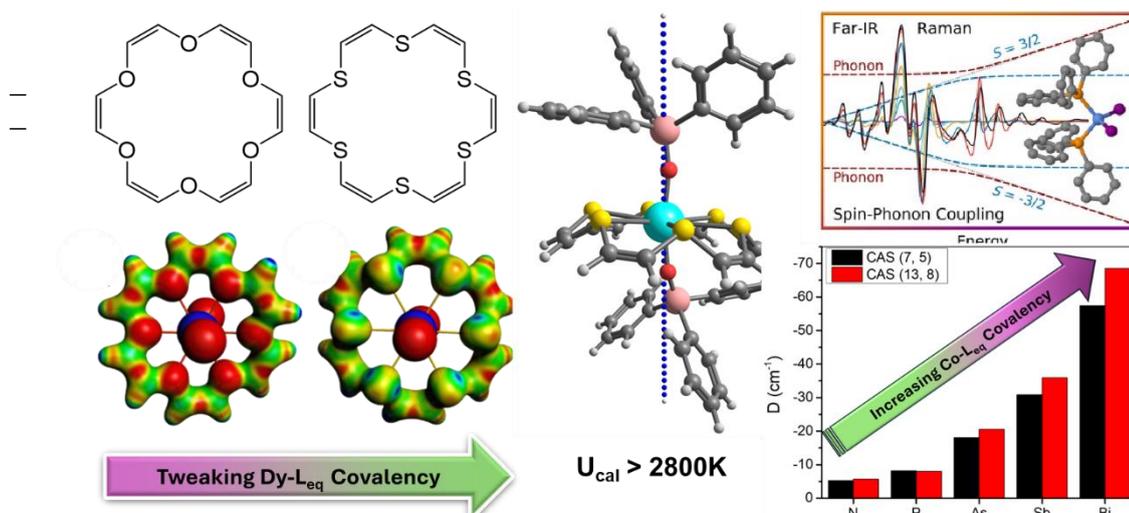
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Heavy p-block Elements in Fine-tuning the Magnetic Anisotropy of Transition Metal and Lanthanide Complexes

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Highly anisotropic mononuclear complexes of the transition metal and lanthanides show a peculiar property of the slow relaxation of magnetization in the absence of the magnetic field and display hysteresis of the molecular origin.¹ These highly anisotropic mononuclear complexes are called Single-Ion Magnets (SIMs), which are highly attractive to explore the quantum effects and have numerous potential applications in information storage devices and molecular spintronics. Accurate modelling of electronic structure and magnetic anisotropy of open-shell d/f-elements is challenging for modern quantum chemistry methods due to the high density of electronic states arising from degeneracy or near degeneracy of the orbitals, proper treatment of the relativistic effects, and subtle metal-ligand covalency. The inclusion of heavy p-block elements in the transition and lanthanide-based SIMs has become a fascinating approach to increasing magnetic anisotropy and SIM performance.² In my presentation, I will highlight how the heavier p-block donor atoms, with their relatively diffuse valence orbitals and more diverse bonding characteristics in the first coordination sphere, introduce the scope for tuning the spin-orbit coupling properties and metal-ligand covalency in molecular magnets.³ I will describe the use of ab initio-based ligand field theory (AILFT) in conjunction with multireference ab initio methods to analyze the metal-ligand covalency (symmetry adapted and central field covalency) in transition metal and lanthanide complexes and how it plays a crucial role in controlling the magnetic anisotropy of these metal complexes.



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Exploring Bis-Guanidinate-Stabilized Zinc(I) Dimer, Zinc(II) and Gallium(III) Hydrides in Catalysis

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In this talk, I present the synthesis of unusual bis-guanidinate stabilized zinc(I) dimer, used as a (pre)catalyst for the dehydroborylation of terminal alkynes¹ and zinc(II) hydride complex as a highly efficient catalyst for the hydrosilylation and hydroboration of cyanamides, representing the first example of cyanamide functionalization using a molecular zinc hydride complex. The active catalyst/key intermediate, a zinc amidinate complex, was isolated and structurally characterized.² Additionally, I will discuss the bis-guanidinate-supported synthesis, reactivity studies, and catalytic applications of gallium(III) dihydride complex.³

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Metal-Organic Framework (MOF) Glasses and Liquids for Sustainable Processes

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Metal-organic frameworks aka MOFs are renowned for their highly ordered crystalline structure, designability, porosity and host-guest chemistry. These crystalline materials are now further being pushed forward in new avenues where the traditional boundary between solid and liquid blurs. The recent discovery of melting MOFs and MOF-based Porous Liquids (PLs) have introduced a new frontier in the field of porous materials. MOF glasses are highly disordered structures that retain the inherent framework connectivity which leverages advantages such as shaping, hierarchical porosity and grain boundary-free monoliths.¹ Often neglected, investigating their melt state can give valuable insights into the melting mechanism.² On the other hand, PLs have been in the hotspot due to their permanent microporosity and flow properties. They merge the properties of solids and liquids which endow them with novel functionalities that are inaccessible otherwise.³ Both, MOF glasses and porous liquids are defined by their common trait i.e. the ability to maintain porosity while offering structural flexibility which allows them to be used in dynamic environments to meet the demands of next-generation chemical processes and energy applications.⁴

In this talk, I will present our efforts toward the development of MOF melts, glasses and porous liquids for sustainable chemical processes.

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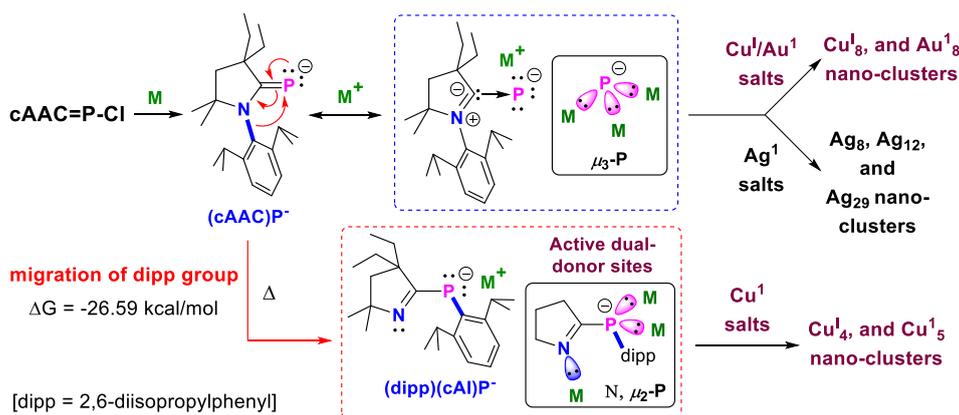
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Monoatomic Phosphorus Anions: A New Horizon of Stabilizing Ligands for Isolation of Novel Transition Metal Nano-Clusters as Light Emitting Materials

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Efficient routes have been developed for the solid state isolation of carbene-supported mono-atomic phosphorus anion $[cAAC=P^-]$,^{1a} and the (aryl)-cyclic alkyl(imino) phosphides $[(Ar)(cAl)P^-]$ ^{1b} from the corresponding carbene-chloro-phosphaalkenes $[cAAC=PCl]$ by alkali metal-mediated direct reduction of the P-Cl bond, and the reductive thermal rearrangement at an elevated temperature, respectively. Both the species have been potentially utilized as the excellent ligands with various modes of coordination to the metal centres affording the syntheses of novel transition metal clusters with different nuclearities, exhibiting promising applications as light emitting materials and photo-redox catalysts.²



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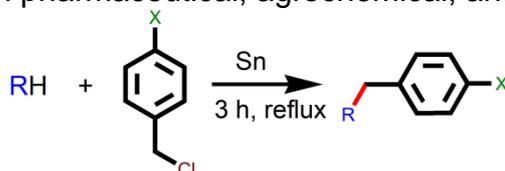
Tin Assisted Multiple C-C Bond-Forming Reactions in a Single Step

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The oxidative-addition reaction between an arylmethyl chloride (RCH_2Cl ; $\text{R} = 1\text{-C}_{10}\text{H}_7$, $2,4,6\text{-Me}_3\text{C}_6\text{H}_2$, $4\text{-MeC}_6\text{H}_4$, $3\text{-MeC}_6\text{H}_4$, C_6H_5 , $4\text{-ClC}_6\text{H}_4$) and tin powder in boiling toluene produces bis(arylmethyl)tin dichlorides, $[(\text{RCH}_2)_2\text{SnCl}_2]$ in good yields [1]. Bis(1-naphthylmethyl)tin dichloride in mesitylene at 160°C undergoes Sn-C homolytic cleavage to generate two 1-naphthylmethyl radicals ($1\text{-C}_{10}\text{H}_7\text{CH}_2^\bullet$), which were trapped by TEMPO ($\text{C}_9\text{H}_8\text{NO}^\bullet$)/4-hydroxy-TEMPO/4-oxo-TEMPO. Subsequently, we utilized the radicals (RCH_2^\bullet) produced in this manner for efficient substitution reactions with electron-rich arenes ($\text{R}'\text{H}$; $\text{R}' = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$, $1,2,4,5\text{-Me}_4\text{C}_6\text{H}$, $1,2,3,4,5\text{-Me}_5\text{C}_6$) to obtain a variety of unsymmetrical diarylmethanes ($\text{RR}'\text{CH}_2$). In the case of anisole or xylenes, iodine mediation is necessary to favor the desired diarylmethane derivatives through Friedel-Crafts reaction [2]. We have recently established a new strategy for obtaining multiple halo-substituted arenes in a single step by directly reacting haloarylmethyl chlorides with arenes and tin powder [3]. Functionalized diarylmethanes have been investigated extensively due to their wide-ranging applications in pharmaceutical, agrochemical, and material sciences [4].



$\text{RH} = \text{Me-substituted arene}; \text{X} = \text{F or Cl}$

No Expensive Catalyst; No Lewis acid

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Orbital engineering of heavier group 14 and 15 cationic compounds for catalytic functions

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We are interested in tuning the frontier electronics of the heavier Group 14 and 15 elements in their regular or low-oxidation states and develop new catalytic manifolds by translating their unique electronic features into creative catalysts.[1],[2] Along this direction in Group 14 chemistry, we have established the intramolecular donor stabilized tetra coordinated Ge(IV) di-cations as Lewis acid catalysts in recent times.[3] Therein, we have reported the preliminary tests on the catalytic hydrosilylation of benzaldehyde using the Ge(IV) di-cations as catalysts. Further investigations reveal that the choice of the donor groups manipulate the extent of Lewis acidity at the Ge centre and thus serve as versatile catalysts for various organic transformations. We have studied element-element cooperative reactivity using heavier Group 15 elements.[4] The cationic distibane and dibismuthane compounds synthesized can activate small molecules. The concepts developed in our group in terms of modulating the geometry and electronics of these positively charged compounds for catalytic applications will be discussed.

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O,S-Chelated Fluorescent Boron Compounds: Synthesis, Characterization and Photophysical Studies

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Tetra-coordinated boron based fluorophores have attracted a great deal of attention due to their properties such as high absorption, emission, electron acceptability, and high stability as well as their applications in fields such as nonlinear optics, organic field effective transistor (OFETs), organic light emitting diodes (OLEDs), photovoltaics, and sensors. Variety of methods have been used to tune the photophysical properties of four-coordinated boron compounds. Among the different approaches studied tuning the chelation (N,N-, N,O, O,O-, N,C-) gained considerable attention. S,O-chelated boron compounds are underdeveloped, in my presentation, I will discuss our recent efforts to make different S,O-chelated tetra-coordinated boron based fluorophores and their applications.

Bio-derived porous carbon nanospheres based catalytic systems for Suzuki-Miyaura cross coupling, nitroarene reduction, and reductive degradation of azo compounds.

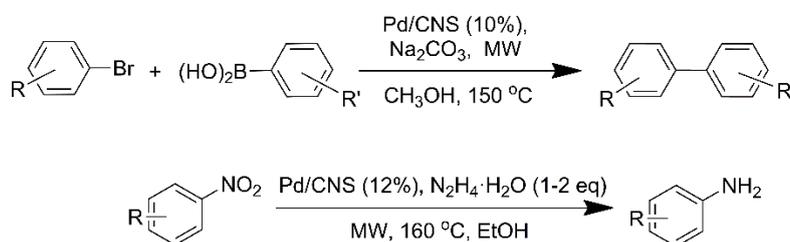
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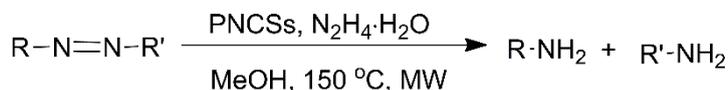
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A new heterogeneous catalyst was prepared by immobilizing Pd metal on the carbon nanospheres (CNSs) derived from areca nut kernel. Without undergoing any additional activation procedures, the CNSs were able to hold 3% of Pd on their surface. The new Pd/CNS catalyst was used as a catalyst for both Suzuki-Miyaura cross coupling¹ of bromoarenes with aryl boronic acids and for the reduction of nitroarenes (Scheme 1). The reactions were carried out with 10-12% Pd/CNS (0.3 - 0.36% actual Pd content) at high temperature (>150 °C) under microwave irradiation. While nitroarenes were reduced into their corresponding amino compounds in 10–20 minutes (conversion up to 100%), the Suzuki–Miyaura reactions produced up to 98% conversion with 10 mol% Pd/CNS catalyst. Further, the catalyst was isolated from the reaction mixture and reused without any significant loss in the activity.²



Scheme 1. Suzuki-Miyaura cross coupling and reduction of nitroarenes

Porous nanocarbon spheres (PNCSSs) derived from onion peel were utilized for metal and oxidant free reductive degradation of azo compounds (Scheme 2). The reductive cleavage is achieved under microwave irradiation, in the presence of PNCSSs catalyst, and hydrazine as reducing agent.³



Scheme 2. Reductive degradation of azo compounds

The details of preparation of catalysts, optimization, and substrate scope in catalytic reactions will be presented.

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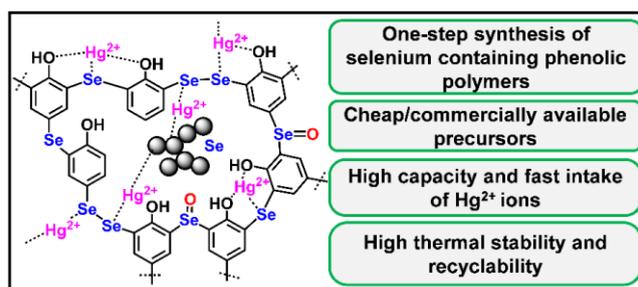
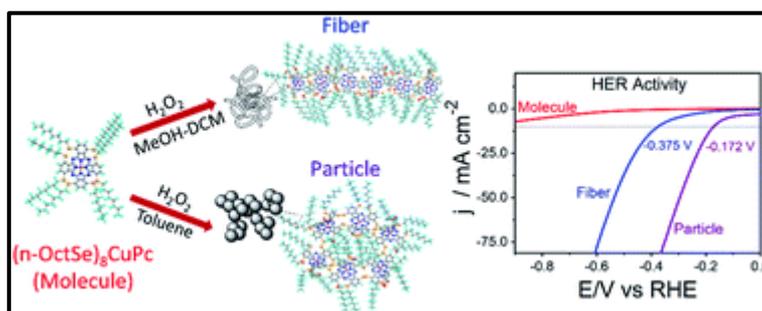
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Structure Functional Aspects of Hierarchically Structured Selenium Containing Polymers

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The properties of polymers are governed by the complex interplay of weak intermolecular forces, such as dispersion, dipole-dipole and hydrogen bonding. These forces drive the formation of self-assembly and subsequent evolution of hierarchically structured materials that show distinct stimulus responsiveness and catalysis. However, architecting functional polymers for high performance applications, not limited to stimulus responsiveness and catalysis, requires the judicious choice of components that constitutes the polymers. I will talk about our recent progress that highlights the role of chemical reactivity of selenium towards the introduction of catalytic sites in polymers and its role as heavy metal ion recognition motif in hierarchically structured selenium containing polymers.



Keywords: Selenium, synthesis, polymers, phenol, phthalocyanine, catalysis

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Secondary Phosphine sulfide stabilized Gold Nanoparticles for Hydrogen Evolution Reaction

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Phosphorus has rich capability of forming organosulphur derivatives. Among these, phosphine sulphides have diverse applications in synthetic, pharmaceutical, and medicinal chemistry.¹ Over time, complexes of these ligands were found to be excellent catalysts for a wide variety of organic transformations but their use as a hydrogen production is newer.^{1,2} This investigation is directed towards the introduction of new family of ligand secondary phosphine sulphide (SPS) to synthesise Au-SPS nanoparticle (6.2 ± 1 nm) and their elucidation as cathode electrocatalyst for hydrogen evolution reactions. The Au-SPS nanostructures were characterised using high resolution transmission electron microscopy (HR-TEM), X-ray diffraction, FTIR analysis, Brunauer-Emmett-Teller (BET) surface area measurements, electron dispersive analysis, and X-ray photoelectron spectroscopy. The electrocatalytic performance was evaluated using cyclic voltammetry (CV), linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS), and Tafel polarization measurements. The results demonstrate an onset potential of 329 mV versus RHE, reached at a current density of 10 mA/cm². Additionally, the Tafel slope was measured at 131 mV/dec, with an exchange current density of 10 mA/cm², remarkable stability (over 500 cycles) and a low charge transfer resistance 11.29 Ω . This catalyst notably reduces cell costs and streamlines the preparation process in comparison to existing high-efficiency platinum and other noble metal-free cathode electrocatalysts.

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Electronic and Steric Modulation of Low-Valent Aluminum Compounds

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The physical and chemical properties of an organometallic compound are significantly influenced by the spatial environment surrounding its metal centers.¹ Consequently, chemists have focused on designing the structural, electronic, and dynamic properties of supporting ligands to harness the potential of organometallic compounds in various fields, including catalysis,² supramolecular chemistry,³ and materials science.⁴ A well-established strategy for tuning electronic properties involves employing different donor ligands, while the spatial environment around metal centers can be modulated using ligands with bulky substituents. In this report, we demonstrate how altering donor ligands around an aluminum center can yield distinct outcomes. The reduction of durylaluminum dibromide coordinated with a cyclic (alkyl)(amino)carbene (CAAC) ligand—specifically, 1-(2,6-diisopropylphenyl)-3,3,5,5-tetramethylpyrrolidin-2-ylidene—results in the formation of open-shell singlet diradicals (**2a** and **2b**, Scheme 1).⁵ In contrast, coordination with an N-heterocyclic carbene (NHC) ligand—1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene—leads to the formation of a near-linear trialuminum system, **4** (Scheme 1).⁶

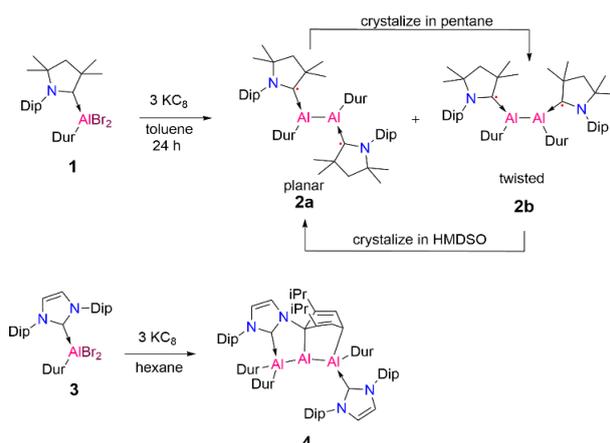
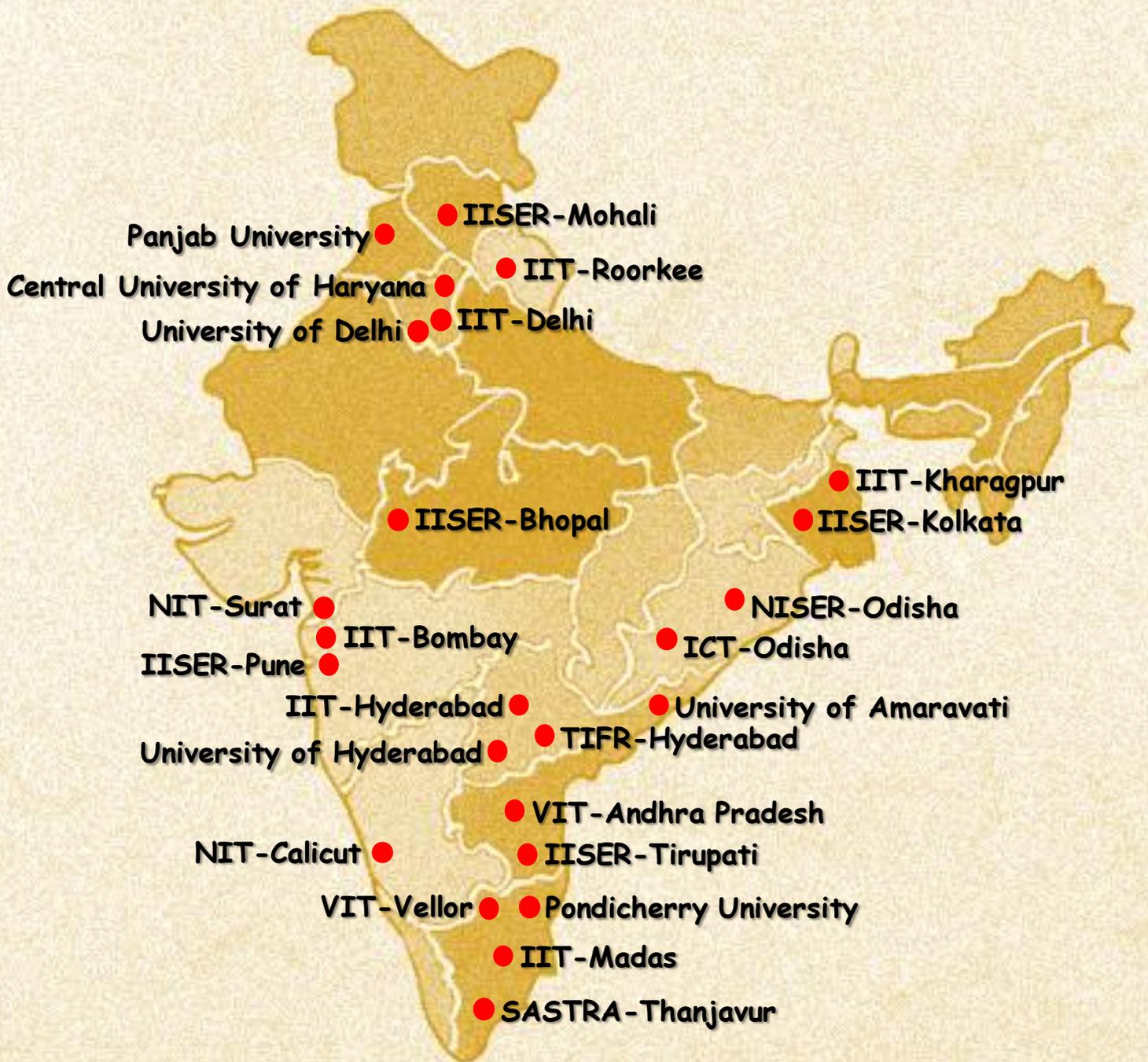


Figure 1 Reduction of CAAC substituted and NHC substituted durylaluminum dibromide.

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Students Participants for the MMM-4



Isomeric Neutral Tetrahedral Pd (II) Cages Assembled by Asymmetric Amido-Oxoacetate Linkers and their Guest Encapsulation Studies

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Designing polyhedral metal-organic cages requires geometrically compatible metal ion-ligand pairs. Understanding self-assembly pathways enhances insights and design strategies. In this regard, we reported self-assembly of isomeric neutral tetrahedral Pd(II) cages by the 2(methylamino)-2-oxoacetate linker molecular formula $[\{Pd^3(N^iPr)_3PO\}(C_3H_5NO_3)_6]$ **1**, forming five major structural isomers. The most stable isomer, Cage **1a**, selectively separates cyclohexane from cyclopentane. MALDI-TOF and UV spectroscopy revealed an intermediate state transitioning from an acetate-bridged cluster to $[\{Pd_3(N^iPr)_3PO\}(C_3H_5NO_3)_6]$. Cage **1** crystallized into two distinct shapes in DCM solvent via slow evaporation, with hydrodynamic radii from X-ray crystallography and 2D DOSY NMR perfectly matching. Only the two lowest-energy isomers predicted by DFT optimization crystallize. Cage **1**'s 86 Å³ cavity selectively encapsulates cyclohexane (1:1 binding) over cyclopentane (2:1 binding), as determined by NMR. Cyclohexane adopts a half-chair conformation when crystallized, with computational studies showing the energy trend: Half-chair < Twist-boat < Boat < Chair.

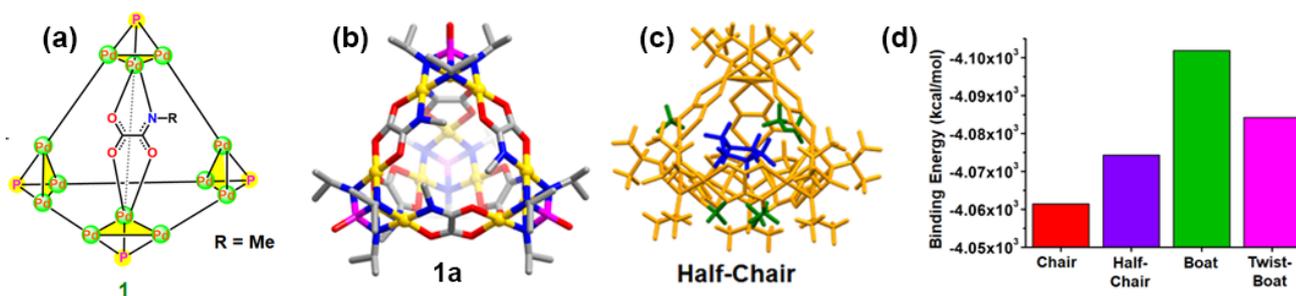


Figure 1 : (a) ChemDraw schematics of Cage **1**. (b) Most stable isomer of Cage **1**. (c) Cage showing Cyclohexane half-chair conformation stabilized in its core. (d) Binding energy diagram calculated for different conformers of cyclohexane.

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Carbon Dots from Medicinal Plant Leaves for Photophysical and Forensic Applications

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Carbon dots (CDs), known for their excellent photoluminescent properties, have received a lot of attention in various fields. The synthesis of carbon dots from medicinal plants provides a sustainable, economical, and biocompatible alternative to chemical synthesis, potentially enhancing functionality through the plant's intrinsic bioactive compounds. This study presents the green synthesis of carbon dots (CDs) from the leaves of a medicinal plant through pyrolysis to underscore the impact on the optical and physicochemical properties of the CDs. The synthesized CDs were characterized using UV-visible spectroscopy and photoluminescence (PL) analysis, which demonstrated excitation-dependent emission, a feature of carbon dots, FTIR, and Raman spectroscopy. Techniques like DLS, TEM, XPS, and XRD are employed to thoroughly investigate the size, morphology, crystallinity, and surface composition of the CDs. The synthesized CDs are explored for forensic applications utilizing their tunable fluorescence and surface versatility.

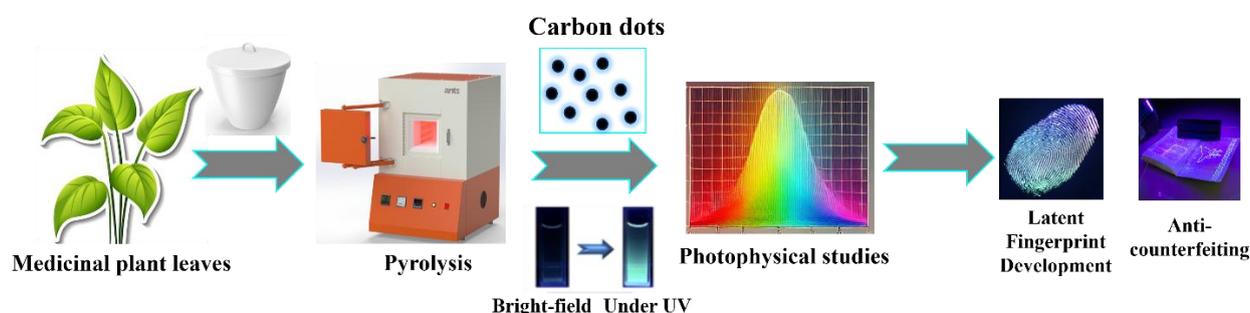


Figure 1 Graphical illustration of the synthesis of carbon dots

Synthesis and studies of covalently linked 3-pyrrolyl BODIPY-BODIPY dyads, triads, and pyrrolyl-BODIPY-incorporated porphyrins

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A series of covalently linked 3-pyrrolyl BODIPY-BODIPY dyads **1**, triads **2**, and *meso*-3-pyrrolyl BODIPY porphyrins **3** were synthesized and explored their physico-chemical properties. Structural analysis revealed distinct molecular orientations that influence electronic interactions and intramolecular singlet-singlet energy transfer. In dyads **1** and triads **2**, efficient energy transfer (up to 98%) occurs from the BODIPY donor to the 3-pyrrolyl BODIPY acceptor, as verified by steady-state and time-resolved fluorescence studies.¹⁻² In *meso*-3-pyrrolyl BODIPY porphyrins, the pyrrolyl-BODIPY unit(s) acts as an energy donor, while the porphyrin core serves as an efficient acceptor with an energy transfer efficiency up to 86%. The presence of multiple pyrrolyl-BODIPY units at the *meso*-positions of the porphyrin led to significant Q-band broadening, enhancing spectral absorption, rapid excitation, and rapid recovery to the ground state. These properties make them promising candidates for advanced photonic and energy-harvesting applications.³ These results will be presented in the poster.

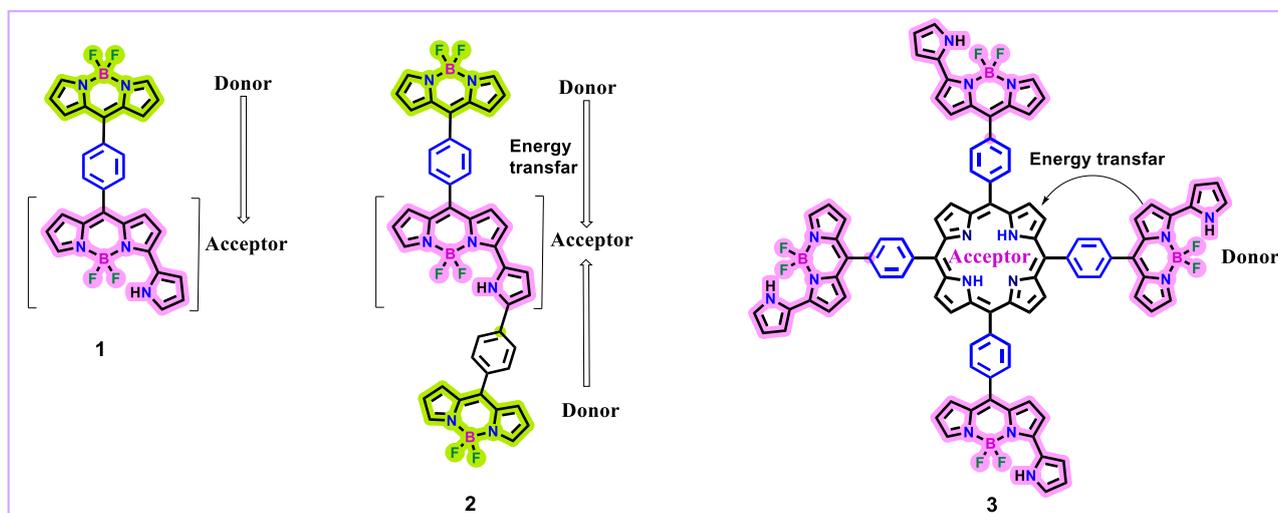


Figure 1: Molecular structures of pyrrolyl BODIPY-BODIPY containing dyad (**1**) and triad (**2**). Pyrrolyl-BODIPY incorporated porphyrin (**3**).

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Vanadyl Quinolinates: Possible Candidates for Qubits

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Molecular spin systems, particularly vanadium(IV) complexes, offer tunable qubits with long coherence times due to d-orbital splitting and a single unpaired electron.¹⁻³ Unlike silicon and diamond defect systems, their interactions can be precisely controlled through synthetic design, making them promising candidates for quantum technologies.^{4,6} Herein, we report the synthesis and detailed characterization of a new oxovanadium(IV) complex, vanadium oxo bis(8-hydroxyquinoline-2-carbaldehyde) [VO(Q-CHO)₂] (**1**), as a potential qubit material. Comprehensive analysis using single-crystal X-ray diffraction and electron spin resonance (ESR) spectroscopy, including pulse-EPR studies, revealed significant spin relaxation (T_1) and phase memory times (T_m) ranging from 0.184 to 0.606 μ s at 5.0 K across various resonant pulse fields, surpassing similar systems (Figure 1). The unique coordination geometry around V(IV) is attributed to these enhanced coherence properties. Efforts are underway to further modify the aldehyde moiety into Schiff bases with various amines to enhance coherence times, offering insights into molecular design strategies for optimized qubit performance.

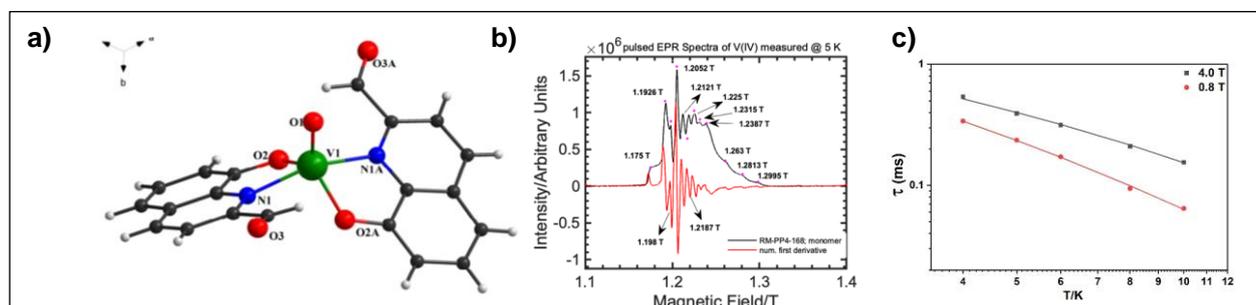


Figure 1. a) Molecular structure of [VO(Q-CHO)₂] (**1**), b) EDFS spectra of a polycrystalline sample of **1** recorded at 5.0 K, and c) Temperature dependence of τ extracted from ac susceptibility measurements for compound **1** at different applied static magnetic field values.

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Acknowledgement:

The pulse EPR studies were done in collaboration with [Dr. Muralidharan Shanmugam](#) & [Prof. Eric J.L. McInnes](#).

Unravelling the Role of Sterically Encumbered Phosphoramides in Tuning the Magnetic Properties of Lanthanide-Based D_{5h} Single-Ion Magnets¹

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Gopalan Rajaraman^{a*} and Ramaswamy Murugavel^{a*}

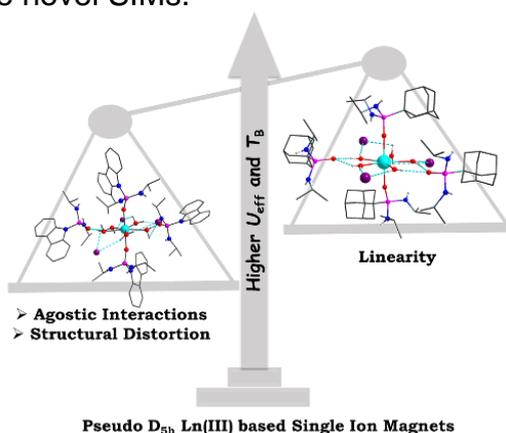
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Isostructural Dy(III) and Er(III) complexes $[L^1_2Ln(H_2O)_5][I]_3 \cdot L^1_2 \cdot (CH_2Cl)_2$ ($Ln = Dy$ (**1**), Er (**3**)) and $[L^2_2Ln(H_2O)_5][I]_3 \cdot L^2_2 \cdot (CH_2Cl)_2$ ($Ln = Dy$ (**2**), Er (**4**)), with distorted pentagonal bipyramidal geometry (D_{5h}) around the central metal were synthesized by utilizing two bulky phosphoramidate ligands, adamantyl phosphoramidate, (Ad)P(O)(NHⁱPr)₂ (**L**¹) and carbazoyl phosphoramidate (Cz)P(O)(NHⁱPr)₂ (**L**²). The resultant complexes were investigated for their magnetic properties in order to elucidate the impact of modification of the coordinating P-O bond environment either by increasing steric bulk and/or introduction of a third P-N bond at the central phosphorus atom. Magnetic studies revealed substantial energy barriers (U_{eff}) of 640 K and 491 K for Dy compounds **1** and **2**, respectively, rendering them as some of the best-performing air-stable SIMs amongst the class of SIMs with D_{5h} symmetry. Compounds **1** and **2** exhibit magnetization blocking (T_B) at 6.5 K and 6 K, respectively, at a sweep rate of 20 Oe/s. Compound **1** benefits from increased lattice intermetallic distances due to bulky adamantyl substituent, but exhibits a significant deviation from linear axial (P)O-Dy-O(P) geometry ($173.7(1)^\circ$). In addition to the deviation from linearity, the incorporation of a bulky adamantane (or carbazole) ligand in complex **1** (or **2**) was found to result in relatively strong Dy...H-C agostic interactions, with distances of 3.698 Å (3.376 Å). These interactions are expected to induce transverse anisotropy. Ab initio CASSCF/RASSI-SO/SINGLE_ANISO calculations offer valuable insights into the dynamics of magnetic relaxation and the impact of axial bulkiness on the anisotropy of D_{5h} systems. Beyond highlighting the crucial role of crystal field and symmetry in achieving high-temperature SIMs, this study also explores how the secondary coordination sphere can be engineered to create novel SIMs.



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Fluorescent Zinc(II) Thione and Selone Complexes for Light-Emitting Applications

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We have synthesized and comprehensively characterized one 1-(anthracene-9-ylmethyl)-3-isopropyl-imidazol-2-selone Zn(II) dichloride complex (**4**) and three 1-(anthracene-9-ylmethyl)-3-isopropyl-imidazol-2-thione Zn(II) halide complexes (**1-3**). All these complexes displayed emission in the crystalline state, with complex **3** showing emission in the yellow region and **1** and **4** in the blue, while **2** gave bluish-green emission. The ligands **L¹** and **L²** were non-emissive in both solution and crystalline state. The photophysical behavior of these four complexes was studied and the quantum yield in crystalline state was obtained. Complex **1** gave the highest quantum yield of 7.72% while complex **4** had the lowest quantum yield of 3.87%. The complexes' crystalline state quantum yield varies with the halide variation coordinated to the metal center as $\text{Cl}^- > \text{Br}^- > \text{I}^-$. The quantum yield for the thione complexes **1-3** is better than the selone complex **4**. TD-DFT natural transition orbital calculations reveal that intra-ligand charge transfer (¹ILCT) mediated through the metal center is responsible for the observed emission behavior.

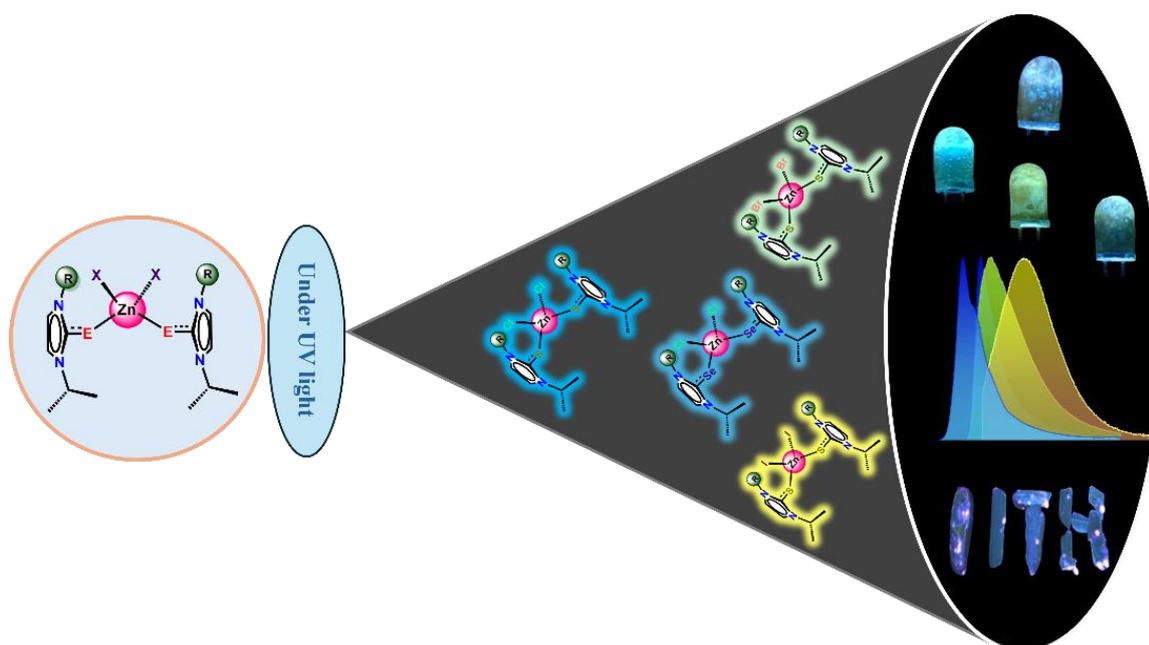


Figure 1: Schematic representation of fluorescent Zn(II) to thione and selone complexes

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Fluorescent Zinc(II)pyrimidazole-2-chalcogenone Complexes: Promising Materials for Light-Emitting Applications

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Organic light-emitting diodes (OLEDs) have gained immense attention for applications in full-color displays and solid-state lighting (SSL).¹ However, the stability issues of organic molecule-based OLEDs limit their operational lifespan. To address this, luminescent metal complexes have been explored, but these often rely on expensive and scarce metals like iridium and platinum.²⁻³ Zinc, being abundant, inexpensive, and non-toxic, presents a viable alternative if designed appropriately.⁴ In this study, we synthesized and characterized Zn(II) pyrimidazole-2-chalcogenone complexes (**1-3**) with distorted tetrahedral geometries. Photophysical analysis revealed blue to cyan emissions, with complexes **1** ($\lambda_{\text{max}} = 454 \text{ nm}$, $\Phi = 7.33\%$) and **2** ($\lambda_{\text{max}} = 487 \text{ nm}$, $\Phi = 8.01\%$) exhibiting superior quantum yields compared to complex **3** ($\lambda_{\text{max}} = 495 \text{ nm}$, $\Phi = 1.2\%$). TD-DFT calculations suggest intra-ligand charge transfer as the primary emission mechanism. These complexes, with excellent air and moisture stability, show significant promise for LED applications.

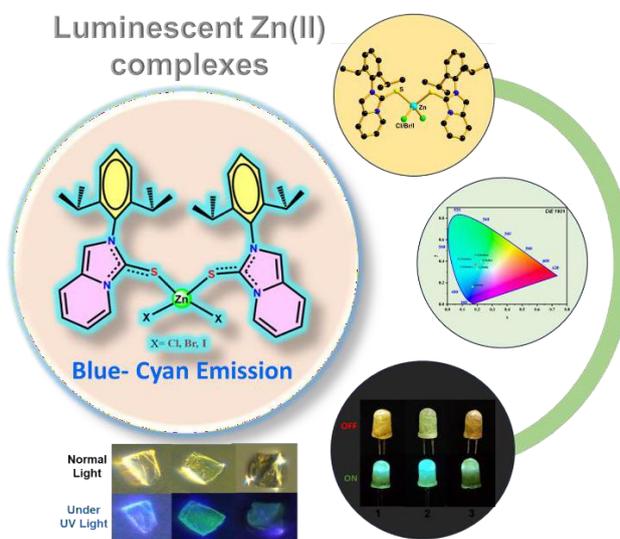


Figure 1. The light-emitting fluorescent Zn(II)Pyrimidazole-2-Chalcogenones complexes.

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Magnetic Behaviour of Mononuclear Cobalt(II) α -Hydroxy Aryl Phosph(on)ates Complexes

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The cobalt phosph(on)ates are of particular interest due to their potential application as single-ion magnets (SIMs)¹. The unique coordination environment, enhanced by hydrogen bonding interactions and influenced by the N-donor ligands, provides a high degree of magnetic anisotropy and slow relaxation dynamics. These features make them promising candidates for applications in molecular magnetism, such as data storage², spintronic devices³, and quantum computing⁴. A series of mononuclear cobalt(II) complexes have been synthesized with various ancillary N-donor ligands which features mononuclear tetrahedral high-spin Co(II) centers. Magnetic measurements reveal that the three complexes possess magnetic anisotropy with negative zero-field splitting parameters, which changes with varying distortion of the pseudo-tetrahedral Co(II) coordination geometry. EPR spectroscopy and theoretical calculations have been used to probe the nature and magnitude of the magnetic anisotropy of these complexes. Further, detailed analysis of the relaxation process indicated the prevalence of the Orbach and Raman process at low temperature. Investigation of the dynamic behavior of the magnetization of these complexes shows that the mononuclear tetrahedral cobalt(II) complexes exhibit field-induced slow magnetic relaxation under an applied dc field, indicating SMM behavior.

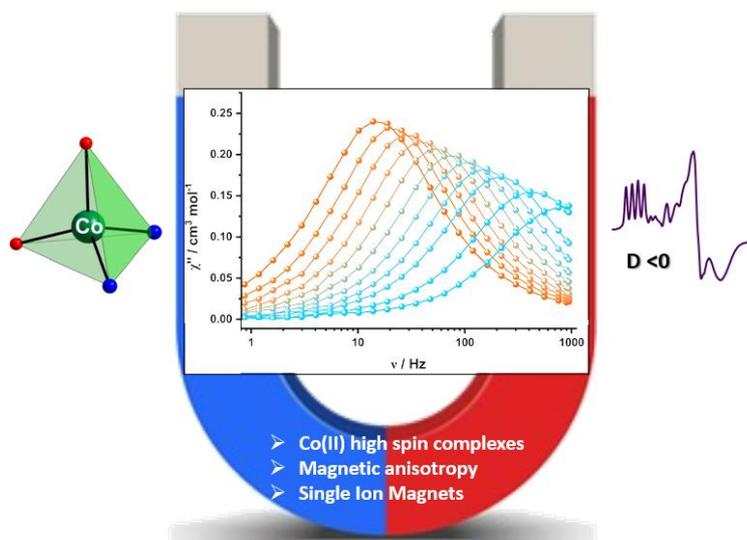


Figure 1. Graphical representation for cobalt(II) based single ion magnets with tetrahedral geometry.

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Temperature-dependent one-pot synthesis of In NPs, green and red InP quantum dots with exceptionally narrow emission full-width at half-maximum (FWHM)

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Abstract: Within the III-V semiconductor nanocrystals, indium phosphide (InP) quantum dots have garnered significant interest owing to their unique characteristics viz., covalency, less toxic, broad emission range, alternative, and effective usage in a variety of applications, such as photovoltaics, light-emitting diodes, and bio-imaging. It has been challenging to selectively produce green InP over red using existing synthetic methods. Herein, we have presented a novel single-step synthesis of green and red-emitting InP. In an interesting observation, we observed that the reaction between InCl_3 and tris(dimethyl)amino phosphine $[(\text{DMA})_3\text{P}]$, assisted by hexamethyldisilazane (HMDS), yielded green and red InP QDs. Unlike conventional synthetic procedures, our preparation method allowed selective production of indium(0) nanoparticles (In-NPs), green or red InP, by controlling the reaction time and temperature. This method produced In-NPs, green InP, and red InP with average particle sizes of 3 to 5 nm with a narrow particle size distribution. The obtained green and red InP exhibited sharp emission at **561 nm** (FWHM = 8.4 nm) and **721 nm** (FWHM = 17 nm), with bandgaps of **2.25 eV** and **1.71 eV**, respectively.

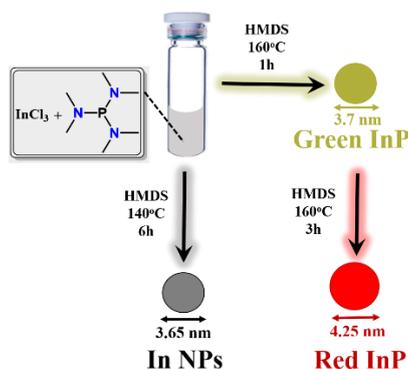


Figure 1: Graphical representation of the synthesis of In NPs, Green InP, Red InP.

References:

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2. G. Almeida, et al., *Nano Lett* **2023**, *23* (18), 8697–8703.

Homochirality-Induced Piezoelectricity in a Single-Component Molecular System

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Organic piezoelectric materials have recently garnered significant attention as potential alternatives to ceramics.¹ However, there are only a handful of reports on single-component molecular crystals exhibiting piezoelectric properties. Introducing homochirality is one of the simplest approaches to achieving piezoelectricity in molecular crystals. Herein, we present an enantiomeric pair of compounds (*R*)-2-(((1-(*p*-tolyl)ethyl)imino)-methyl)phenol (**^RPTIMP**) and (*S*)-2-(((1-(*p*-tolyl)ethyl)imino)-methyl)phenol (**^SPTIMP**) crystallizing in the noncentrosymmetric $P2_12_12_1$ space group making them suitable for piezoelectric studies. In contrast, the racemic mixture of these compounds, *Rac*-2-(((1-(*p*-tolyl)ethyl)imino)methyl)phenol (**^{Rac}PTIMP**), crystallizes in the centrosymmetric $P2_1/n$ space group. The noncentrosymmetry of both **^RPTIMP** and **^SPTIMP** was confirmed through second harmonic generation (SHG) measurements, showing the SHG efficiencies of 0.11 and 0.12, respectively, relative to standard potassium dihydrogen phosphate (KDP). Piezoelectric coefficient (d_{33}) measurements on a powder-pressed pellet of **^SPTIMP** resulted in a d_{33} value of 4.7 pC N⁻¹. The piezoelectric energy harvesting experiments performed on the poled thermoplastic polyurethane (TPU) composite films of **^SPTIMP** resulted in a maximum voltage output of 7.04 V for the 15 wt % **^SPTIMP**-TPU composite device. The energy storage efficacy was also tested by successfully charging a 10 μ F capacitor within 100 s using the best-performing 15 wt % **^SPTIMP**-TPU device.

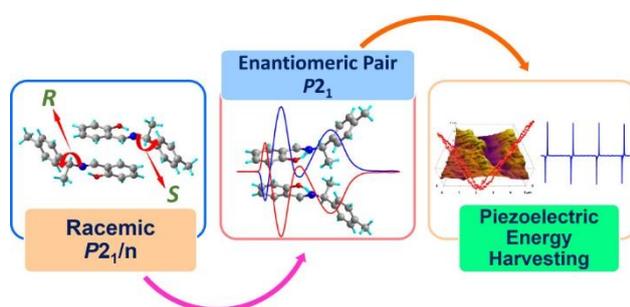


Figure 1. A pair of enantiomeric Schiff base compounds R/SPTIMP were synthesized and shown to exhibit piezoelectric properties. The polymer composites of SPTIMP in thermoplastic polyurethane showed piezoelectric energy harvesting properties with good open-circuit output voltages, which were further utilized for capacitor charging experiments.

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Temperature-dependent one-pot synthesis of In NPs, green and red InP quantum dots with exceptionally narrow emission full-width at half-maximum (FWHM)

Bantumelli Prachuritha, Billakanti Srinivas, Anjali George, and Krishnamurthi Muralidharan*

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Abstract: Within the III-V semiconductor nanocrystals, indium phosphide (InP) quantum dots have garnered significant interest owing to their unique characteristics viz., covalency, less toxic, broad emission range, alternative, and effective usage in a variety of applications, such as photovoltaics, light-emitting diodes, and bio-imaging. It has been challenging to selectively produce green InP over red using existing synthetic methods. Herein, we have presented a novel single-step synthesis of green and red-emitting InP. In an interesting observation, we observed that the reaction between InCl_3 and tris(dimethyl)amino phosphine $[(\text{DMA})_3\text{P}]$, assisted by hexamethyldisilazane (HMDS), yielded green and red InP QDs. Unlike conventional synthetic procedures, our preparation method allowed selective production of indium(0) nanoparticles (In-NPs), green or red InP, by controlling the reaction time and temperature. This method produced In-NPs, green InP, and red InP with average particle sizes of 3 to 5 nm with a narrow particle size distribution. The obtained green and red InP exhibited sharp emission at 561 nm (FWHM = 8.4 nm) and 721 nm (FWHM = 17 nm), with bandgaps of 2.25 eV and 1.71 eV, respectively.

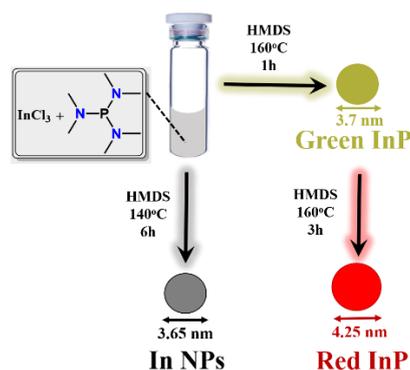


Figure 1: Graphical representation of the synthesis of In NPs, Green InP, Red InP.

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- G. Almeida, et al., *Nano Lett* **2023**, 23 (18), 8697–8703.

In-situ Spectroscopic and Microscopic Investigation on The Aging Reaction of Schiff Base and Its Optical Waveguiding

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Organic Schiff bases have been one of the centerpieces of research owing to excellent luminescent properties for photonic and optoelectronic devices. Extensive research exploiting their multi-stimuli responsiveness has been reported, but the 'green' synthesis approach has seldom been explored. Herein, we explore the aging of a Schiff base reaction through in situ monitoring by means of simple spectroscopic and microscopic techniques to understand its mechanistic aspects from the macroscale down to the microscale level. We have employed UV-Vis DRS, FTIR, Fluorescence, and Raman spectroscopy to showcase the real-time changes observed during the aging process. For the first time, we have displayed real-time microscopic observations of the aging process. Branched homostructures were produced by the self-assembly method, which acted as multi-input/output channel optical waveguides. Our work reflects the possibility of designing such molecules for modern-day photonic integrated circuits through an inexpensive green route.

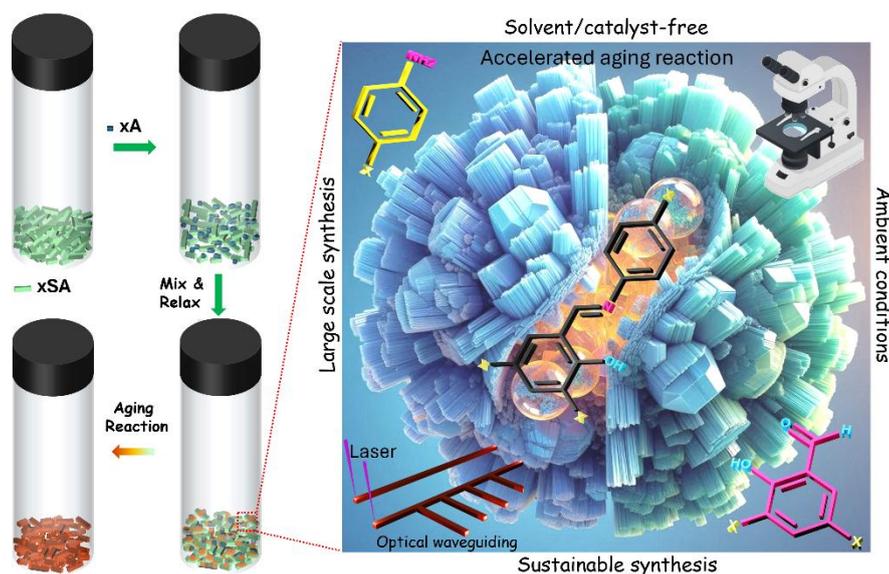


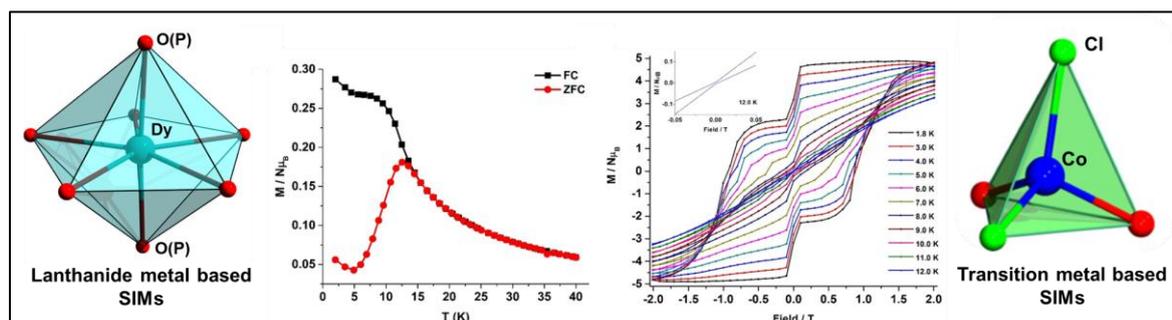
Figure 1 Graphical illustration of the accelerated aging process and its in-situ monitoring.

Enriching Single Ion Magnetism in Ln-phosphonamides by Crystal-Field Manipulation at RM Group

Presented by Brinda Goyal

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Single Ion Magnetism (SIM) offers an energy-efficient, cost-effective solution for data storage and processing which has seen significant advancements over the past two decades. Recent research has shifted focus from polynuclear clusters to mononuclear complexes, with ligand design emerging as a key factor in controlling the geometry and crystal field around the paramagnetic center, enhancing the anisotropic energy barriers of SIMs. In 2016, our group reported an air-stable, distorted D_{5h} Dy(III)-based complex with remarkable magnetic properties, a record energy barrier of 735 K for reversal of magnetization and a blocking temperature (T_B) of 12 K.¹ The complex also exhibited a butterfly-shaped hysteresis loop with high coercivity. This can be attributed to the anisotropy around the Dy(III) ion enhanced by the axially of phosphonamide ligands. Application of hydrostatic pressure distorted the linearity of O-Ln-O bond angle, compromising the magnetic properties and highlighting the delicate balance required for optimal SIM performance.² We also studied the impact of secondary ions by replacing large iodide anions with smaller chloride and bromide ions, which decreased both U_{eff} and T_B values due to stronger hydrogen bonding in the chloride analogue.³ Additionally, modifying the ligand environment by substituting the *t*-butyl group with bulkier groups like adamantyl or carbazolyl led to further distortion due to agnostic interactions, compromising the magnetic properties of such complexes.⁴ Beyond rare earth-based SIMs, our group has also developed cost-effective, air-stable Co(II)-based complexes with modified phosphine oxide ligands, achieving field induced magnetic properties.⁵ Our research underscores the critical role of structural factors in controlling the magnetic properties of SIMs, particularly in the context of ligand design and heavy ion effects.



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A ligand-modulated Mn-based complexes for preferential electro and photochemical reduction of CO₂ to valuable products

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A redox-active ligand was specifically designed to maintain the correct electronic balance in an Mn(I)–carbonyl complex¹, ensuring its photostability and water solubility. This design enabled the Mn–carbonyl complex to efficiently reduce CO₂, with a high Faradaic efficiency of approximately 88%. The reaction preferentially produced carbon monoxide (CO) as the sole C1 product. Importantly, the complex was effective in pure water and could even reduce CO₂ from flue gas sources². This development opens up the potential for more efficient and sustainable CO₂ conversion technologies. Moreover, first-row transition metal-based photocatalysts are promising for efficient CO₂ reduction, but designing such catalysts is challenging due to issues with oxidation state stability. This study presents a Mn(II)-based molecular catalyst, Mn(apap)₂Br₂, for visible light-driven CO₂ reduction. The catalyst features a bulky apap ligand, which distorts the Mn(II) site and forms hydrogen bonding networks, enhancing its catalytic performance. X-ray diffraction provides detailed structural insights. When combined with an Ir-based photosensitizer and a sacrificial electron donor, the catalyst achieves optimized CO production (TON ~ 636) in water-DMA media, outperforming H₂ production by ~20:1. Spectroscopic studies reveal reductive electron transfer as the main mechanism. The Mn(apap)₂Br₂ complex remains stable during extended photocatalysis, even as the photosensitizer degrades³. This catalyst design, which toggles between Mn(II) and Mn(I) states, offers a robust and selective photocatalytic solution for CO₂ conversion, with the potential for expanding the development of durable CO₂-activating catalysts.

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How do quantum chemical descriptors shape hydrogen atom abstraction reactivity in cupric-superoxo species? A combined DFT and machine learning perspective

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Oxygen activation, a crucial function performed by enzymes, prompts the synthesis of biomimetic models utilized to investigate structure–activity relationships, with a particular focus on metal-superoxo species resulting from O_2 interaction with the metal center. Among others, cupric-superoxo species have been extensively studied, showcasing diverse examples and potent catalytic capabilities. While quantum chemical calculations have helped in understanding the mechanistic aspect of their reactivity, recent advances in machine learning (ML) tools have substantiated this further and offered potent predictive power. The development of machine learning tools and associated quantum descriptors for open-shell paramagnetic catalysts is rarely pursued due to the complexity involved. However, if achieved, it has the potential to fundamentally change the existing paradigm in catalytic design and development. In making this connection, a detailed hydrogen atom transfer (HAT) reaction instigated by $[(\text{TMPA})\text{Cu}(\text{II})-\text{O}_2^{\cdot-}]$ (TMPA = tris(2-pyridyl methyl)amine) (Figure 1) species and its analogues gains relevance as they offer a unique set of diverse reactivity pathways among structurally similar cupric-superoxo species. In this study, we embark on a comprehensive exploration of reactivity mechanisms employing the DFT method (B3LYP/TZVP) with five distinct catalysts and three varied substrates, resulting in combinations that lead to fifteen different reactions for the HAT reaction. [1] The reactivity of cupric-superoxo species was found to be correlated not only with the rate-limiting HAT barrier but also with the competitive dimerization barrier. Our comprehensive analysis of mechanisms offered a rationale for the experimentally observed reactivity and the setting of goals for developing suitable ML models. In making this connection, we have arrived at fifteen quantum chemical descriptors, including exchange interaction (J), sterics, hydrogen bonding, and various thermodynamic parameters derived from DFT calculations. Our multivariate linear regression (MLR) model accurately predicts catalytic reactivity towards HAT using these quantum chemical descriptors based simply on ground state geometry. The H-bonding interactions, along with the free energy of the HAT/PT/ET reaction ($\Delta G_{\text{PCET}}/\Delta G_{\text{PT}}/\Delta G_{\text{ET}}$), were found to yield excellent results for accuracy ($R^2 = 0.90$), setting a stage to study multinuclear paramagnetic catalysts. For the first time, this study provides valuable insights not only into the reactivity of metalloenzymes but also offers design clues to enhance the reactivity of transient species using the ML approach.

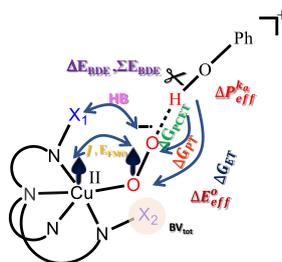


Figure 1. Schematic representation of encoding the catalyst structure and various quantum chemical descriptors employed.

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Design, Synthesis, and Antibacterial Activities of Multi-functional C2-Functionalized 1,4-Naphthoquinonyl Organoseleniums

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Quinones and organoseleniums always fascinated the scientific community due to their unique redox behavior and applications in biology and materials.¹ Herein, a practical and efficient strategy for C₂-selenylation of 1,4-naphthoquinones has been explored. This coupling reaction of two redox structural motifs, such as 2-bromo-1,4-naphthoquinone with diaryl diselenide or ebselen has been achieved by avoiding transition metal catalysts and high temperatures. Photophysical investigations have been performed on selected C₂-selenylated naphthoquinones. Synthesized organoselenium shows good antibacterial potential against *S. aureus* ATCC 29213 with MIC 0.5 µg/mL and a selectivity Index of >200.²

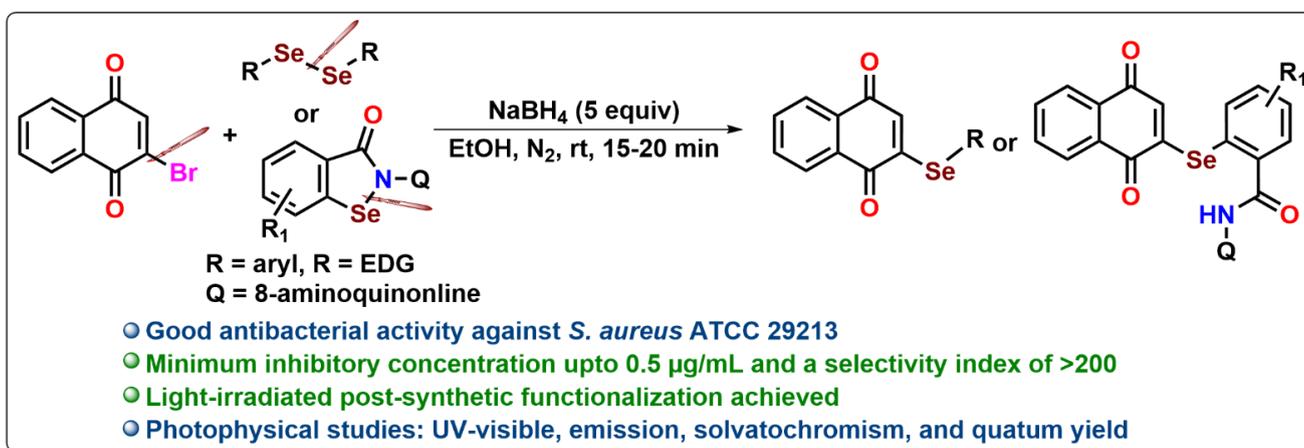


Figure 1 C2-Selenylation of 1,4-Naphthoquinone with Diaryldiselenides and Ebselens

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pH-responsive supramolecular switch of a rationally designed dipyrroethene-based chromophore

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This work represents a synthetic strategy to access a novel class of pH-responsive, dual-state emissive (DSE), highly fluorescent pyrrole-based chromophores *via* diformylation of dipyrroethenes (DPE) followed by condensation with various aniline derivatives. The DPE-based chromophores exhibit a large Stokes' shift and maintain good fluorescence quantum yields. Remarkably, these chromophores demonstrate reversible colourimetric changes and a fluorometric 'on–off–on' switch in response to pH variations. Various spectroscopic techniques, optical microscopy, X-ray crystallography, and computational studies revealed that the synthesized molecules adopt a two-dimensional conformation due to the presence of strong $\pi\cdots\pi$ stacking and hydrogen bonding interactions, allowing them to function as flexible molecular hosts. Under acidic conditions, selective protonation of imine bonds and subsequent complexation with the counter anion enhance the host–guest interactions, resulting in a stable three-dimensional supramolecular structure. Notably, the reversibility of these molecules under basic conditions showcases the robustness and potential applications of these chromophores in various fields, ranging from the design of finely tuned pH-responsive degradable polymers to self-healing materials, as well as sensing and molecular devices.

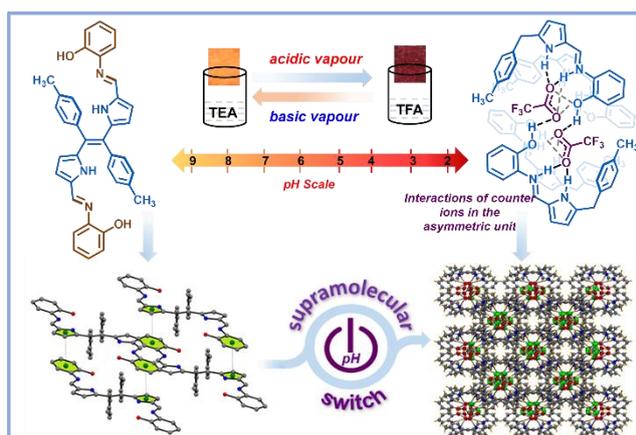


Figure 1 pH responsive supramolecular switch of newly DPE based chromophores: from colorimetric changes to crystal-to-crystal transitions

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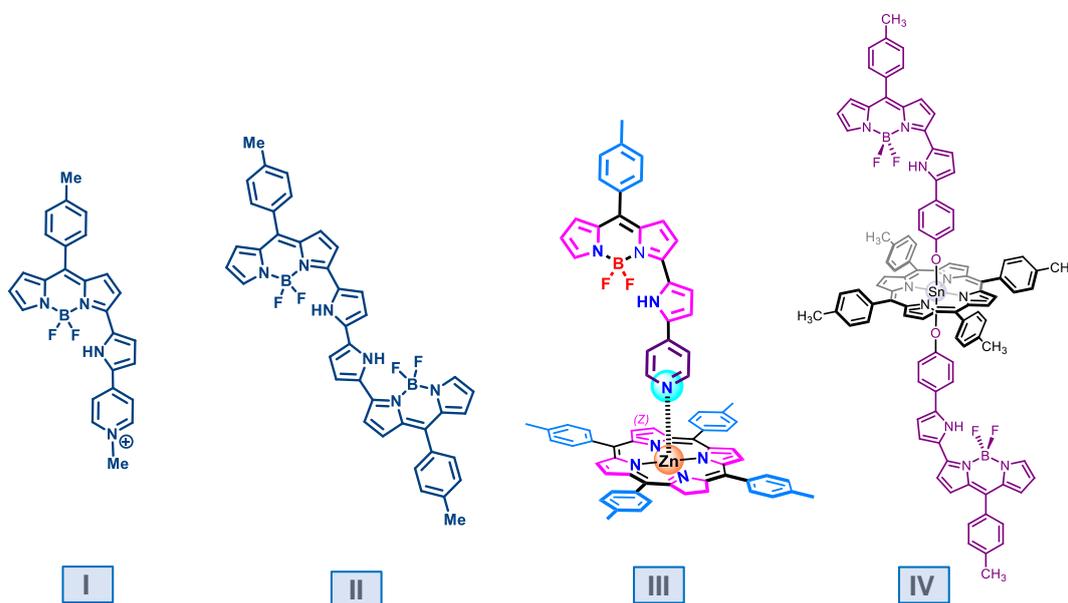
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Advanced 3-Pyrrolyl BODIPY Sensors: Unraveling Charge Transfer and Coordination Chemistry with Metal Porphyrins"

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Our research domain explores the design and synthesis of 3-pyrrolyl-BODIPY derivatives, highlighting their potential as versatile fluorophores and advanced materials for various applications. Specifically, we demonstrated the exceptional performance of *o*-N-methylated *p*-pyridyl 3-pyrrolyl BODIPY derivative¹ **I** as a highly selective and sensitive sensor for picric acid (HPA), with remarkable sensitivity (LOD = 7.90 pM) and binding affinity ($K_a = 4.94 \times 10^8 \text{ M}^{-1}$). We recently synthesized very novel covalently linked near-infrared (NIR)-absorbing 3-pyrrolyl BODIPY dimers **II** which exhibit rapid charge separation on a picosecond timescale, facilitated by intradimer electronic interactions and solvent-mediated symmetry breaking charge transfer. These long-lived charge-separated states present promising applications in energy conversion. We also synthesized axially bonded 3-pyrrolyl-BODIPY-porphyrin conjugates by varying linker groups and central metal ions **III**, **IV** to tailor coordination geometry, electronic coupling, and photophysical properties. These works will be presented in our poster.



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Benzoimidazolyl Organoseleniums: Antioxidant Activity and Catalysts for Selective Iodination of Arenes and Nitro-Michael Reaction

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Benzamide-derived organoseleniums have shown promising catalytic as well as biological activity.¹ The activation mode of these organoseleniums is chalcogen bonding² by the selenium center and the presence of an amid functional group makes them more Lewis acidic.³ Here, we have explored the synthesis and catalytic activity of benzimidazole-derived organoselenium. Among all the synthesized organoseleniums bis(2-benzoimidazolyl) diselenide shows prominent activity, which may be due to the planarity present in benzimidazole diselenide which can make it more Lewis acidic. Additionally, the presence of NH functionality interacts with the substrate during the transformations. Organoselenium bis(2-benzoimidazolyl) diselenide exhibited thiol peroxidase hydrogen peroxide reducing antioxidant activity with a reduction rate of $18.6 \pm 1.9 \mu\text{M/s}$ better than benzamide-based organoseleniums. The synthesized diselenide also activates *N*-iodo-succinimide toward the regioselective, monoiodination of electron-rich arenes and activation of nitroalkene for nitro-Michael reactions for the first time.

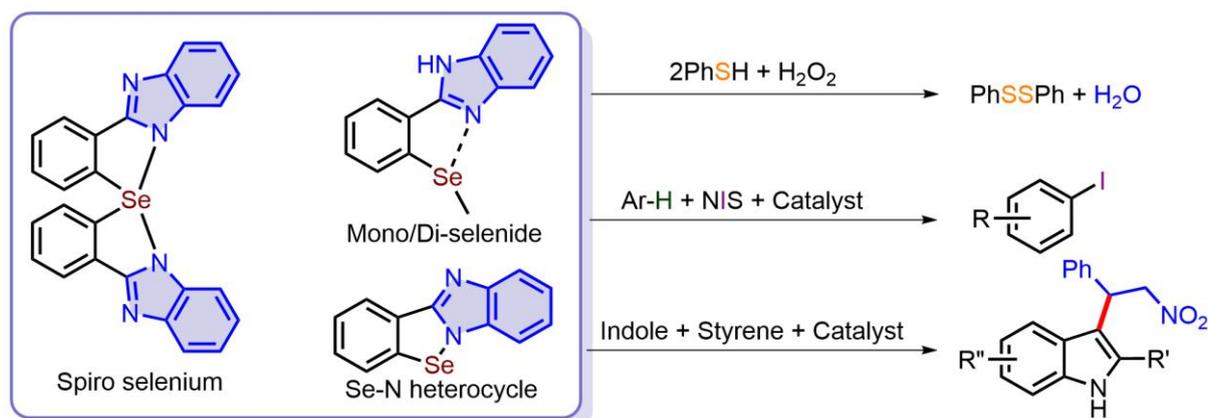


Figure 1 Synthesis and catalytic activity of benzoimidazolyl-derived organoselenium compounds

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Engineering Single-Molecule Toroids: A Main-Group Metal Ion Strategy for Stabilizing Ferrotoroidal Ground States with Enhanced FT-AFT Energy Gaps

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Single-molecule Toroids (SMTs) represent a pivotal class of molecules characterized by exotic physical behaviors and electrically tunable quantum states, offering significant potential for emerging quantum technologies.¹ However, achieving SMTs, particularly those with ferrotoroidal (FT) ground states, remains a significant challenge due to the stringent structural requirements.¹ While {Dy₃} triangles are known to exhibit toroidal moments, attaining an FT state where two or more {Dy₃} units connect to form a conrotatory magnetic chiral state is exceptionally rare. Herein, we report a novel molecular complex, [M^{III}₇Ln^{III}₆(N-med)₆(ClCH₂COO)₆(NO₃)₆(OH)₁₂(H₂O)₆]₃Cl (Ln = Dy (**1**) and Gd (**2**), M = Ga^{III}), with complex **1** exhibiting a rare FT ground state. The inclusion of main group metal ion Ga^{III} ions forms a {Ga₃} triangular buffer, creating a unique sandwich design where the {GaDy₆} hourglass core is encapsulated between two {Ga₃} triangles. This arrangement significantly reduces the h/r ratio, enhancing the ferrotoroidal-antiferrotoroidal (FT-AFT) energy gap to 0.39 cm⁻¹, the largest reported to date. *Ab initio* CASSCF calculations predict toroidal blocking up to 0.41 T, validated by micro-SQUID single-crystal measurements showing a clear hysteresis loop opening within 16–128 mT/s. These findings highlight a novel design strategy where incorporating main-group Ga^{III} ions with higher Lewis acidity offers precise control over the FT-AFT gap, paving the way for engineered SMTs.

References

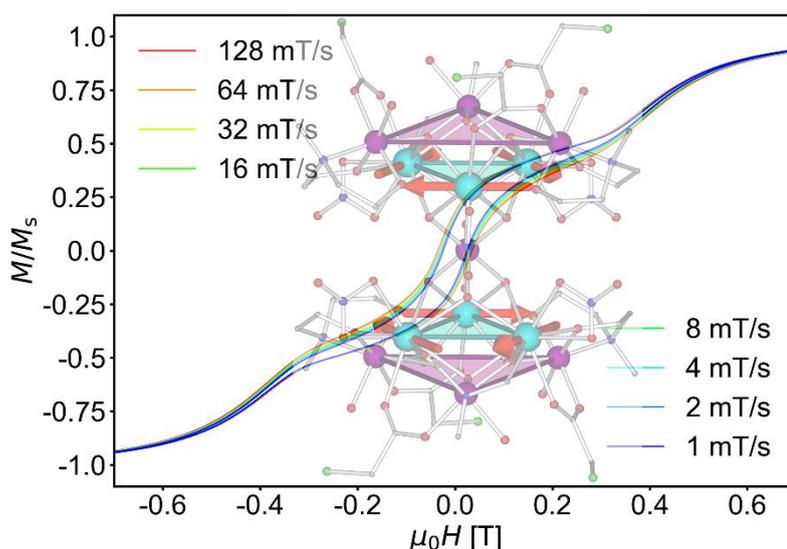


Figure 1: Magnetic anisotropy axis orientation and magnetization hysteresis curve exhibit an S-shaped profile characteristic of the ferrotoroidal state.

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Sulfur and Selenium Ligated Copper(I) Complexes: Synthesis and Applications

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N-heterocyclic carbene (NHC) derivatives of the main group elements of sulfur and selenium have attracted considerable attention. They exhibit strong σ -donor and π -acceptor properties. They can also act as bridging ligands and coordinate with multiple metal centers.^{1,2} These ligands are most stable compared to NHC and phosphine-based ligands. In this context, a series of sulfur and selenium-based tri-coordinated mononuclear copper(I)-*N*-heterocyclic chalcogenone catalysts ($[\text{Cu}(\text{X})(\text{L}^1)_2]$ and $[\text{Cu}(\text{X})(\text{L}^2)_2]$, {where $\text{L}^1/\text{L}^2 =$ anthracene tagged imidazole thione/selone, $\text{X} = \text{Cl}, \text{Br}, \text{I}$ }) were synthesized along with a cationic tetra-coordinated mononuclear copper(I)-*N*-heterocyclic chalcogenone catalyst ($[\text{Cu}(\text{L}^3)_2]\text{PF}_6$ { $\text{L}^3 =$ pyridyl substituted isopropyl imidazole thione}). These catalysts were characterized using FT-IR, NMR spectroscopy, and single-crystal X-ray diffraction techniques. Further, to understand the influence of ancillary ligands (sulfur and selenium based) and catalysts coordination environment, we have performed the [3+2] cycloaddition reaction between aryl azide and phenylacetylene using the catalysts. Notably, we observed that tri-coordinated mononuclear catalysts with bromo and iodo ligands demonstrated superior catalytic activity compared to their chloro ligand counterparts. However, the tetra-coordinated ionic catalyst exhibited exceptional catalytic efficiency, outperforming the neutral tri-coordinated Cu(I) halide complexes. The mechanistic study disclosed the crucial roles of a six-membered cyclic transition state of the copper(I) catalyst for high reactivity.



Figure 1: Copper(I)-*N*-heterocyclic chalcogenone catalysts [3+2] cycloaddition reaction

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Achieving Ambient Stability and Suppressing Spin-Phonon Coupling in Dyprosocenium SIMs via MOF Encapsulation

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Detailed ab initio Complete Active Space Self-Consistent Field (CASSCF) calculations, combined with periodic Density Functional Theory (DFT) studies, have been conducted on the $[(Cp^*)Dy(Cp^{iPr5})]^+$ [1] molecule encapsulated within a metal-organic framework (MOF). These comprehensive analyses revealed that MOF encapsulation significantly enhances the stability of these otherwise fragile molecules while preserving their effective magnetic moment (U_{eff}) values. Notably, this encapsulation effectively suppresses the critical vibrational modes typically responsible for reducing the blocking temperature. [2] This suppression presents a previously unexplored strategy for developing a new generation of Single-Molecule Magnet (SIM)-based devices, potentially revolutionising the field.

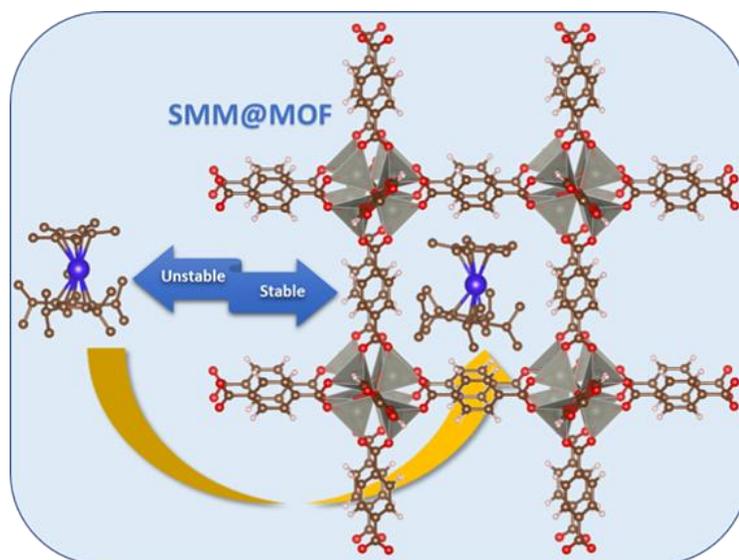


Figure 1 Stabilization of Dy-complex inside MOF

References:

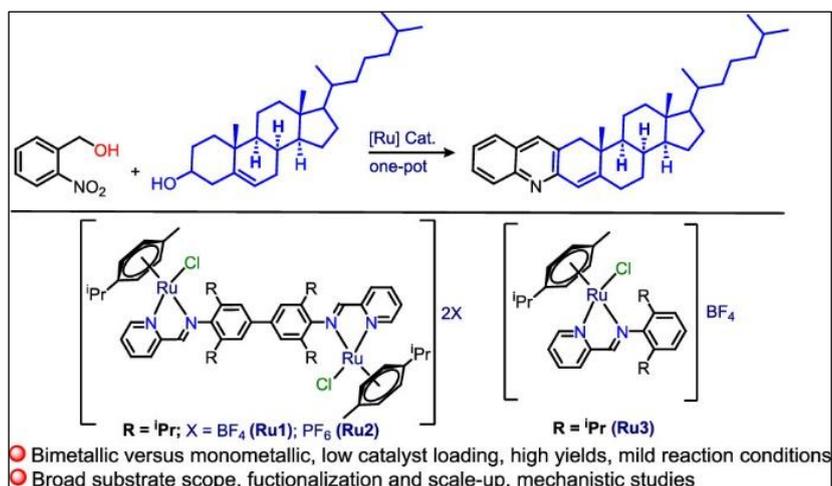
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A Dinuclear Ru(II) Schiff-Base Complex Catalyzed One-pot Synthesis of Quinolines through Acceptorless Dehydrogenative Coupling of Secondary Alcohols with 2-Nitrobenzyl Alcohol

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Abstract: Development of efficient synthetic protocols for N-heterocyclic compounds, particularly quinoline derivatives, remains a key focus in synthetic organic chemistry due to their wide-ranging applications in pharmaceuticals, agrochemicals, dyes, and more.¹ Existing methodologies for quinoline synthesis, including the Friedlander reaction and metal-catalyzed acceptorless dehydrogenative coupling (ADC), face challenges such as harsh reaction conditions, limited selectivity, and reliance on air-sensitive ligands or toxic additives.²⁻⁵ Herein, we report a novel bimetallic ruthenium-based catalytic system for the one-pot synthesis of quinolines from 2-nitrobenzyl alcohol or 2-aminobenzyl alcohol under mild, sustainable conditions.⁶ For the first time, the cooperative effects of bimetallic catalysts (**Ru1** and **Ru2**) are systematically compared with their mononuclear counterpart (**Ru3**), revealing significantly enhanced catalytic efficiency, higher selectivity, and broader substrate scope. Furthermore, this catalytic approach was successfully extended to late-stage functionalization of biologically active steroid derivatives, demonstrating its practical utility. Mechanistic insights were gained through controlled experiments and spectroscopic analyses, shedding light on the role of metal-metal synergy in catalytic performance. This work establishes a sustainable and efficient strategy for quinoline synthesis while showcasing the potential of bimetallic systems in advancing modern synthetic methodologies.



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N-alkyl Induced Luminescent Gold(I) Complexes for Blue Light Emitting Applications

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The intriguing light-emitting capabilities of gold N-heterocyclic carbene (NHC) complexes have attracted a lot of interest for their application in organic light-emitting diodes (OLEDs) and light-emitting electrochemical cells (LECs).¹⁻² A number of factors, including the coordination number of gold, hydrogen bonding, aurophilic contacts, and $\pi \cdots \pi$ stacking, affect the luminescence of Au-NHC complexes. Particularly useful for effective white light OLEDs in lighting and display applications are blue-emitting gold NHC complexes.³ Here, we synthesize and characterize *N*-(9-anthracenyl)-*N*-(*n*-alkyl) imidazol-2-ylidene gold(I) chloride (alkyl = *n*-butyl (**1**), *n*-pentyl (**2**), *n*-hexyl (**3**), a blue-emitting mononuclear gold(I)-NHC chloride complex. Hydrogen bonding, aurophilic contacts, and CH \cdots π interactions drive the unusual molecular packing of these complexes; $\pi \cdots \pi$ stacking is seen in **1-3**.⁴ All complexes show high thermal stability and emit blue light in solution and crystalline states, with complex **1** displaying the highest quantum yield (22.4%) compared to **2** (9.9%) and **3** (14.98%). Theoretical studies revealed the electronic basis of their luminescence, and a blue-emitting thin film and LED fabricated using **1** demonstrated emission in the blue region with CIE coordinates near NTSC standards.

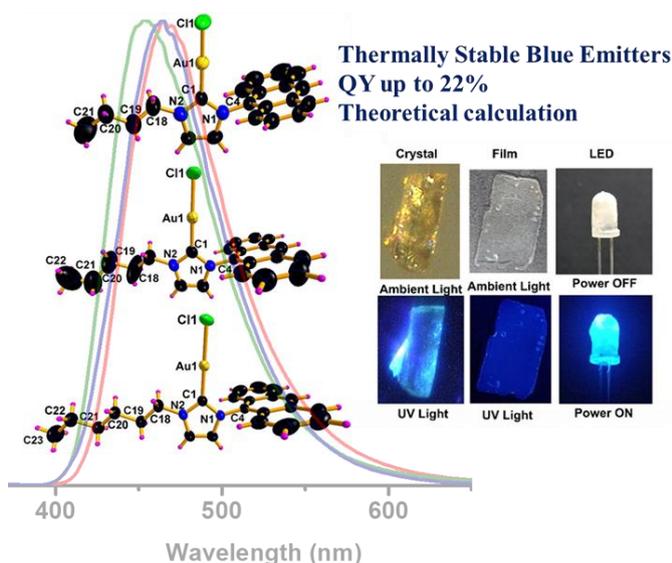


Figure 1. The light-emitting application of Gold(I) complexes

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Light Weight Composite Materials for Aerospace Applications

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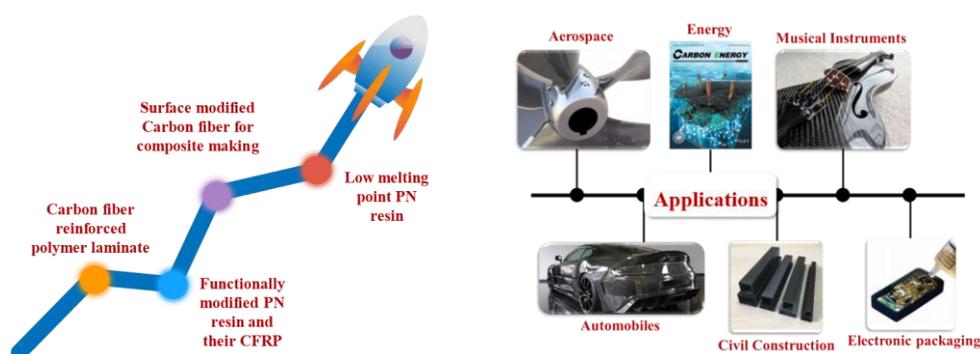
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The aerospace industry is focused on developing advanced lightweight composite materials, particularly those using Phthalonitrile (PN) resins, known for their excellent thermal stability and mechanical strength. Recent advancements involve incorporating boron, phosphorus, and silicon to enhance these properties. Boron improves thermal stability and flame retardancy¹, phosphorus reduces smoke production², and silicon adds flexibility, making PN resins suitable for high-temperature applications³. However, challenges such as high melting points and brittleness in these resins limit their processability⁴. Low melting point PN resins have been developed to improve compatibility with liquid molding techniques like Resin Transfer Molding (RTM). These resins maintain excellent thermal stability, mechanical strength, and flame retardancy, especially when combined with silicon-modified carbon fibers⁵. Ongoing research aims to improve curing efficiencies and explore new synthetic methods to further enhance their application in



aerospace technology.

Figure 1: Development of light weight composite materials and their potential applications

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Selective removal of lead ions from wastewater using phosphate-based organic polymers

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Abstract

Heavy metals are used in many industries, such as electronics, automobiles, and pose severe health and environmental hazards due to uncontrolled release into the environment. Unlike organic pollutants that naturally degrade over time, heavy metal salts usually bioaccumulate and threaten the health of the ecosystem. Lead, due to its toxicity, even in parts per billion (PPB) levels is one of the most toxic and common heavy metals found in water. Phosphate-based organic polymers are interesting systems for the removal of pollutants from water.^{1, 2} To counter the issue of lead contamination in water, phosphate-based organic polymers **P1**, **P2** and **P3** have been synthesized by the room-temperature condensation reaction of diphenyl phosphorochloridate with hydroquinone, biphenol, and phloroglucinol respectively. These polymers have been utilized for lead removal from water. Among the polymers, **P3** exhibited the highest maximum adsorption capacity (q_{\max}) of 305 mg/g, whereas **P1** and **P2** showed q_{\max} of 77 mg/g and 45 mg/g. In conclusion, this work establishes triaryl phosphate-based polymers as versatile and highly effective nontoxic adsorbents for lead removal, making them promising candidates for real-world water treatment applications.

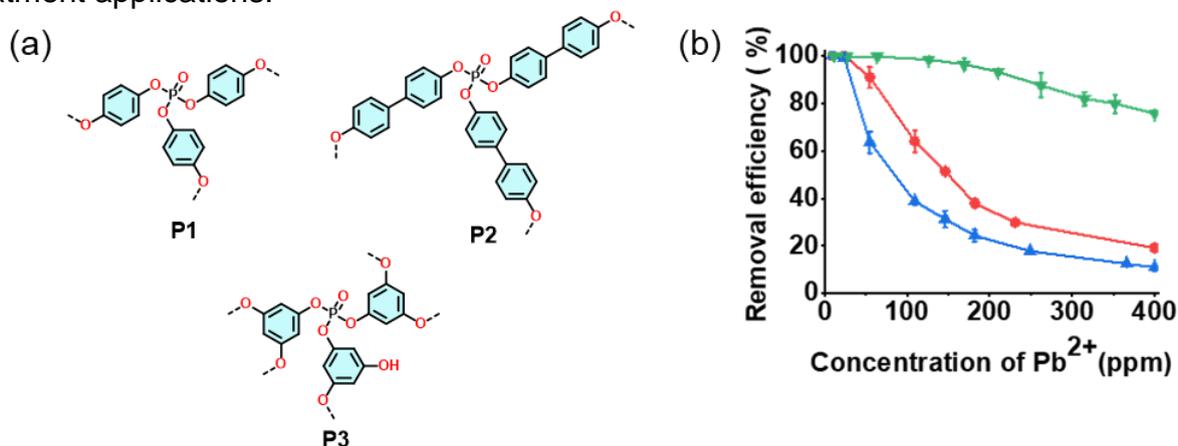


Fig 1. (a) Repeating unit for Polymer **P1**, **P2** and **P3** and (b) Influence of initial concentration of Pb²⁺ on removal efficiency for **P1-P3**

(—●— P1, —▲— P2, —▼— P3)

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Diversity in Caesium Coordination Polymers of Iminopyrrolyl Ligand

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Among alkali metals, lithium, sodium, and potassium complexes were extensively investigated over a prolonged timeframe for their structural diversity along with their implementation in several organic transformations.¹ However, heavier congeners, namely caesium (Cs) compounds, are merely established as strong bases like CsOH, Cs₂CO₃ and [CsN(SiMe₃)₂] in a wide spectrum of organic reactions.² Recently, Brønsted basic character of [CsN(SiMe₃)₂] is utilized to deprotonate various organic substrates which leads to eye-catching polymeric networks due to higher polarizability, larger ionic radius of caesium ion and affection of Cs⁺ cation toward π -electron cloud (caesium cation- π interaction).³⁻⁵ Here, we study the fine-tuning of iminopyrrolyl ligand scaffold that favours a unique alteration in the caesium coordination polymers from a 2D sheet (**1**), an infinite ladder chain (**2**), and a well-connected 3D cage (**3**). Subsequently, caesium complexes were found to be competent catalysts in the ROP of *rac*-lactide and ϵ -caprolactone.

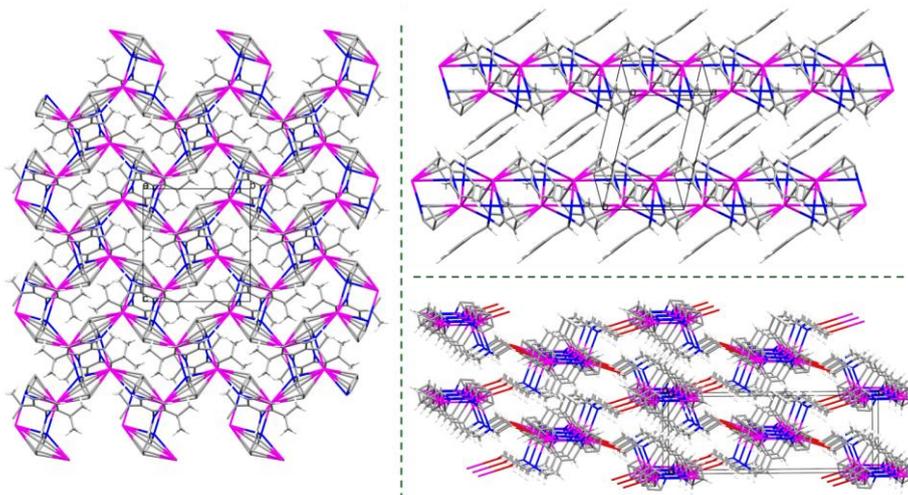


Figure 1. Representation of Caesium Coordination Polymers of Iminopyrrolyl Ligand

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Design, Synthesis, and Molecular docking of Novel Chalcone-based Ebselen analogs as Potential anti-cancer agents

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Cancer remains a life-threatening disease and the second leading cause of human death after cardiovascular disorders. Over recent decades, numerous anticancer agents have been developed to target various enzymes and receptors involved in cancer progression¹. Among these, angiogenic factors such as COX-1, EGF, and HIF have attracted significant attention due to their critical roles in promoting cancer growth, metastasis, and resistance to therapy². Targeting these pathways simultaneously offers a promising strategy for effective cancer treatment. In this study, we synthesized a series of novel chalcone-based ebselen conjugates and performed molecular docking analyses to evaluate their interactions with the enzymes. Among the four synthesized conjugates, the derivative containing an anthracene moiety demonstrated exceptional binding affinities, with binding energies of -14.20, -11.18, and -10.34 kcal/mol for COX-1, EGF, and HIF, respectively. These results suggest that the anthracene-containing conjugate holds significant promise as a potent anticancer agent.

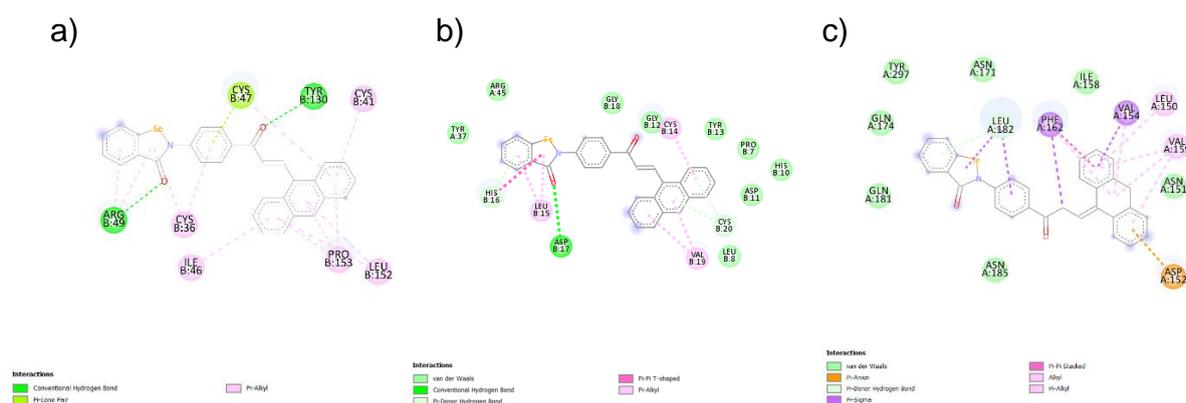


Figure 1: Docking poses of the chalcone-ebselen conjugate containing an anthracene moiety with: a) COX-1 b) EGF c) HIF

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Design and Application of Organotelluroxane Macrocycle in Electrochemical HER

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The increasing global energy demand highlights hydrogen gas as a promising solution for future needs.¹ A discrete lipophilic organotelluroxane macrocycle has been identified as an efficient catalyst for the hydrogen evolution reaction (HER) via proton reduction.² The macrocycle is synthesized through chloride abstraction from bis(*p*-methoxyphenyl) tellurium dichloride, (*p*-MeOC₆H₅)₂TeCl₂, using silver salts AgMX₄ (MX₄=BF₄⁻ and ClO₄⁻). This process generates dicationic tetraorganoditelluroxane units *in situ* that assemble into 12-membered macrocycles, [((*p*-MeOC₆H₄)₂Te)₂(μ-O)(μ₂-F₂BF₂)₂]²⁺ (2) and [((*p*-MeOC₆H₄)₂Te)₂(μ-O)(μ₂-O₂ClO₂)₂]²⁺ (3), bridged by weak anions (μ₂-MX₄) and stabilized by Te–(μ₂-BF₄/ClO₄) secondary interactions. The anions above and below the macrocycle plane balances the charge. At higher temperatures, the reaction predominantly yields telluronium salts R₃TeX [X = BF₄⁻ (4), ClO₄⁻ (5)]. The macrocycle and its associated telluronium salts were characterized using ¹⁹F NMR and high-resolution mass spectrometry (HRMS), confirming their structural stability in solution. Notably, macrocycle 2 demonstrates remarkable electrocatalytic efficiency for HER in an organic medium, utilizing *p*-toluene sulfonic acid as a proton source.

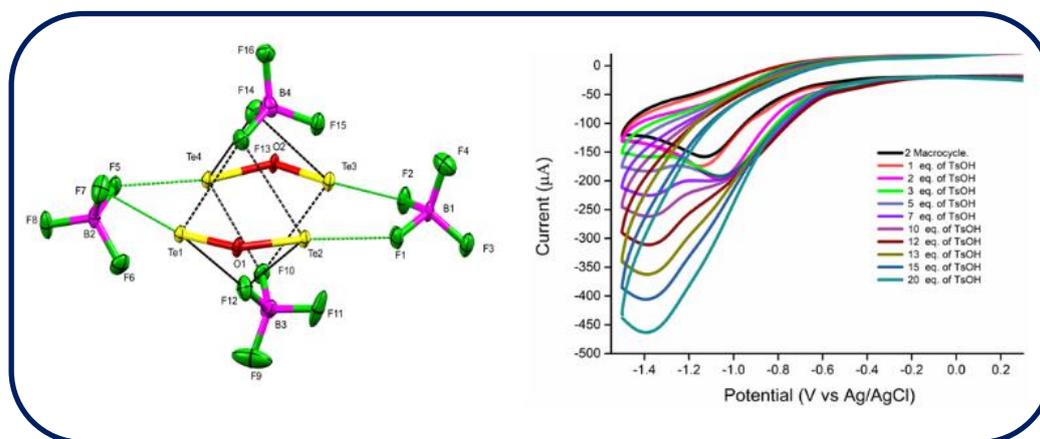


Figure-1: Graphical Abstract

References:

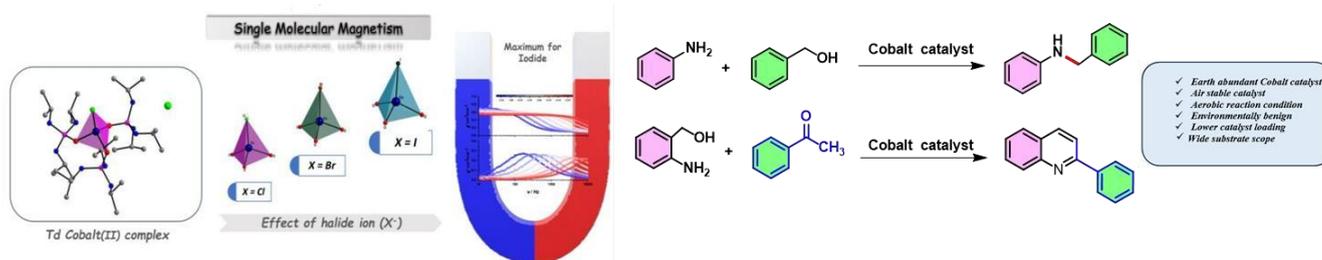
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Synthesis, structure, catalytic and magnetic properties of phosphoramidate derived four coordinate mononuclear cationic cobalt (II) complexes

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Materials that can retain their magnetization at the molecular level just like bulk magnets are called single molecular magnets (SMM).¹ These materials exhibit promising applications in high-density information storage,² molecular spintronics,³ and quantum computing.⁴ Monometallic complexes based on 3d transition metal ions can exhibit appreciably enhanced magnetic anisotropy due to the stabilization of an unquenched orbital moment. Understanding and controlling magnetic anisotropy at the level of a single metal ion is vital if the miniaturization of data storage is to evolve into transformative technologies.⁵ In this regard, three novel cationic mononuclear tetrahedral cobalt (II) complexes [Co(L)₃X]X (L= tris-isopropyl phosphoric triamide and X = Cl, Br, and I) have been synthesized using a rational approach to acquire information on the single-ion magnetic behavior. A detailed study of the variation in the dynamic magnetic properties of the Co(II) ion in a tetrahedral ligand field has been carried out by changing the halide ligand [X = Cl (**1**), Br (**2**), I (**3**)]. Field sweep data shows the maximum SMM behavior for complex **3**. The axial zero-field splitting parameter D was found to vary from -9.62 cm⁻¹ in **1** to -7.38 cm⁻¹ in **2** and -9.84 cm⁻¹ in **3**. Besides, the utility of Co(II) complexes as homogeneous catalysts for various organic transformations has been explored, for example, these complexes were found to display good catalytic activity toward the synthesis of amines and quinolines. Complex **2** was found to be more efficient for the synthesis of amines in comparison to complexes **1** and **3**. A wide array of alcohols and amines were successfully reacted to result in the formation of amines in good yields. Complex **2** was also found to be highly efficient for the synthesis of quinolines with a low catalyst loading. Although various cobalt complexes are explored for such organic transformation reactions, phosphoramidate ligand-containing complexes are still unexplored.



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Strategic Design of Zinc (SVNIT-1) and Cadmium (SVNIT-2) Metal-Organic Frameworks for Enhanced, Reversible, and Multi-Phase Iodine Sequestration

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Abstract

Radioactive iodine isotopes, such as ^{129}I and ^{131}I , are generated during nuclear fission and present significant health hazards due to their high volatility, bioaccumulation potential, and long-term persistence in both gaseous and aqueous environments. The efficient removal of iodine across multiphase environments poses a significant challenge, especially in polar aqueous systems where conventional materials typically exhibit limited effectiveness. To overcome this challenge, a novel bidentate precursor, 4,4'-(((2,3,5,6-tetramethyl-1,4-phenylene)bis(methylene))bis(azanediyl))dibenzoic acid (PMBADH_2), was designed with strategically incorporated -NH linkages to strengthen iodine interactions across vapor, organic, and aqueous phases. Using PMBADH_2 , two isostructural metal-organic frameworks (MOFs), $\{[\text{Zn}_2(\text{PMBADH}_2)_4(\text{DMF})_2] \cdot 4\text{DMF}\}_n$ (SVNIT-1) and $\{[\text{Cd}_2(\text{PMBADH}_2)_4(\text{DMF})_2] \cdot 4\text{DMF}\}_n$ (SVNIT-2), were synthesized, with scalable production methods developed to facilitate practical applications. The synthesized MOFs were thoroughly characterized using SCXRD, PXRD, FTIR, XPS, BET, and TGA techniques, which validated their structural integrity and functional attributes. SVNIT-1 exhibited exceptional iodine removal efficiencies, with capacities of 6.5 g g^{-1} in the vapor phase, 2.8 g g^{-1} in organic solvents, and 2.5 g g^{-1} in aqueous media, including seawater. SVNIT-2 demonstrated comparable performance, achieving iodine removal capacities of 6.1 g g^{-1} in the vapor phase, 2.6 g g^{-1} in organic solvents, and 2.4 g g^{-1} in aqueous media, including seawater. Extensive studies on desorption, recyclability, and stability confirmed the durability and reusability of both MOFs. Mechanistic investigations using FTIR, PXRD, Raman, UV-DRS, XPS, and ESR highlighted the critical role of -NH linkages in facilitating iodine adsorption through strong host-guest interactions, emphasizing the potential of these MOFs to address iodine contamination across diverse environments.

Key Words: SVNIT-1 and 2, MOFs, Iodine Adsorption, -NH Linkage Precursor, Multi-Phase Iodine Sequestration.

A Multi-functional Zn(II) - Metallogel for Organic Dye Adsorption and Catalytic CO₂ Fixation under Ambient Conditions

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Metallogels, a type of viscoelastic material having unique properties, that make them suitable for applications in areas like catalysis, electrochemical devices, dye adsorption, sensing, etc. [1] Among the different porous materials used for dye adsorption, metallogel has emerged as an excellent adsorbent due to its porous nature and ease of synthesis. [2] Using metallogel as a catalyst has an advantage due to its heterogeneous nature. [3] A novel multi-responsive Zn(II) metallogel was synthesized by utilizing a new amino acid-based gelator Na₂HL, {H₃L = 2-(3,5-di-tert-butyl-2-hydroxybenzylamino) pentanedioic acid}. Metallogel was characterized using different techniques, including rheology, FTIR, FESEM, TEM, AFM, BET, PXRD, and TGA-DTA. The metallogel exhibited a self-healing and self-sustaining nature. Xerogel, the dried form of gel, demonstrated a very good uptake of Congo red,^[4] an anionic dye (126.5 mg/g). Kinetics, isotherm, and thermodynamics aspects of CR adsorption were investigated. Adsorption isotherm and kinetic studies suggested that the adsorption process followed the Langmuir adsorption model and pseudo-second-order kinetics, respectively. The Zn(II) metallogel also exhibited excellent recyclability without a significant loss of adsorption capacity. The xerogel was also employed as a heterogeneous catalyst in the chemical fixation of carbon dioxide with epoxide under solvent-free conditions. A good to excellent yield was obtained for this reaction. Thus, this study signifies the dual functionality of metallogel as both an adsorbent for dye removal and a catalyst for the conversion of Carbon dioxide to form cyclic carbonates.

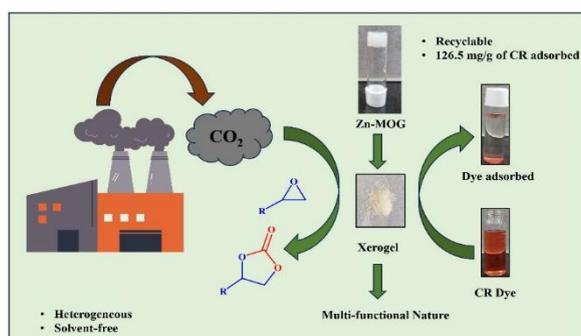


Figure 1. Zn-MOG used in CR dye adsorption and CO₂ fixation.

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'CENTROSYMMETRIC' ANISOLE-SUBSTITUTED FERROCENYL PUSH-PULL BARBITURATE AND THIOBARBITURATE DYES FOR SECOND HARMONIC GENERATION

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Anisole-substituted ferrocenyl (thio)barbiturate dyes FcABA, FcATBA, FcADMBA, and FcADMTBA were synthesized and structurally characterized by ^1H , ^{13}C -NMR, ESI-Mass, and single crystal X-ray diffraction analysis. FcADMBA and FcADMTBA dyes (N-methylated dyes) were crystallized as the centrosymmetric triclinic system while the non-methylated dyes were more amorphous. Also, absorption and emission solvatochromism were done to examine the Intramolecular Charge Transfer (ICT) process, one of the key factors to get Second Harmonic Generation (SHG). Absorption solvatochromism of all the dyes showed that the hydrogen bond donor solvents and chlorinated solvents showed a bathochromic shift in all the dyes which shows that they could be good NLOphores in those solvents. Thermogravimetric analysis (TGA) showed that the barbiturate dyes are more stable than the corresponding thiobarbiturate dyes. The cyclic voltammetry analysis revealed that FcABA, FcADMBA, and FcADMTBA are almost reversible systems with a current ratio of 0.94, 0.97, and 0.99 respectively, FcATBA is quasi-reversible with a current ratio of 0.80. In addition, the theoretical calculations were done to correlate the experimental results using various functionals like B3LYP, CAM-B3LYP, M06, and LC-BLYP with the 6-31G(d,p) basis set and the outcomes showed B3LYP/6-31G(d,p) level of theory is suitable for the synthesized dyes and the results are summarized in **Fig. 1**.

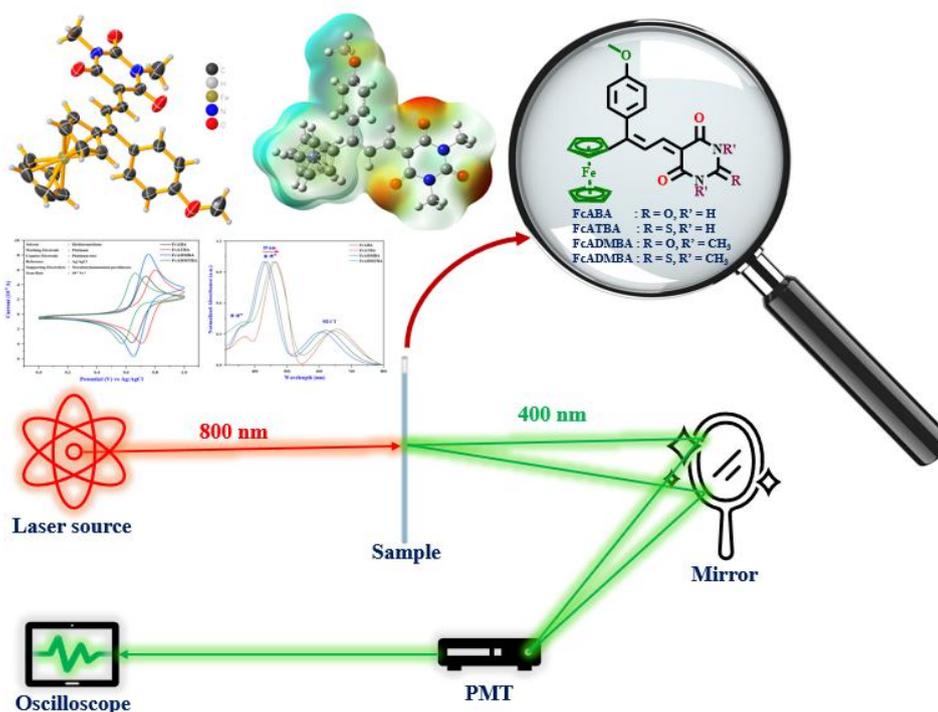


Fig. 1 Anisole-substituted Ferrocenyl Barbiturates for Non-Linear Optics

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Silver Nanoclusters Stabilized by Carbene-phosphaalkenides Ligands: Structural Insights and Functional Properties

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The exploration of silver nanoclusters (NCs) stabilized by innovative ligand frameworks has unveiled a fascinating realm of structural diversity, electronic properties, and potential applications. Herein, we report the isolation and characterization of a range of silver nanoclusters (Ag_{12} , Ag_{29} , Ag_{10} , and Ag_8) stabilized by cyclic alkyl(amino) carbene (cAAC)-phosphaalkenides.^{1,2} These clusters exhibit distinct structural motifs, including the unprecedented 3-fold symmetry in the Ag_{12} clusters and the unique arrangement of atoms in the Ag_{10} cluster. The tri-cationic Ag_{12} cluster demonstrates remarkable stability and luminescent properties, while the Ag_{10} cluster highlights a new geometry, providing insights into silver cluster evolution. Additionally, the neutral Ag_8 and Ag_{29} clusters showcase paramagnetic behavior due to their unique electronic structure. Spectroscopic investigations, including single-crystal X-ray diffraction, UV-visible absorption studies, EPR, and XPS, reveal their mixed-valence nature and delocalized electronic interactions. Furthermore, these clusters exhibit promising luminescent characteristics, highlighting their potential applications in sensing and optoelectronics.

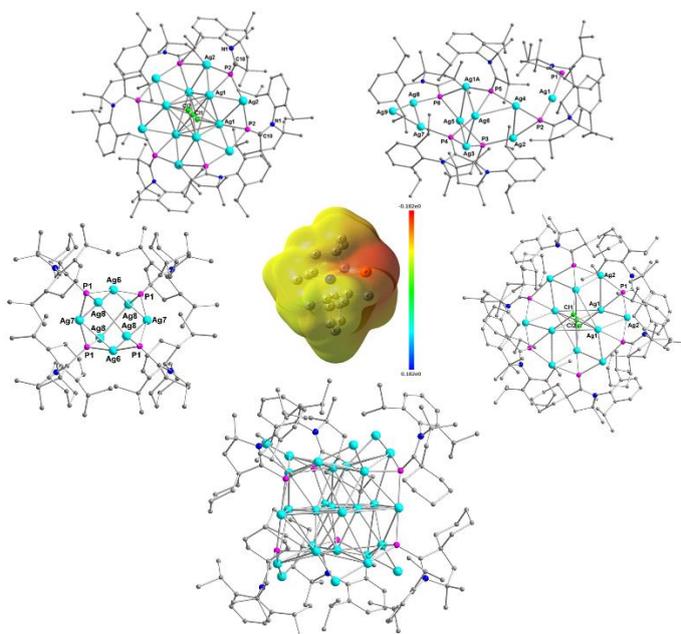


Figure 1 Structural representations of Ag NCs (Ag_{12} , Ag_{29} , Ag_{10} , and Ag_8) stabilized by carbene phosphinidenides, illustrating their distinct geometries and nuclearities.

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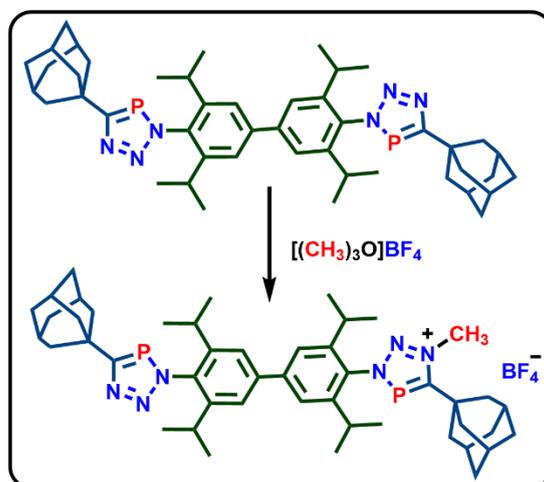
3H-1,2,3,4-Triazaphosphole Constructs Derived from Sterically Encumbered Aryl Polyazides: Synthesis, Structure and Reactivity

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Abstract: Starting from sterically hindered aniline derivatives containing one or more Ar-NH₂ moieties, a series of aryl-azides have been synthesized. The reactions of these mono-, di-, and tri-aryl azides, ArN₃, (ArN₃)₂, and (ArN₃)₃ with phosphalkynes R-C≡P (R = adamantyl or 2,4,6-tri-*t*-butylphenyl) yielded mono-, bis-, and tris-triazaphosphole assemblies. All the products are formed under ambient conditions under prolonged stirring. Representative triazaphospholes can be selectively alkylated with Meerwein's reagent on the most nucleophilic nitrogen atom to yield stable 1,2,3,4-triazaphospholenium cations. These compounds were characterized by multinuclear NMR spectroscopy (¹H, ¹³C, ³¹P, ¹⁹F and ¹¹B), mass spectrometry, and photophysical studies. Molecular structures of representative compounds have also been determined by single crystal X-ray crystallography. Additional DFT, TD-DFT and NICS calculations were performed and the result were found to be in agreement with our experimental findings.



Scheme.1 Synthesis of triazaphospholenium tetrafluoroborate

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A Nitrogen-Rich Fused Triazolo-Pyrimidine Explosive (TPX): Synthesis, Characterization and Energetic Properties

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Nitrogen-rich fused energetic molecules with extended conjugated systems that usually offer high performance and low sensitivity have captured the attention of the energetic materials community.^{1,2} Despite their potential, synthesizing many of the reported fused energetic molecules remains challenging due to their intricate synthetic pathways involving toxic chemicals like cyanogen bromide, nitroacetonitrile, tert-butyl hypochlorite, etc.³ Also, starting materials required for synthesizing such fused-ring energetic compounds are difficult to synthesize.⁴ In this work, we have synthesized a novel fused-ring energetic compound, N-(7-amino-6-nitro-5-oxo-4,5-dihydro-[1,2,4]triazolo[1,5-a]pyrimidin-2-yl)nitramide (TPX, **2**) in good yield via a simple and straightforward synthetic route using commercially available 3,5-diamino-1,2,4-triazole and ethyl cyanoacetate. Further, energetic salt formation allowed us to fine-tune the overall energetic performance and stability of TPX. The molecular structures of TPX and its ammonium salt were confirmed through single-crystal X-ray diffraction. An examination of the physicochemical and energetic properties revealed that TPX and its energetic salts are insensitive (IS = >40 J, FS = >360 N) to mechanical stimuli with good energetic performances and acceptable thermal stabilities. The detonation properties of hydrazinium (**4**, $V_d = 8611 \text{ m s}^{-1}$, $P = 29.46 \text{ GPa}$) and hydroxylammonium salts (**5**, $V_d = 8613 \text{ m s}^{-1}$, $P = 30.81 \text{ GPa}$) were significantly better than the traditional insensitive explosive TATB ($V_d = 8179 \text{ m s}^{-1}$, $P = 30.50 \text{ GPa}$) and were approaching the performance of the benchmark explosive RDX ($V_d = 8795 \text{ m s}^{-1}$, $P = 34.9 \text{ GPa}$). Theoretical analyses, including Hirshfeld surface analysis, 2-D fingerprint plots, and NCI analysis, were conducted to gain insights into the structural and energetic features of crystallized compounds.

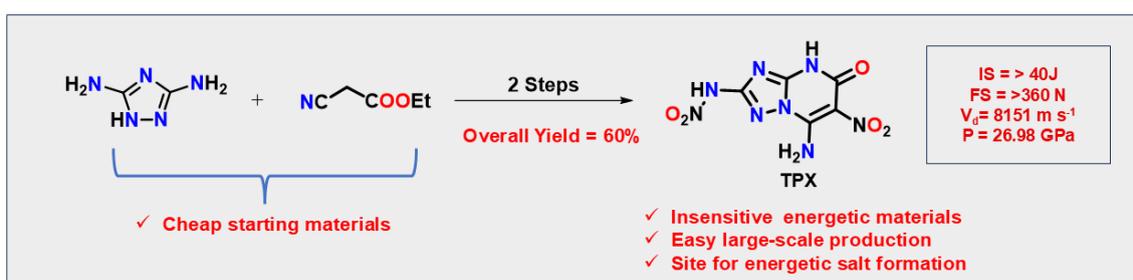


Figure 1 Synthesis pattern of TPX

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A Low-Temperature Organic Soluble Precursor Based Synthetic Strategy to Impurity-Free Pristine and Transition Metal Doped Lead Apatites of LK-99 Type

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The recent claim of copper-doped lead apatite (LK-99) as an ambient pressure room temperature superconductor has garnered widespread attention.^{1,2} However, the signature of superconductivity is supposed to have been derived from a small quantity of Cu₂S impurity present in the system, which involves a very high-temperature, multistep synthetic route.³ Hence, we propose a soft synthetic approach⁴ to develop single-phase lead hydroxyapatite (**Pb-HA**) and transition metal-doped lead hydroxyapatites through solution thermolysis. A new one-dimensional polymeric lead phosphate, Pb[μ-dtbp)₂]_n (**1**), is used as a single-source precursor. The solution thermolysis of **1** with required amounts of PbO and transition metal phosphates/oxides yields **Pb-HA** and transition metal-doped LK-99 analogues, respectively, without any phase impurities. This study presents a foundation for a mild synthetic approach to introduce divalent transition metal ions to lead hydroxyapatite structure with better control over the metal-to-ligand ratio compared to previously known high-temperature methods and better perspectives to the purported superconductivity of copper-doped lead apatite.

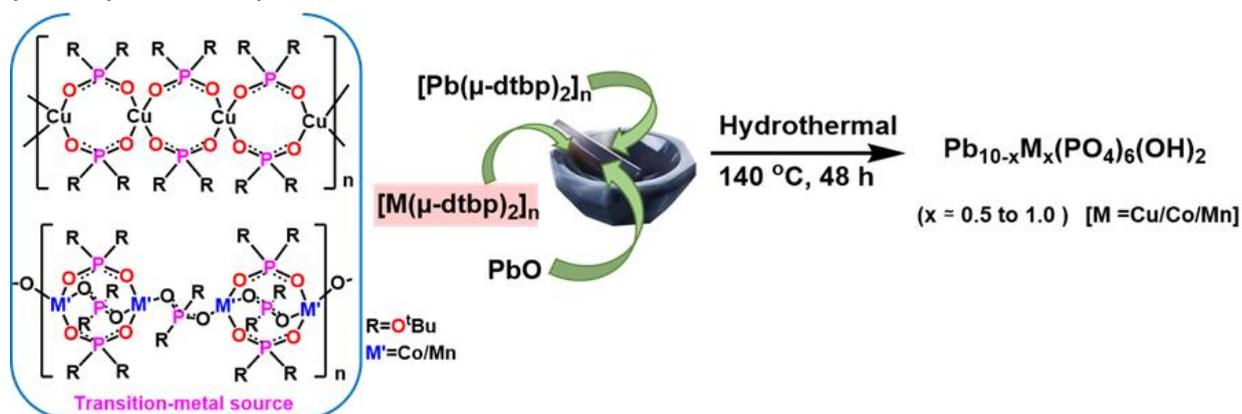


Figure 1: Synthesis route of transition metal doped lead hydroxyapatite through a solution-based method.

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Tellurium Empowered Catalysis for Enantioselective Seleno- Michael Addition Reaction

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Organochalcogens (chalcogens = S/Se/Te) have shown applications in various fields, namely as potent antioxidants, reagents or catalysts in synthetic organic chemistry and materials.¹ The discovery of chiral organoselenium reagents for enantioselective functionalization of alkenes has led to the design of numerous chiral organoselenium reagents and catalysts.² The development of a new organotellurium catalysts,² which has not been explored before, not only provides an alternative to the existing organocatalysts but also leads to a distinct chemical reactivity. Here, an organotellurium catalyst consisting of a chiral quinine auxiliary displays remarkable activity for the enantioselective delivery of reactive arylselenols as a Michael donor in common solvents such as dichloromethane and acetonitrile. The developed chiral organotellurium-catalyzed arylselenol addition to alkenes shows a broad substrate scope as electron-rich and deficient arylselenols and diversely substituted enones are amenable to the reaction conditions. Control experiments, ⁷⁷Se, and ¹²⁵Te NMR, suggest that non-bonded Te...Se interaction between catalyst and arylselenol seems responsible for accelerated and highly enantioselective delivery of arylselenol to enone.

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Mechanistic Study of C-H Bond Activation by Non-Heme Iron and Manganese Oxo Complex: Impact of Oxidation States

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Hydrocarbons are among the most abundant and cost-effective sources of feedstock for organic compounds. However, their utilization is hindered by the challenge of breaking the strong C-H/O-H/N-H bonds, which are characterized by high kinetic stability and robust thermodynamic resilience. [1-2] High valent metal-oxo species are key intermediates that can activate C-H/O-H/N-H bond. High-valent manganese, iron and cobalt-oxo intermediates serve as promising templates for designing biomimetic molecular catalysts tailored to C-H bond activation. [3-5] We present a detailed DFT analysis of key parameters influencing high-valent metal-oxo-mediated C-H activation and oxygen atom transfer (OAT) reactions. Using DFT calculations, we examine the electronic structures of $Mn^{IV}=O$, $Fe^{IV}=O$, and $Co^{IV}=O$ complexes to evaluate their potential for enhanced catalytic activity. Additionally, we investigate the mechanistic pathways for the initial C-H bond activation and OAT reactions of methane, cyclohexadiene, and dimethyl sulfide. To further elucidate the reactivity of these species, we employ molecular orbital (MO), non-covalent interaction (NCI), and steric parameter (% buried volume) analyses. This study underscores advancements in utilizing high-valent metal-oxo species for activating inert C-H bonds and facilitating OAT reactions. [6] The significant exchange of metal electrons and structural parameters during transition states can control reactivity and can help to design catalysts with better efficiency/selectivity for catalytic reactions.

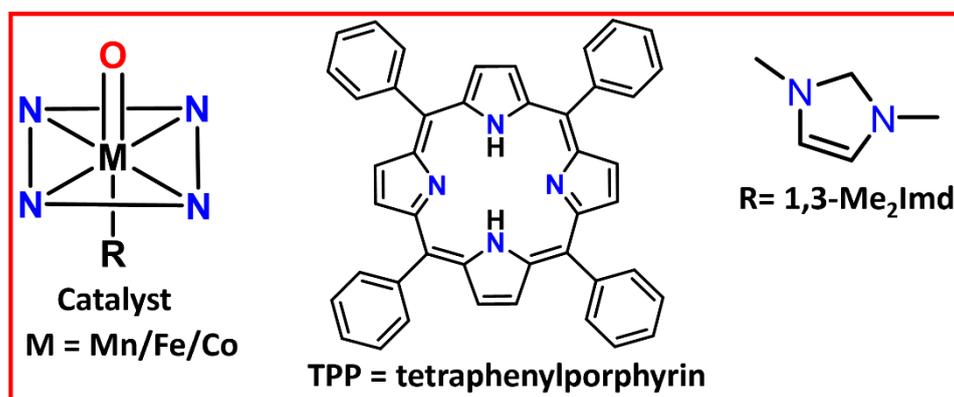


Figure 1 Structures of the species discussed in this work.

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Fine-Tuning the FT-AFT Gap in {CrDy6} Complex through Electron Donating and Withdrawing Group Effects: A Combined Experimental and Theoretical Approach

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Toroidal states hold great promise for spin qubits, magnetoelectric coupling, spintronics, quantum sensing, etc, but stabilizing them at the molecular level remains challenging^{1,2}. Enhancing toroidal moments requires long-range vortex ordering or sufficient dipolar coupling to control magnetic anisotropy. In our recent work, we studied {MLn₆} complexes and found, for the first time, a ferrotoroidal ground state in a molecule. Compared to ferrotoroidal (FT) states, other states must be much higher in energy, ensuring a large FT-AFT (antiferrotoroidal) gap for application³. However, no known chemical strategies exist to increase this gap. We introduced Cl, Br, I, and CH₃ groups at the para position of the parent ligand (o-toluic acid) in similar structures to explore how electron-donating and withdrawing groups affect this gap⁴. Direct current (DC) magnetic measurements and theoretical calculations (RASSCF/RASSI_SO/SINGLE_ANISO/POLY_ANISO) demonstrated that as the height-to-radius (h/r) ratio decreases, inter-triangle dipolar coupling units strengthen, leading to an increase in the FT-AFT gap.

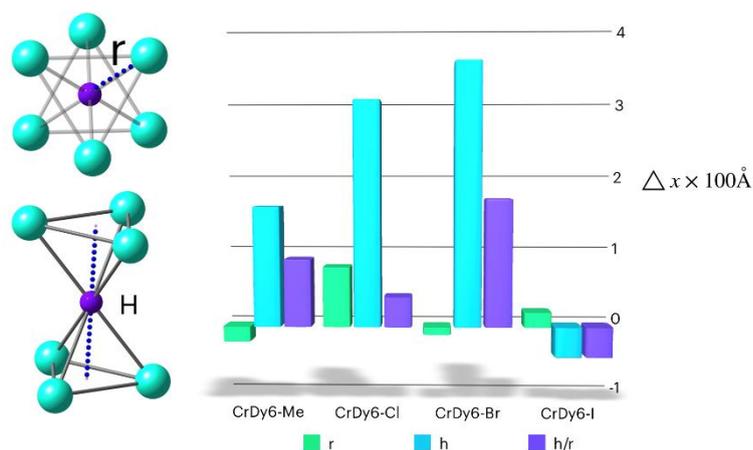


Figure 1. The r, h, h/r ratio of substitute {X-CrDy6} (X = Me, Cl, Br, I) relative to reported {CrDy6}

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Air and Water stable Bis(germylenes): Syntheses, Reactivity, and Photophysical Properties

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Bis(germylenes) refers to compounds with two germylene centers, while germylenes refer to those with a single germylene center.¹ The oxidation of germylenes using elemental chalcogens leads to germacarbonyl compounds. Although the chemistry of air and water stable germylenes and germacarbonyl compounds has been explored, bis(germylenes) and bis(germacarbonyl compounds) stable under ambient conditions have not yet been isolated.² This study, therefore, presents the first examples of air and water stable bis(germylenes) **5-9** and bis(germacarbonyl compounds) **10-12**. The bis(germylene monochloride) **5** is synthesized from bis(dipyrromethene) **4**; compound **5** reacts with alcohols, phenol, and sodium pyrrolide, yielding bis(germylene alkoxides) **6-7**, bis(germylene phenoxide) **8**, and bis(germylene pyrrolide) **9**, respectively. Bis(germylenes) **7** and **9** also react with elemental sulfur and selenium under ambient conditions, affording bis(germacarbonyl compounds) **10-12**. The optical properties of compounds **4-12** are investigated experimentally and computationally. Comprehensive details of all these studies will be shown during the poster presentation.

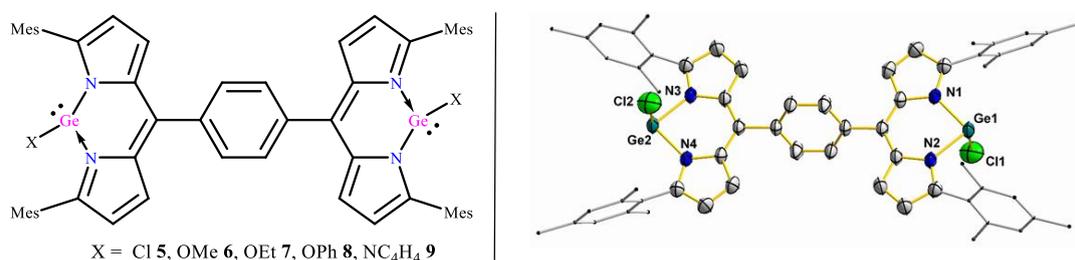


Figure 1. Air and water stable bis(germylenes) **5-9**, and the molecular structure of Bis(DPMGeCl) **5**. All hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at the 50% probability level. Data collection temperature: 300 K

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Mononuclear Copper(II) Phosphinates Bearing N-Donor ligands: DNA Binding and Cleavage, Cytotoxicity and Nanoencapsulation

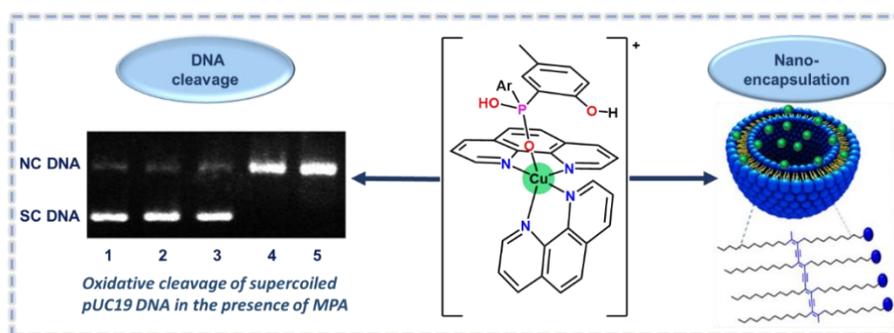
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Mononuclear Cu(II) phosphinate based compounds, viz., [Cu(H₂L₁)₂(Py)₂] (**1**), [Cu(OAc)(H₂L₁)(Cl-tpy)] (**2**) and [Cu(H₂L₁)(Phen)₂]H₂L₁ (**3**), where Py = pyridine; Cl-tpy = 4'-chloro-2,2':6',2''-terpyridine and Phen = 1,10 phenanthroline monohydrate, have been isolated by reacting Cu(OAc)₂·2H₂O with various N-donor ligands in the presence of bis(2-hydroxy-5-methylphenyl)phosphinic acid (**H₃L₁**).¹⁻³ Owing to the bioavailability and biocompatibility of copper, these compounds have been tested for DNA cleavage, cytotoxic activity, and nanoencapsulation.^{4,5} The oxidative DNA cleavage ability of complexes **1-3** has been studied by incubating them with supercoiled (SC) pUC19 DNA (40 μM). The highest oxidative DNA cleavage ability of **3** is related to its strong partial intercalation of 1,10-phenanthroline rings as they are available in higher concentrations on the DNA surface to generate the reactive oxygen species (ROS). **3** encapsulated in a polydiacetylene-supported liposome nanocarrier (**Lip-(3)**), improves biocompatibility and anticancer activity while addressing poor solubility and toxicity concerns. The spherical nanoparticles (~93 nm), which were characterized by UV-Vis, TEM, DLS, and EDX studies, exhibit stability, efficient encapsulation, and suitability for targeted drug delivery.



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Phenothiazine/Phenoxazine Embedded Porphyrinoids

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Porphyrins are 18π aromatic macrocycles containing four five membered pyrroles connected via four *meso* carbons. The electronic properties of porphyrins can be altered by suitable modifications at the periphery of the porphyrin or in the core. One such interesting modification is to introduce polyaromatic hydrocarbon/heterocycle (PAH) in place of one or more pyrrole rings of the porphyrinoids and the resulted polyaromatic hydrocarbon/heterocycle embedded porphyrinoids¹. In this poster, we will be presenting (a) synthesis and studies of phenothiazine embedded porphyrins called here as phenothiazinophyrins² and phenothiazine/phenoxazine embedded heteroporphyrins^{3,4}, (b) Phenothiazine/ Phenothiazine sulfone embedded dithiasmaragdyrins⁵ and (c) phenothiazine embedded calixpentaphyrins⁶(2.1.1.1.1). NMR studies showed that these macrocycles are nonaromatic, and exhibits panchromatic absorption features spanning the visible and NIR regions in both their neutral and protonated forms. Redox study showed that these macrocycles are electron rich in nature and can be oxidised easily. These results will be summarized in the poster.

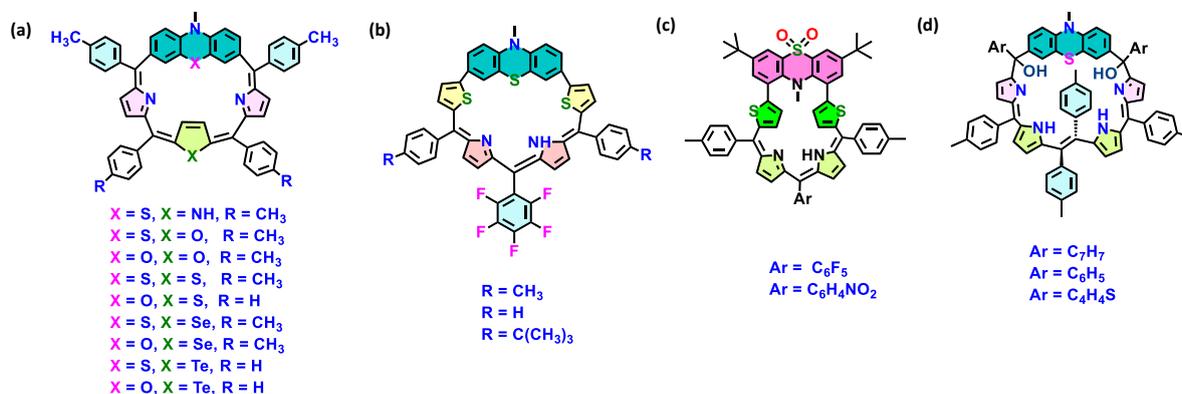


Figure 1. Molecular structures of phenothiazine/phenoxazine embedded macrocycles

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**Isoelectronic Analogues of Carbene using 5,6-bis(diisopropylphosphino)acenaphthene Ligand**Nilanjana Mukherjee,^a Moumita Majumdar*^aDepartment of Chemistry, Indian Institute of Science Education and Research (IISER),
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We have been interested in electron-rich cationic main-group compounds that serve as cationic donor ligands toward transition metal centers.^{[1],[2a,b]} Such transition metal catalysts show strong implications in Lewis-acid catalysis. In this direction, the Group 15 Pn(I) cations (Pn = N, P, As, Sb, and Bi), and Group 16 Ch(II) di-cations (Ch= S, Se, Te) which are isoelectronic with the donor-stabilized carbenes, have emerged recently.^[3a,b] Although the donor-stabilized N(I), P(I), and As(I) cations have been known in the literature, the Sb(I) and Bi(I) cations have remained as fleeting species due to their spontaneous reduction to the corresponding elemental states. Recently, we have reported the stabilization of the elusive Sb(I) cation using bis(diisopropylphosphino)acenaphthene as the supporting ligand.^[4] The dual role of bis(diisopropylphosphino)acenaphthene ligand as a reducing agent as well as in stabilization facilitated the isolation of the Sb(I) cation. The rich electronics available at the Sb(I) cation have led to its coordination towards transition metal ions.^[4] The reactivity of the Sb(I) cation towards transition metal ions, main-group compounds, and bond activation chemistry will be discussed.^[5] The synthetic routes developed for the isolation of Chalcogen(II) di-cations and their reactivity study will be covered (*unpublished results*).

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Ferroelectricity in an Amine-Boronic Acid Co-crystal

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Boronic acids, known for their nontoxicity, are environmentally friendly and are promising candidates for developing all-organic ferroelectric materials due to their capacity to form polar co-crystals.¹ Herein, we present the first report of ferroelectricity in an amine-boronic acid co-crystal, **AP·FPBA**, containing 2-aminopyrimidine (AP) (acceptor) and 4-formylphenyl boronic acid (FPBA) (donor). **AP·FPBA** crystallizes in the polar orthorhombic $Pca2_1$ space group and shows a distinctive rectangular polarization vs. electric field (P - E) hysteresis loop with saturation polarization of $0.37 \mu\text{C cm}^{-2}$. Piezoresponse force microscopic studies revealed the presence of the microscopic polar domain structures of **AP·FPBA** along with the amplitude-bias butterfly and phase-bias hysteresis loops. Furthermore, the piezoelectric energy harvesting experiments show the nanogenerator attributes of **AP·FPBA** with a resultant open circuit voltage of 6.8 V. The capacitance of **AP·FPBA** was measured to be 13.05 pF, which led to its utility for charge storage applications.

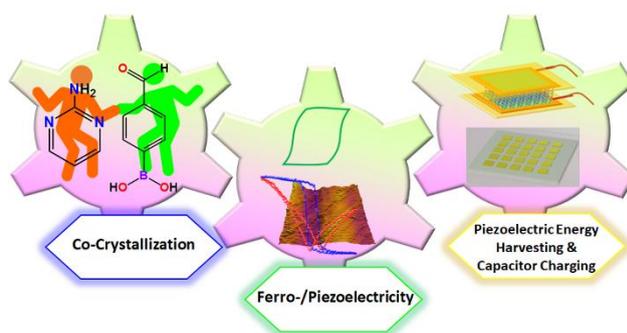


Figure 1 Amine-boronic acid co-crystal **AP·FPBA** containing 2-aminopyrimidine (AP) and 4-formylphenyl boronic acid (FPBA), crystallizing in ferroelectrically active orthorhombic $Pca2_1$ space group, which has been further explored for piezoelectric energy harvesting and capacitor charging.

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Unveiling C-C Coupling in Redox-Active Bis(α -Iminopyridine) Tin Complexes

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Our group have been interested in low-valent Sn(II) chemistry stabilized within bis(imine) based redox-active ligand systems.^[1] We have obtained a bisstannylene from the reaction between the bis(α -iminopyridine) ligand and the Sn[(NSiMe₃)₂]₂ through ene-amide transformation.^[2] Such ene-amide stabilized stannylene exhibit dipolar behavior leading to the formation of Sn(II) di-cation. The ene-amide derivative has been utilized for the stabilization of a highly nucleophilic stannylene.^[3] We have now observed C-C coupling reactions^[4] in the ene-amide stabilized polystannylene systems via radical pathway.^[5] The C-C coupling occurs at the ligand backbone of the polystannylenes leading to the formation of intensely colored compounds. The compounds have been fully characterized using single crystal X-ray diffraction techniques in the solid-state and multi-nuclear NMR spectroscopy in the solution-state. The origin of the absorbance for such polystannylenes have been rationalized from time-dependent density functional theory of their optimized geometries. We have isolated intermediates which helps to rationalize the reaction mechanism for the coupling reaction. All these studies will be detailed in the poster.

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Sterically Crowded 3-Pyrrolyl BODIPYs, Fluorescent BODIPY tetrads, 3-Pyrrolyl BODIPY-Ru(II) Complexes and Metal Helicates

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Oligopyrrolic ligands form metal complexes which show applications in major fields of research such as energy, and medicine. Dipyrin ligand containing two pyrrole rings is one of the most successful oligopyrrolic ligand that forms coordination complexes with wide range of metals and non-metals.¹ Few years back, we have reported synthesis and functionalization of 3-pyrrolyl BODIPYs. In this poster, we present synthesis and studies of a series of sterically crowded hexaarylated *meso*-aryl 3-pyrrolyl BODIPYs (**I**) and their photophysical and electrochemical properties.² We also present synthesis of novel phenyl bridged bis(3-pyrrolyl BODIPY)s and their use in synthesis of more complex fluorescent tetrads (**II**) containing two BODIPY units and two 3-pyrrolyl BODIPY units.³ Synthesis and properties of Ru(II) complex of pyrrolyl dipyrin and bichromophoric 3-pyrrolyl BODIPY-Ru(II) complexes (**III**) also will be presented.⁴ Finally, we also present bis-Cu(II) and bis-Zn(II) complexes **IV** of hexapyrrolic ligands which were stabilized in a double helical fashion.^{5,6} These results will be summarized in this poster.

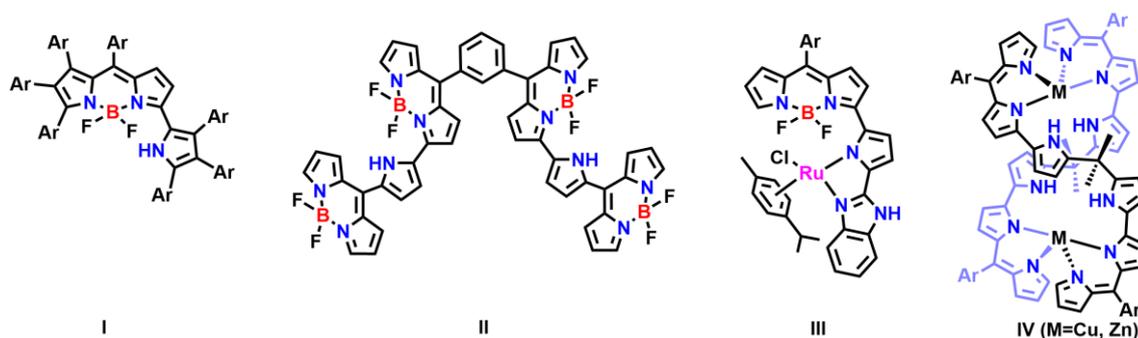


Figure 1 Molecular Structures of hexaarylated 3-pyrrolyl BODIPY **I**, tetrad **II**, BODIPY-Ru(II) complex **III** and bis metal complexes of Cu(II) and Zn(II) **IV**.

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Synthesis and Studies of Expanded Carbaporphyrinoids

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Carbaporphyrinoids, formed by replacing one or more pyrrole rings with benzene rings, exhibit distinctive physicochemical and coordination properties compared to pyrrole-containing porphyrinoids. Incorporation of benzene rings into the macrocyclic framework can occur *via* either a 1,3-linkage (*m*-benzporphyrinoids) or a 1,4-linkage (*p*-benzporphyrinoids). Our synthetic efforts have yielded 28π *p*-benzithiahexaphyrin(1.1.1.1.1)s (**1a-d**) with Möbius aromaticity, as well as a series of core-modified *m*-benzicalixhexaphyrin(1.1.1.1.1)s (**2a-e**) exhibiting non-aromatic characteristics.^{1,2}

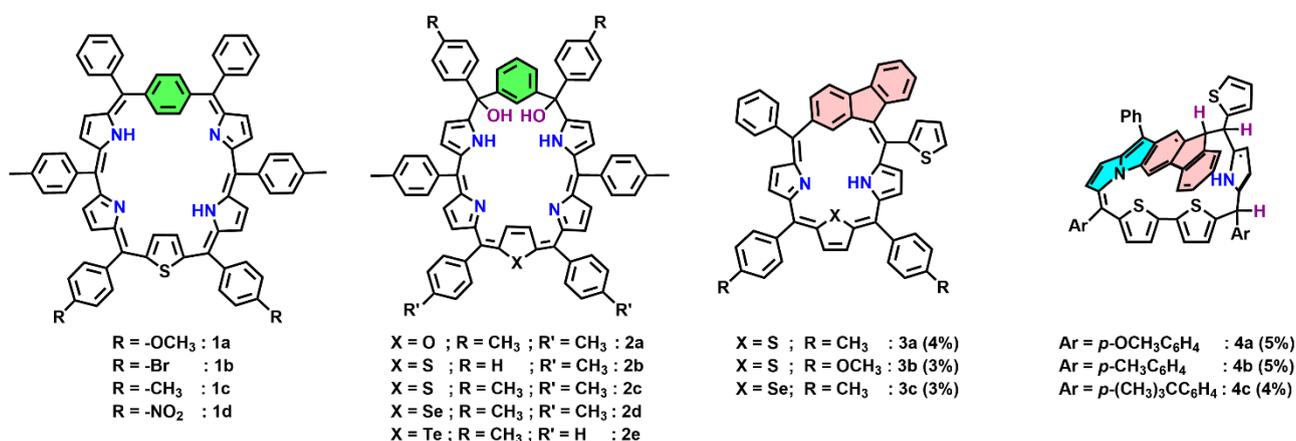


Figure 1: Molecular structures of carbaporphyrinoids 1-4.

Introduction of polycyclic aromatic hydrocarbons (PAHs), such as the fluorene in place of the benzene ring into the porphyrinoid framework, resulted in carbaporphyrinoids with significantly altered structural, spectroscopic, chemical and coordination properties compared to benziporphyrinoids. We synthesized a series of non-aromatic *meso*-fused thia- and selenabenzihomoporphyrin(2.1.1.1)s (**3a-c**).³ Additionally, we synthesized novel pyrrolizino-fluorene-embedded dithiacalixcorrole(1.0.1.1)s (**4a-c**).⁴ The findings of these works will be discussed in this poster.

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Reactivity of Amidinate-Supported Tetrylenes with Organoboron dihalide

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N-heterocyclic silylene (NHSis) chemistry has advanced significantly over the last 20 years. In 1994, West and Denk made the first NHSi discovery.^[1] Since then, several academic and industrial research groups have investigated their possible uses in coordination chemistry, synthesis, and catalysis, indicating the beginning of a new era in low-valent main-group chemistry. The electron acceptor and donor character of NHSis is indicated by its two-coordinate Si (II) core, which has one vacant *p*-orbital and one electron pair. It has been noted that the reports of NHSi's effect against boron halides are quite rare. However, H.Roesky and co-workers reported the reaction of arylhaloborane with LSiCl which results in the formation of borylhalosilane.^[2] Similarly, we envisioned the reaction of amidinato silylene with carbazole-substituted boron halide which results in borylhalosilanes formation. Also to play with the steric and electronics of the ligand, we tried the effect of different substituents on silylene (-*O*^tBu, -N(SiMe₃)₂, -Cbz, -Si(SiMe₃)₃). Moreover, it has been observed that a GeBr₂ precipitate forms while pursuing a higher analog of group 14, such as germylene, due to the increasing inert pair effect down the group.

The reaction mechanism can be explained by the insertion of Si(II) into the B-Br bond, followed by the rearrangement of amidinate from Si to B center and migration of the other halide atoms from the B to Si atom. The borylhalosilanes produced by this rearrangement are helpful precursors for functionalizing the boryl-ligated SiCl₃ or SiX₂ groups, which are typically challenging to prepare using other widely used metathesis reactions.

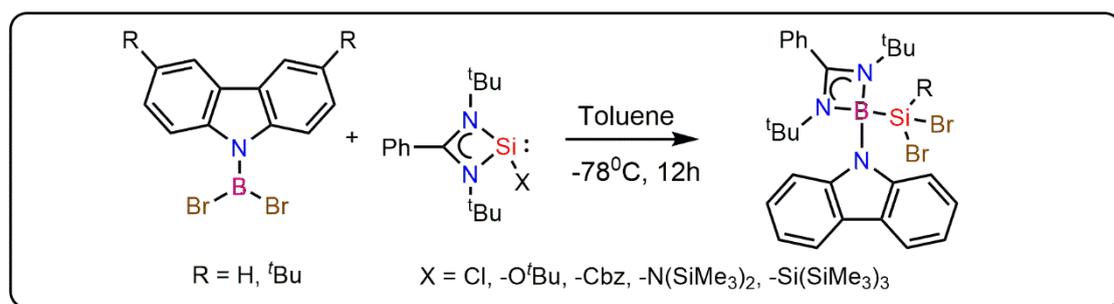


Figure 1. Synthesis of Borylhalosilanes

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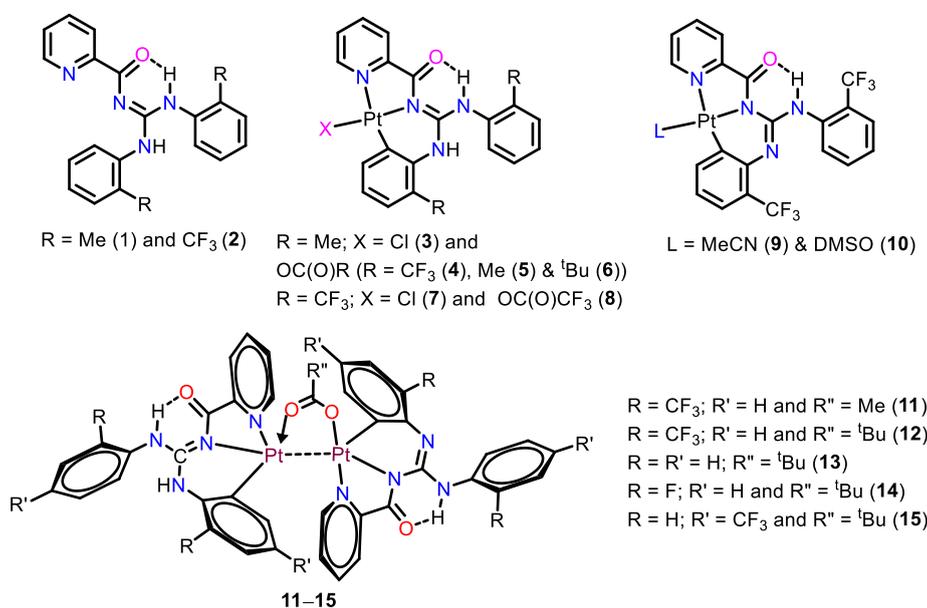
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[6,5] CNN Platinum(II) Pincer Complexes Ligated by Picolinamide Directed N-Arylguanidinate Ligands: Synthesis, Structural Features, and Photophysical Properties

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A comprehensive study was undertaken to understand how the nature of substituents in guanidines **1** and **2** affects their reactions with $\text{PtX}_2(\text{DMSO})_2$ ($\text{X} = \text{Cl}, \text{OC}(\text{O})\text{CF}_3, \text{OC}(\text{O})\text{Me}$ and $\text{OC}(\text{O})^t\text{Bu}$), revealing insights into product diversification. The reactions of **1** with $\text{PtX}_2(\text{DMSO})_2$ ($\text{X} = \text{Cl}, \text{OC}(\text{O})\text{CF}_3, \text{OC}(\text{O})\text{Me}$ and $\text{OC}(\text{O})^t\text{Bu}$) in methanol or toluene at $>65^\circ\text{C}$ afforded **3–6**. The analogous reactions of **2** with $\text{PtX}_2(\text{DMSO})_2$ afforded either mononuclear **7** and **8** or dinuclear **11** and **12**. Compound **8**, upon reaction with acetonitrile at ambient temperature, facilitated the loss of $\text{CF}_3\text{C}(\text{O})\text{OH}$ resulting in the formation of **9** that contains a dianionic guanidinate ligand. The reactivity study of **8** with DMSO is being studied to obtain **10**. Compounds **13–15** are being prepared following the procedure established for **11** and **12**. The new complexes were characterized by elemental analysis, IR spectroscopy, and multinuclear NMR spectroscopy. Molecular structures of **3, 4, 6–9** and **11** and **12** were characterized by SCXRD. The photophysical properties of the new pincer complexes are being studied to understand the influence of guanidinate(1–) versus guanidinate(2–) backbone of dinuclear complexes upon the MMLCT due to the presence of Pt...Pt interaction.¹ This work is aimed at continuing our interest in understanding organometallic reactivity and photophysical properties of organo-palladium and -platinum complexes ligated by guanidinate ligands.^{2,3}



Scheme 1 Types of [6,5] CNN platinum(II) pincer complexes Isolated/envisioned for photophysical studies

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C₂-symmetric p-terphenyl based amine derivatives and their Schiff bases: Potential building blocks for COFs and MOFs

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Covalent-organic frameworks (COFs) represent a relatively new class of porous polymers, which are solely constructed from organic building units via strong covalent bonds, and are of great interest for the applications in gas storage, catalysis, gas separation, chemo-sensing and opto-electricity.^{1,2} The basic building blocks used for the synthesis of a COF must meet two requirements: (a) the functional groups should be chosen in such a way that they can condense in a reversible fashion and (b) the structural integrity of the rigid core of the building blocks should be well preserved throughout the synthesis process. π - π Stacking is the dominant driving force to obtain higher periodicity in the COFs, especially in 2-D COFs in which 2-D sheets are stacked over one another. Our research group has earlier contributed to this area by loading bulky isopropyl groups on tetra-arylamino pyrene, 1,3,5-triarylamino benzene based azo-linked or imine-linked covalent organic polymer for nitroaromatics sensing and CO₂ adsorption.³⁻⁵

The present work involves developing synthetic strategies for diverse C₂-symmetric p-terphenyl based amine derivatives such as bis(2,6-diisopropylamine)terphenyl and their other variants via Suzuki coupling. These linkers with long N...N distances are suitable for synthesizing COFs with larger voids. The presence of orthogonal alkyl chains shall further aid in restricting interpenetration of the networks apart from providing a hydrophobic environment inside the channels of the framework solids. An extension of the utility of these building blocks in MOF chemistry has been achieved by converting them to corresponding Schiff bases. These C₂-symmetric Schiff bases afford a variety of copper(I) and (II) framework structures.

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Synthesis, structure, and piezoelectric properties of a highly fluorescent aluminum(III) 8-hydroxyquinoline tetramer

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Piezoelectric materials convert mechanical stress into electrical energy, but traditional inorganic types face brittleness and toxicity, spurring interest in molecular alternatives.^{1,2} Although numerous phosphonium and aminophosphonium-based complexes³ have been studied for their piezoelectric properties, aluminum covalent compound complexes are rarely recognized as piezoelectric despite the extensive literature on aluminum clusters⁴⁻⁶. Herein, we report a piezoelectrically active aluminum quinolate molecular complex, $[\text{Al}_4(\text{Q-CHO})_8(\mu^2\text{-OH})_4]$ (**1**), crystallized in a non-centrosymmetric space group ($P\bar{4}21c$). This system exhibits promising energy-harvesting capabilities, generating an open-circuit voltage of 1.8 V and a peak power density of $0.24 \mu\text{Wcm}^{-2}$ in a sandwich device configuration (Figure 1). Additionally, photophysical studies of **1** demonstrate its unique optical properties, including strong fluorescence emission, making it a multifunctional material with potential applications in energy harvesting and optoelectronics. Our findings highlight the potential of discrete metal-organic complexes to advance piezoelectric technologies and bridge the gap between mechanical and photophysical energy conversion.

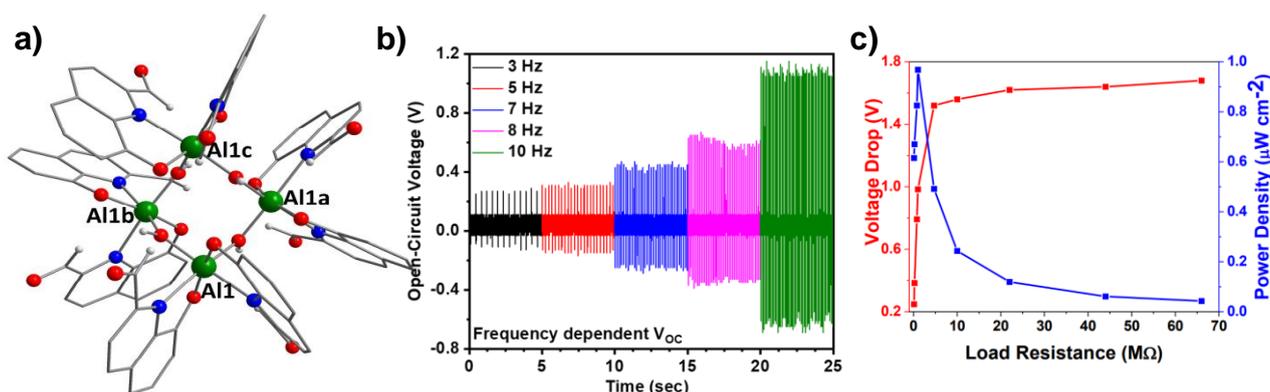


Figure: a) Molecular structure of $\text{Al}_4(\text{Q-CHO})_8(\mu^2\text{-OH})_4$ (**1**), b) Frequency-dependent V_{PP} profile of **1** device at 21 N applied force, and c) Obtained load resistance-dependent peak voltage and calculated peak power density for **1** device.

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N-Acetimidamide Functionalized 4-Amino-3,5-dinitropyrazole as an Oxygen Containing Cation for Thermally Stable Energetic Salts

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Nitrogen-rich heterocyclic skeletons are proficient frameworks for constructing High energy density materials (HEDMs) owing to their high heat of formation, density, and stability.¹ However, balancing energetic performance with stability is a significant challenge in this field. To overcome this obstruction, ionic energetic materials (IEMs) offer a viable approach by leveraging the complementary properties of their cations and anions. N, O-rich cations are desirable for the synthesis of high-performing energetic salts. However, they are comparatively marginalized and less promoted than their anionic counterparts, resulting from their complicated synthetic procedures.² The challenges in designing oxygen-rich energetic cations are addressed in this work, where 4-amino-3,5-dinitropyrazole (ADNP) was utilized as a building block for a novel N, O-rich cationic precursor by coupling it with acetimidamide, which can bear a positive charge via N-functionalization approach. Further modification of performance is achieved by combining it with different N, O-rich anions. The synthesized ADNP-based cation showed significant improvement in energy (oxygen balance) and stability (thermal and physical) in comparison to commonly used N-rich cations and some of the neutral acidic analogues, in the targeted IEMs. All the compounds (**2-15**) were fully characterized, and their energetic properties were calculated. Furthermore, compound **9** ($\rho = 1.84 \text{ g cm}^{-3}$; $D_v = 8699 \text{ m s}^{-1}$; $P = 31.1 \text{ Gpa}$) shows the highest energetic properties (comparable to RDX) and best correlation between stability and energetic performance among all synthesized compounds. This work represents an innovative advancement in the field of ionic energetic materials (IEMs) and is expected to accelerate further research and development in this challenging area.



Figure 1 Strategic combination of the oxygen-rich energetic cation with tetrazolate-based anion to form energetic salt with promising performances.

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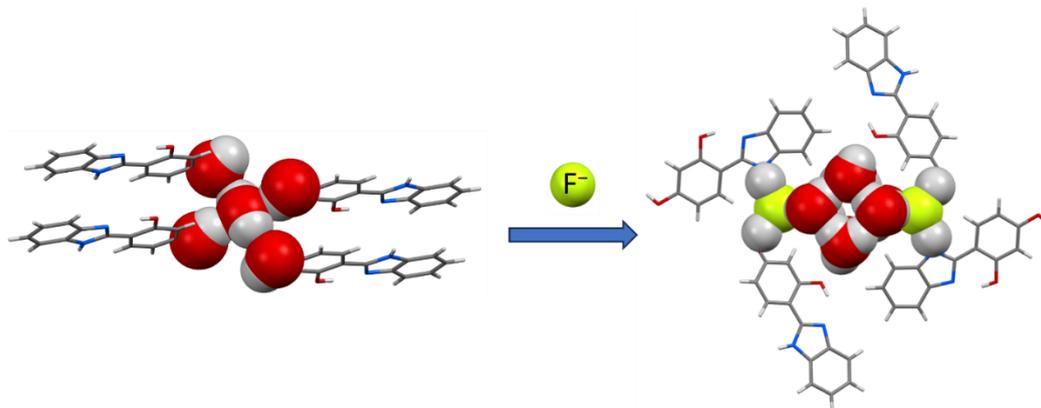
Structural and optical studies of fluoride ion binding using *N*-heteroaromatic ligands

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Fluoride (F^-) ions are essential in various chemistry, biology, and health science applications.¹⁻³ They are key trace elements, and their deficiency and excess can lead to significant health problems. The WHO has recommended limiting fluoride intake to below 1.5 ppm. Herein, we center on two crucial *N*-heteroaromatic systems, 8-hydroxyquinoline and imidazole. These compounds show a strong affinity for different anions due to their acidic hydroxyl (OH) and amine (NH) protons. In our study, we synthesized three receptor ligands: 5-(1H-benzo[d]imidazol-2-yl)quinolin-8-ol, 5-(benzo[d]thiazol-2-yl)quinolin-8-ol, and 4-(1H-benzo[d]imidazol-2-yl)benzene-1,3-diol, and assessed their ability to bind F^- ions.⁴ These ligands selectively interact with F^- ions, forming specific fluoride complexes that we analyzed through SCXRD, NMR spectroscopy, and UV-vis spectroscopy. The structural analysis indicated that F^- ions are firmly integrated into the ligand structure via NH, OH, and aryl-CH hydrogen bonds. ¹H NMR studies confirmed that NH and OH serve as the main F^- binding sites, as observed by the disappearance of their proton signals upon the addition of TBAF. UV-vis spectroscopy also demonstrated the ligands' sensitivity to F^- at concentrations of $\geq 0.5 \mu\text{M}$.⁴



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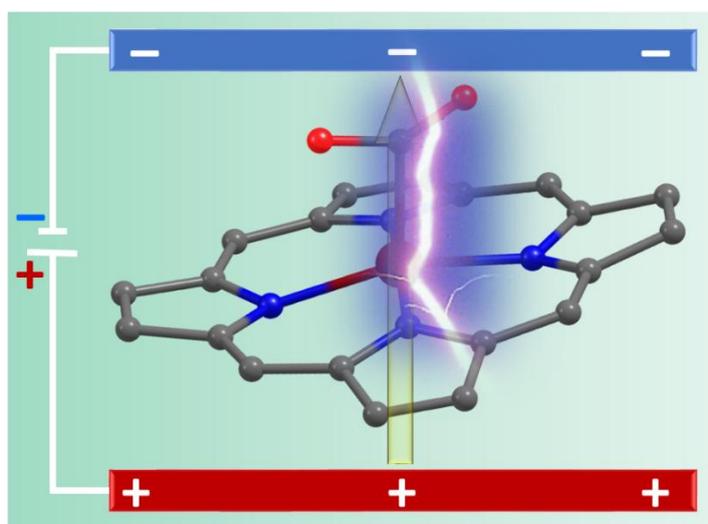
Role of Oriented(Local) Electric Field to Drive CO₂ Activation in Low-Valent Iron Porphyrin Systems

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Electrochemical CO₂ reduction to CO is a promising strategy for sustainable carbon utilization, yet its efficiency is highly dependent on catalyst design. In this study, we investigate the mechanistic pathways of CO₂-to-CO conversion catalyzed by three low-valent synthetic Fe-porphyrin systems: Fe-TPP (1), Fe-p-TMA (2), and Fe-o-TMA (3). Our findings reveal that Fe-o-TMA (3) exhibits the highest catalytic efficiency, followed by Fe-p-TMA (2) and Fe-TPP (1). This trend is attributed to the enhanced local electric field (LEF) induced by the o-TMA substituents, which significantly lower activation energy barriers and facilitate CO₂ reduction. To further elucidate the role of electrostatics, we analyze the effect of an oriented external electric field (OEEF). Remarkably, Fe-TPP under an applied field of 0.46 V/Å mimics the catalytic performance of Fe-o-TMA, demonstrating that external fields can modulate reactivity and enhance catalytic efficiency. These insights underscore the interplay between electronic structure, geometric effects, and electrostatics in governing catalyst performance. Overall, this work provides a mechanistic foundation for rational catalyst design, highlighting the potential of leveraging both intrinsic molecular properties and external stimuli to optimize electrochemical CO₂ reduction.



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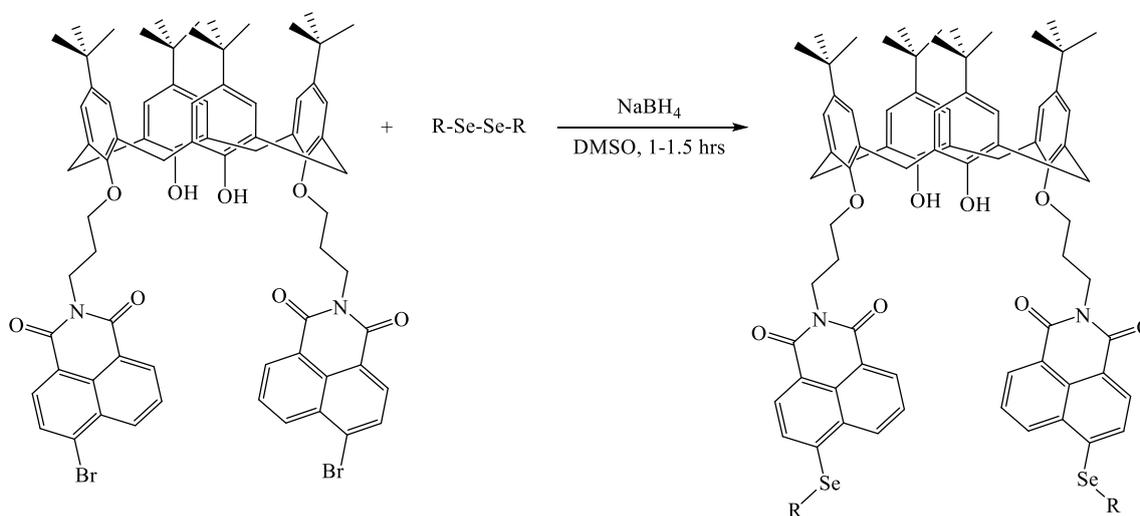
Calix[4]arene in-built naphthalimide conjugated with organoselenium derivatives for heavy metal sensing application

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Calix[4]arene-conjugated naphthalimide sensing probes have gained attention for their ability to detect various substances, including heavy metals, dyes, and both anions and cations. Similarly, organoselenium derived probes have advanced due to their effective metal ion chelation, making them ideal for metal ion sensing. The combination of organoselenium compounds with Calix[4]arene-conjugated naphthalimide can enhance both the structural and chemical properties of the probe, improving its sensing capabilities. In this study, (**figure-1**), we synthesized three novel organoselenium (aliphatic/aromatic and heterocyclic) based Calix[4]arene - conjugated naphthalimides. These derivatives were characterized using a variety of spectroscopic techniques, including FT-IR, UV-Visible, ¹H NMR, ¹³C NMR, and ⁷⁷Se NMR, providing valuable insights into their structural features and potential for sensing applications.



R = -ph, -n-octyl, -CH₂-pyridine

Figure-1: Synthetic strategy of Calix[4]arene in-built naphthalimide conjugated with organoselenium derivatives

Deciphering the Mechanism of Selective L-Arginine Oxidation by Iron-(IV)-Oxo Intermediates

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The ethylene-forming enzyme (EFE) in pseudomonads and fungi is a unique Fe/αKG oxygenase with a dual function. Fukuda et al. (1992) proposed a mechanism where EFE primarily converts its co-substrate into ethylene and CO₂, utilizing all four oxidizing equivalents from O₂. It also catalyzes a secondary reaction, oxidizing 2OG to succinate while breaking down L-Arg into guanidine and pyrroline-5-carboxylate (P5C). Though L-Arg is directly involved only in the secondary reaction, it is essential for ethylene formation. The product ratio of ethylene, succinate, and P5C was 2:1:1.

Certain mutations in the ethylene-forming enzyme (EFE) can shift its activity toward the L-arginine oxidation (RO) pathway. While the wild-type enzyme primarily facilitates ethylene formation, these mutations enhance the oxidation of L-Arg, leading to increased production of succinate, guanidine, and pyrroline-5-carboxylate (P5C). This suggests that structural changes in EFE can modulate its dual-function mechanism, favoring either ethylene synthesis or L-Arg oxidation, depending on the specific mutation.

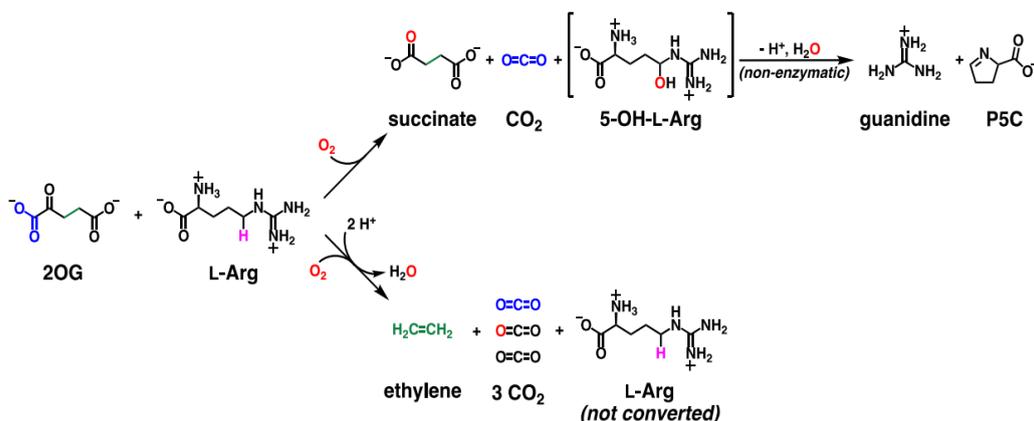


Figure 1 Reaction scheme diversion for EFE (Fe/ αKG) enzyme

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Investigating the Influence of Oriented External Electric Fields on Modulating Spin-Transition Temperatures in Fe(II) SCO Complexes: A Theoretical Perspective

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Spin-crossover complexes, valued for their bistability, are extensively studied due to their numerous potential applications. A primary challenge in this molecular class is identifying effective methods to adjust the spin-transition temperature, which frequently falls outside the desired temperature range. This typically necessitates intricate chemical design and synthesis or the use of stimuli such as light or pressure, each introducing its own set of challenges for integrating these molecules into end-user applications. In this work, we aim to address this challenge using an oriented external electric field (OEEF) as one stimulus to modulate the spin-transition temperatures. For this purpose, we have employed both periodic and non-periodic calculations on three well-characterized Fe(II) SCO complexes namely [Fe(phen)₂(NCS)₂] (**1**, phen = 1,10-phenanthroline), [Fe(bt)₂(NCS)₂] (**2**, bt = 2,2'-bi-2-thiazoline) and [Fe(py)₂phen(NCS)₂] (**3**, py = pyridine) possessing similar structural motif of {FeN₄N'₂}. To begin with, DFT calculations employing TPSSh functional were performed on complexes **1** to **3**, and the estimated low-spin (LS) and high-spin (HS) gaps are 24.6, 15.3 and 15.4 kJ/mol, and these are in the range expected for Fe(II) SCO complexes. In the next step, OEEF was applied in the molecule along the pseudo-C₂ axis that bisects two coordinated -NCS groups. Application of OEEF was found to increase the Fe-ligand bond length and found to affect the spin-transition at particular applied OEEF. While the HS state of **1** becomes the ground state at an applied field of 0.514 V/Å, the LS state lies at a higher energy of 1.3 kJmol⁻¹. While the DFT computed T_{1/2} for the optimised geometry of **1**, **2** and **3** were found to be 134.6 K, 159.9 K and 111.4 K respectively, at the applied field of 0.6425 V/Å T_{1/2} increases up to 187.3 K, 211.0 K and 184.4 K respectively, unveiling hitherto unknown strategy to tune to the T_{1/2} values. Further, calculations were performed with complex **1** adsorbing on the Au(111) surface. The formation of an Au-S bond during adsorption significantly stabilises the low-spin (LS) state, hindering the observation of spin-crossover (SCO) behaviour. Nonetheless, the application of OEEF reduces this gap and brings the T_{1/2} value closer to the desired temperature. This offers a novel post-fabrication strategy for attaining SCO properties at the interface.

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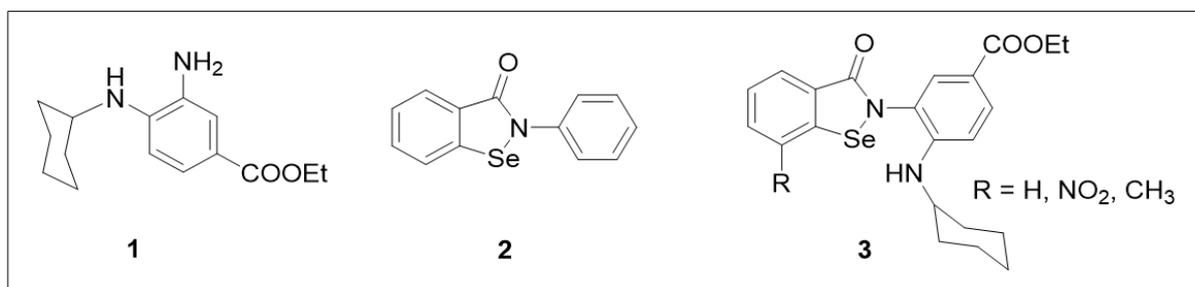
Synthesis and Glutathione Peroxidase-like Antioxidant Activity of Ferrostatin-Based Organoselenium Compounds

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ABSTRACT: Ferroptosis is an iron dependent programmed cell death characterised by the accumulation of lipid peroxidation products and glutathione depletion.¹ Recent studies have shown that ferroptosis is closely related to pathophysiological processes of many diseases such as neurodegenerative diseases, tumours, blood disease, kidney injury.² This leads to the study of radical trapping antioxidants that effectively suppress ferroptosis by trapping peroxy radicals which is responsible for chain propagation. Recently, Ferrostatin-1 (**1**) was reported as the first potent inhibitor of ferroptosis due to their ability to slow the accumulation of lipid peroxides.^{1,3} Dixon and collaborators demonstrated the efficacy of ebselen (**2**) in blocking the death induced by erastin and RSL3, inducers of ferroptosis.¹ Therefore, we synthesized more functionalised ferrostatin-based organoselenium compounds **3** and evaluation of their antioxidant properties by using UV-Visible spectroscopic techniques.



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PNP-Mn(I) Catalysed Base Free *N*-Alkylation of Amines using Alcohols and *N*-Methylation of Amines

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The catalytic coupling of amines with alcohols via the hydrogen borrowing method offers distinct advantages, notably the absence of a need for an external hydrogen source and the production of water as the sole byproduct. The transition metals most commonly employed in this catalytic process are ruthenium¹ and iridium². However, the development of similar catalytic systems utilizing non-precious, earth-abundant metals remains comparatively underexplored. Herein, we report a non-noble metal homogeneous catalytic system for the *N*-alkylation of amines with alcohols, facilitated by a Mn^I pincer complex [Mn(CO)₃{*o*-Ph₂PC₆H₄C(O)N(C₆H₄PPh₂-*o*)}*K*^{3-P,N,P}] **1** featuring a Bala-Hari Bisphosphine. The reaction operates under base-free conditions at 80 °C, enabling efficient transformations to *N*-alkylated products with good to excellent yields within 12 h. This system exhibits broad substrate scope, accommodating a wide range of alcohols and anilines and has been successfully applied to the synthesis of indoles, dibenzylpiperazine, and dialkylation of diamines. Additionally, selective mono *N*-methylation of amines was achieved under mild conditions using methanol as an inexpensive C₁ source.

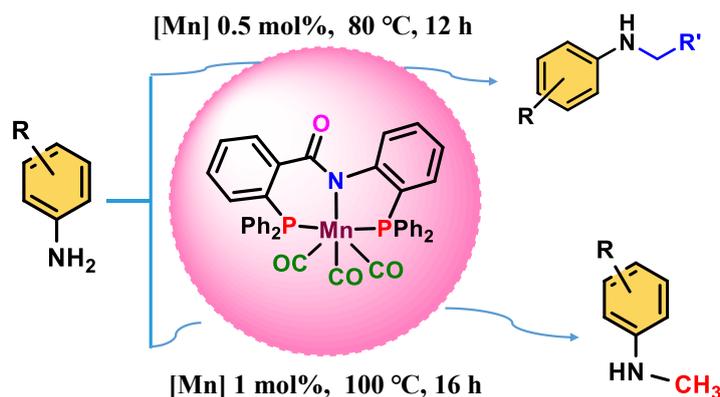


Figure 1 *N*-alkylation of amines with alcohols by **1**

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A Machine Learning Approach to Decipher the Origin of Magnetic Anisotropy in Three-Coordinate Cobalt Single-Ion Magnets

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Single Molecule Magnets (SMMs) serve as vital models for permanent magnets and are key to compact information storage and molecular spintronics. A critical factor in SMM behavior is magnetic anisotropy, especially the axial zero-field splitting parameter (D) in mononuclear transition metal complexes.[1] Low-coordinate mononuclear complexes, in particular, exhibit higher anisotropy and blocking temperatures compared to other molecular classes. However, predicting the sign and magnitude of the D value is a challenging task due to the influence of donor atom properties and structural parameters.[2] To address this, an initial dataset of 90 Co(II) complexes was curated and expanded to 614 complexes through optimization techniques. Attempts to predict D values and their classifications using traditional magneto-structural correlations were inadequate. Machine learning (ML) tools were employed to identify seven critical descriptors influencing D values: bond lengths (BL1, BL2, BL3), bond angles (BA1, BA2, BA3), and the parameter ϕ . This dataset was shuffled and split, with 80% used for training and 20% for testing. The ML model achieved over 90% accuracy in D value prediction and over 95% in classification, offering a deeper understanding of the relationship between structural features and magnetic properties in SMMs.

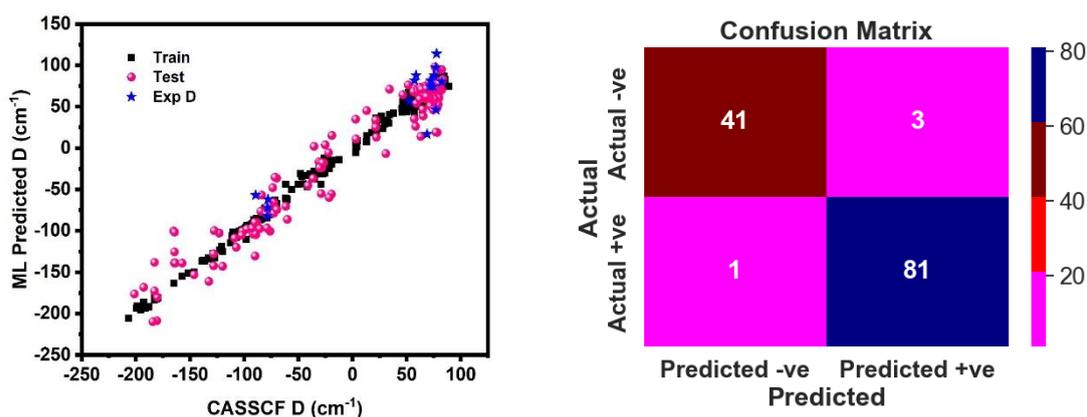


Figure 1. (a) Scatter plots illustrate the comparison between ML-predicted, CASSCF-calculated D , and experimentally reported values within both training and testing datasets. (b) Binary confusion matrix with an actual sign on the y-axis and predicted sign on the x-axis

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Reversible Switching Between a Self-Assembled 2-Catenane and the Constituent Coordination Rings

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2-Catenanes (Hopf link) are composed of two macromonocyclic or macropolycyclic rings that are mechanically interlocked.¹ Reversible conversion between a 2-catenane and its constituent rings is a rare phenomenon. Guest-binding/-sequestering as a concept for reversible conversion between a 2-catenane and the constituent macromonocyclic ring is conceptualized and successfully demonstrated in this work. A pair of C-shaped bis-monodentate ligands of comparable sizes and a linear bis-monodentate ligand complimenting to the terminal-lengths of C-shaped ligands have been identified. One pot complexation of cis-protected Pd(II), C-shaped neutral ligand and linear neutral ligand (2:1:1 ratio) in water resulted in an octa-cationic 2-catenane where two tetra-cationic macromonocyclic coordination rings are interlocked forming 2-catenane. When the reaction was performed in presence of a selected di-anionic guest molecule, it resulted in a guest bound coordination ring instead of the 2-catenane. One-pot complexation of cis-protected Pd(II), C-shaped di-cationic ligand and linear neutral ligand (2:1:1 ratio) in water resulted in a hexa-cationic electron deficient macromonocyclic coordination ring in the absence of guest but a guest bound coordination ring was formed in the presence of the di-anionic guest. Addition of the guest to the preformed catenane resulted in the separation of the two rings to favour the guest-bound ring. This guest bound ring can be reverted to 2-catenane by sequestering the bound guest using the electron deficient hexa-cationic coordination ring.

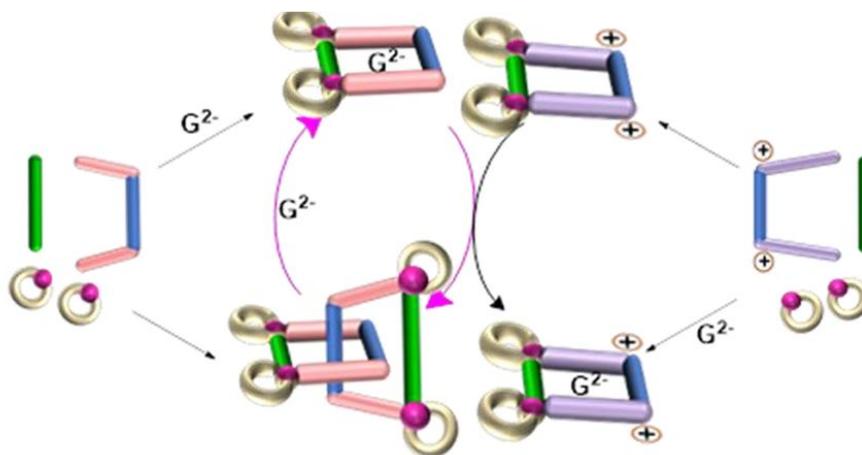


Figure 1 Stimuli responsive switching between a 2-catenane and the constituent rings.

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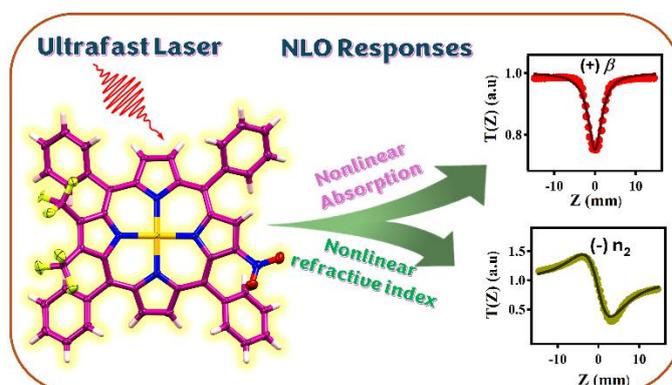
Electron-Deficient β -Trisubstituted Porphyrins: Synthesis, Spectral, Structural, DFT, Electrochemical Studies and Their NLO Application

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Developing novel NLO materials exhibiting strong NLO responses and high stability is urgently required to meet the demands of various applications across different fields.¹ In this regard, porphyrins emerge as promising candidates for nonlinear optical applications. This is attributed to their highly delocalized aromatic π -electron systems, substantial stability, conformational flexibility, and potential for versatile structural modifications.² Our group explored the NLO properties of unsymmetrical porphyrins with push-pull groups.² The present work illustrates the synthesis of β -trisubstituted porphyrin, viz. 2,3-bis(trifluoromethyl)-12-nitro-5,10,15,20-tetraphenylporphyrin ($H_2TPP(NO_2)(CF_3)_2$) and its metal complexes (Co^{II} , Ni^{II} , Cu^{II} , and Zn^{II}) and their characterization by various spectroscopic techniques and single crystal XRD and exploring their intensity-dependent third-order NLO properties. Unsymmetrical electron-deficient antipodal β -trisubstituted porphyrins showed interesting photophysical and electrochemical properties. Intensity-dependent third-order nonlinear optical studies demonstrated that the asymmetric β -substituted electron-deficient porphyrins exhibited a significant two-photon absorption coefficient ($\beta = 0.04 - 8.10 \times 10^{-10} \text{ m/W}$) and two-photon absorption cross-section ($\sigma_{2PA} = 0.02 - 1.67 \times 10^6 \text{ GM}$). Additionally, the materials display a self-defocusing negative nonlinear refraction ($n_2 = (-) 1.08 - 40.27 \times 10^{-17} \text{ m}^2/\text{W}$). These results suggest that synthesized porphyrins hold the potential for advanced applications in photonic devices and other optoelectronic technologies.



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Post-translational Modification: Covalent Modification of Amino Acids in Cytochrome P460 Cofactor Maturation

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Post-translational modification (PTMs) in c-type cytochrome P460 through covalent cross-linking involves the heme porphyrin ring itself at *meso*-carbon with Lys amino acid of the protein.^[1] The site-directed mutagenesis of Lys with Tyr or Leu does not cross-link and leads to catalytic inactivity for NH_2OH oxidation.^[2,3] The origin of heme-Lys cross-link with leans of the functional and co-factor electronic structure remains elusive to date, and its study is highly demanding for mapping the artificial enzyme design. Specifically, the role of cross-link needs a virtuous theoretical prediction that has triggered the exciting advances in enzyme chemistry, particularly mechanistic insight.

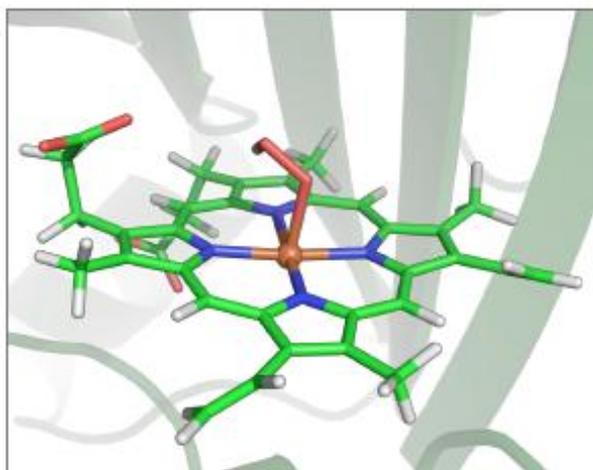


Figure 1: Active site for cyt P460 intermediate from *Nitrosomonas europaea*. PDB ID: 8GAR

To this extent, we have studied the dynamics and mechanism for maturation of cross-linked cyt P460 as well as spectroscopic validation of intermediate observed by experimental studies using QM/MM calculation.

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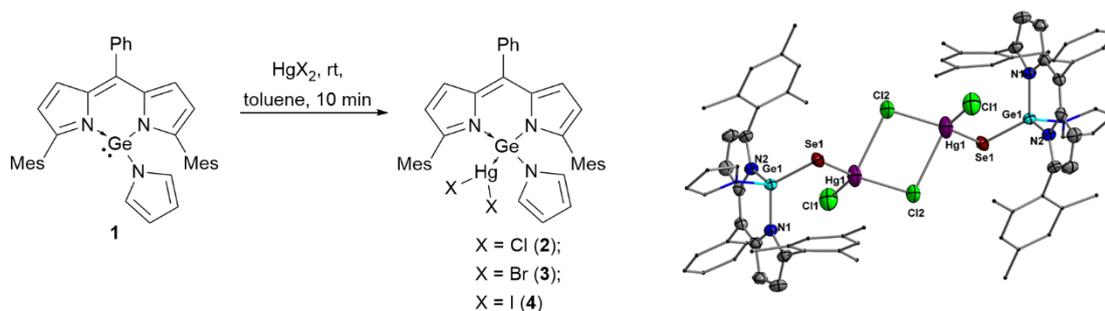
Germylene and Germacarbonyl Compounds as Complexing Agents for Mercury Remediation

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Metallylenes contain a lone pair of electrons on the central group 14 element. Their oxidation using elemental chalcogens leads to heavier analogs of carbonyl compounds with an M=E bond (M = Si, Ge; E = O, S, Se, Te). With lone pairs of electrons on the E atoms, these compounds can also act as Lewis bases.¹ While various metal complexes involving germynes and germacarbonyl compounds as ligands are known, their mercury complexes are hardly known.²⁻³ While planning to isolate such missing complexes, it was also thought that if they can be obtained as species stable under ambient conditions using air and water-stable germynes and germacarbonyl compounds, the utility of these compounds for mercury remediation can also be pursued. Execution of this plan favorably afforded anticipated results, which are described here. DPM stabilized germylene pyrrolide **1** and germacarbonyl compounds **5-6** with Ge=E bonds react with mercury(II) halides to produce mercury halide complexes **2-4** and **7-12**, respectively (E = S **5**, Se **6**; Scheme 1). This complexation occurs even at low mercury concentrations, and most mercury complexes formed exhibit reasonable stability in water. Because of all these aspects, mercury remediation using compounds **1** and **5-6** became possible. ICPMS studies have shown that these germanium compounds can remove over 99% mercury from contaminated water samples containing approximately 20 mg/L of mercury halide within 10 minutes. Details regarding the synthesis, characterization, and mercury remediation will be presented in the poster.



Scheme 1. Syntheses of dipyrinatogermylene pyrrolide **1** and germacarbonyl compounds **5-6** stabilized mercury halide complexes **2-4** and **7-12**, respectively.

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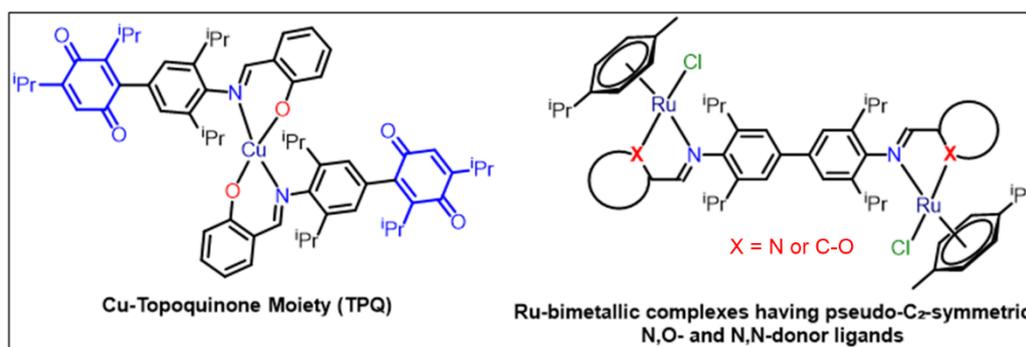
Homogeneously Catalyzed Organic Transformations at RM Group

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Our group has been investigating the chemistry of C_2 -symmetric 2,2',6,6'-tetraisopropylbenzidine, a sterically demanding platform for Schiff-base ligands that stabilizes low-coordinate metal centers. Initially, we synthesized a Cu (II)-topoquinone complex based on a C_2 -symmetric salicylaldimine ligand featuring TPQ-like side arms.¹ This complex efficiently catalyzes the oxidation of primary benzylic amines to secondary imines under ambient conditions, as confirmed by quenching experiments and DFT studies. Building on this, we explored pseudo- C_2 -symmetric N, O- and N, N-donor ligands² for the synthesis of Ru-bimetallic complexes. These bimetallic systems exhibit significantly enhanced catalytic activity compared to their monometallic counterparts due to cooperative effects, demonstrating their potential in diverse catalytic transformations often even in solvent such as water. Notably, these catalysts display high efficiency in reductive amination,³ chemoselective transfer hydrogenation of aldehydes,⁴ quinoline synthesis,⁵ and α/β -alkylation reactions.⁶ Additionally, microwave-assisted hydrogenation significantly accelerates reaction rates.⁷ Ligand design and metal cooperativity play critical roles in optimizing catalytic performance and reusability.

Beyond C_2 -symmetric ligand systems, we are currently investigating the catalytic activity of Co (II)-phosphoramidate and Ru (II)-carbazoyl phosphine complexes for hydrogen borrowing reactions, further broadening the scope of efficient and sustainable catalytic methodologies.



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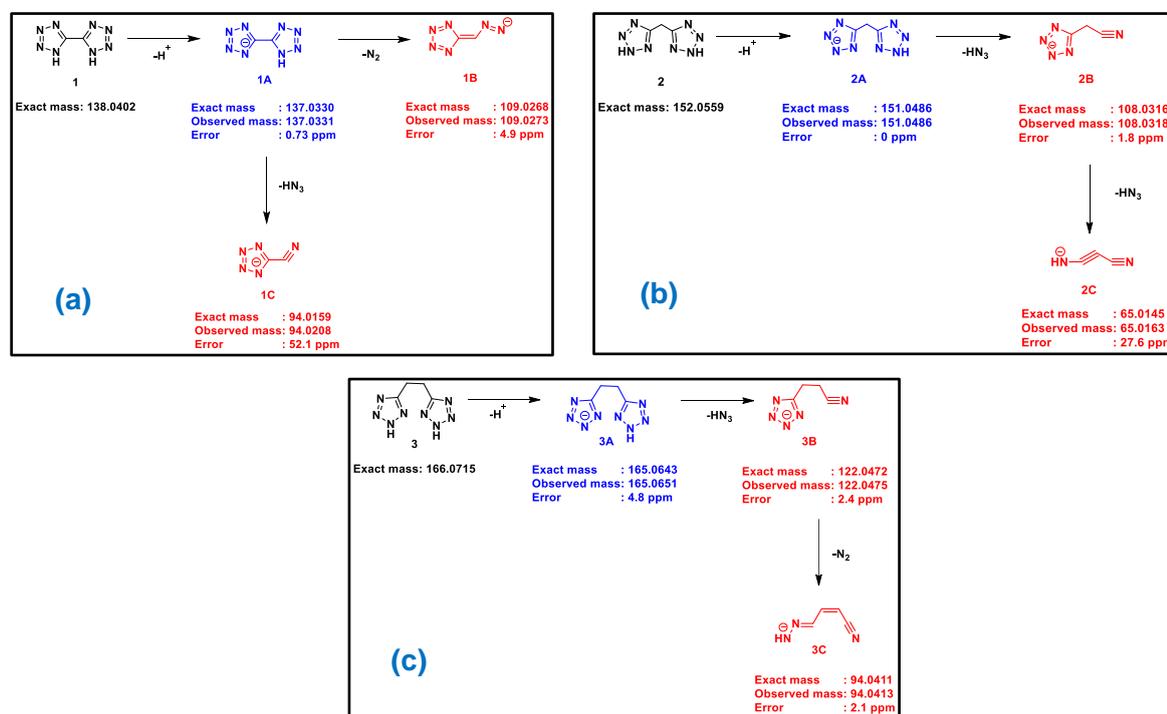
Fragmentation of Nitrogen-rich bridged energetic azoles

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Nitrogen-rich heterocycles, particularly tetrazole-based high-energy density materials (HEDMs) offer high performance, low sensitivity, and are environmental-friendly. However, many nitrogen-rich energetic heterocycles are sensitive to external stimuli. Gaining insights into the potential anomalous thermal or kinetic behavior of such molecules is essential for designing new HEDMs and their practical applications. We investigated the influence of introducing an alkylidene bridge between the energetic nitrogen heterocycles on the decomposition mechanism and pathway of different bridged tetrazoles. Fragmentation pathways of 5-(Tetrazol-1-yl)-2H-tetrazole, 1,2-Bis(5-tetrazolo)methane, and 1,2-Bis(5-tetrazolo)ethane, were investigated using high-resolution mass spectrometry (HRMS). The deduced fragmentation pathways are shown in Scheme 1. Stability comparisons were made using the HOMO-LUMO gap and electrostatic potential (ESP) values from computational calculations. The observed stability trend is: 5-(Tetrazol-1-yl)-2H-tetrazole (1) < 1,2-Bis(5-tetrazolo)methane (2) < 1,2-Bis(5-tetrazolo)ethane (3). This study confirmed that the introduction of various bridges between the two heterocyclic rings enhanced conjugation, thereby making them more stable. In addition, the number of catenated carbon atoms in the bridge connecting the two heterocyclic rings influences the stability of the compounds.



Scheme 1 Fragmentation pathways of compounds 1 (a), 2 (b), and 3 (c)

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Magnesium-porphyrin as an efficient photocatalyst for the transformation of CO₂ to cyclic carbonates and oxazolidinones under ambient conditions

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Carbon dioxide significantly contributes to global warming and tackling climate change through the chemical conversion of CO₂ is challenging. Carbon capture and sequestration are the most effective methods for reducing atmospheric CO₂ levels.¹ Different homogeneous and heterogeneous catalytic systems, including metal complexes (e.g. metal salens and metal porphyrins), metal oxides, organocatalysts, and ionic liquids, have been developed for the cycloaddition of CO₂ and epoxides/aziridines.² Employing a simple and efficient Mg-porphyrin as a photocatalyst for the cycloaddition of CO₂ with epoxides and aziridines to generate cyclic carbonates and oxazolidinones under solvent-free and ambient temperature and pressure conditions presents a promising strategy for producing valuable synthetic products and active pharmaceutical agents. This greener and sustainable approach applies to a wide range of substrates, including terminal and internal epoxides and aziridines.³

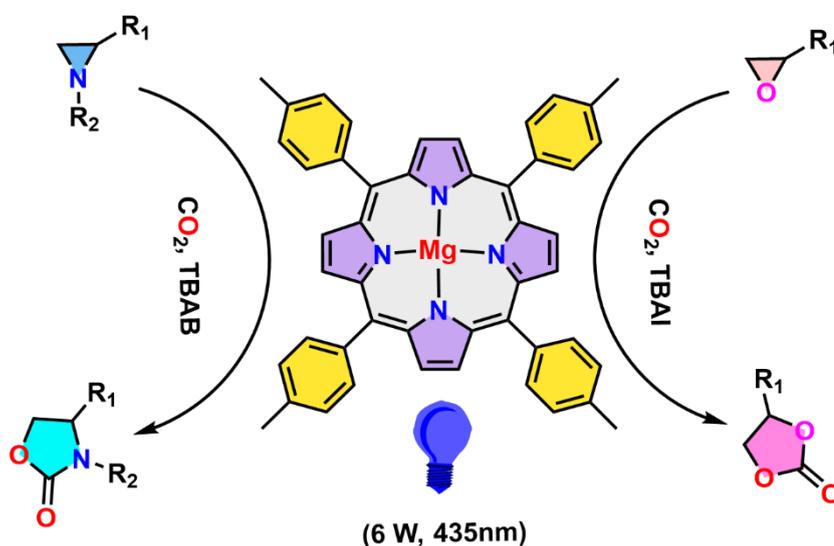


Figure 1 Photocatalysis driven by Magnesium-porphyrin

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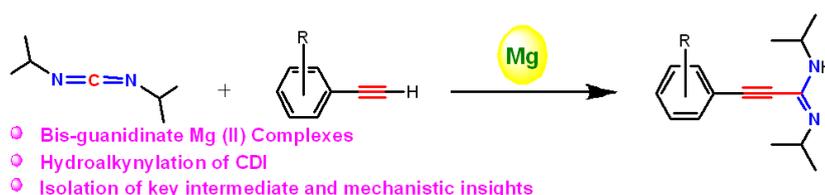


Advancements in Magnesium Catalysis: Bis-Guanidinate Amido Complexes for Selective Organic Transformations, and Mechanistic Insights

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Abstract. A new bis-guanidinate-stabilized amido magnesium (II) complex was synthesized and characterized, demonstrating promising catalytic capabilities in C–C coupling reactions and other organic transformations.^{1,2} This complex served as an effective pre-catalyst for the coupling of terminal alkynes with carbodiimides, yielding propiolamide products in moderate to good yields. Through the course of this reaction, the first example of bis-guanidinate magnesium acetylide, involved as the active catalysts and bis-guanidinate magnesium propiolamidate intermediates were isolated and structurally characterized using advanced spectroscopic and crystallographic methods, which helped propose a plausible catalytic mechanism. Further reactivity studies revealed the complex's ability to form a unique magnesium propiolamidate derivative upon reaction with isocyanates. This work highlights the versatility of bis-guanidinate-supported magnesium compounds in facilitating C–C and C–N bond formation, broadening the scope for their applications in organic synthesis and catalysis.



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Non-Linear Optical Studies on Ferrocene Appended Chiral/Achiral Naphthalimide D- π -A Chromophores: Combined Experimental and Computational Studies

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The second harmonic generation (SHG) specific in chiral compounds is emerging, as they crystallize in non-centrosymmetric crystal systems, satisfying the foremost criteria for SHG. In this report, a new series of ferrocene (Donor) appended chiral and achiral D- π -A push-pull Naphthalimide (Acceptor) chromophores Fc-Ph-R (**1** and **3**) and Fc-CH=C(CN)-Ph-R (**2** and **4**), where R=Naphthalimide, were synthesized and spectroscopically characterized using FT-IR, HR-Mass and ^1H , ^{13}C NMR. Single crystal X-ray diffraction (XRD) analysis revealed that **3** and **4** (chiral) crystallized in non-centrosymmetric space groups. The intramolecular charge transfer process (ICT) between ferrocene and naphthalimide was studied using the solvatochromism technique that revealed positive solvatochromism for all the chromophores^{1,2}. The redox properties were determined by cyclic voltammetry showing one-electron transfer from the ferrocene to ferrocenium ion ($\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$). Kurtz-Perry powder technique for chiral chromophores (**3** and **4**) showed enhanced SHG efficiency, 6-7.5 folds higher than the achiral systems (**1** and **2**) as we expected. Computational studies using density functional theory (DFT) showed that the calculated outcomes were in good agreement with experimental data. Because of their large first hyperpolarizability (β) values and SHG efficiencies, the chiral versions of D- π -A chromophores are of great interest in optoelectronics and the results will be presented.

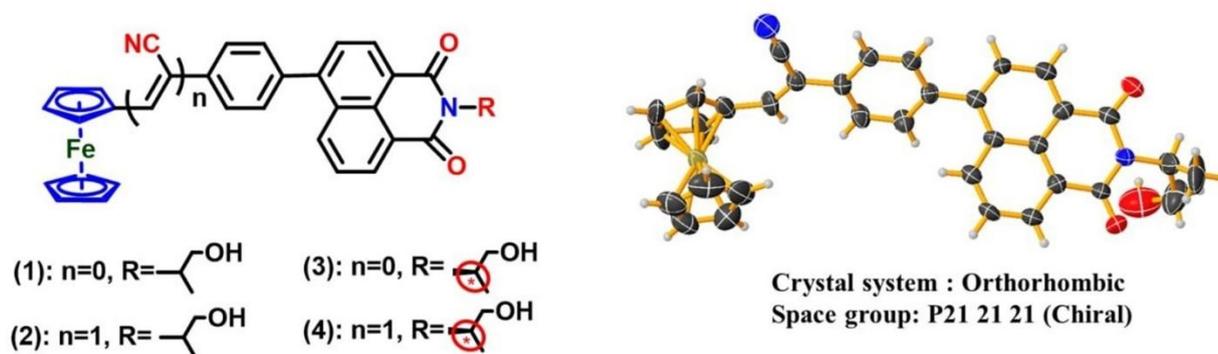


Figure 1: Ferrocene appended achiral/chiral Naphthalimides

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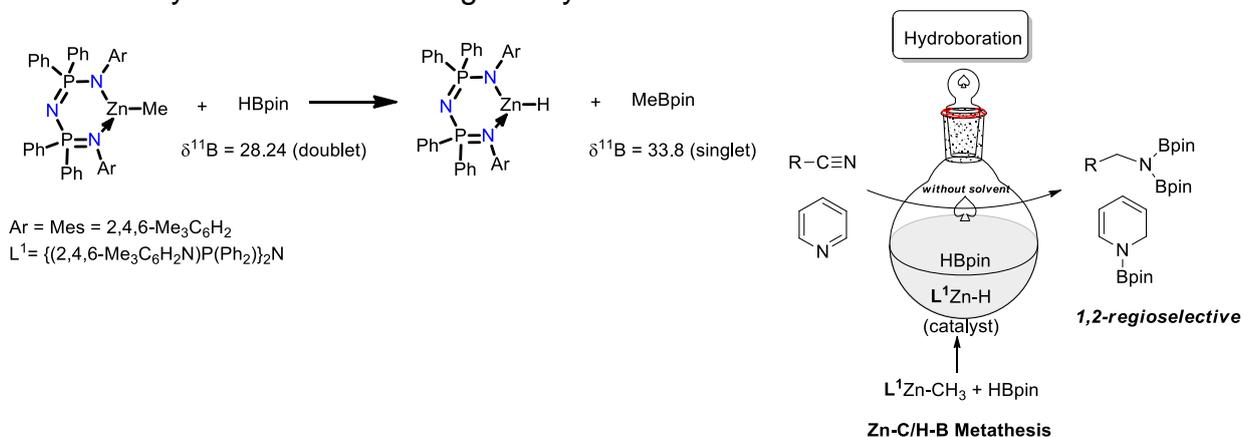
Regioselective Hydroboration of N-Heteroarenes Using Heteroleptic Zinc Bis(phosphinimino)amide Complexes

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Zinc, an environmentally friendly and earth-abundant base metal, has garnered significant attention in catalysis due to its affordability, biocompatibility, and mild nucleophilic properties. In recent years, Zinc complexes have emerged as a versatile catalysts, facilitating key transformations such as hydrosilylation, hydroboration, and hydroamination of unsaturated substrates.¹⁻² In order to design an efficient catalyst, choice of ligand always play an integral role to control the reactivity and selectivity. In this study, we present low-coordinate, neutral zinc complexes supported by bis(phosphinimino)amide ligands, specifically designed to ensure thermodynamic and kinetic stabilization. These complexes effectively catalyze the 1,2-regioselective hydroboration of N-heteroarenes, along with dihydroboration of nitriles and hydroboration of imines, carbonyls, esters, and pyridines. Mechanistic insights were obtained through detailed control experiments, with intermediates characterized by NMR, HRMS, X-ray crystallography, and computational studies. These results highlight the potential of zinc-based complexes as sustainable and efficient catalysts for advanced organic synthesis.



Keywords: Zinc alkyl, Hydroboration, Reaction mechanism.

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Thiazoline Derived $N_{thio}^{\ominus}N^{\ominus}C_{Ph}$ Dianionic Pincer Palladium(II) Complexes: Efficient Catalyst for Quinolines Synthesis

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Quinoline and its derivatives are significant class of heterocyclic compounds that contain nitrogen and have a variety of physiological and pharmacological properties, including antimalarial, antiviral, and anticancer actions.^[1] Though there are several methods were available to synthesize quinoline derivatives, it suffers from the use of unstable aldehydes, strong oxidants or additives, high temperatures, and inert atmosphere conditions. Recently, the development of transition-metal mediated acceptor less dehydrogenative coupling (ADC) process paved the way to achieve quinolines synthesis through mild reaction conditions using commercially available starting materials.^[2]

In this regard, herein we report the synthesis and characterization of new class of dianionic ligand derived from thiazoline moiety and its homoleptic and heteroleptic palladium(II) complexes (Figure 1). Palladium(II) complexes were found to be an excellent catalyst (low catalyst loadings, high TON and tolerance to functional groups) for the synthesis of 2-substituted quinolones (15 examples) via ADC. The detailed synthetic procedure and catalytic activity will be presented.

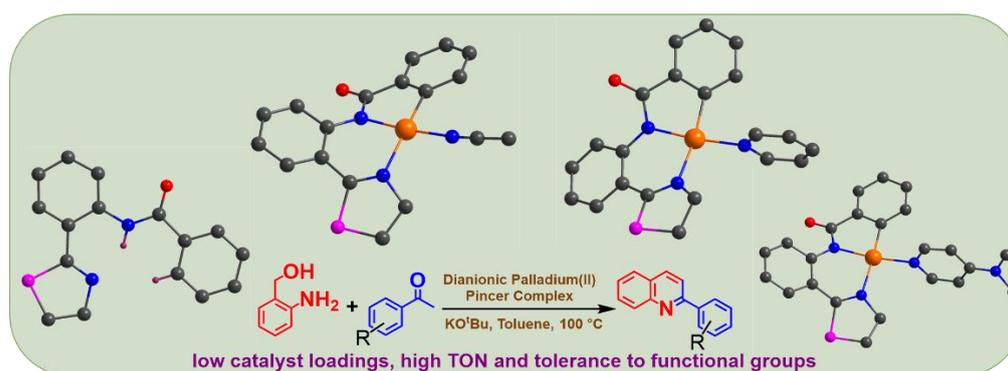


Figure 1: Dianionic Palladium(II) Complexes Mediated Synthesis of Substituted Quinolines

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Synthesis and Characterization: Bis-Guanidinate Ligands in Aluminum Complexes

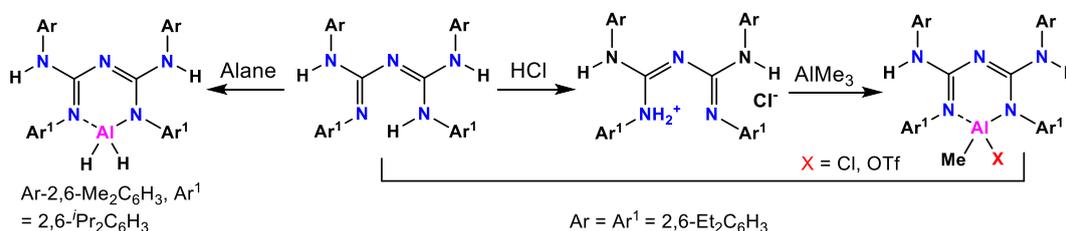
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Bis-guanidinate ligands promote unique advantages in coordination chemistry and catalysis, with significant industrial relevance due to their stability and reactivity. This work presents a novel synthetic protocol for bis-guanidinate stabilized aluminum complexes, synthesizing a series of bis-guanidinate salts and further developing bis-guanidinate aluminum mixed halide-alkyl,¹ and hydride complexes.² These were fully characterized via NMR spectroscopy, mass spectrometry, and X-ray diffraction analysis, confirming their robust coordination modes. The resulting complexes demonstrated efficient catalytic efficiency in key organic transformations, showcasing aluminum's potential in sustainable organometallic chemistry. This study lays the groundwork for expanded applications of bis-guanidinate aluminum complexes in catalysis.



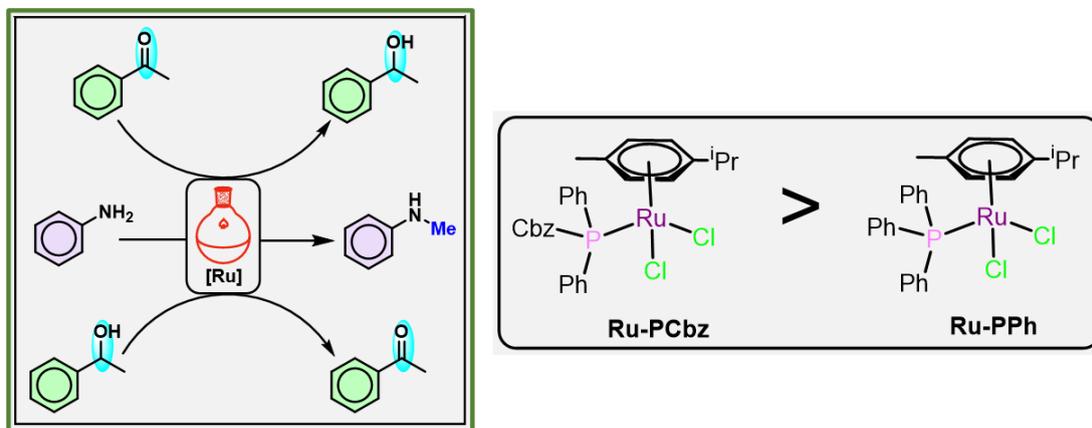
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Air-stable diphenyl-N-carbazoyl phosphine derived ruthenium (II) *p*-cymene complex as a versatile catalyst for hydrogen borrowing reactions

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Borrowing hydrogen methodology has emerged as a versatile and powerful technique to synthesize value added organic compounds in recent times.^[1] The ligands that are widely explored for making organometallic complexes are Schiff bases,^[2] NHCs,^[3] phosphines^[4] and arenes.^[5] It is a challenge to synthesize airstable phosphine ligands for complexes which can catalyze organic reactions at low catalyst loading. Considering the above factors, the Ru(II) complex [(*p*-cymene)RuCl₂(PPh₂Cbz)] (**Ru-PCbz**) (Cbz = N-Carbazoyl) has been synthesized and characterized using various spectroscopic and analytical techniques. The molecular structure of **Ru-PCbz** has been deduced from single crystal X-ray diffraction studies. This air-stable complex is found to be a good catalyst for N-methylation of aniline, transfer hydrogenation of ketone and dehydrogenation of alcohol. To ascertain the role of carbazoyl group in the reactions studied, we have carried out a comparative study of **Ru-PCbz** with a known Ru(II) complex [(*p*-cymene)RuCl₂(PPh₃)] (**Ru-PPh**), where **Ru-PCbz** performs much better than **Ru-PPh** as a catalyst. The plausible mechanistic pathway of these reactions has been deduced by trapping the intermediates using various spectroscopic tools.



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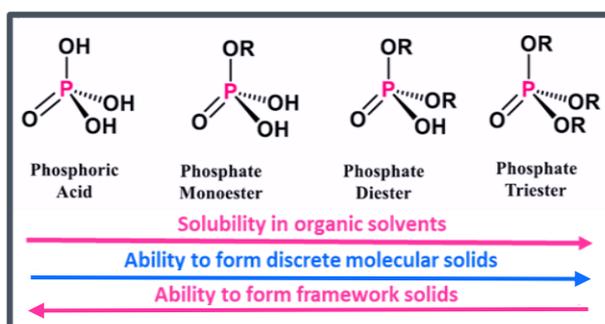
Molecular and ceramic phosphate research for energy applications at RM Group

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The development of renewable, highly efficient, and environmentally friendly energy storage and conversion technologies is crucial for addressing current energy and environmental challenges. Over the past two decades, transition metal phosphates and phosphonates have attracted considerable attention as efficient electrodes due to their low cost, environmental benignity, high stability, unique physicochemical characteristics, and tunable multifunctionality. In our research group, we have extensively investigated the use of organophosphate ligands—such as monoesters (ROPO_3H_2), diesters ($(\text{RO})_2\text{PO}_2\text{H}$), and triesters ($(\text{RO})_3\text{PO}$)—which form discrete molecules or clusters (and occasionally polymeric or layered materials) when reacted with different metal ions.¹ These organophosphate compounds are inherently highly soluble than their inorganic counterparts. By modifying the ligand design or adjusting the reaction conditions, we have been able to control the nuclearity and assembly of the molecular metal-organophosphates. These fine-tuned variations have led to enhanced electrocatalytic performance and provided valuable mechanistic insights into how the structure of the active sites affects both the geometric and electronic configurations of the molecular catalyst.^{2,3} Additionally, these molecular complexes have been employed to prepare metal phosphate materials using a thermolytic Single Source Precursor (SSP) approach. The alkyl groups on the phosphate ligands make these complexes thermally labile and organic-soluble, allowing them to be calcined at temperatures below 250°C to produce phase-pure metal phosphates. This method offered precise control over the M:P ratio and morphology of the derived ceramic materials by adjusting the reactant ratio and reaction conditions.^{4,5,6} The electrocatalytic performance and stability of various molecular and ceramic phosphate materials have been studied to understand the synergistic effects generated by the structure, composition, and morphology of the metal phosphates.



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Ferrocene Conjugated T-Shaped (D- π -A- π -D) and (D-A- π -A- π -A-D) Chromophores: The Effect of Multi Donor-Acceptor in Linear, Nonlinear Optical Studies and Theoretical Calculations

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The ferrocene appended T-shaped indanedione substituted with *n*-butyl amine and additional cyanovinylene substituted chromophores [D- π -A- π -D (**1**), D-A- π -A- π -A-D (**2**)] were synthesized and characterized in nonlinear optical (NLO) point of view. Because, the light manipulation in NLO is applied for many applications like optical communication, laser, etc. The single crystal X-ray diffraction studies confirm the structure of the chromophore **2**, which shows the centrosymmetric space group in P-1 space group^{1,2}. In addition, many dihedral angles and various non-covalent interactions were observed, which suppress the antiparallel alignment and enhance the SHG efficiencies. The intramolecular charge transfer process of the chromophores **1-2** were tested in photophysical studies using various solvents, which shows a red shift with a more significant effect in emission spectra. In emission spectra, dual emission was observed as an evidence of twisted intramolecular charge transfer (TICT) process. Because of the multidonor- π -acceptor system, chromophore **2** exhibits 2.6 times higher SHG efficiencies in NLO measurement compared to the reference potassium dihydrogen phosphate (KDP). The HOMO, LUMO along with dipole moment, polarizability and hyperpolarizability values were calculated from B3LYP//6-31+G** level of theory. Hence, the synthesized T-shaped chromophores with multidonor- π -acceptor system greatly influence in NLO point of view, which may be actively utilized for optoelectronic applications. The results will be presented.

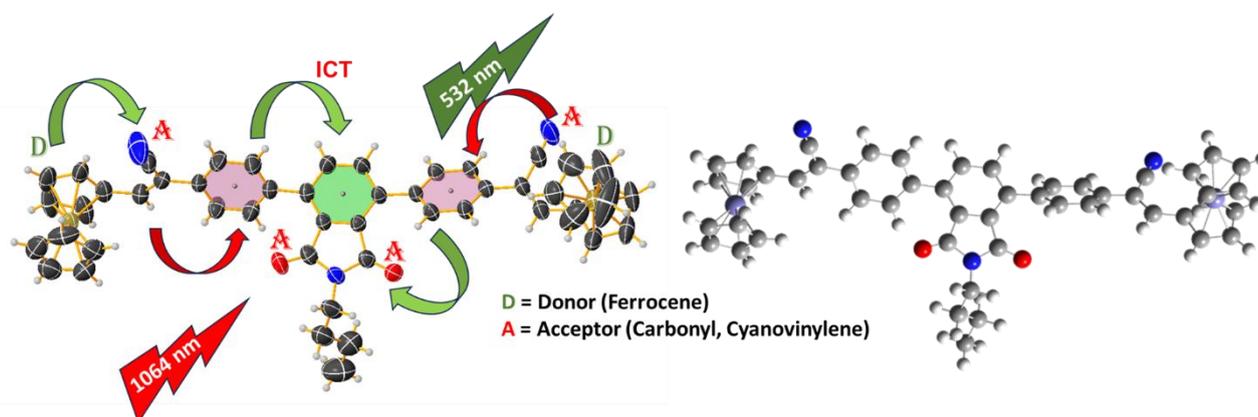


Figure 1 T-Shaped ferrocenyl appended indanedione chromophore

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Pd-Catalyzed Skeletal Rearrangement via C(sp³)-C(sp³) Activation to Access α,β -Unsaturated δ/γ -Lactone

The activation of non-polar aliphatic C-C bonds represents a significant challenge that remains to be addressed in the field of Pd(II) catalysis. In this study, we present a dual ligand approach as a means of addressing this issue. The process entails lactonization of cyclobutane and cyclopropane carboxylic acid via the activation of non-polar C(sp³)-C(sp³) bond despite the high feasibility of both *ortho*-C(sp²)-H and β or γ -C(sp³)-H activation. Density Functional Theory (DFT) calculations were performed to reveal the mechanistic insights and elucidate the role of dual ligands in facilitating this challenging transformation.

Copper Redox Mediators for Photovoltaic Performance in DSSCs: DFT and TDDFT Studies

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Dye-sensitized solar cells present a promising avenue for addressing the escalating need for clean energy solutions. [1-2] These innovative cells offer a sustainable approach to meet the rising demands for environmentally friendly power sources. An assessment was conducted on a copper complex containing a hexadentate ligand, serving as a redox shuttle, alongside triphenylamine-based organic dyes in the construction of DSSC. [3] This study thoroughly investigates the electronic structures and photovoltaic properties of copper redox shuttle along with triphenylamine dyes by performing DFT and TDDFT calculations. [4-5] The copper system, $[\text{Cu}(\text{bpyPY4})]^{2+/+}$, analyzed in this study, is anchored by the hexadentate polypyridyl ligand bpyPY4 (6,6'-bis(1,1-di(pyridine-2-yl)ethyl)-2,2'-bipyridine), studied as a redox shuttle (RS). The assessed redox potential for $[\text{Cu}(\text{bpyPY4})]^{2+/+}$ is -4.67 eV. This indicates that the dye can effectively undergo regeneration by transferring electrons from the redox shuttle's reduced form to the dye's oxidized form. The photovoltaic efficiency has been analyzed about various factors, including the energy gaps between the HOMO and LUMO, the excited-state oxidation potential ($E^{\text{dye*}}$), electron injection ability (ΔG_{inj}), electron regeneration (ΔG_{reg}), light harvesting efficiency, short-circuit current density (J_{sc}) and the open-circuit voltage (V_{oc}). This study sheds light on present-day developments and forthcoming prospects in utilizing 3d transition metal-based redox shuttles, presenting them as compelling candidates for integration with organic dyes in DSSCs.

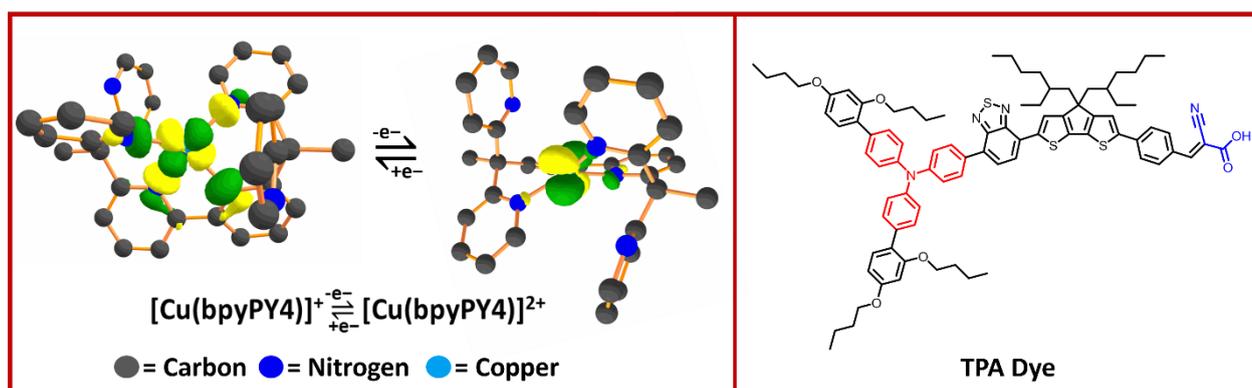


Figure 1 $\text{Cu}^{\text{(II/I)}}$ redox system bearing a hexadentate polypyridyl ligand (6,6'-bis(1,1-di(pyridine-2-yl)ethyl)-2,2'-bipyridine, bpyPY4) as a Redox Shuttle with Triphenylamine donor-based dye.

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Exploring Spin Transport Characteristics of Mixed-Valence $\{V^{IV}-V^{III}\}$ Magnetic Dimer: Probing the Interplay of Magnetic-Exchange and Double-Exchange Effects

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This study delves into the exploration of coherent transport properties of single-molecule junction (SMJ – Figure 1) devices featuring the molecule $[(Me_3tacn)_2V_2(CN)_4(\mu-C_4N_4)]$ (**1**).^{1,2} Employing a combination of DFT, ab initio CASSCF/NEVPT2 and NEGF calculations, we explored the spin state energetics, magnetic properties, and quantum transport characteristics of these complexes, aiming to uncover their potential applications in molecular spintronics devices.³⁻⁶ The complex **1**, upon one-electron reduction (**1**_{red}), exhibited Robin-Day class III mixed-valence magnetic dimer characteristics. The neutral state displayed strong antiferromagnetic coupling, which switched to ferromagnetic upon reduction. DFT calculations revealed an antiferromagnetic exchange interaction of -97 cm^{-1} between the V^{IV} centres, consistent with the experimental reported value of -112 cm^{-1} . The TD-DFT calculations confirmed strong intervalence charge transfer in reduced state, making $S = 3/2$ the ground state with the double-exchange parameter, $B \gg J$. Quantum transport studies showed greater conductance in the high-spin state ($S_T = 1$) compared to the broken symmetry state ($S_T = 0$) in **1**, attributed to the presence of β -empty states in the conduction band near Fermi energy. The **1**_{red} exhibited an enhanced spin transport characteristics due to complete electron delocalization between the V centres.

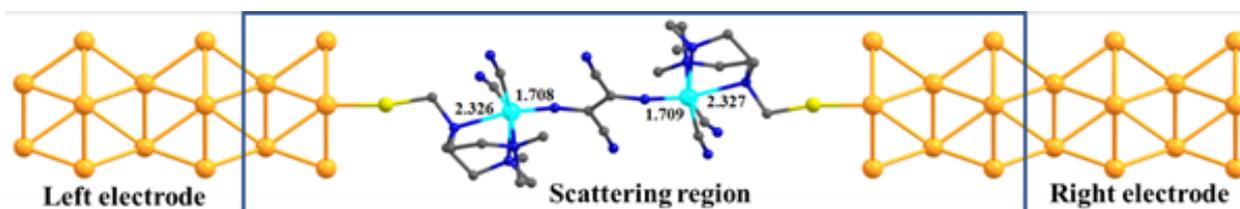


Figure 1. SMJ device to compute the quantum transport properties through the complex **1**_{red}.

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Self- Assembled Ln(III)₄ Phosphinate Square Grids (Ln= Er,Dy and Tb):A class of Lanthanide Clusters exhibiting SMM/ SMT Behavior

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Three tetranuclear Ln(III) clusters were obtained by reaction of bis[α- hydroxyl (p-bromophenyl)methyl] phosphinic acid with subsequent LnCl₃.6H₂O salts using pivalate as co-ligand. Single crystal diffraction studies shows the formation of Ln₄ squares [Me₄N]₂[Ln₄(μ₂-η¹ :η¹-POR)₈(η²-CO₂Bu^t)₄(μ₄-CO₃)] where [Ln= Er(1),Dy(2) & Tb(3)]. Direct current magnetic susceptibility measurements reveals a remarkable ferromagnetic interaction between Dy(III) in (2) and Tb(III) in (3) and antiferromagnetic interaction between Er(III) in 1. Furthermore, dynamic magnetic susceptibility measurements confirm SMM behavior of Dy(III) complex (2) in both 0 and 1200 Oe applied magnetic field, while the Er(III) and Tb(III) complexes shows the SMT behavior with a mixed magnetic moment.

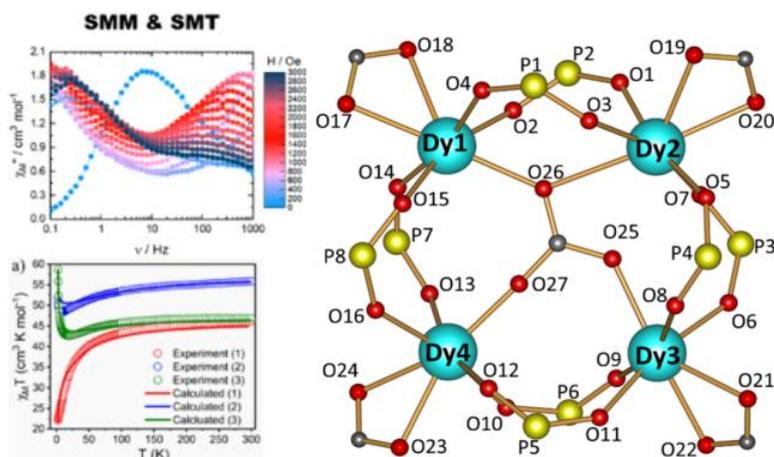


Figure 1: Graphical Abstract

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Synthesis and Characterization of Metal doped Hydroxyapatite using a Hydrothermal method

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Hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (**HA**) is a compound of biological importance as it forms the major component of bones. Hence **HA**-based materials are important for the bone defect restoration due to their stability, good biocompatibility, and bone induction potential.¹ Traditionally, the synthesis of HA involves harsh reaction conditions, such as elevated temperatures, high pressures, and multi-step processes, which can limit the scalability and efficiency of these methods. Our group has previously utilized mild single step solvothermal method for synthesis of **HA** by using thermolabile nature of di-tert butyl phosphate (dtbp)-based calcium complex, $[\text{Ca}(\text{dtbp})_2(\text{H}_2\text{O})_2 \cdot \text{H}_2\text{O}]_n$ (**1**).² To enhance the performance of **HA**, like antimicrobial activity, doping has been introduced to **HA** lattice. In this work we propose the synthesis of calcium apatite doped with four different metal ions by solution thermolysis of **1** in the presence of CaO and different transition metal phosphates³, giving clean phase of **HA** doped with different metals $\text{Ca}_{10-x}\text{M}_x(\text{PO}_4)_6(\text{OH})_2$ ($\text{M}=\text{Co}, \text{Mn}, \text{Zn}$ or Cu). Synthesis provides the utility of thermolabile dtbp metal complexes as a single-source precursor (SSP) for uniform doping into hydroxyapatite structure for their applications in biologically important materials.

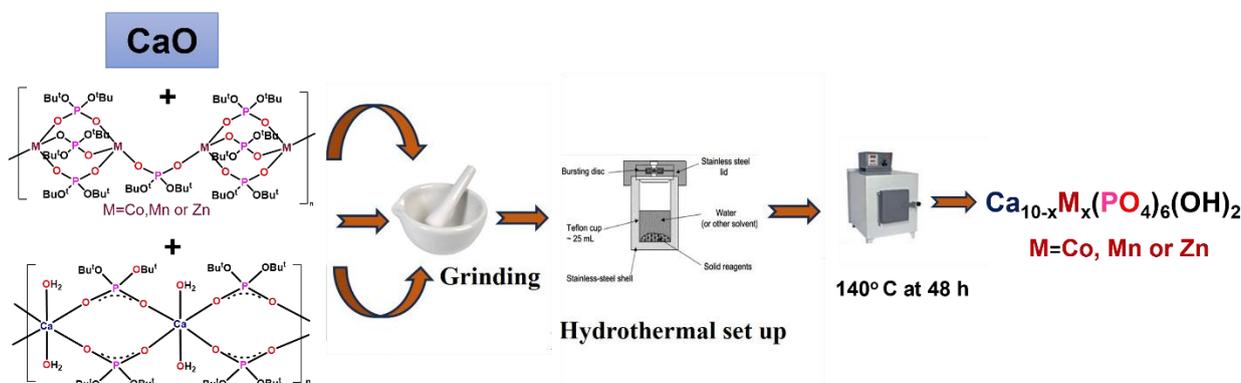


Figure 1. Synthesis of metal doped hydroxyapatite via hydrothermal method

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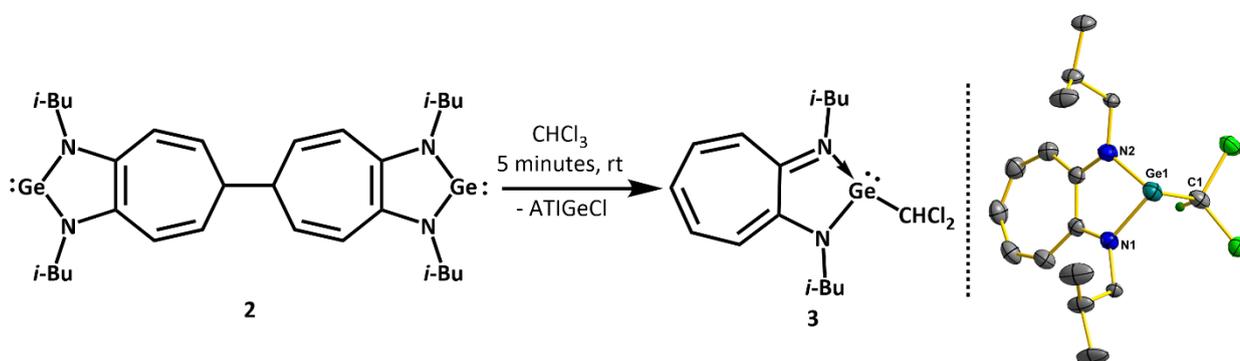
Activation of the E-X Bonds of Molecules by a Bis(germylene) (E = C, Ga, Ge, Sn, Ag and X = Cl, Br, I)

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Germylenes, low-valent germanium compounds, can activate bonds of various small molecules because of their reactive nature. However, the potential of bis(germylenes) in facilitating chemical bond activation remains unexplored¹⁻². This poster addresses this missing by presenting details on the isolation of bis(germylene) **2** and its ability to activate C-X (X = Cl, Br, I) and M-Cl (M = Ga, Ge, Sn, Ag) bonds in small molecules and metal halides (Scheme 1).



Scheme 1. Activation of the C-H bond of chloroform by bis(germylene) **2** and the molecular structure of compound **3**.

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Silver- π Interactions for assembling Hybrid material: A Novel Approach for Enhanced Electrocatalytic Nitrate reduction to Ammonia

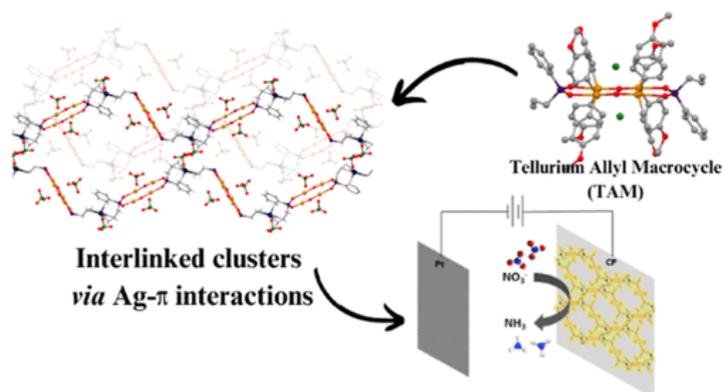
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Ammonia is an indispensable feedstock for fertilizer production and one of the most ideal green hydrogen-rich fuels. This work presents a functionalized Tellurium Allyl Macrocycle (TAM) that acts as molecular building blocks, which are interlinked via Ag- π interaction to establish Ag-TAM. Silver is coordinated to two allyl groups and a phenyl ring in η^2 mode. Ag-TAM showed electrocatalytic activity for the conversion of nitrate to ammonia with a high Faradaic efficiency of 94.6% with good longevity, proving that interlinking of macrocycles via metal- π interaction improves the catalytic activity. Further, DFT studies gave mechanistic insights and possible cooperative catalysis occurring between two Ag centers.



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A Highly Moisture-stable Ferroelectric Ammonium Phosphate Salt showing Piezoelectric Energy Harvesting and Sensor Applications

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Ferroelectric phosphate-based materials are known for their biocompatibility, dipole switching, and high thermal stability. In this context, we report a novel organic ferroelectric material, diisopropylammonium bis(4-nitrophenyl) phosphate (**DIPA-BNPP**), crystallizing in the monoclinic C2 space group. **DIPA-BNPP** exhibits a high second harmonic generation (SHG) efficiency of 2.5 times higher than that of potassium dihydrogen phosphate (KDP). The ferroelectric nature of **DIPA-BNPP** was confirmed by the observation of a rectangular P-E hysteresis loop, which gave a saturated polarization value of 6.82 μCcm^{-2} . The ferroelectric polar domains of **DIPA-BNPP**, along with the bias-dependent amplitude butterfly and phase hysteresis loops, were visualized by piezoresponse force microscopy (PFM). Furthermore, the polydimethyl siloxane (PDMS) composites of **DIPA-BNPP** resulted in a maximum open-circuit output voltage (VOC) of 9.5 V for its best-performing 10 wt% **DIPA-BNPP**-PDMS device. This piezoelectric nanogenerator device exhibits a high electrical energy conversion efficiency of 5.34 %, which is the first observation of this kind for a polymer composite of an organic ferroelectric material. Additionally, the 10 wt% **DIPA-BNPP**-PDMS composite exhibits efficient charge-storage capabilities as demonstrated by charging a 22 μF capacitor followed by the flash lighting of bright LEDs. The high sensitivity and responsivity of the **DIPA-BNPP**-PDMS device during the impact measurements further enabled its application as a rotations per minute (RPM) sensor.

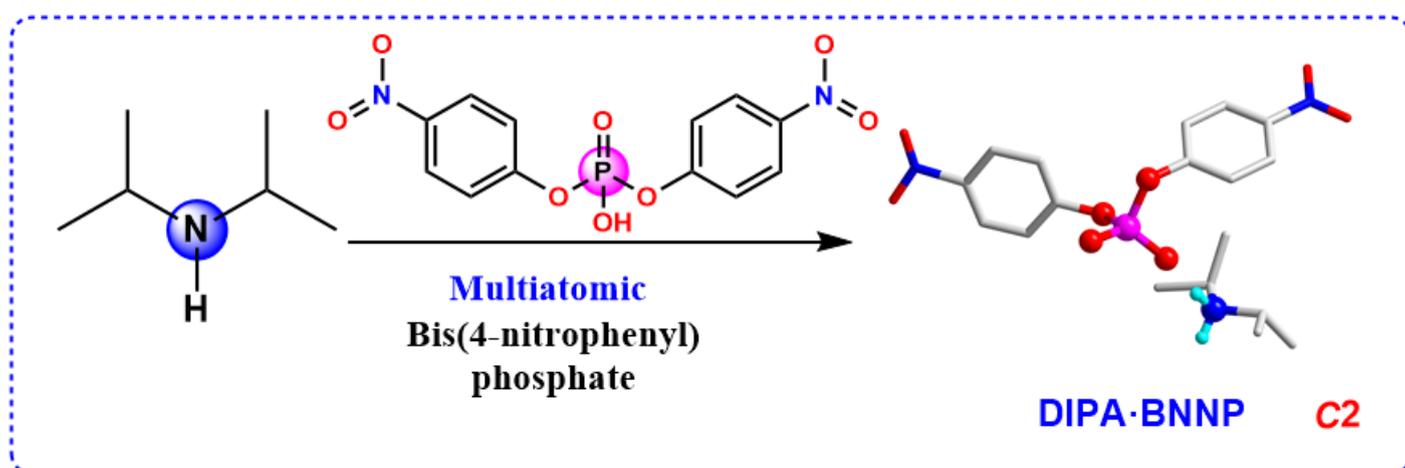


Figure 1: Synthetic scheme for the preparation of the ferroelectric **DIPA-BNPP**.

References:

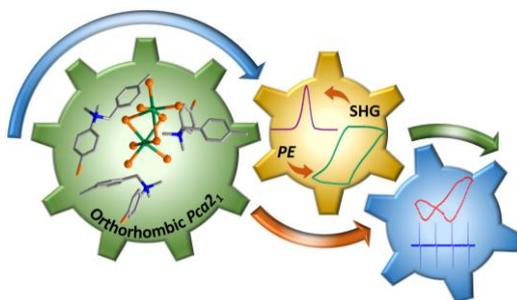
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Ferroelectricity and Piezoelectric Energy Harvesting of an $A_3M_2X_9$ type 0D Bromobismuthate Hybrid with Bulky Organic Quaternary Amine

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Organic-inorganic hybrid ferroelectric compounds of the halobismuthates family have emerged as a focal point of research owing to their reduced toxicity and distinctive optical characteristics. This study presents a novel ammonium hybrid perovskite, [BPMBDMA]·[Bi₂Br₉]¹, which exhibits both ferro- and piezoelectric properties and crystallizes in the polar noncentrosymmetric *Pca*2₁ space group. The nonlinear optical (NLO) activity of [BPMBDMA]·[Bi₂Br₉] was corroborated through second harmonic generation (SHG) measurements evidencing its noncentrosymmetric structure, which was further substantiated by piezoresponse force microscopy analyses. Ferroelectric *P-E* hysteresis loop investigations conducted on a thin film sample of [BPMBDMA]·[Bi₂Br₉] revealed a saturation polarization (*P*_s) as much as 11.30 μC cm⁻² at ambient temperature. To explore the piezoelectric energy harvesting capabilities of [BPMBDMA]·[Bi₂Br₉], composite materials were fabricated using polylactic acid (PLA) as a matrix. Notably, a device comprising 10 wt% [BPMBDMA]·[Bi₂Br₉] in PLA demonstrated a remarkable output voltage of 24.6 V and a peak power density of 13.65 μW cm⁻². The practical applicability of this device's output performance was further evaluated through a capacitor charging experiment, wherein a 10 μF capacitor was charged within 160 seconds.



A novel room-temperature ferroelectric Halobismuthate(III) compound, [BPMBDMA]·[Bi₂Br₉], was synthesized and found to possess excellent ferroelectric and piezoelectric properties. Its polylactic acid (PLA) composites demonstrated strong potential for piezoelectric energy harvesting with high open-circuit voltage and power density, making it ideal for self-powered devices.

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SYNTHESIS, STRUCTURE AND PROPERTIES OF CORE-MODIFIED NORROLES AND EXPANDED *p*-BENZIPORPHYRINOIDS

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We developed a straightforward route to synthesize the 22-oxanorroles **1** and 22-oxabenzonorroles through the oxidation of corresponding new open-chain oxabilanes.^{1,2} On the other hand, the oxidative cyclization of thiabilanes yielded the unique piperazine bridged thianorrole dimer **2** instead of thianorrole monomer.³ The spectral studies indicated that 22-oxanorroles **1** and 22-oxabenzonorroles are aromatic in nature whereas thianorrole dimers **2** are non-aromatic in nature.

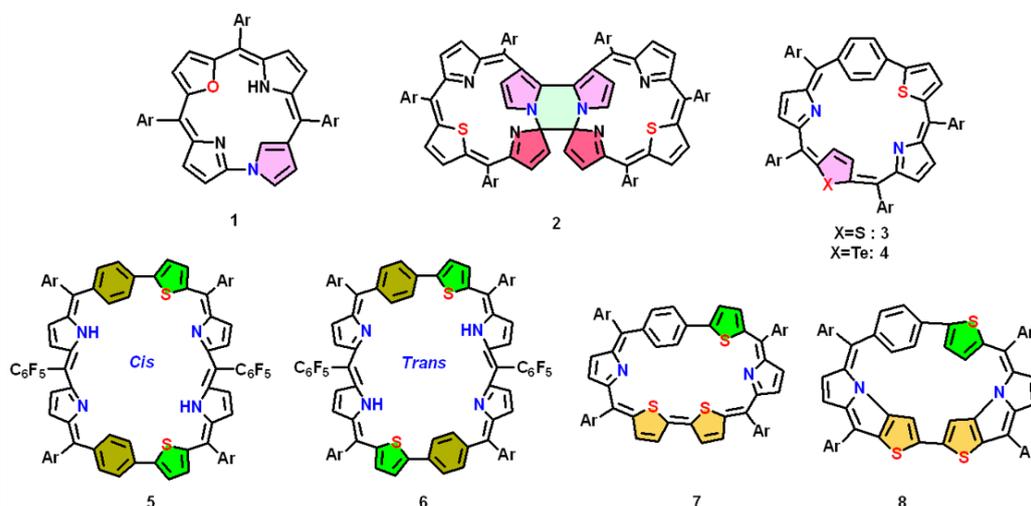


Figure 1 Molecular structure of norroles and expanded *p*-benziporphyrinoids.

We have also synthesized moderately aromatic *p*-benzi dithiasapphyrin **3** and *p*-benzi tellurathiasapphyrins **4** by condensing *p*-benzithiophene diol with 16-thia/ telluratripyrrane under acid-catalyzed reaction conditions.⁴ Further, two structural isomers, namely, the *cis*- and *trans*-isomers **5** & **6** of di-*p*-benzidithiaoctaphyrins, were synthesized *via* the two-step condensation pathway.⁵ The aromatic trithia *p*-benzihexaphyrins **7** and nonaromatic doubly N-fused trithia *p*-benzihexaphyrins **8** were synthesized in one pot condensation reaction.⁶ The synthesis, structure and spectral properties of macrocycles **1-8** will be discussed in this poster.

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Nickel(II)– hydrazineylpyridine catalyzed regioselective synthesis of α -benzyl substituted β -hydroxy ketones via Fenton free radical reaction

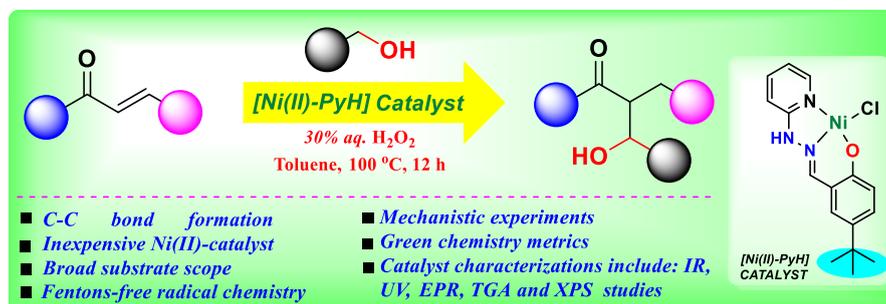
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Abstract: A Ni(II)-hydrazineylpyridine (Ni(II)-PyH) catalyzed intermolecular Fenton free-radical mediated regioselective C-C bond formation is reported to provide α -benzyl substituted β -hydroxy ketones, i.e., α -addition products selectively from α , β -unsaturated ketones and alcohols. The oxidative properties of hydrogen peroxide enable this transformation with catalyst recyclability. The reaction lacks significant side products, demonstrating high selectivity for α -addition products. High functional **group** tolerance with both aliphatic and aromatic substrates. The catalyst structure is characterized using IR, UV, EPR and XPS studies. The thermal stability of the catalyst is up to 290 °C, confirmed via TGA study. The green metrics of the reaction showed 90% of the atomic economy with a turnover frequency of 165.



Our objective is to achieve α -benzyl substituted β -hydroxy ketones without prevailing cyclization or condensation reactions. Here, we report the design and direct synthesis of novel hydrazineylpyridine-based Nickel (II) catalysts. Then, these complexes were utilized for the catalytic activity in organic reactions. Serendipitously, we found that the aldol reaction afforded regioselective synthesis of α -benzyl substituted β -hydroxy ketones using α , β -unsaturated ketones and alcohols in good to excellent product yield.

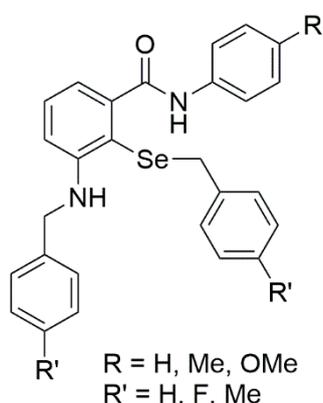
Benzylamine-Substituted Organoselenium Compounds with Antioxidant and Antibacterial Activity

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ABSTRACT: Glutathione peroxidase¹ (GPx) enzymes are selenoproteins and have preventive antioxidant functions *in vivo* i.e. peroxide decomposing antioxidants. A wide range of GPx mimics organoselenium compounds have been investigated for diseases associated with oxidative stress.²



Recently, we synthesized benzylamine-substituted organoselenium compounds with multifunctional antioxidant properties, including radical-trapping and hydroperoxide-decomposing activities. After evaluating their antioxidant properties, the compounds were tested for their *in vitro* biological activities. All benzylamines were maintained cell viability above 60%, making them suitable for further investigation. Notably, they demonstrated significant *in vitro* antibacterial activity against gram-negative *Escherichia coli* and gram-positive *Staphylococcus aureus*. Furthermore, *in silico* studies showed these compounds exhibited promising Moldock scores.

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Fluorescent Probe for Selective Fluoride and Hydroxide Binding

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Anion sensing and recognition have evolved as an emerging research topic in recent decades, particularly in developing sensors for water-soluble toxic reagents. Among the anions, the fluorides and hydroxides have profound significance in various environmental and physiological fields. Sodium fluoride and organofluorides have been known for a long past to control the growth of insects, but they failed to improve the quality of any plants. Inorganic and organofluorides were reported to cause developmental anomalies in the eyes of the chick embryos and also responsible for the neurobehavioral defects in the larvae of *Zaprionus indianus*.^{1,2} In this regard, it is important to know the exact concentration of these anions in real water samples. Many Fluorescent probes have been designed to detect the fluorides and hydroxides, but most of them tend to have high value of limit of detection.³⁻⁵

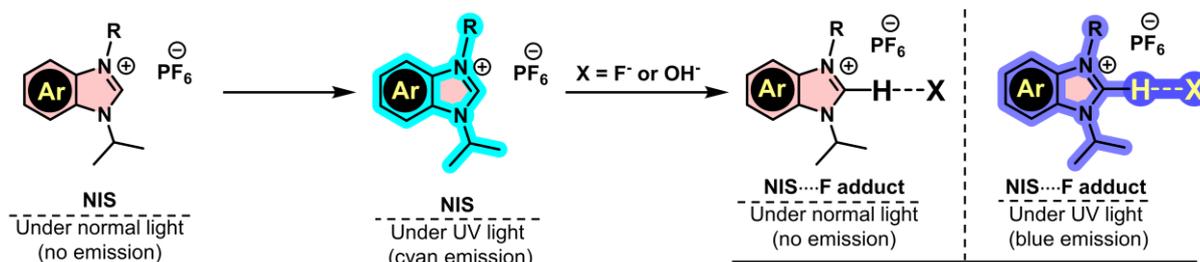


Figure 1: Schematic representation of the light emitting property of NIS on treating with F[−] or OH[−] anion.

In this work, we have designed imidazolium based ionic compound **NIS** and studied its efficacy as a fluorescent probe for F[−] and OH[−] anions, shown in **Figure 1**. Our study reveals that **NIS** have a strong binding affinity for the OH[−] ($K = 2.5 \times 10^4 \text{ M}^{-1}$) compared to F[−] anions ($K = 1.0 \times 10^4 \text{ M}^{-1}$), where K represents binding constant, and have considerably low limit of detection. The emission spectra of **NIS** observed at 471 nm in acetonitrile at 25 °C shifts to lower wavelength (388 nm) when treated with increasing concentration of anions (F[−] or OH[−]).

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B-N Fused Anthracene as Functional Linker for Viologen Type Compounds: NIR Emission and Electrochromism

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B-N Lewis pair fused polyaromatics are among the most contemporary classes of π -conjugated molecules. Owing to their intriguing electronic structure and photophysical properties they have attracted significant interest for applications in optoelectronics, singlet oxygen generation, bioimaging and therapeutics. Over the last several years, our group has developed B-N fused anthracene, pyrene, and fluorene derivatives, and investigated their properties.^[1-4] As a continuation of this project, we have now pursued further functionalization of B-N fused anthracenes with pendant pyridyl group with the aim of (i) examining the effects of electron-withdrawing N-heterocycles and their Lewis acid complexes on the electronic structure and optoelectronic properties and (ii) exploring the compounds as π -extended analogues of redox-responsive viologens.

Detailed investigations revealed that electron withdrawing pyridyl groups attached to B-N Lewis pair-fused anthracenes further lower their LUMO energy level and consequently result in bathochromic shifts in the absorption and emission bands. These effects become even more prominent upon quaternization. Owing to the lower LUMO levels, these compounds also undergo reduction at less negative potentials. Structural similarities with viologen systems inspired us to investigate their electrochromic behaviour. Electrochromism is the ability of a material to change colour or opacity upon applying an electrical stimulus. Among various reported organic and inorganic electrochromic materials, viologen dication systems are particularly interesting as they can undergo two reversible reductions to create radical and neutral species, respectively. We studied in detail the electrochromic properties of the new viologen-like molecules through spectroelectrochemical measurements, and constructed a solution based electrochromic device. Specifics of these investigations will be discussed in this poster.

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MMM-4 Conference IIT Bombay

Early Researcher Lecture (ERL) Schedule (8 minutes oral presentation + 2 minutes Q&A session)

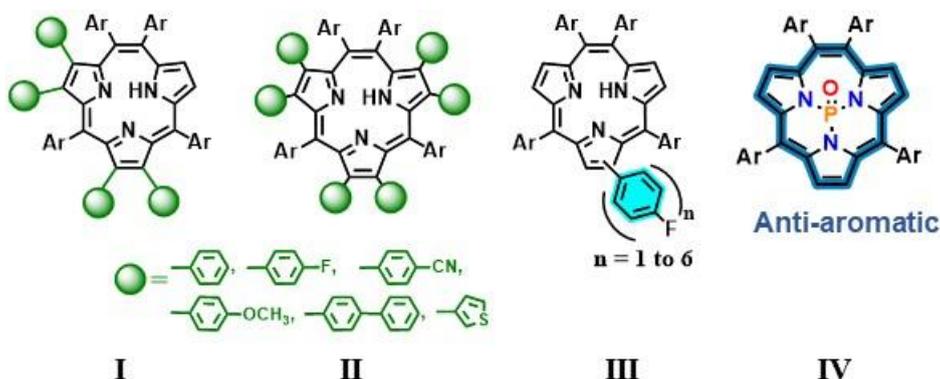
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| Savi Chowdhury | S VISHNU | Amisha Bansal | Rohan Kumar Meher | Manu Goyal | Deepali Sharma | Vijaya TR | Vijaya TR |
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| | Calvin Samuel P | | | | Chandan Das | | |
| | ERPA MANOJKUMAR | | | | | | |
| | Vasu Malhotra | | | | | | |

Effect of β -substitution on Structure, Spectral and Redox properties of Triphyrins(2.1.1)

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Triphyrins(2.1.1) are contracted congeners of porphyrins containing three pyrrole rings connected via four *meso* carbons in 14 p electron conjugation.¹ We developed conditions for regioselective bromination of triphyrin(2.1.1). Notably, slight adjustments in the reaction conditions resulted in the formation of unsymmetrical tetrabromo triphyrin, which was then used to synthesize sterically crowded octaarylated triphyrins² (I). Further, sterically crowded decaaryl triphyrins³ (II) were synthesized by coupling β -hexabromo triphyrin(2.1.1) with various arylboronic acids. A series of β -arylated triphyrins(2.1.1) with varying number of p -fluorophenyl groups from one to six were synthesized, and explored their structure, spectral and redox properties.⁴ Lastly, a series of antiaromatic $P^V=O$ complexes of triphyrin (IV) and its β -substituted derivatives were synthesized.⁵ The synthesis, spectral, electrochemical and theoretical studies of all these compounds will be discussed in the presentation.



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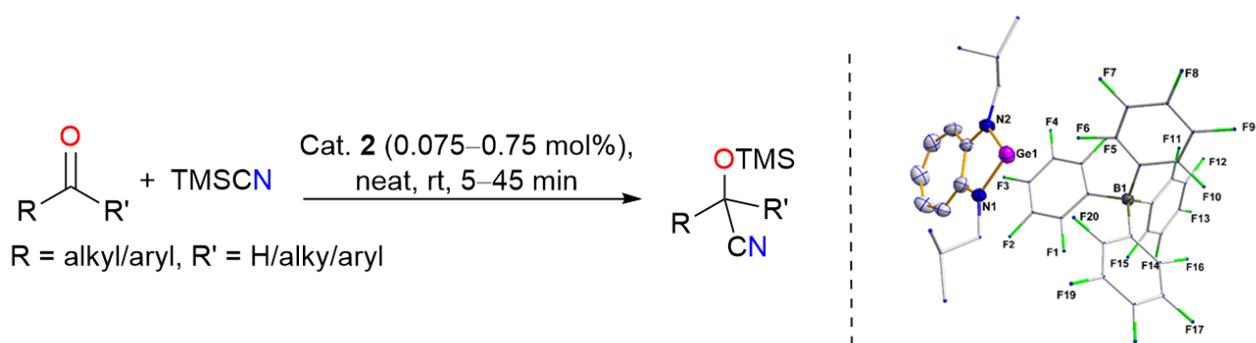
ATI Stabilized Germylene Cation: An Effective Catalyst for the Cyanosilylation of Aldehydes and Ketones

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In the past few years, many low-valent germanium compounds have been used as catalysts for organic transformations, including hydroboration, hydrosilylation, and cyanosilylation.¹⁻³ Concerning cyanosilylation, the highest TOF value of approximately 6000 h⁻¹ has been reached using Ge(II) catalysts and other low-valent main-group catalysts.⁴ We present here ATI ligand stabilized germylene cation, [(*i*-Bu)₂ATIGeB(C₆F₅)₄] (**2**), as a catalyst that offers a TOF of 15840 h⁻¹ for the aliphatic aldehydes, that was found during our attempts to discover a more effective low-valent main-group catalyst for the cyanosilylation of aldehydes and ketones (ATI = aminotroponimate; Scheme 1). It thus becomes the most effective low-valent main-group catalyst for aldehyde and ketone cyanosilylation. According to DFT calculations, compound **2**'s germanium atom has a significant charge localization, which accounts for its high catalytic activity. The germylene cation [(*i*-Bu)₂ATIGeB(C₆F₅)₄] (**2**) was synthesized by reacting [(*i*-Bu)₂ATIGeCl] (**1**) with NaB(C₆F₅)₄. Single-crystal X-ray diffraction studies (Scheme 1) and multinuclear NMR spectroscopy have been used to characterize compound **2**. The poster presentation will include comprehensive information about the synthesis, characterization, and catalysis applications.



Scheme 1: Cyanosilylation of aldehydes and ketones using catalyst **2** (left). Molecular structure of compound **2** (right)

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Effects of High-Temperature Oxidation on the Performance of Bismuth Telluride Thermoelectric Materials

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Thermoelectric materials due to their ability to directly transform heat into electricity, offer an efficient and sustainable approach to energy harvesting and waste heat recovery in various applications. Bismuth telluride (Bi_2Te_3) is a thermoelectric material with excellent thermoelectric efficiency in the temperature range 200-400 K due to its complex electronic structure and low thermal conductivity. Though the thermoelectric property of Bi_2Te_3 is exceptional, its thermal stability deteriorates at temperatures beyond 350 °C. The loss of thermal stability can significantly affect the thermoelectric efficiency of Bi_2Te_3 . In this study, we synthesized Bi_2Te_3 nanoparticles by a solvothermal method and evaluated their thermal stability from room temperature to 700 °C using TG-DTG (thermogravimetric-differential thermogravimetric) analysis. The synthesized Bi_2Te_3 nanoparticles were characterized using Powder X-Ray Diffraction (PXRD) (Figure 1a) and their morphology evaluation using Scanning Electron Microscopy (SEM) (Figure 1d and e) showed that the hexagonal and rhombus-shaped particles were stacked on one another. The TG-DTG analysis showed that above 350 °C, Bi_2Te_3 nanoparticles undergo a two-stage weight gain with peaks at 395 °C and 457 °C (Figure 1b). The PXRD data (Figure 1c) of TGA residue obtained after the initial weight gain at 395 °C correspond to peaks of Bi_2TeO_5 , Te, and Bi_2O_4 revealing that the weight gain results from the oxidation of Bi_2Te_3 nanoparticles. The formation of oxides with the increase in temperature reveals the increased oxidation susceptibility of Bi_2Te_3 nanoparticles at elevated temperatures.

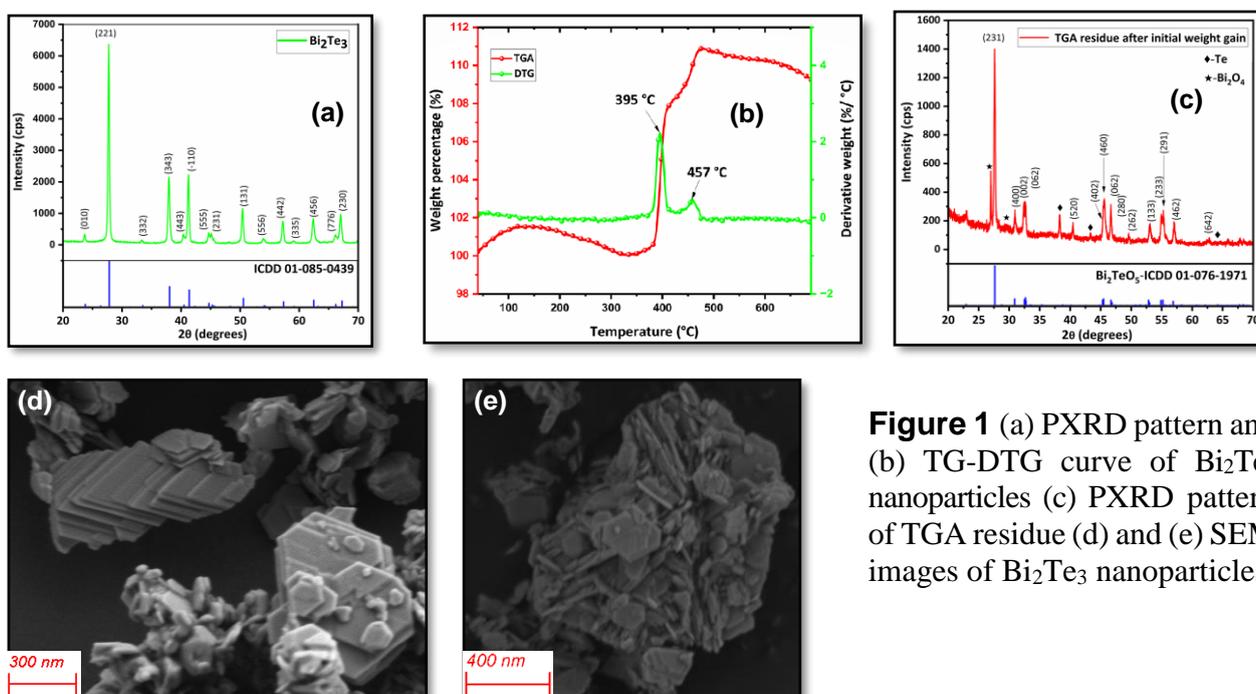


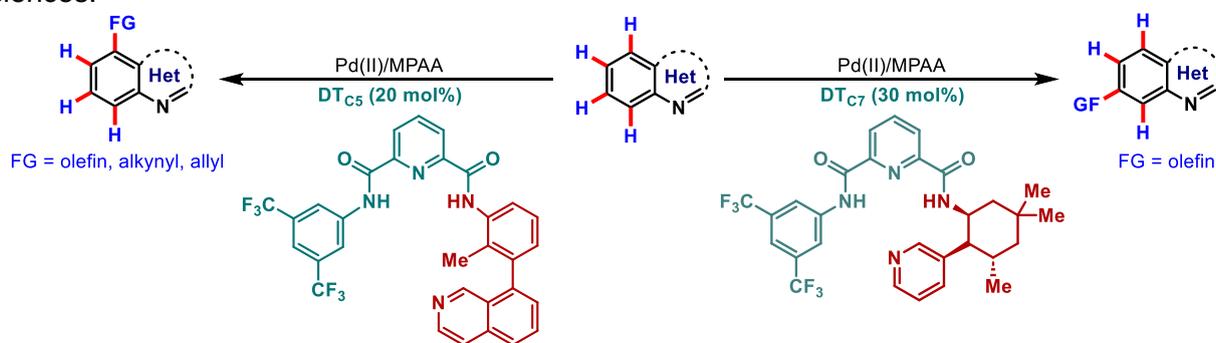
Figure 1 (a) PXRD pattern and (b) TG-DTG curve of Bi_2Te_3 nanoparticles (c) PXRD pattern of TGA residue (d) and (e) SEM images of Bi_2Te_3 nanoparticles.

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Engineering Catalytic Template for Distal C-H Functionalization of Fused Heterocycles

As privileged pharmacophores for diverse biological targets, fused heterocycles are particularly dominant within the realm of drug discovery¹. In contrast to electronically biased heterocyclic C - H bonds², remote benzocyclic C - H bonds on bicyclic azaarenes are especially difficult to differentiate due to the lack of intrinsic steric and electronic biases³. This presentation focuses on the development of innovative template designs that enable the modular differentiation and functionalization of adjacent remote (C5 vs C7) and positionally similar (C3 vs C7) positions on bicyclic azaarenes through careful modulation of distance and geometry. By strategically engineering isoquinoline-based directing templates, we demonstrate improved control over C5 site-selectivity in olefination reactions, overcoming traditional challenges associated with electronic and steric biases in both azaarenes and olefinic coupling partners. The efficacy of this template was further demonstrated by achieving alkynylation and allylation with acyclic trisubstituted alkenes for the first time at the distal C5 position. Notably, the ring dynamics of the 3,3,5-trimethyl-substituted cyclohexane ring within the directing template framework are instrumental in facilitating activation at the distal C7 position. This work not only provides valuable insights into the mechanistic aspects of template-assisted C - H activation but also offers practical solutions for the streamlined synthesis of complex azaarene derivatives, with potential applications in pharmaceutical and material sciences.



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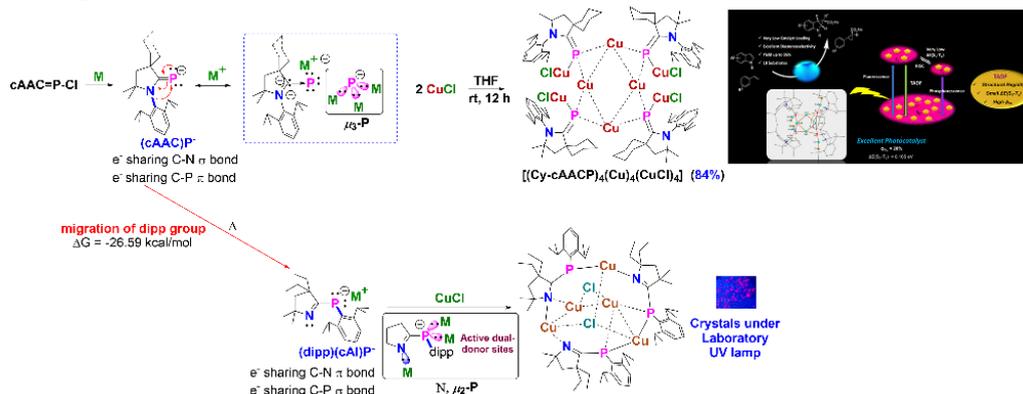
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Carbene-Chloro-Phosphinidenes: A Precursor for Generating Alkali Metal Phosphinidenides and (Aryl)-Cyclic Alkyl(Imino) Phosphides as Stabilizing Ligands Toward Isolation of Novel Luminescent Cu^I Clusters

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Carbene chloro-phosphinidenes serve as precursors for synthesizing alkali metal-phosphinidenides, which can act as sources of mono-anionic phosphorus, functioning as stabilizing ligands in the formation of various metal clusters. In this context, the P- atom possesses three lone pairs of electrons, enabling μ_3 -P type coordination with metal centers. This arrangement permits the creation of diverse coinage metal clusters with varying nuclearities. The mono-anionic phosphorus, $cAAC=P^{-1}$, has been utilized as a stabilizing ligand to produce a novel Cu(I)₈ cluster, which exhibits TADF properties and a PLQY of 20% at room temperature. The redox-active Cu(I)₈ nanocluster has also been employed as a photocatalyst for the stereoselective cyclopropanation of N-protected indoles and unactivated styrenes through carbene transfer reactions derived from the corresponding diazoesters. Additionally, we have developed an efficient method for the alkali metal-mediated reductive dehalogenation of carbene-chloro-phosphinidene, followed by thermal rearrangement that results in the thermodynamically favored migration of the Dipp-group from the N to the P-center. This process yields alkali metal complexes of (aryl)-cyclic alkyl(imino) phosphides [(Ar)(cAl)P⁻]. In this context, we report the synthesis of a pentanuclear copper cluster stabilized by (aryl)-cyclic alkyl(imino) phosphide ligands, demonstrating luminescence properties with a PLQY of 11% at room temperature.



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Visible light mediated cycloaddition reactions: Heterogeneous Catalysis

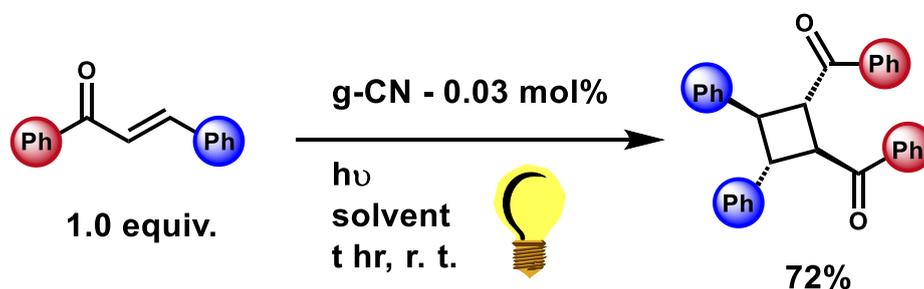
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We explored the efficacy of $g\text{-C}_3\text{N}_4$ ^{1,2,3} in the photocatalytic [2+2] cycloaddition of chalcone derivatives with styrene derivatives. The reactions proceeded under visible light irradiation⁴, yielding cyclobutane derivatives with good to moderate yields. Notably, the $g\text{-C}_3\text{N}_4$ catalyst demonstrated remarkable recyclability, maintaining its catalytic activity over five consecutive cycles without any significant loss in performance. These findings highlight the potential of $g\text{-C}_3\text{N}_4$ as a sustainable and efficient photocatalyst for organic transformations, offering a promising avenue for the development of green synthetic methodologies.

Figure 1: Cycloaddition of chalcones



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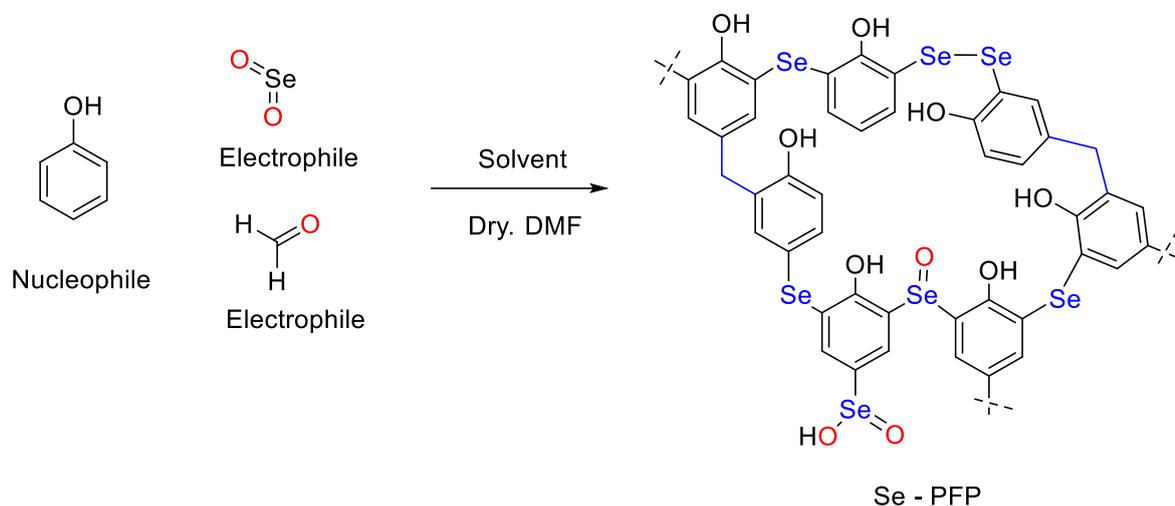
Hierarchically structured selenium-containing phenol-formaldehyde polymers for Hg²⁺ adsorption

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Mercury contamination poses a serious environmental and health risk, necessitating the development of effective adsorbent materials that bind Hg²⁺ ions. This study focuses on synthesizing selenium-containing phenol-formaldehyde polymers (Se-PFP) as potential adsorbents for mercury removal. Four different polymers were synthesized by varying the selenium dioxide concentration (10 mmol to 20 mmol), while keeping the phenol and formaldehyde concentrations fixed at 10 mmol, in DMF at 130°C. This resulted in highly porous materials with a specific surface area of up to 114.535 m²/g. The adsorption of Hg²⁺ ions was found to be rapid, occurring even at low pH (3.0). Characterization of the polymers was conducted using various techniques, including thermogravimetric analysis, differential scanning calorimetry, X-ray diffraction, FTIR spectroscopy, and FE-SEM, which confirmed the material's structural integrity and surface morphology. These results suggest that selenium-containing phenol-formaldehyde polymers hold promise as effective adsorbents for mercury removal.



Keywords:

Organoselenium compounds, Selenium dioxide, Phenol formaldehyde resins, Mercury, Adsorption.

Evaluation of Catalytic Activity of a Cerium(III) Phosphinate and a Cerium(IV) Phosphostibonate for Mild, Selective Sulfoxidation

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Phosphorus-based ligands have been an area of topical research, aiding in the assembly of interesting molecular architectures.¹ Here, a Ce(III) phosphinate $[\text{Ce}^{\text{III}}_3(\text{Ph}_3\text{CHPO}_2)_6\text{Cl}_3(\text{CH}_3\text{OH})(\text{H}_2\text{O})_8]$ (**1**), having a rare triangular architecture has been isolated by the reaction of a phosphinic acid with Ce(III) salt. Subsequently, the reaction of Ce(III) salt with a phosphostibonate yielded a heterometallic, hexanuclear cerium oxo-cluster $[\text{Ce}^{\text{IV}}_6(p\text{-ClC}_6\text{H}_4\text{Sb}^{\text{V}})_4(\mu_4\text{-O})_4(\mu_3\text{-O})_4(t\text{-BuPO}_3)_8(\mu_2\text{-OCH}_3)_8]$ (**2**).² The molecular architecture of **2** showcased an interesting correlation with platonic solids, wherein the Ce(IV), Sb(V), and P(V) ions were found to be present in vertices of an octahedron, a tetrahedron, and a cube, respectively. Under mild conditions, **1** and **2** exhibited the capability to act as catalysts for sulfoxidation with high conversion for various substrates. They were also found to catalyze the oxidation of toxic 2-chloroethyl ethyl sulfide (CEES) to nontoxic 2-chloroethyl ethyl sulfoxide (CEESO) with high selectivity.



Figure 1 Graphical abstract

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A ligand-modulated Mn-based complexes for preferential electro and photochemical reduction of CO₂ to valuable products

Chandan Das, Prof. G. K. Lahiri*, and Prof. Arnab Dutta*

A redox-active ligand was specifically designed to maintain the correct electronic balance in an Mn(I)–carbonyl complex¹, ensuring its photostability and water solubility. This design enabled the Mn–carbonyl complex to efficiently reduce CO₂, with a high Faradaic efficiency of approximately 88%. The reaction preferentially produced carbon monoxide (CO) as the sole C1 product. Importantly, the complex was effective in pure water and could even reduce CO₂ from flue gas sources². This development opens up the potential for more efficient and sustainable CO₂ conversion technologies. Moreover, first-row transition metal-based photocatalysts are promising for efficient CO₂ reduction, but designing such catalysts is challenging due to issues with oxidation state stability. This study presents a Mn(II)-based molecular catalyst, Mn(apap)₂Br₂, for visible light-driven CO₂ reduction. The catalyst features a bulky apap ligand, which distorts the Mn(II) site and forms hydrogen bonding networks, enhancing its catalytic performance. X-ray diffraction provides detailed structural insights. When combined with an Ir-based photosensitizer and a sacrificial electron donor, the catalyst achieves optimized CO production (TON ~ 636) in water-DMA media, outperforming H₂ production by ~20:1. Spectroscopic studies reveal reductive electron transfer as the main mechanism. The Mn(apap)₂Br₂ complex remains stable during extended photocatalysis, even as the photosensitizer degrades³. This catalyst design, which toggles between Mn(II) and Mn(I) states, offers a robust and selective photocatalytic solution for CO₂ conversion, with the potential for expanding the development of durable CO₂-activating catalysts.

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Graphene based Framework for Adsorbed Natural Gas Storage

-Deepali Sharma

Methane is a promising future fuel due to its high energy density and cleaner combustion compared to traditional fossil fuels. However, challenges in efficient storage and safe transportation hinder its practical use, necessitating advanced storage materials. Methane is typically stored as Compressed Natural Gas (CNG), Liquefied Natural Gas (LNG), and Adsorbed Natural Gas (ANG). ANG offers a safer, cost-effective alternative by using porous materials to adsorb methane at lower pressures (35–60 bar), relying on advanced adsorbents with high uptake and structural integrity. Metal-Organic Frameworks (MOFs), known for high surface areas and tunable pores, show excellent methane uptake in powder form but lose efficiency when pelletized, with issues like low gravimetric efficiency and structural instability under high-pressure cycles. Graphene based Frameworks (GFs) offer a novel solution, combining graphene's chemical stability and functionalization flexibility with reticular chemistry. Despite their potential, GOFs remain underexplored for ANG applications. This presentation will present the methane storage performance of GF for ANG storage performance.

Synthesis, Characterization, and Catalytic Performance of Aluminum Alkoxide [(AlMe₂(μ-OCHPh₂))₂] in the Ring-Opening Polymerization of ε-Caprolactone

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Abstract: Aluminum alkoxide complexes are widely recognized for their effectiveness in catalytic efficiency in the ring-opening polymerization (ROP) of ε-caprolactone. In this work, the aluminum alkoxide [(AlMe₂(μ-OCHPh₂))₂] was synthesized from the diphenylmethanol and 2M trimethylaluminum in toluene are treated with toluene. The resultant complex was characterized using ¹H NMR and ¹³C NMR spectroscopy to confirm its structure. Its catalytic activity toward the ROP of ε-caprolactone (ε-CL) was investigated, high efficiency in promoting polymerization. The ε-CL conversion percentage was quantitatively determined using ¹H NMR spectroscopy. Because of the metal center's strong Lewis acidity, aluminum alkoxides are more active than other aluminum-based initiators. High polymerization activity and excellent control over the polymerization process are frequently observed in aluminum alkoxide.

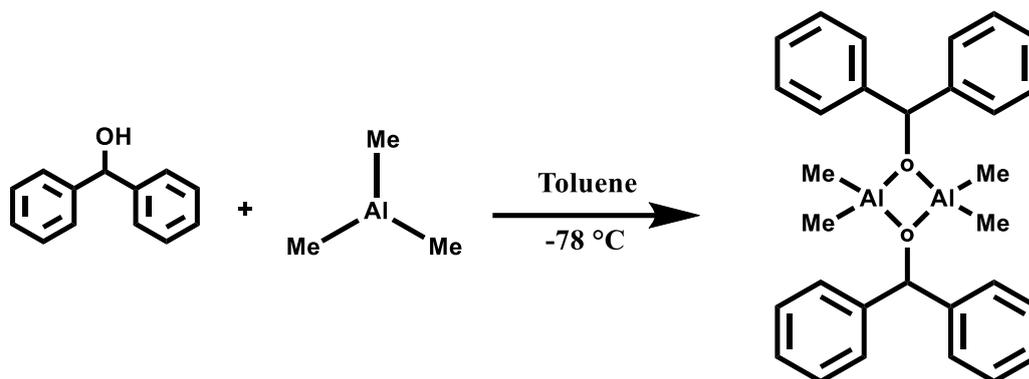


Figure 1: Synthesis of [(AlMe₂(μ-OCHPh₂))₂].

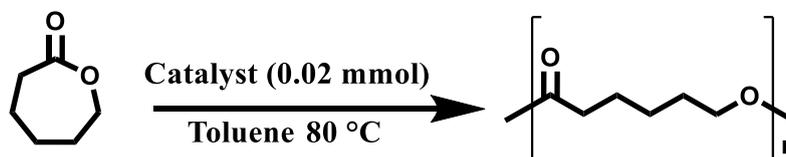


Figure 2: Preparation of Polycaprolactone.

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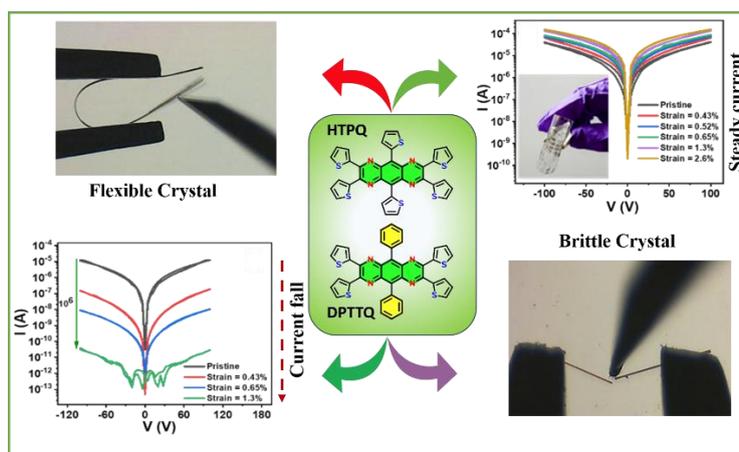
Pyrazinoquinoxaline derivatives for flexible electronic devices: effect of mechanical properties of the crystals on device durability

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Exploring the structure-property relationship in p-type organic semiconductors marks a significant stride in the advancement of molecular electronics. Among these, mechanically flexible single crystals of π -conjugated molecules hold immense potential for advanced organic electronics. Pyrazinoquinoxaline (PQ) derivatives, versatile building blocks for π -conjugated systems, demonstrate good semiconductor performance in OFETs. This study presents the synthesis, characterization, mechanical property analysis, and device application of two novel pyrazinoquinoxaline (PQ) derivatives, DPTTQ and HTPQ. HTPQ exhibits exceptional elastic flexibility. Conversely, two polymorphic forms of DPTTQ crystals display brittle fracture when subjected to a similar stress. Specifically, DPTTQ molecules adopt a β -sheet packing, while HTPQ presents a γ -packing with corrugated arrangement. Field-effect charge transport measurements reveal a p-type charge transport in both derivatives, with HTPQ achieving a hole mobility of 0.01 cm²/Vs, exceeding DPTTQ by an order of magnitude. This variance in the field effect mobility can be directly correlated to the difference of crystal packing bringing out a clear structure-property correlation. Importantly, HTPQ's flexibility enables durable device fabrication, retaining conductivity over 60 strain cycles, underscoring its potential for flexible electronics. These findings highlight the promise of semiconducting organics with γ -packing for achieving both better mobility and elasticity for integration into organic electronic devices.



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Design and Syntheses of Phosphazane-Azo Macrocycles: Insights Into Their Photophysical Behavior

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Since the last decades, phosph(III)azane dimers of the type, $[CIP(\mu-NR)]_2$ have proven to be excellent building blocks for the formation of a variety of inorganic macrocycles. While the *cis-trans* equilibrium is significantly influenced by solvents and their electronic effects, temperature, and often large activation barriers hinder this equilibrium, resulting in the formation of kinetic products.¹ Substitution reactions with diols, diamines, or amino-alcohols lead to the formation of monomeric, simple dimeric, or hexameric macrocycles, depending on the spacers and their kinetic effects.² However, there is a lack of investigation into the host-guest chemistry of these macrocycles. This study focuses on our efforts to incorporate a photoactive linker into the assembly of the P_2N_2 macrocycle, which may facilitate the detection or sensing of guest molecules through luminescence properties. To achieve this, we designed and synthesized a series of acyclic and cyclic compounds containing azo and phosphazane moieties, and examined their photoswitching behavior.

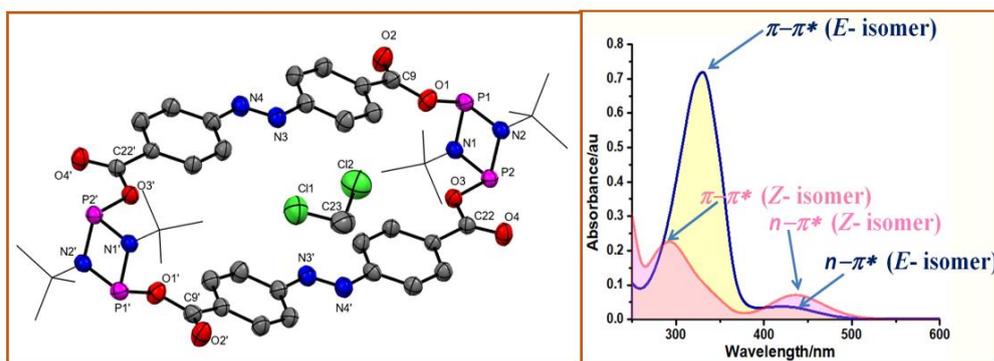


Figure 1. An example of azo-phosphazane macrocycle and its *E-Z* photoisomerization behavior.

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Deciphering the Origin of Double Exchange and Magnetic Exchange in a $[\text{Fe}_3]$ Cluster Using Density Matrix Renormalization Group (DMRG) Approach

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Multinuclear transition metal clusters have significant potential for small molecule activation, electron transfer in biological systems, and magnetic data storage devices. In particular, mixed-valence iron clusters are known to couple spin components through double-exchange, stabilizing high-spin states. This unique property makes them highly suitable for applications as single-molecule magnets.^{1,2} In this study, a combination of advanced multireference methods, including Density Matrix Renormalization Group configuration interaction (DMRG-CI), multiconfiguration pair density functional theory (MC-PDFT), and state-averaged complete active space self-consistent field (SA-CASSCF), was employed to investigate a mixed-valence trimeric iron cluster, $[(18\text{-C-6})\text{K}(\text{thf})_2][(\text{t}^{\text{bs}}\text{L})\text{Fe}_3]^{3-}$. These methods helped identify key properties such as spin ladder, double exchange, and zero-field splitting of the complex. A very strong double exchange interaction with $B = 248 \text{ cm}^{-1}$ was obtained from SA-CASSCF(19,16) calculation which is in excellent agreement with the experimental maximum of $\sim 250 \text{ cm}^{-1}$ from the intra-valence charge transfer (IVCT) band.

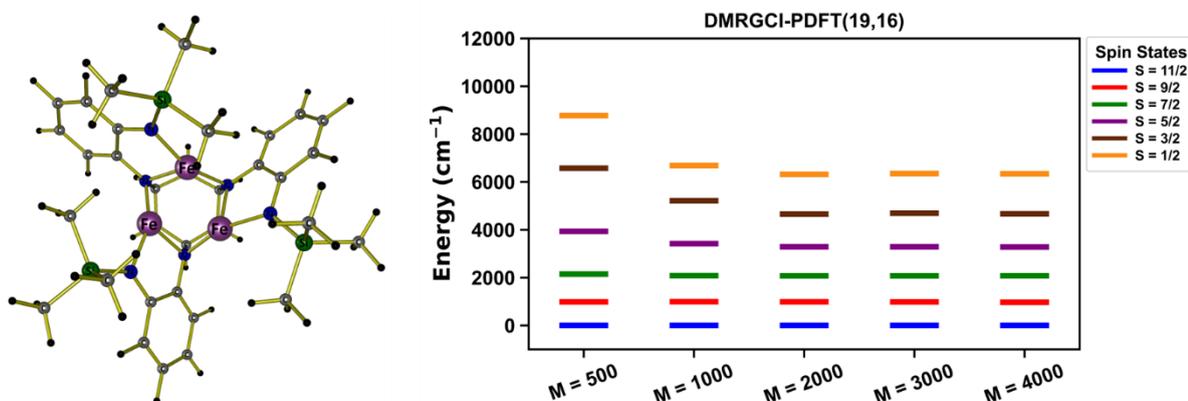


Figure 1 Crystal structure of the $[(\text{t}^{\text{bs}}\text{L})\text{Fe}_3]^{3-}$ (left) and the DMRGCI-PDFT computed spin ladder (right).

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Electrostatic modulation of redox potential

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Optimizing redox potentials is crucial for efficient electrocatalysis. While modifying ligands or metal centres can tune redox potentials, thereby minimising overpotential, this often leads to a trade-off with catalytic rates due to underlying molecular-scale relationships.^{1,2} An effective strategy to overcome this key bottleneck is to incorporate a non-redox active metal ion functioning as an electrostatic modulator which tunes the redox potential without impacting kinetics.^{3,4} However, these kinds of systems are synthetically challenging, and synthetic tractability of s-block metal ions incorporation is also difficult. The present work uses density functional theory and charged sphere model, to quantify the influence of distance-dependent electrostatic effects on the reduction potentials of a bimetallic Cu (II) model system. The system includes a dipicolylamine (DPA) ligated bimetallic Cu(II) complex, wherein the Cu(II) centres are bridged by an aliphatic diamine (NH₂-(CH₂)_n-NH₂) linker of varying chain lengths (n = 0 to 10). The calculated reduction potentials in non-aqueous solvation environments were found to vary linearly with the reciprocal of the Cu-Cu intermetallic distance, suggesting a strong distance-dependent electrostatic interaction between the two metal centres. The predicted shifts in the one-electron redox potential as a function of the chain length in the model system were experimentally validated with synthesis and cyclic voltammetry studies of two bimetallic Cu(II)(DPA) analog bridged by 1,4-diaminobutane and 1,8-diaminooctane respectively in acetonitrile.

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Oxidative Coupling of Isonitriles with 2-Amino-phenols and thiophenols Giving Benzoxazoles and Benzothiazoles Catalyzed by Cobalt (II) Complexes in Air

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Abstract

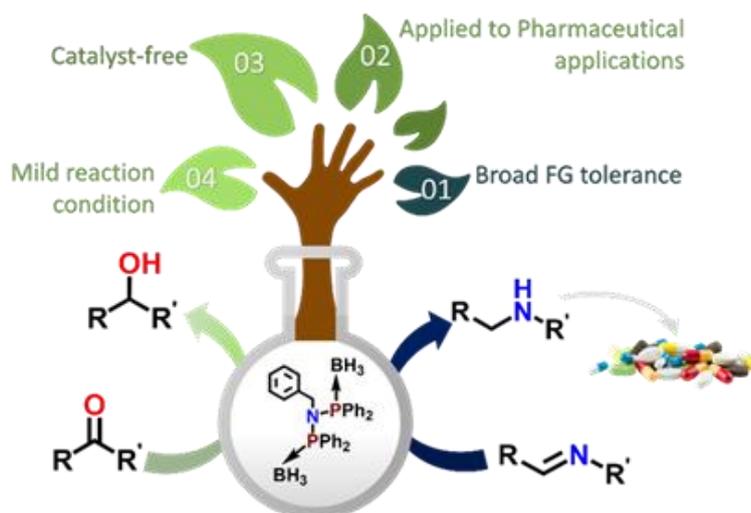
A large variety of benzoxazoles and benzothiazoles (**4** - **33**) were synthesized by aerobic oxidative coupling of isonitriles with 2-aminophenols and 2-aminothiophenols in moderate to excellent yields (ca. 24 – 98 %) using well-defined cobalt (II) complexes supported over mixed N-donor tetradentate tripodal ligand derived from triazole and cyclohexylamine moieties namely, {[N¹,N¹-(CH₂Ph)₂-N²,N²-(1-CH₂Ph-1,2,3-C₂N₃H-4-CH₂)₂-cyclohexane-1,2-diamine]CoX}X, X = Cl (**2**) and Br (**3**), at 1 mol % of the catalyst loading at 50 °C in CH₃CN after 18 h of the reaction time. The complex (**2**) consistently exhibited superior yields (ca. 98 – 32 %) than the complex (**3**) (ca. 81 – 24 %) for the same pair of 2-aminophenol and 2-aminothiophenol substrates in reaction with the same isonitrile variant. Interestingly, the 2-aminophenol substrates showed a broader variation of the product yields (ca. 93 – 24 %) than the 2-aminothiophenol substrates (ca. 98 - 48 %). The isonitrile variation study showed the aliphatic substrates exhibited higher yields for the pair of representative 2-aminophenol [ca. 93 – 36 % (**2**) and ca. 81 – 28 % (**3**)] compared to respective aromatic substrates [ca. 32 % (**2**) and ca. 30 – 24 % (**3**)]. Similar trend was also observed for the 2-aminothiophenol substrates [aliphatic: ca. 98 – 71 % (**2**) and ca. 88 – 43 % (**3**) and aromatic: ca. 81 – 65 % (**2**) and ca 67 – 48 % (**3**)]. Proposed mechanism shows that the reaction proceeds through a formation of cobalt (III) superoxo intermediate followed by a Hydrogen Atom Transfer (HAT) step from 2-aminophenol moiety to cobalt (III) superoxo species.

Hydroboration of Ketones and Imines Using Amidophosphineborane under Catalyst-Free Conditions

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Hydroboration is a vital reaction in organic synthesis, enabling the addition of B-H bonds to unsaturated carbon-carbon and carbon-heteroatom bonds (e.g., C=O,¹ C=N²). Among these, the hydroboration of ketones and imines is particularly attractive for its ability to produce secondary alcohols and amines, making it widely applicable across industries such as natural products, pharmaceuticals, agrochemicals, polymers, and dyes.³ While numerous catalysts, including transition metals⁴ and main-group elements,⁵ have been established for hydroboration, several are unsustainable, delicate to air and moisture, and incompatible with large-scale applications.⁶ This has encouraged interest in catalyst-free hydroboration methods. Even though pinacolborane (HBpin) is a common reagent for catalyst-free hydroboration, its sensitivity, cost, and high quantity requirements limit its use. Recent studies demonstrated amidophosphine boranes as cost-effective, air- and moisture-stable alternatives.⁷ Inspired by this, we study catalyst-free hydroboration of ketones and imines using amidophosphine boranes under mild conditions.



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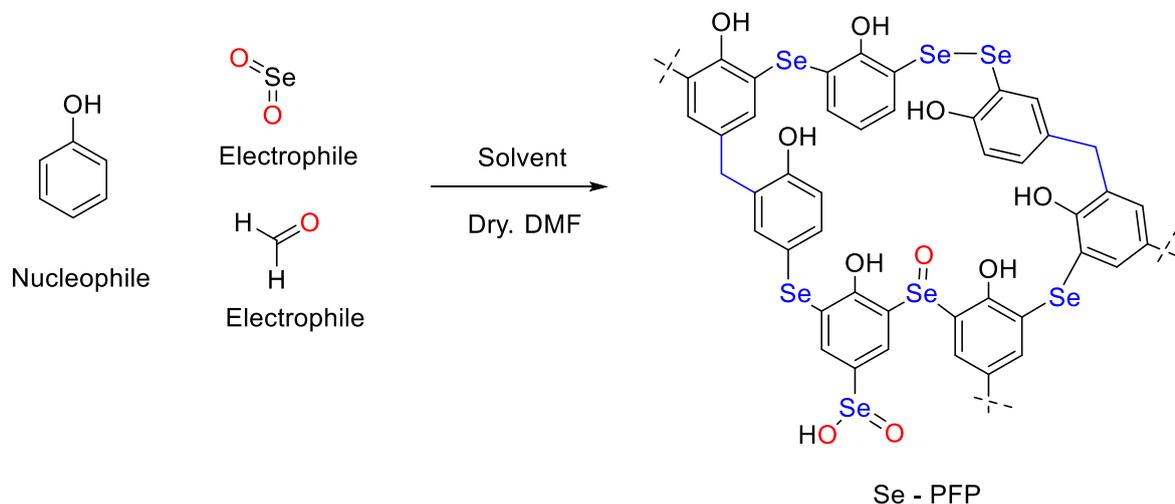
Hierarchically structured selenium-containing phenol-formaldehyde polymers for Hg²⁺ adsorption

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Mercury contamination poses a serious environmental and health risk, necessitating the development of effective adsorbent materials that bind Hg²⁺ ions. This study focuses on synthesizing selenium-containing phenol-formaldehyde polymers (Se-PFP) as potential adsorbents for mercury removal. Four different polymers were synthesized by varying the selenium dioxide concentration (10 mmol to 20 mmol), while keeping the phenol and formaldehyde concentrations fixed at 10 mmol, in DMF at 130°C. This resulted in highly porous materials with a specific surface area of up to 114.535 m²/g. The adsorption of Hg²⁺ ions was found to be rapid, occurring even at low pH (3.0). Characterization of the polymers was conducted using various techniques, including thermogravimetric analysis, differential scanning calorimetry, X-ray diffraction, FTIR spectroscopy, and FE-SEM, which confirmed the material's structural integrity and surface morphology. These results suggest that selenium-containing phenol-formaldehyde polymers hold promise as effective adsorbents for mercury removal.



Keywords:

Organoselenium compounds, Selenium dioxide, Phenol formaldehyde resins, Mercury, Adsorption.

Zinc and Gallium Hydrides: Catalytic Breakthroughs and Mechanistic Revelations

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We present the development of a bis-guanidinate zinc hydride complex as a highly efficient catalyst for the hydrosilylation and hydroboration of cyanamides under mild conditions. This work marks the first reported example of cyanamide functionalization catalyzed by a molecular zinc complex. The active catalyst/key intermediate a zinc amidinate complex, was isolated and structurally characterized.¹ Additionally, we report the synthesis of a bis-guanidinate-supported mononuclear gallium(III) dihydride complex, which catalyzes the hydroboration of diverse organic substrates under solvent-free conditions, producing borylated products in high yields. An intermediate gallium formamidinate mono-hydride was identified and characterized by NMR, HRMS, and X-ray diffraction.² These findings underscore the significant catalytic potential of bis-guanidinate zinc and gallium complexes in organic transformations.

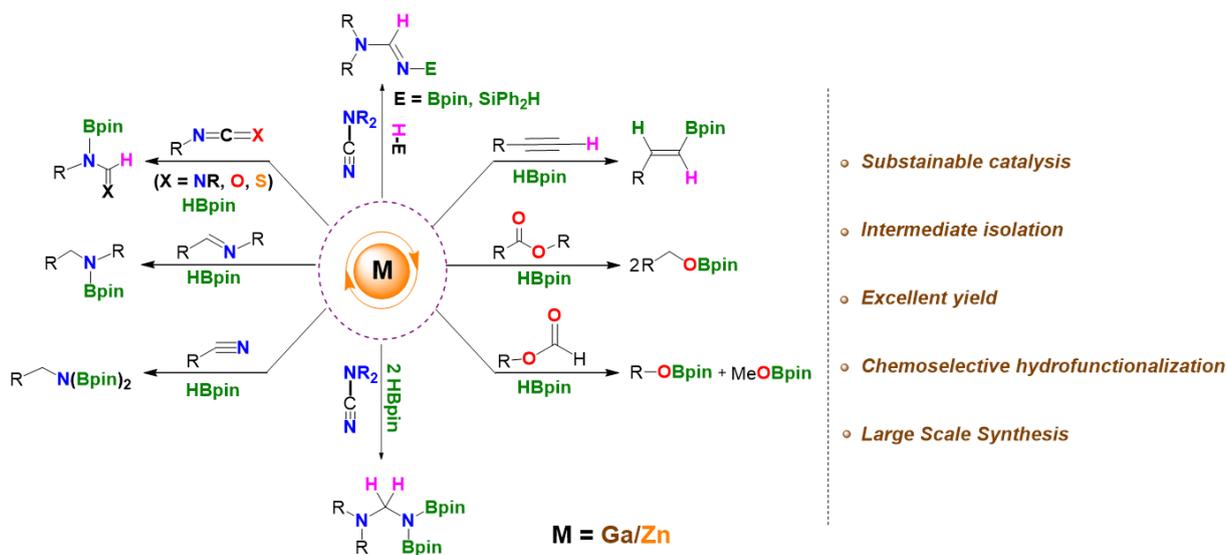


Figure 1 Zinc and Gallium Catalyzed Organic Transformations.

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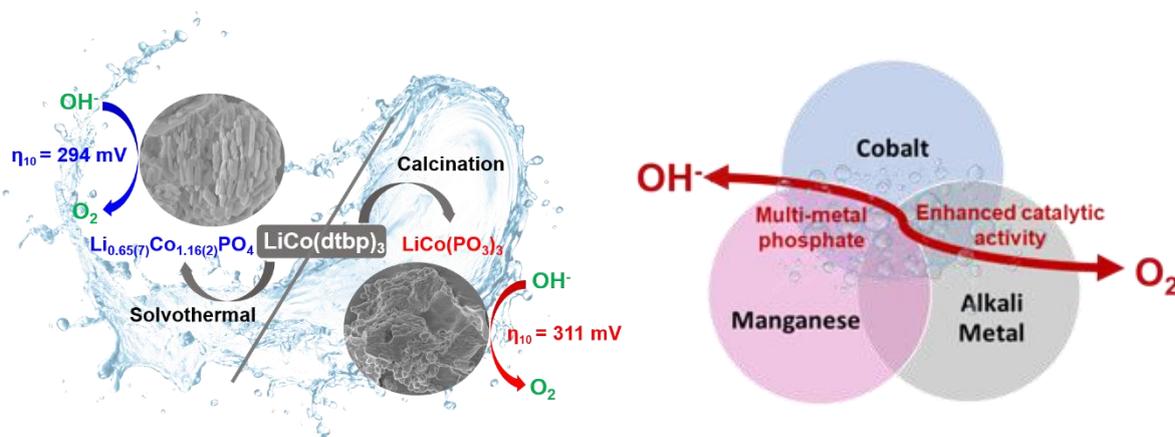
Thermally Labile Organic-Soluble Heterometal Diorganophosphate-Derived Efficient Electrodes for Oxygen Electrocatalysis

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Transition metal phosphate materials have gained immense interest in catalysis, energy conversion and storage devices. The facile functionalization of PO_4 and/or P-OH groups along with their low-cost, high stability, unique physicochemical characteristics and tuneable multifunctionality make them ideal candidates for outperforming the state-of-art technologies. However, rational design strategies to achieve heterometal phosphate with controllable structure and morphology still profess a challenge. The existing synthetic methodologies such as solid-state synthesis, solvothermal, sol-gel method and template synthesis require complex, high temperature or hazardous synthesis with very limited control over the M/P ratio and assembly apart from the issue of phase separation at higher loadings. Therefore, we have extended the simple, non-evasive thermolytic Single Source Precursor (SSP) approach for synthesising heterometal phosphate materials by hybridizing suitably designed metal di-organophosphate complexes as synthons to isolate alkali-Co/Mn/Zn-phosphate materials of different compositions, including those with lithium-ion deficiency by decomposition at low temperatures. The alkyl groups on the phosphate ligands render these complexes both thermally labile and organic-soluble allowing their calcination at very low temperatures (e.g., below 250 °C) to yield phase-pure metal phosphates.¹ By this methodology, heterometal phosphates with attendant $\text{M}':\text{M}'':\text{P}$ ratios (e.g., Li/Na-MPO₄, Li/Na-M_x(PO₃)₃ and Li/Na-M_xM'_{7-x}(HPO₄)_a(PO₄)_b (M, M' = divalent transition metal) and morphology have been isolated by controlling the decomposition temperature, nature of solvent and the ratio of the starting materials. Detailed electrocatalytic performance and stability towards OER/ORR have been studied to elucidate the synergistic effect generated by the structure, composition, and morphology of heterometal phosphate.^{2, 3}



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Intramolecular Phosphine stabilized Ge(IV) mono-cations as Ambiphilic ligand towards Au(I)

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Main group-transition metal co-operativity has been a promising sector of fundamental research during the past decade. Placing electron deficient moiety adjacent to a transition metal has been known to remarkably influence its electronics.¹ The σ -accepting nature or Z-type character of the main group-based ligands grabbed attention as the M \rightarrow Z interaction controls the reactivity at the metal center. Contemporary research is very much invested in designing cationic ligand frameworks,² apart from the traditional neutral and anionic ligands. Due to the presence of positive charge, it is expected to serve as a better acceptor ligand. Very recently, we reported rare penta-coordinated Ge(IV) mono-cations, stabilized intramolecularly by phosphine donor ligand.³ Additionally, phosphine group has the inherent authority to tune the electronics of the system as it can feature both donor and acceptor functionalities by varying the associated R group. In this work, we explore the possibility of the two Ge(IV) mono-cations, one featuring the *i*Pr moiety and the other Ph group, serving as ligand towards transition metal (say, Au). The corresponding gold complexes were synthesized and characterized by single crystal XRD and multi-nuclear NMR techniques. The impact of the R group on the bonding scenario between Ge and Au center and the reactivity across the bond will be discussed in detail.⁴

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Zn(II) Pyridinoxy Imidazolium Complexes for CO₂ Cycloaddition towards challenging Epoxides under Ambient Conditions

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The escalating levels of CO₂ and global warming pose severe environmental challenges. Addressing this, research is increasingly focused on converting CO₂ into valuable chemical products. Beyond Carbon Capture and Storage (CCS), converting CO₂ into value-added products (CCUS) offers more excellent benefits. CO₂ can be reduced to methanol, formic acid, and methane or oxidized into amides, cyclic carbonates, and polycarbonates, leveraging its abundance, sustainability, and non-toxicity as a C1 source.¹⁻² Various metal complexes, including pincer, salen, salophen, and phenolate ligands, have been investigated for CO₂ conversion. Our research group is focusing on the (non)innocent amidine/NHC based ligands which are hitherto useful for the various C-C bond cross-coupling reactions.³ Recently, we have shown that cyclic carbonates can be prepared quantitatively using an octahedral cobalt-NHC complex as catalysts with TBAB as a cocatalyst with an exceptional TON (666,667) and TOF (52,713 h⁻¹) in the conversion of terminal epoxides and CO₂.⁴ Building on this, we have developed pyridonate-functionalized tetrahedral Zn(II)-imidazolium complexes, which exhibit high efficiency in CO₂ cycloaddition reactions with challenging terminal epoxides. This catalyst demonstrates a broad substrate scope with >99% selectivity for various epoxides and maintains reusability for at least six cycles. Here, we will discuss in detail the synthesis, catalytic activity and mechanism of the cyclic carbonate preparation.

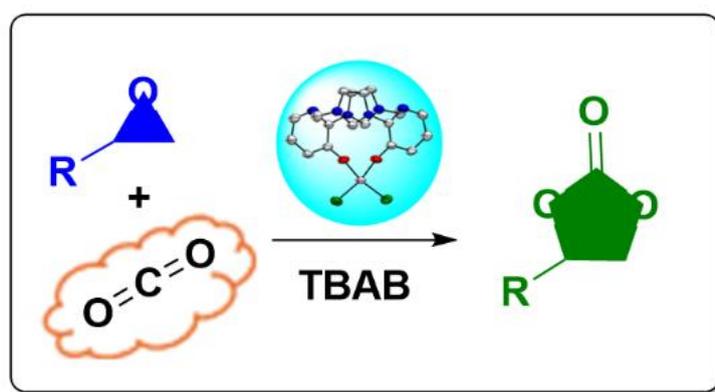


Figure 1 : Conversion of epoxides into cyclic carbonates

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Directing Group Strategy for the Isolation of Organoselenium(VI) Benzoselenonates: Metal-Free Catalysts for Hydrogen Evolution Reaction

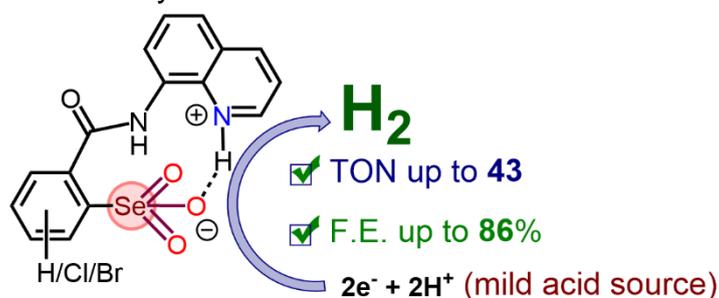
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Abstract:

Currently, the very high demand for energy and the recent abrupt climate change enforce society to utilize a renewable and environment-friendly fuel H₂ gas. Recently, the demand for H₂ gas production has been immense as it could serve as an alternative, carbon-free green fuel (95 metric tons in 2022).¹ H₂ production is an intriguing approach to converting electrical energy to chemical energy (H₂). In this regard, scientists have developed a detailed mechanistic understanding to develop efficient electrocatalysts to produce hydrogen gas by reducing protons. However, non-innocent ligands or organic molecules have recently gained attention for hydrogen evolution reactions. These molecules could form a hydride intermediate (hydride with main group elements: N, P, S) and unlock the new catalytic possibilities by avoiding the M-H bond formation to follow the ligand-centered HER.² Very recently, we explored ligand-centered HER by metal-free hexavalent organoselenium Se(VI) electrocatalysts for hydrogen evolution reaction.³ The unique ability of selenium to act as an electron reservoir and adjust its coordination site during the catalytic reaction could play a crucial role in the catalytic reaction.



- Stable organoseleniums(VI)
- Overpotential **500-570 mV**
- 4th-Period electrocatalysts
- Less deprotonating DMF solvent

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Cross-Coupling of Carbodicarbene: Synthesis of Electron-Deficient Diradicaloids

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Zerovalent carbon compounds, unlike divalent carbenes, possess two non-bonding electron pairs at the central carbon atom, which when stabilized by two carbenes are known as carbodicarbenes.¹ Herein, we present a nickel(0)-catalyzed strategy for the cross-coupling of NHC/CAAC-based carbodicarbene² (NHC = N-heterocyclic carbene and CAAC = cyclic(alkyl)(amino)carbene) with different aryl halides resulting in aryl-substituted cationic carbodicarbene derivatives. These derivatives can be electrochemically oxidized to the corresponding radical-dications, which may then follow different modes of radical-radical dimerization depending on the aryl motif employed, yielding carbon/nitrogen- and nitrogen/nitrogen-centered diradicaloids. Furthermore, this coupling strategy is extended to the synthesis of *p*-phenylene- and *p,p'*-biphenylene-bridged carbon/carbon-centered electron-deficient diradicaloids (see below scheme). The π -conjugated spacer plays a critical role in regulating the triplet population at room temperature by tuning the singlet-triplet gap, resulting in EPR inactivity for *p*-phenylene derivative and EPR activity for *p,p'*-biphenylene derivative. Nearly two decades after the introduction of carbodicarbenes as donor-stabilized atomic carbon equivalents by Tonner and Frenking,³ we demonstrate their cross-couplings with an array of aryl halides and present a modular methodology for the systematic synthesis of various electron-deficient diradicaloids.

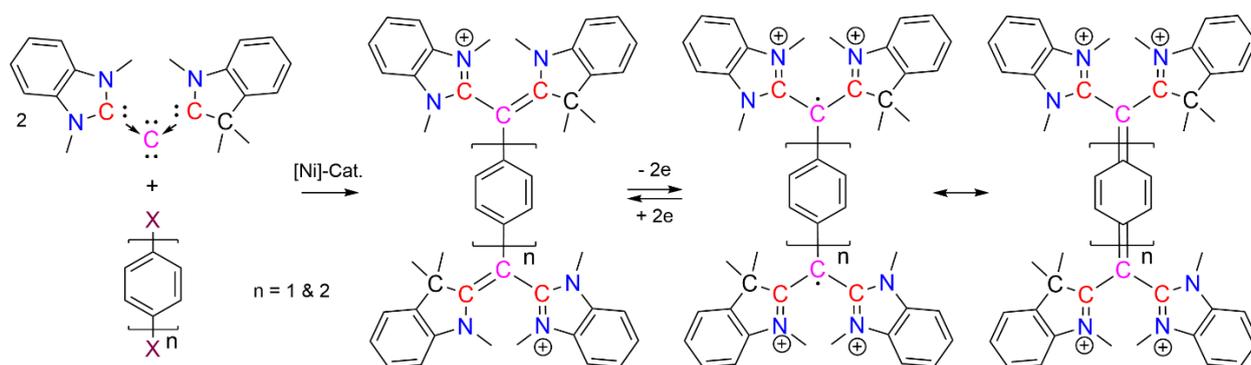


Figure 1 Cross-coupling of carbodicarbene and redox transition of corresponding derivatives. (Counter anions are omitted for clarity)

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Quantifying Magnetic Anisotropy of Series of Five-coordinate Co^{II} ions: Experimental and Theoretical Insights

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Stabilizing large easy axis type magnetic anisotropy in molecular complexes is an extremely challenging task, yet it is crucial for the development of molecular-based information storage devices and its applications in molecular spintronics. Achieving this requires a profound understanding of electronic structure and the relationships between structure and properties, to develop magneto-structural correlations. Herein, we report a series of five-coordinate distorted square pyramidal Co^{II} complexes [Co(L)(X₂)]·CHCl₃ (where X = Cl(**1**), Br(**2**), or I(**3**)), all exhibiting axial anisotropy (D). The D was quantitatively determined for all members of the series (**1** = -72; **2** = -67 and **3** = -25 cm⁻¹) using a high-precision Cantilever Torque Magnetometer (CTM) which is firmly supported by magnetic susceptibility, and EPR measurements. The study of the magnetization relaxation dynamics reveals the presence of field-induced slow relaxation of magnetization. Theoretical calculations on **1-3** and certain model complexes shed not only the electronic structure but also provide the influence of steric and electronic effects in modulating the D values. Overall, these studies open new avenues for designing next-generation Co^{II} complexes with improved D values and a reduced |E/D| ratio.

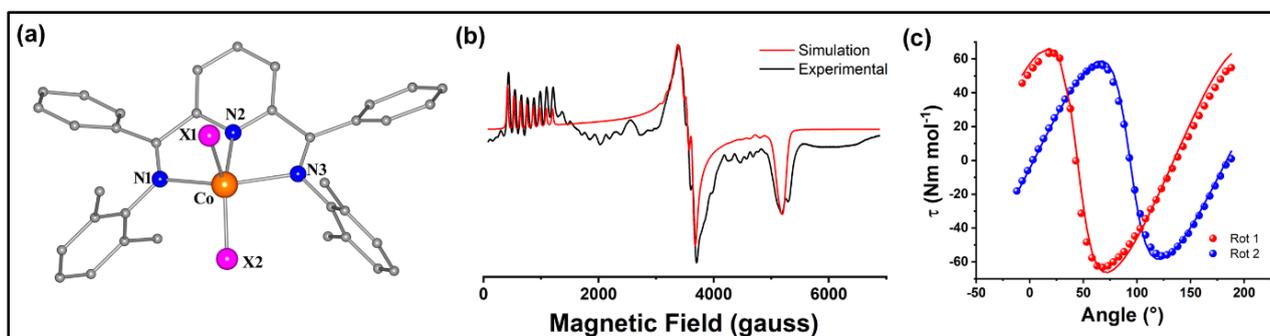


Figure 1: (a) Representative molecular structure of complex **1-3**. Solvent moiety and hydrogen atoms are omitted for clarity (b) X-band EPR spectrum of magnetically diluted **2-dil** at 5.0 K (c) Torque signals for **2** at 2.0 K and in a magnetic field of 4 T. The solid line are the best-fit curves for Rotation 1 and 2.

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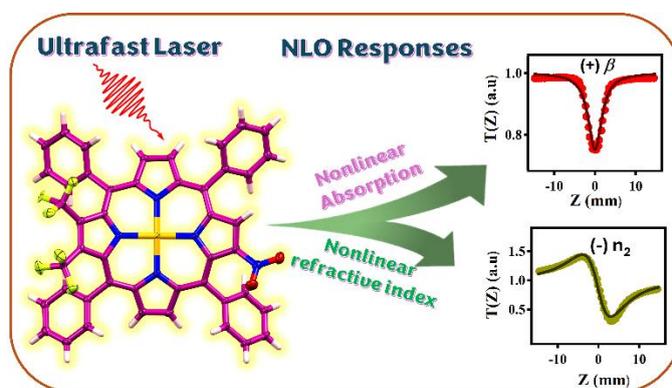
Electron-Deficient β -Trisubstituted Porphyrins: Synthesis, Spectral, Structural, DFT, Electrochemical Studies and Their NLO Application

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Developing novel NLO materials exhibiting strong NLO responses and high stability is urgently required to meet the demands of various applications across different fields.¹ In this regard, porphyrins emerge as promising candidates for nonlinear optical applications. This is attributed to their highly delocalized aromatic π -electron systems, substantial stability, conformational flexibility, and potential for versatile structural modifications.² Our group explored the NLO properties of unsymmetrical porphyrins with push-pull groups.² The present work illustrates the synthesis of β -trisubstituted porphyrin, viz. 2,3-bis(trifluoromethyl)-12-nitro-5,10,15,20-tetraphenylporphyrin ($H_2TPP(NO_2)(CF_3)_2$) and its metal complexes (Co^{II} , Ni^{II} , Cu^{II} , and Zn^{II}) and their characterization by various spectroscopic techniques and single crystal XRD and exploring their intensity-dependent third-order NLO properties. Unsymmetrical electron-deficient antipodal β -trisubstituted porphyrins showed interesting photophysical and electrochemical properties. Intensity-dependent third-order nonlinear optical studies demonstrated that the asymmetric β -substituted electron-deficient porphyrins exhibited a significant two-photon absorption coefficient ($\beta = 0.04 - 8.10 \times 10^{-10} \text{ m/W}$) and two-photon absorption cross-section ($\sigma_{2PA} = 0.02 - 1.67 \times 10^6 \text{ GM}$). Additionally, the materials display a self-defocusing negative nonlinear refraction ($n_2 = (-) 1.08 - 40.27 \times 10^{-17} \text{ m}^2/\text{W}$). These results suggest that synthesized porphyrins hold the potential for advanced applications in photonic devices and other optoelectronic technologies.



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Self-assembly and anticancer activity studies of dinuclear rhenium organometallic supramolecules

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The design and synthesis of clinical Pt(II)-based metallodrugs including cisplatin and its derivatives are well-known for its significant chemotherapeutic efficacy in cancer diagnosis. However, there is a rising need for alternative anti-cancer metal complexes not only to overcome the drawbacks of these drugs including drug resistance and toxic side-effects on healthy organelles but also which will possess ideal mechanism of action, high selectivity and stability. In this regard, several other metal complexes containing copper, gallium, palladium, ruthenium, titanium, gold, and silver as central metal ion have proven to address the limitations of platinum-based drugs.¹ Among these, efforts have been directed towards developing Re(I) tricarbonyl complexes as potential anti-cancer agents due to their intriguing rich photophysical properties, thermodynamic stability, kinetic inertness, and one-step synthesis.^{2,3} Moreover, fluorinated compounds continue to receive considerable attention in medicinal chemistry owing to their remarkable enhancement in biological properties achieved through fluorine incorporation.⁴ Herein, the synthesis via a simple one-pot self-assembly approach and biological evaluation of fluorinated and non-fluorinated dinuclear Re(I) tricarbonyl metallocycles are presented. The fluorinated metallocycle displayed significant anticancer activity against human cervical cancer cells compared to its non-fluorinated analogue, exhibiting greater efficacy than the clinically used cisplatin.

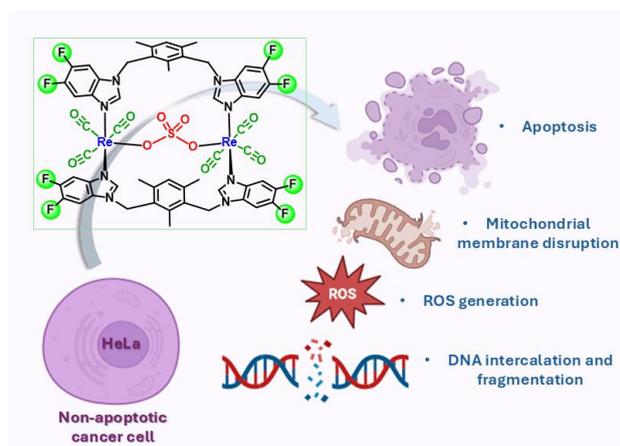
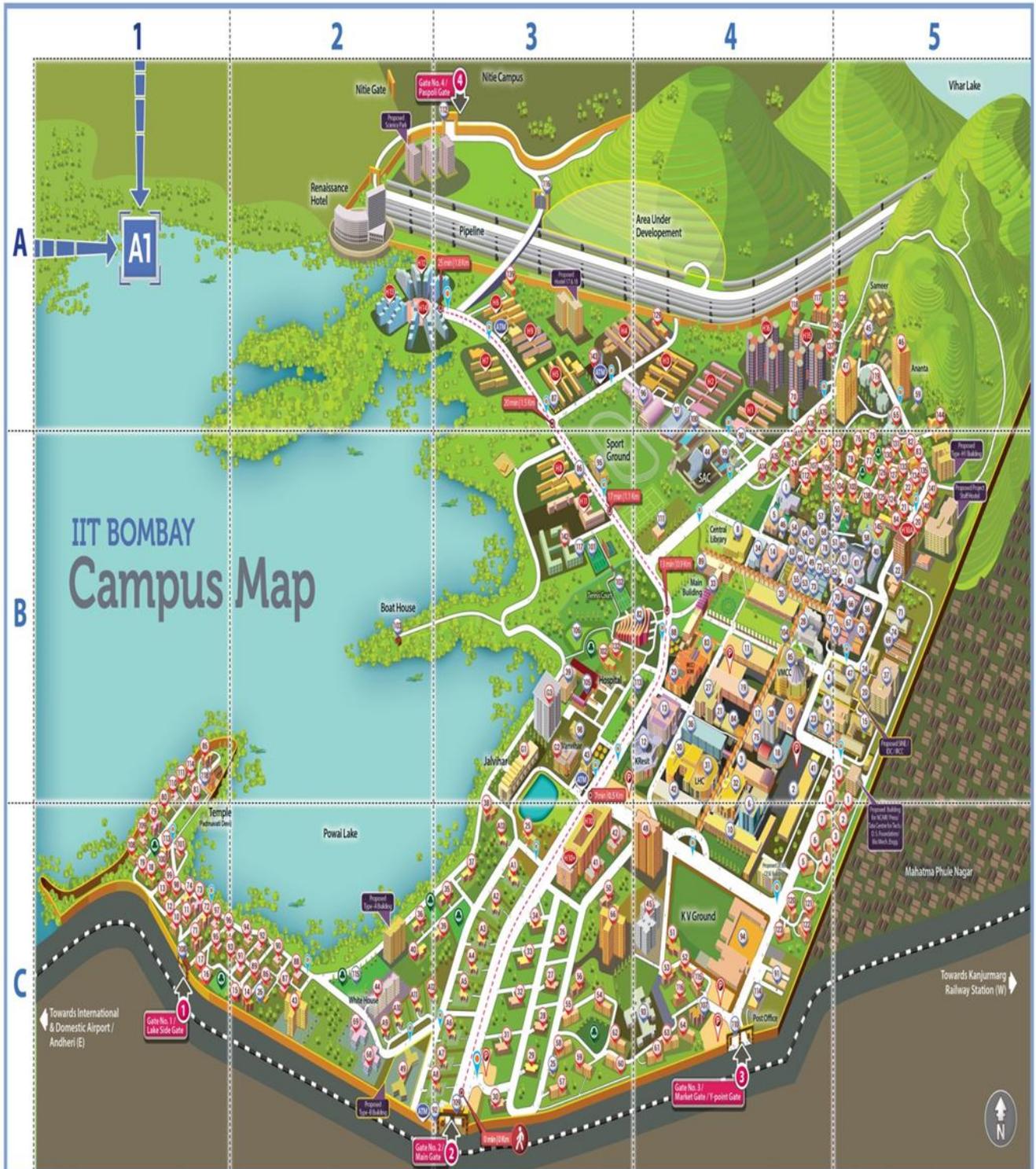


Figure 1 Graphical representation of the modes of activity of the fluorinated rhenium(I) rhenium metallocycles on human cervical (HeLa) cancer cells.

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Conference on Main-group Molecules to Materials-4



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