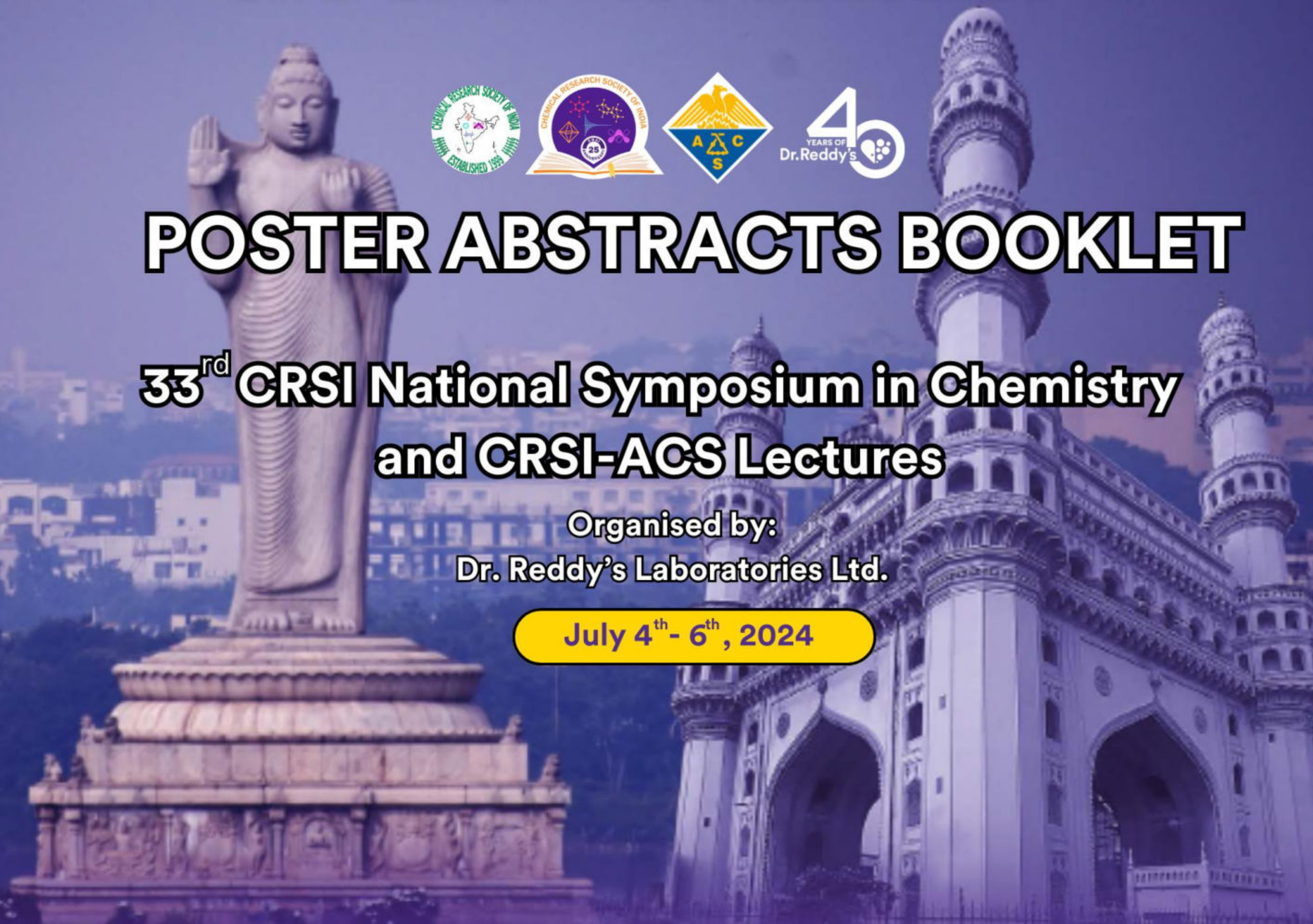

POSTER ABSTRACTS BOOKLET

33rd CRSI National Symposium in Chemistry and CRSI-ACS Lectures

Organised by:
Dr. Reddy's Laboratories Ltd.

July 4th- 6th, 2024

Low Platinum Loading ZnO/CQDs Bifunctional Electro-Catalyst Towards OER and ORR Impacting Zinc-Air Battery

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Architecting efficient and economical nano-electrocatalyst for oxygen electrocatalyst is the most promising approach for the widespread application of green energy conversion devices. Herein, we have reported low platinum loaded ZnO/CQDs nanocomposite for the significant oxygen electro-catalysis. During overall catalytic process, Pt-ZnO/CQDs nanoelectrocatalyst is improving over potential of $\Delta E_{\mathrm{ORR\text{-}OER}}= 0.60 \pm 0.02$ V vs. RHE. In last, fabricated Zinc-Air Battery is with bifunctional catalyst showing high areal power density of 147 mW cm^{-2} with high specific capacity of590 mAh cm^{-2} indicating suitable candidature as a cathode material for Zinc-Air Battery.

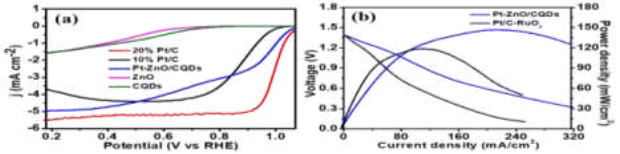

Figure: **(a)** CLSV of PtNP-ZnO/CQDs**,** ZnO, CQDs and commercially available10 &20 % Pt-C catalyst.

(b) Polarization curves and corresponding areal power plots

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1. Subhajit Sarkar, Ashmita Biswas*, et al. ACS Nano* **2022** *16* (5), 7890-7903.

Synthesis, Characterization, and Catalytic Degradation of Methyl Orange with H_2O_2 by an Oxidovanadium(IV) Schiff Base Complex Derived from Glycine

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Environmental concerns are raised worldwide by the discharge of wastewaters from the textile industry that contain organic contaminants.[1-2] Azo dyes, the largest group of synthetic pigments makes up more than 50% of all commercial dyes are extensively employed by the textile industry.[3] The VO^{2+} ion interacts with H_2O_2 in Fenton-type reactions to form hydroxyl radicals.

A Schiff base oxidovanadium(IV) complex derived from glycine and salicylaldehyde with phenanthroline as co-ligand viz. [VO(salgly)(phen)]·$4H_2O$ (**1**) (where salgly is a Schiff base derived from salicylaldehyde and glycine, phen is 1,10-phenanthroline) was and characterized by spectroscopic techniques such as FT-IR and UV-vis. The structure of the complex was determined by single crystal X-ray diffraction. The complex showed good catalytic activity for the degradation of methyl orange (MO) in presence of hydrogen peroxide.

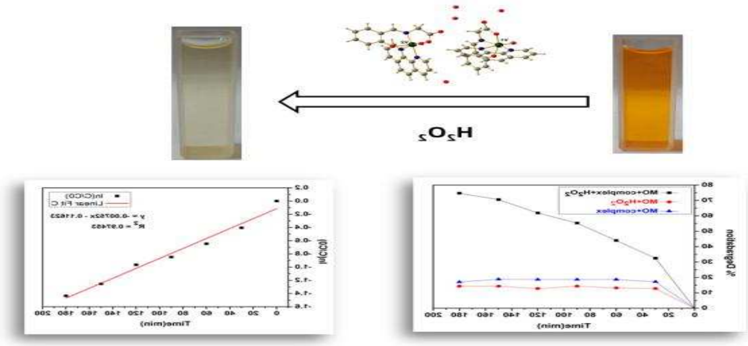

Figure 1: Catalytic Degradation of Methyl Orange by [VO(salgly)(phen)]·4H_2O (1) in presence of H_2O_2

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"All-organic" Electrode Material Toward High-Performing Rigid to Flexible Supercapacitor Devices

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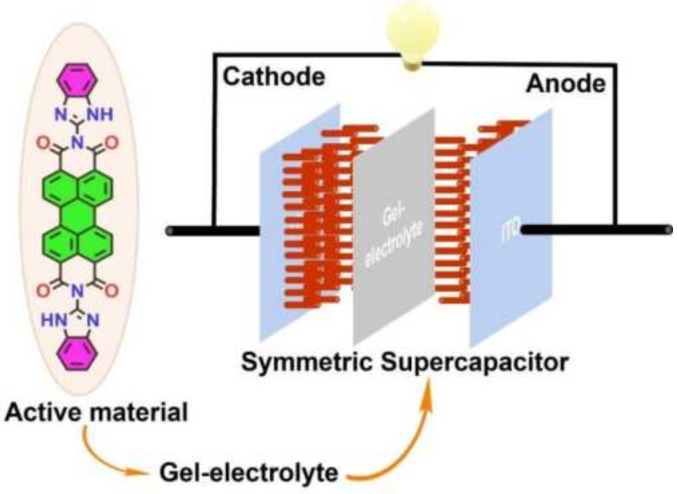
Abstract: The donor–acceptor π-conjugated organic materials are considered intriguing electrode materials for reversible energy storage applications owing to their excellent charge transfer ability, high electrical dipole moment, and good electrical conductivity. Such redox behavior can be utilized in designing and fabricating hybrid supercapacitor devices. We, herein fabricate low-cost, rigid to flexible, and symmetrical supercapacitors (SCs) using perylene diimide-2-amino benzimidazole (PDI-AB, **1**) with a device configuration of (ITO/PDI-AB//PMMA-$LiClO_4$-PC//PDI-AB/ITO), where poly(methyl methacrylate)-based PC-$LiClO_4$ gel used as electrolyte-cum separator. As-fabricated PDI-AB-based rigid supercapacitors exhibit specific capacitance (C_S) of 28.28 mF/g at a current density of 0.5 mA/g with an energy density of 24.5 mWh/kg at a power density of 2.5 W/kg. The devices show nearly 96% retention of C_S even after 2,000 cycles indicating the excellent cyclic stability and robustness of the devices. Similarly, the flexible SCs show a C_S of 25.59 mF/g at a current density of 0.5 mA/g with an energy density of 22.21 mWh/kg and a power density of 2.5 W/kg. The PDI-AB exhibits a lower bandgap of 2.45 eV in comparison to pristine PDI (2.99 eV) resulting in enhanced redox behavior owing to the extended π-conjugation. The current study will offer new avenues toward 'all-organic' active electrode materials for flexible, compact, lightweight, 'on-chip' supercapacitors and optoelectronic devices.



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Impact of surfactants in modulating the viscoelastic properties of Fmoc-Phe hydrogels

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Supramolecular gels, arising from the self-assembly of low molecular weight (LMW) gelators, have garnered significant interest in various fields including biosensors, drug delivery systems, optical sensors, and tissue engineering. These hydrogels are formed through non-covalent interactions between self-assembled molecular networks. In this study, we investigated the impact of different surfactants - sodium dodecyl sulphate (SDS), Cetyltrimethylammonium bromide (CTAB), and Triton-X-100 - on the viscoelastic properties of hydrogels composed of Fluorenylmethoxycarbonyl group conjugated Phenylalanine (Fmoc-Phe). By varying the surfactant concentration relative to its critical micelle concentration (CMC), we explored its influence on Fmoc-Phe self-assembly and viscoelastic behavior. Rheological analysis indicated that the viscoelastic property of the Fmoc-Phe hydrogel was significantly modulated in the present of different surfactants. Morphological analysis revealed that surfactant nanoparticles were embedded within the fibrils of Fmoc-Phe hydrogels. Biophysical techniques such as UV-visible spectroscopy, circular dichroism (CD), Fourier-transform infrared spectroscopy (FT-IR), and fluorescence measurements provided insights into the interaction between

surfactants and Fmoc-Phe, influencing viscoelastic properties. The development of hydrogel-surfactant composite gel materials holds promise for diverse biomedical applications, particularly in drug delivery and tissue engineering contexts.

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Know Your Insulin: Proposing A Self-Investigated Insulin

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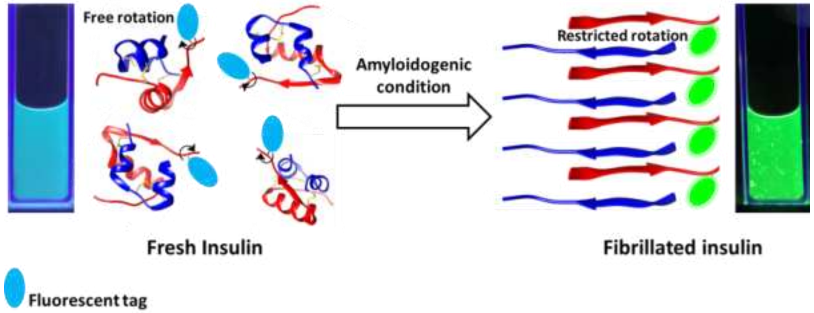
Unintentional purchase of improperly stored degraded or fibrillated insulin causes financial losses and life-threatening risks. Detecting degraded insulin is challenging due to its visual similarity to fresh insulin. Prefibrillar insulin populations, present in the early stages of insulin aggregation, are particularly cytotoxic, causing severe pathophysiological conditions. Thus, monitoring these prefibrillar populations is crucial for consumers to ensure the quality of their insulin dosage before injection. We introduce a chemically modified human insulin with aggregation-induced emission (AIE) property for real-time monitoring of insulin quality.[1,2] A significant visual transition from cyan-colored fresh insulin to green-colored fibrillated insulin is observed under UV lamp irradiation due to a bathochromic shift in fluorescence spectra. The presence of a conjugated fluorescent moiety and its spatial arrangement influence the insulin's photophysical property, allowing users to assess insulin quality personally. This advancement empowers users to make informed decisions about their diabetes management, potentially preventing life-threatening complications and safeguarding patients' health.



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Oxazine-based probe for the colorimetric detection of toxic mercuric ions

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Mercury is known for its toxic effect on human health. Exposure to elevated levels of mercury through drinking water leads to a lack of appetite, loss of weight, muscular incoordination, unstable gait, and lameness. Exposure to elevated levels of mercury affects the central nervous system, and neurological disorders in children including Parkinson's disease, Alzheimer's disease, ALS, Lupus, Rheumatoid arthritis, and Autism. Therefore, there is a need to develop portable sensors for its detection. Optical sensors particularly those, that displays a visible color change are simple and portable devices, that can detect the presence of toxic ions like mercury ions in remote locations. Such portable, simple convenient sensors, which can be used for naked eye detection, and use inexpensive instruments are vital for monitoring drinking water in rivers, lakes, ponds, and other water bodies for the presence of toxic ions like mercury. Although a variety of sensors are available, still there is a need to develop new types of sensors, particularly those, which can be regenerated easily through convenient techniques like light. Given the toxicity of mercury and the regeneration abilities of photochromic compounds, our group has designed a light-sensitive probe based on the photochromic oxazine derivative. Photochromic oxazine is a family of photochromic molecules, which are known to exist in OX (colorless, closed) and IN (colored, open) forms. The open form is known to interact with metal ions, while the close IN form has low

interaction with metal ions. However, OX form on interaction with metal ion produces the colored IN form. Exposure to visible light IN forms a complex with metal ions releases metal ions and regenerates the probe. So, a photochromic oxazine-based probe was successfully designed and its mercury ion complexation ability in water was explored through various techniques. The results of this study will be presented.

Nitronaphthalimides Increase Nitric Oxide Bioavailability by Nitrite Donation: Potential Implications in Cardiovascular Complications

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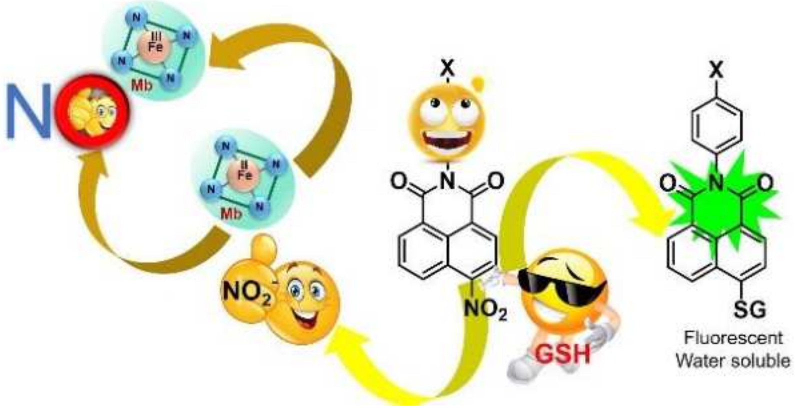
Nitric Oxide (NO) is an important gaseous signalling molecule in mammalians. Since the discovery that human body utilizes plasma nitrite (NO_2^-) as a precursor of NO for hypoxic vasodilation (Hypoxic vasodilation is the mechanism by which NO is produced from NO_2^- by Haem (II) proteins: Haemoglobin, Myoglobin etc.), this alternative pathway for the generation of NO has drawn attention of scientific community and is specifically important under Cardiac ischemia. Therefore, exploring the therapeutic capability of nitrite donors in conditions of hypertension, stroke, heart attack etc. would be interesting and might provide newer insights in the development of drugs for cardiovascular complications. Here, we have synthesized small molecules which act as nitrite donors as promising candidates for applications in cardiovascular complications such as cardiac ischemia and others. These molecules release nitrite (increase NO bioavailability) with the assistance of biological thiol (Glutathione, GSH) which leads to the formation of fluorescent GSH adducts. Formation of fluorescent adducts provide added novelty to these compounds because of their self-reporter property which assists in tracking cellular localization of these molecules. Cellular studies in HeLa and Endothelial cells indicate a promising drug-like response of these synthetic molecules.



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A fluorescent benzothiazole dimer for sensing lead ions in an aqueous solution

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In recent decades, optical probes with diverse structure segments with plausible fluorescence readouts have been comprehensively examined and extensively reported in the literature. Biomedical sectors have been using such fluorescent probes for screening various samples. Among such sensors, those consisting of benzothiazole segments are unique and dependable sources of optical probes for examining disorders by imaging cells and their organelles. Fluorescent sensors are also widely for monitoring toxic ions in environmental and biological samples. It is a well-accepted fact that toxic heavy metals like lead, mercury, and rubidium cause significant pollution, and their detection and analysis are very tough using recent techniques like atomic absorption and atomic emission spectroscopy. However, by utilizing an optical probe with a suitable cavity size for retaining the metal ions and an appropriate group to coordinate with the signaling unit, we can detect the ions at trace concentration levels. In theory, optical probes for metal ions can be colorimetric or fluorometric, however, many reports only utilize one technique for the detection process. The

development of metal ion sensors for transition metals like lead ions has garnered some interest. To create a probe for lead ions, a suitable cavity was created using benzothiazole units, benzene rings, and spacer units. The benzene spacer was linked with two benzothiazole units at meta positions, forming a suitable cavity for lead ions and the donor atoms that coordinate it. The optical signal produced by the probe with benzothiazole units in the form of color was studied using UV-vis spectroscopy and the change in fluorescence signals was studied using fluorescence spectroscopy. Overall, the study describes the design and synthesis of a tweezer-shaped probe for the detection of lead ions in an aqueous solution.

Amine functionalised luminescent carbon dots - white light emission and sensing applications

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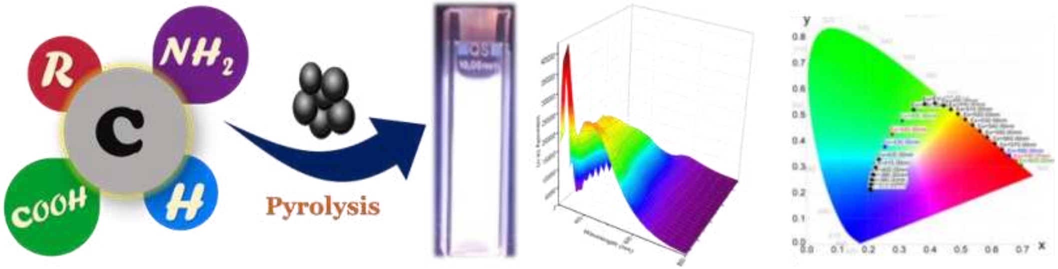
A prominent member of carbon nanomaterial family, Carbon dots (CDs), a ‘zero dimensional’ nanomaterial has attracted great attention since its discovery in 2004. Owing to their excellent optical properties, biocompatibility, low toxicity, and high luminescence quantum yield with enhanced photostability, it finds application in the field of sensing, bioimaging, laser, LED, and energy storage devices. One of the major flaws encountered while using conventional fluorescence dyes is photobleaching during fluorescence imaging. This can be overcome by photostable CDs. Moreover, the high quantum yield from CDs further aids in the localisation of particles for super resolution microscopic applications. Fluorescence emission from CDs ranges from blue to near-IR region and this emission variation has been attributed mainly to its size and surface functional groups. Both the wavelength-dependent and wavelength-independent fluorescence emission of CDs has been studied as they offer several advantages. In this work we report the synthesis of CDs by pyrolysis method using aromatic amino acids as precursors under controlled temperature. They displayed a wide range of fluorescence emission from blue to green region. The CDs were characterised mainly by TEM, IR, XRD and relevant spectroscopic techniques. The photoluminescence properties of CDs were studied using UV-visible and steady state and time resolved fluorescence spectroscopy. Under UV 365 nm excitation, an intense white fluorescence was observed, and the emission spectra seemingly depends on the excitation wavelength. This feature highlights the existence of different chromophoric units in the CDs. The detailed steady state and time resolved fluorescence studies will be presented.



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Probing acidic systems: Molecular interaction analysis with thermal lens

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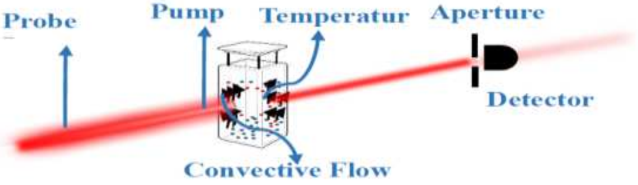
Abstract:

Intermolecular interactions, encompassing hydrogen bonding, dipole-dipole interactions, and van der Waals forces, exert significant influence on solvent properties, solvation behaviour, and solute reactivity. The interplay between solvent structure, composition, and chemical reactions is quite a difficult task to determine yet important for understanding the phase equilibria, molecular organization, and the dynamics of chemical processes. Thermal lens (TL) spectroscopy, an ultra-sensitive technique utilizing femtosecond lasers, probes molecular properties as well as interaction at molecular level due to nonlinear heating. Here, we explore the intricacies of molecular-level interactions in acidic systems and their binary mixtures with water, as well as the impact of superheating on their electrochemical properties through TL spectroscopy. Our findings unveil an optimized binary acidic mixture with enhanced electrochemical properties. Ultimately, this research aims to advance our understanding of molecular interactions in acidic systems.



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pH-Dependent Haloperoxidase-like Activity of Vanadium Pentoxide Nanostructures

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Vanadium pentoxide (V_2O_5) nanoparticles as haloperoxidase started to gain attention due to their ability to prevent marine biofouling. In the presence of bromide ions and hydrogen peroxide, V_2O_5 nanowires catalyse the oxidation of bromide ions to hyperbooks acid (a reactive halogen species) and serve as an alternative approach to conventional anti-biofouling agents. Previous reports suggested Bromo peroxidase- like activity but there were no studies on other halogens. Herein, we synthesized V_2O_5 nanostructures of different morphologies via coprecipitation and hydrothermal methods. The synthesized materials were characterized using various techniques such as TEM, SEM, PXRD, IR, and UV-Visible spectroscopy. We intended to study HPO activity through phenol red assay at varying pH from 4 to 8. Results showed that V_2O_5 nanoparticle was like native vanadium haloperoxidases enzyme and exhibited selectivity in their capability to oxidise halogens. At pH=5, both Cl and Br get oxidised. At pH=6, oxidised only Br and at pH 7.3 oxidized both Br and I. At pH=8, it was able oxidise only Iodine, which corresponds to the obtained tetra-halogenated phenol red. This particular study was not reported anywhere.

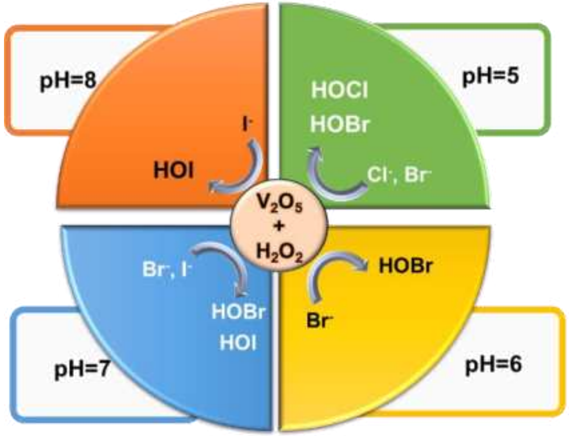

Figure 1: Illustration of pH-Dependent HPO-like activity of V_2O_5.

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High mobility and ON/OFF ratio of solution-processable p-channel OFETs from Pyrene, anthracene and triphenylamine based D-π-D triads

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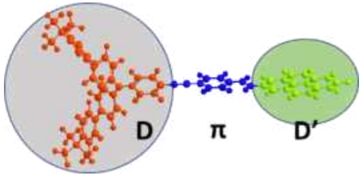
Organic field-effect transistors (OFETs) represent a promising candidate for next-generation electronic applications because of the intrinsic advantages of organic semiconductors such as solution processability, mechanical stability and large-area fabrication. Enormous attempts have been devoted to enhancing the chemical stability and charge transporting properties of active layer. In this present investigation, we have designed and synthesized a series of unsymmetrical D-π-D small molecules, comprising triarylamine and anthracene/pyrene units. The structural effects of these molecules are systematically investigated by changing the substituents and spacers. Ethynylene and ethenylene bridges are chosen as spacers between triarylamine and anthracene/pyrene units to increase rigidity and conjugation. D-π-D molecules have been synthesized via a series of Wittig-Horner and Sonogashira cross-coupling reactions and characterized through various spectroscopic techniques. Solubility of the molecules informs that they are promising candidates for economical solution processing. All functionalized D-π-D systems possess good electrochemical reproducibility with an optimum bandgap of ~ 2.7 eV. All compounds exhibited the highest HOMO levels with an average value of ca. -5.21 to -5.44 eV. Pyrene and anthracene connected tert-butyl phenyltriarylamine showed the highest lying HOMO levels, which facilitates charge carrier injection into the electrodes. Optimized geometry and charge distribution of the molecules are

envisioned by density functional theory. OFETs were fabricated through solution-processable methods and displayed promising performance with charge carrier mobility μ_h up to 3.6 cm^2/Vs, on/off ratio of 10^7, and lowest V_T of -3 V.



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From Solution to Microstructures in Minutes: Microdroplet-Derived Stand-alone Surfaces for Simultaneous Water Harvesting and Treatment

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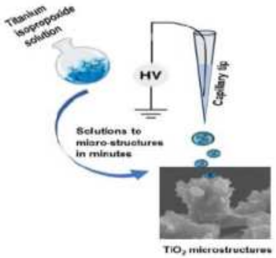
Abstract:

We present a straightforward and eco-friendly method to transform a titanium tetraisopropoxide (TTIP) solution into superhydrophobic TiO_2 microstructures by ambient microdroplet deposition. When cooled, the micro-pillars on the surface act as nucleation sites for condensing humidity to form droplets. However, the microstructures facilitate efficient water runoff despite TiO_2's hydrophilic character, by a combination of surface hydrophobicity and gravity. Additionally, the photocatalytic TiO_2 surface resists biofilm formation and degrades the contaminants, offering long-term collection of safe water and its purification, which has been demonstrated with examples. This approach was also successfully applied to other metal oxides, highlighting universality of the process.

Figure or Scheme



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Metal Organic framework-Carbon dots conjugates for Recognition of REACH Chemicals

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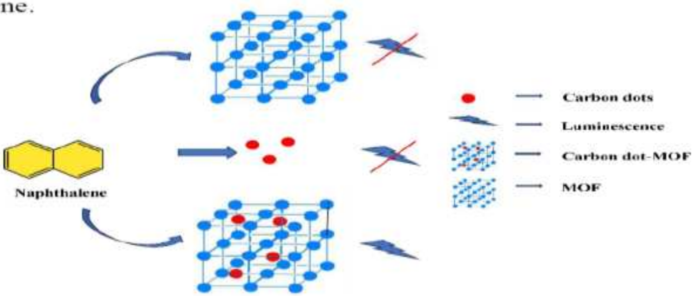
Abstract:

The European Union (EU) enacted the Registration, Evaluation, Authorization, and Restriction of Chemicals, or REACH (EC 1907/2006), safety regulation to forbid the use of specific harmful chemical substances in goods produced, sold, and imported into the EU. Hence REACH acts as a body to ensure the safety of the usage of chemicals in cosmetics, furniture, paints etc. Due to the limitations of sensors present for these chemicals, there is a need for new sensors.[1,2] This work focuses on the use of fluorescent sensors based on Metal-Organic Frameworks (MOFs)-Carbon dots conjugates. The metals used for the MOF synthesis are chosen from the lanthanide series for their inherent fluorescence properties. The carbon dots known for their excellent fluorescence property, in conjugation with MOFs, show increased fluorescence. This fluorescence system shows turn-on fluorescence with naphthalene, a restricted chemical. This method is found to be efficient over the available SERS sensors for naphthalene.



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Design, synthesis, and tunable self-assembly of a diamino diacid-based short cyclic peptide

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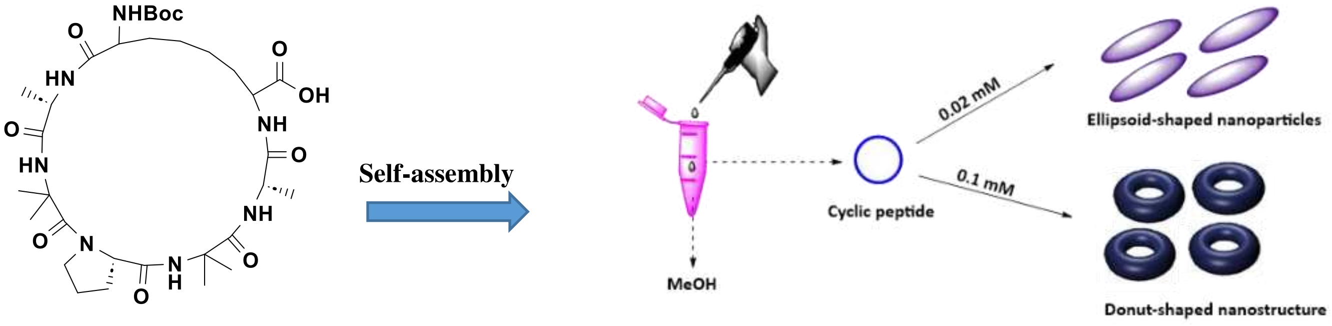
The restricted conformations of macrocyclic peptides confer improved metabolic stability, membrane permeability, and target selectivity compared to their linear counterparts. Among the myriad designs explored, cyclic peptides stand out as promising candidates for various applications ranging from drug delivery to materials science. The diamino diacid residues are formed from two α-amino acid units, which are coupled with a linker. They have been used as external templates for synthesizing short cyclic peptides (CP). We have used a diamino diacid for the preparation of a cyclic heptapetide with an aliphatic chain connecting the two terminal α-amino acid units. The properties of this cyclic peptide were compared with that of the corresponding linear peptide (LP). It was found that the CP showed concentration dependent self-assembly resulting in the formation of different nanostructures at different concentrations. These self-assembled nanostructures were characterized using FESEM, AFM, DLS, and FTIR. The study showed that the self-assembling behaviors of the cyclic and linear peptides are significantly different. Both the CP and the LP have very low critical aggregation concentrations (CAC), which were measured using fluorescence and DLS. The conformations of the CP and LP were analyzed at different concentrations using CD spectroscopy and marked differences were observed in their native conformations at different concentrations and solvents. These results will be presented.



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Synthesis of C_3N_5 through Various Routes and development of C_3N_5 Composites for Improved Photocatalytic Dye Degradation Performance

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Carbon nitride materials have emerged as promising candidates for photocatalytic applications. In this study, we synthesized carbon nitride through various synthetic routes and investigated the resulting effects on its morphology and chemical properties. The high nitrogen content and narrower band gap of g-C_3N_5, compared to g-C_3N_4, establish it as a distinctly nitrogen-rich semiconducting material. The optical absorption characteristics of g-C_3N_5, inherently dependent on the number of stacking layers, enable a tunable bandgap, enhancing its light-harvesting ability in the visible region. These properties offer significant advantages for photocatalytic applications.

Furthermore, we synthesized a composite of C_3N_5 with metal chalcogenides and examined its unique characteristics. Our findings reveal substantial insights into the material's potential applications, particularly in environmental sustainability, providing significant benefits for eco-friendly technologies.

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Metal Organic Frameworks Based Triboelectric Nanogenerator

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Harnessing mechanical energy from the surroundings shows significant promise as a power supply for micro and nanoscale devices. The triboelectric nanogenerator (TENG) operates based on the principles of triboelectrification and electrostatic induction. Metals and polymers have mostly dominated the conventional triboelectric series, but there is a need for novel materials to expand this series and enhance the TENG performance. Herein, we have synthesized a zeolitic imidazole framework (ZIF-67) via a room temperature solvent-assisted method and analyzed its structural and chemical properties. A simple vertical contact mode S-shaped TENG device was fabricated with the help of additive manufacturing process. Here, ZIF-67 served as the positive triboelectric layer, while Teflon/PDMS served as the negative triboelectric layer. The multi-unit S-TENG device was used for self-powered recognition of different gaits through digital signal processing. The device based on ZIF-67 and Teflon produced a voltage of 118 V, a current of 1.7 mA, and a power density of 15 mW cm^2 at a load resistance of 50 MΩ. By capturing the gait patterns of diverse volunteers, the S-TENG device assisted in accurately identifying various gaits to mitigate the risk of falls and injuries, particularly among children wearing flip flops equipped with the S-TENG technology while playing in a park. Furthermore, it was employed to charge a commercial capacitor to power a wristwatch and was attached to a robotic gripper for object identification.

Keywords: Metal organic framework, Triboelectric nanogenerator, Power Source, Solvothermal

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Molecular Versus Supramolecular: Chirality induction in Nano-size Trizinc(II)porphyrin Trimers

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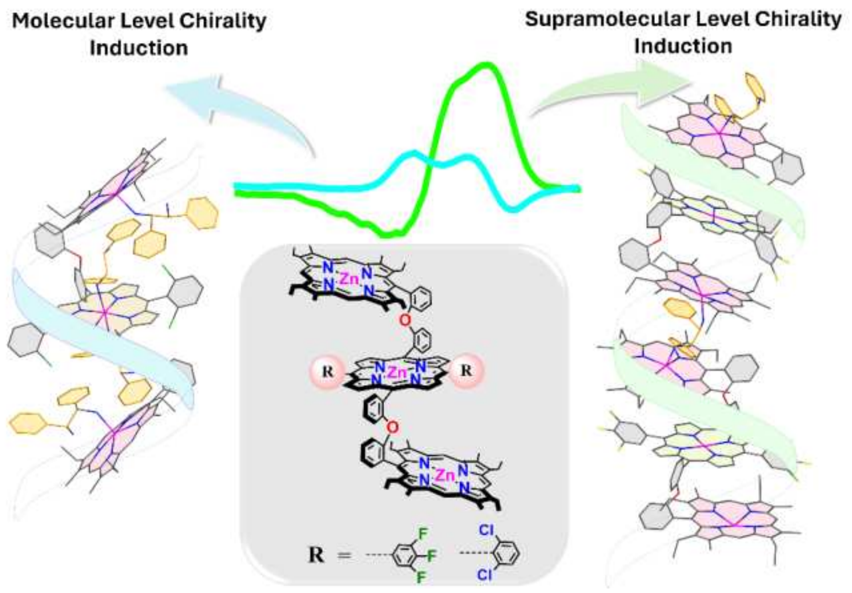
Supramolecular chirogenesis is one of the most important interdisciplinary fields to be looked into, because of its occurrences in many natural (DNA double helix, heme proteins, secondary α-helix structure of proteins, etc.) and artificial systems. Exciton Coupled Circular Dichroism (ECCD) is a nonempirical spectroscopic method that is based on detecting the through-space exciton interaction between helically oriented independently conjugated chromophores. Control of molecular to supramolecular level chirality induction has been realized just by subtle modification in a nano-size porphyrin trimer. The architecture of the host dictates the fate of supramolecular chirogenic process. A threefold increase in circular dichroism intensity is noted for the polymer compared to the monomer. This finding is substantiated by X-ray structural analysis and DFT calculations.



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Multi-Functional Hydroxyquinoline-Derived Small Molecule Nano Dot for Alzheimer's Disease Detection and Treatment.

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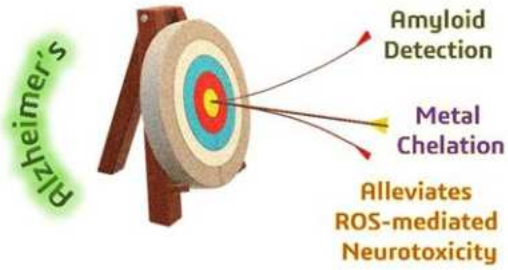
In the pursuit of effective Alzheimer's disease (AD) diagnostic tools, we offer a multipotent small-molecule fluorescence probe designed to target lysosomes, important organelles implicated in AD pathology specifically. When interacting with amyloid-β (Aβ), this hydroxyquinoline-derived probe exhibits a distinctive turn-on fluorescence response, allowing for sensitive and precise detection of AD. The probe's design makes use of the specific lysosomal abnormalities seen in Alzheimer's disease, providing a viable technique for early-stage diagnosis. Theoretical analyses like Molecular Docking and Molecular Dynamics Simulation confirmed the molecule's reactivity towards Aβ and found excellent interactions with the peptide. *In vitro* and cellular studies showed that this biocompatible molecule effectively reduces ROS (Reactive Oxygen Species) and attenuates



amyloid toxicity. The molecular tool given here has enormous potential for furthering our understanding of AD pathophysiology and allowing the development of novel diagnostic techniques for improved patient outcomes.

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Temperature dependent tuning of Secondary Nucleation to modulate mechanical stiffness of supramolecular hydrogel

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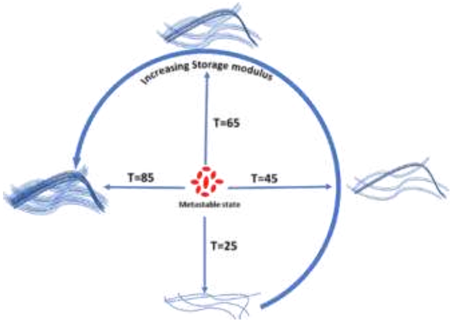
Fine tuning of micro-/macroscopic properties of supramolecular systems requires precise mechanistic understanding of the phenomena which remains a major challenge. Seed-induced surface catalysis has been an established phenomenon in the propagation of amyloid fibrils. This principle has been mimicked in the fine tuning of topology and the mechanical stiffness of a hydrogel system.[1] Temperature dependent control on propagation kinetics of amyloid fibril was established by Linse *et al.*[2, 3]

Herein, we conferred significant control on molecular level self-assembly using temperature as the stimulus. By varying the temperature, microscopic topology was tuned which further tuned hierarchical self-assembly to modulate mechanical stiffness of a hydrogel by slanting self-assembly pathways. We developed a synthetic, self-assembled system akin to amyloid propagation to tune secondary nucleation-elongation which in turn tuned microscopic topology henceforth mechanical stiffens using temperature as the stimulus. This mechanically tuned hydrogels can have applications in mechanobiology, drug delivery, tissue engineering, nanomedicine, cell culture, etc..[4-8]



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An Electronic Device Incorporating Flexible Organic Single Crystals for Ultrasensitive Detection of NO_2

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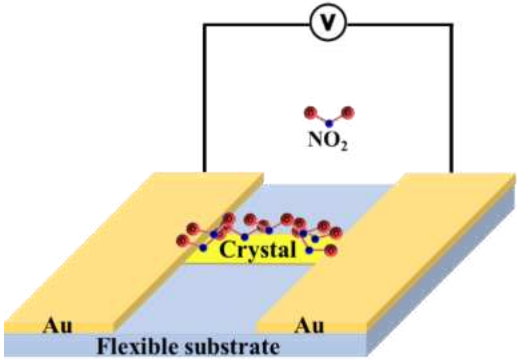
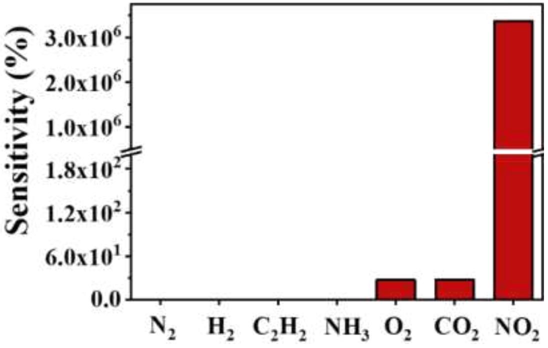
Organic electronic devices are emerging as viable replacements for inorganic counterparts due to simple and low-cost processing, versatile molecular design, and ease of control of physical properties. Organic crystalline materials (OCMs) exhibit superior device performance and are seen as promising candidates for future flexible electronics.[1] Compared to conventional single crystals, flexible organic single crystals exhibit structural bending, curling, and twisting in response to external stimuli while maintaining their intact macro-structures.[2] Despite the latest developments in understanding the fundamental principles governing flexibility in organic single crystals, they are rarely employed in electronic devices. Herein, we present an electronic device incorporating the flexible single crystals of a Schiff base having intramolecular charge transfer (CT) properties for detecting NO_2 gas. The crystals' potent CT interactions were indispensable in determining their optoelectronic properties, such as green fluorescence and high electrical conductivity. Our findings have significant implications for both the ecosystem and public wellness due to the high toxicity of NO_2. The device is cost-effective, power-efficient, and has a high sensitivity of 3.36×10^6 % at 1 ppm of NO_2 with a limit of detection of 67 ppb. The flexibility of the synthesized crystals allowed their integration into flexible substrates, expanding their uses in the realm of flexible wearables and smart electronics such as e-skin and soft-robotics, which have the potential to spark a worldwide revolution.





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Synthesis of Organic and Organic-inorganic Hybrid π-conjugated Semiconducting Materials for Optoelectronic Devices

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Organic solar cells (OSCs) have attracted much attention due to several technological advantages of light weight, flexibility, large-area fabrication via simple solution deposition techniques. The development of novel photoactive materials and device engineering in the last few years, the power conversion efficiencies (PCEs) of OSCs have currently reached over 19% for single-junction cells,[1] demonstrating their great potential in future applications. The major problem of biphasic bulk-hetero junction (BHJs) solar cell is the optimized morphology is thermodynamically unstable and the progressive macrophase separation of donor (D) and (A) leads to a decrease of PCE and stability of OSCs.[2] Therefore, control of the active layer morphology is an important parameter for realizing good performance and stable commercially viable OSCs. Single material organic solar cells are an important alternative to make large scale organic solar cells, are composed of only one organic material that serves as both the light-absorbing layer and the charge transport layer, eliminating the need of complex device architectures and multiple interfaces that can cause performance degradation and device instability.

On the other hand, Two-dimensional (2D) organic-inorganic hybrid perovskites, which incorporate functional organic cations, have emerged as a new type of semiconducting material useful for optoelectronic devices such as solar cells, LEDs, and photodetectors. We studied a lead-based 2D perovskite structure, Dion-Jacobson type, incorporating simple terphenyl diammonium salts as organic spacers. Type II heterostructures formed by organic semiconducting ligands and in 2D perovskites can offer separated charge transport channels for holes and electrons. This work gives valuable insights into the charge transport mechanisms of type II heterostructures and paves the way toward optoelectronic device applications for such Dion−Jacobson-type 2D perovskites.[3]

Keywords: Renewable energy, organic solar cells, π-conjugated materials, 2D dion-jacobson perovskite, p-n heterojunction, charge transport properties

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Supramolecular Lanthanide-Based Gel and Xerogel Systems: Towards Efficient White Light Emitting Materials

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Abstract: Supramolecular Lanthanide-Based Gel and Xerogel Systems: Towards Efficient White Light Emitting Materials

Luminescent materials play a pivotal role in modern technological applications, from display screens to bio-imaging. Among these, white light emitting materials have garnered significant interest due to their versatile utility. While various approaches have been explored to achieve white light emission, supramolecular gels present distinctive advantages owing to their viscoelastic properties and facile processability. Lanthanide-based systems, renowned for their characteristic photoluminescence, offer a promising avenue for generating white light. In this study, we propose the incorporation of lanthanides into supramolecular gels to create efficient white light emitting systems. Our methodology allows for rapid synthesis at ambient conditions, distinguishing it from existing methods that often require complex procedures or elevated temperatures. Preliminary investigations on two such systems have shown that it is indeed possible to achieve white light emitting gels using a sensitizer, a facially amphiphilic surfactant and three carefully chosen metal ions. The present work involves optimization of these components in order to develop white light emitting xerogels.

This work underscores the potential of supramolecular gels as platforms for developing advanced luminescent materials with diverse applications.

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Engineering luminescent lanthanide on chitosan thin films: A possible new age band-aid materials

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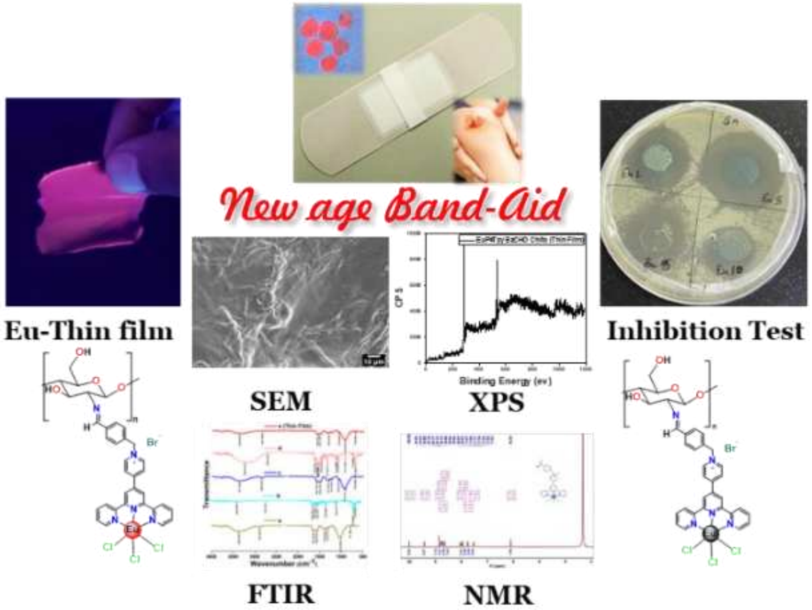
Stimuli-responsive light-emitting materials are of great interest owing to their potential use in encryption, multilevel security and biomedical applications. Stable chitosan thin films can be promising substrates for creating materials. Herein we present a novel method to synthesize flexible self-standing films consisting of Europium complexes functionalised with aldehyde that are used to append using Schiff base reaction with free amine on the chitosan surfaces. Comprehensive characterization employing FTIR, NMR, XPS, SEM, UV-spectroscopy, and fluorescence spectroscopy was conducted to elucidate the structural and optical properties of these films. The films are biodegradable and biocompatible (low cytotoxicity for HaCaT cells). These luminescent thin films can be integrated into drug delivery systems, enabling real-time monitoring of drug release and distribution within the body via imaging. Additionally, these films were used for triggering therapeutic properties (anti-microbial) and thus could be used as a new age band-aid material.



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Supramolecular self-assembly for light harvesting application

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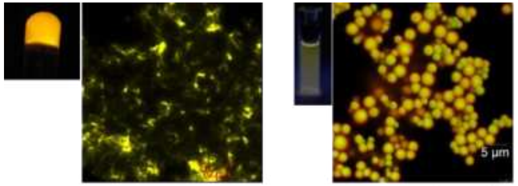
Abstract: Multiple components self-assembled supramolecular assembly formed by various non-covalent interactions has attracted attention for developing materials with advanced functional properties. Charge transfer (CT) interaction-based co-assemblies/co-crystals are enormously getting investigated for intriguing biological, photocatalytic, and luminescence properties. Artificial light harvesting self-assembly has attracted attention as a synthetic mimic of the natural photosynthesis process and supramolecular soft materials, metal organic framework (MOF), inorganic-organic hybrid materials *etc.* are reported for developing light harvesting systems. In our work, supramolecular light-harvesting hydrogel and microspheres are developed by directional, non-covalent interactions of multiple components. In the light harvesting hydrogel, energy transfer was observed from sensitizer to green emitting Tb(III) to red emitting Rhodamine B dye. Whereas, emitting co-assembly was formed from the charge transfer interaction of the bis-naphthyl dipicolinic amide (DPA) derivative as donor and tetracyanobenzene as an acceptor. The generation of green emission was observed from the charge transfer interaction of donor and acceptor. Crystal structural analysis of the co-crystal shows the alternative pi-pi stacking arrangement of DPA and TCNB. The green luminescent microspheres were further doped with red emitting dye, and energy transfer was observed from green CT complex to red pyronin Y dye. These materials can be interesting for further applications in optoelectronics and sensing.



RhB doped TbCholate Xerogel

Pyronin Y doped CT microsphere

Figure: Confocal microscopic images of light harvesting hydrogel and charge transfer co-assembly

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Efficient aerobic oxidation of biomass derived alcohols over Magnesium-chromium-based hydrotalcite materials

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Currently, there's a surge of interest in converting lignin model compounds, especially those with alcohol functionality, into valuable products such as cinnamaldehyde, veratraldehyde, and vanillin.[1] Consequently, there's a pressing need to develop and assess a catalyst that is structurally and thermally stable while also being highly recoverable and reusable.[2] Hydrotalcite (HT) is a type of material made up of divalent and trivalent metal ions arranged in octahedral sheets with anions between them. It shows promise as a catalyst or support for different organic transformations. HT-based multi-metal oxides, including those containing transition metals, exhibit both acid-base and redox properties. For example, chromium-based hydrotalcite has strong basic properties because the Cr^{3+} ions are bigger and have similar electronegativity, which makes it suitable for alcohol oxidation reactions. [3]

In this study, we systematically investigated the solvent-free oxidation of benzhydrol using a series of MgCr-HT catalysts, both molybdate intercalated and molybdate free. Various MgCrMo catalysts with different concentrations of molybdate loading (0.014, 0.05, 0.1, and 0.15) were prepared. The presence of the layered HT structure was confirmed through powder XRD, while interlayer molybdate was detected via FT-IR and XPS studies. Structural morphology was further analyzed through SEM and TEM analysis.

The resulting catalysts were then evaluated for the oxidation of benzhydrol as model compounds. Optimum reaction conditions led to a maximum conversion of benzhydrol (97%) with exclusive selectivity towards benzophenone, achieved using the MgCrMo(0.15) catalyst. Extending the study to biomass-derived alcohols, namely cinnamyl alcohol and 3,4-dimethoxybenzyl alcohol, showed comparable catalytic activity.

In summary, the molybdate-stabilized MgCr-HT catalyst demonstrated potential, stability, and efficacy in converting alcohols into value-added products while maintaining its activity over five reaction cycles.

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Synthesis and Characterisation of Stable Metal-Radical Complexes by EPR Spectroscopy

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Abstract:

Transition metal complexes have garnered significant research attention due to their intriguing electronic and magnetic properties. Among these, stable complexes[1] stand out, offering insights into their structural and spectroscopic characteristics through techniques like Electron Paramagnetic Resonance (EPR) and elucidation of the molecular structure by refining SC-XRD data. EPR spectroscopy is a precious tool for characterizing unpaired electrons of both radicals and paramagnetic transition metal complexes. The assistance from signal fitting tools is inevitable regarding the cognizance derived from EPR spectroscopic analysis. This abstract provides an outlook into various stable metal-radical complexes and EPR spectral analysis methodology, focusing on signal fitting through simulation using EasySpin[2] based on MATLAB software (Figure 1). This integrated approach achieves a deeper understanding of the electronic structure and magnetic behaviour of the stable metal-radical complexes various radical ligands, offering valuable insights for applications in areas such as catalysis and molecular electronics.

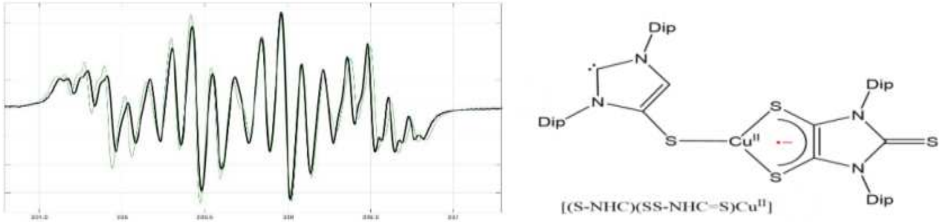

Figure 1. Experimental (dark black line) and simulated (green line) EPR spectra of complex [Cu^{II} (S-NHC)(SS-NHC=S))] at room temperature in THF.

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Room Temperature Synthesis and Low Thermal Conductivity in Nanocrystalline Ag_3CuS_2

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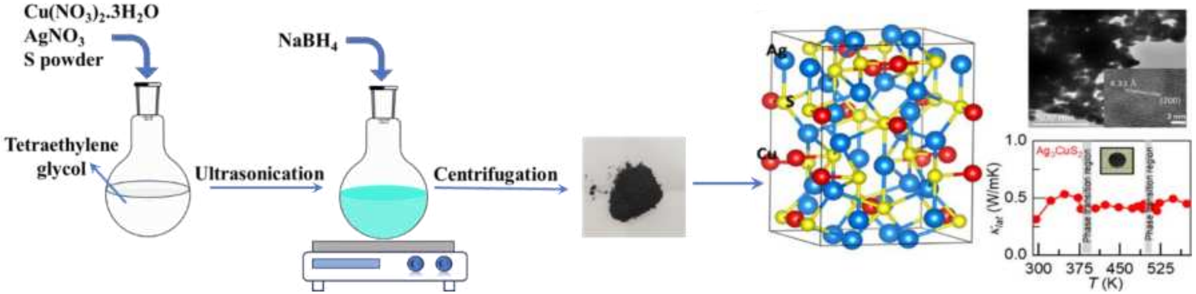
Nobel metal-based chalcogenides have been recognised as an important class of materials in the recent past in the field of thermoelectrics. These materials are typically synthesised by i) high-temperature solid-state reactions and ii) soft chemical methods where temperature requirements are lower than those of solid-state reactions (generally below 400 ºC). Herein, we present a facile surfactant-free, room-temperature and scalable synthesis of nanocrystalline Ag_3CuS_2. The as-synthesised spark plasma sintered (SPS) sample exhibits ultralow thermal conductivity of ~0.31 W/m.K at room temperature, which is lower than its bulk counterpart. To comprehend such low thermal conductivity, we carried out sound velocity and low-temperature heat capacity measurements. We found that Ag_3CuS_2 exhibits low sound velocity (~1124 m/s at room temperature). Moreover, the analysis of low-temperature heat capacity data shows non-Debye-like behaviour and indicating the presence of three low-energy Einstein modes. The synergistic effects of lattice anharmonicity, low-energy localized vibrational modes, and nanoscale grain boundary scattering leads to low thermal conductivity in Ag_3CuS_2. Such a low thermal conductivity material could be useful for optoelectronics, thermal barrier coating, and thermoelectric applications.

Figure or Scheme



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Synthesis, characterization, and catalytic evaluation of glucopyranosylamine-derived Mo(VI) complex toward organic sulfide oxidations

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A new glucopyranosylamine-derived ditopic ligand (bis(4,6-O-ethylidene-β-D-glucopyranosylamine)-1,4-dihydroxy-2,5-dibenzylidene (H_6L)) and it's coordinatively flexible dinuclear octahedral molybdenum complex ($(MoO_2)_2H_2L(D)_2$, (D = solvent)) has been synthesized. Recrystallization of the complex from dimethylformamide (DMF) yielded single crystals of coordination polymer (CP) $[(MoO_2)_2H_2L(DMF)]_n$, where the sixth coordination sites are occupied by Glu-OH3 and DMF. The solution-state studies revealed the presence of a discrete system, while the solid-state studies supported the polymeric nature, which is backed by density functional theory (DFT) calculations. To the best of our knowledge, this is the first report on the polymeric molybdenum complex of glucopyranosylamine-derived ligand (Figure 1). The experimental spectral data of Mo-complex matches with the theoretically generated spectra/values within the accepted range. The quantum chemical calculation for cooperative effect (ν_{ce}) revealed the affinity of both the metal centers for the ligand's electron density, causing the

largest weakening of the axial bond formed by the solvent molecule. This fact has been further evaluated experimentally by exploring the catalytic aspects of the dinuclear Mo(VI) complex.

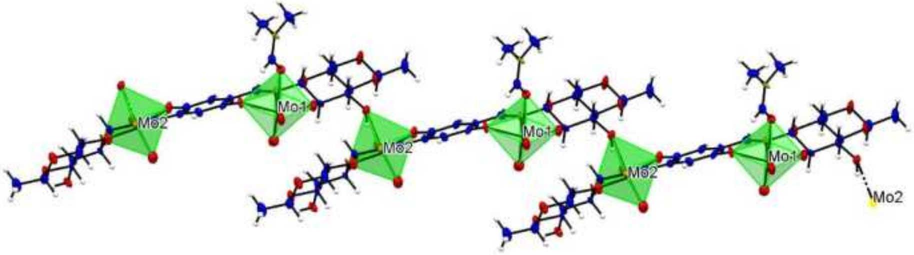

Figure 1: 1D-Coordination polymer $[(MoO_2)_2H_2L(DMF)]_n$

Exsolved Ni-Ru Alloy from Nickel-Ruthenium co-doped $SrFeO_{3-\delta}$ Perovskite: A Potential Hydrogenation Catalyst

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Perovskite oxides are a fascinating group of mixed metal oxides with the general formula ABO_3 and enormous potential as ferromagnetic, energy storage, and catalytic materials. Partial substitution of appropriate cations at the A or B sites produces multi-component perovskites ($A_{1-y}A'_yB_{1-x}B'_xO_3$) with variable structures and properties compared to its pristine oxides.[1] Strontium ferrite ($SrFeO_3$) is an important family of perovskite with tuneable physicochemical properties and promising applications in diverse fields.[2] The doping of different transition metals on B sites of $SrFeO_{3-\delta}$, stabilises the perovskite structure and potentially improves the properties of the materials. Under the reducing environment at high temperature, the availability of B-site metal ions on the perovskite surface has been enhanced by the exsolution process, thereby improving the performance of the particular reaction.

In the present work, the synthesis of Ni and Ru co-doped $SrFeO_{3-\delta}$ ($SrFe_{1-x-y}Ni_xRu_yO_{3-\delta}$) perovskite materials were achieved through sol-gel combustion followed by annealing treatment.[3] The resulting materials exhibited a cubic perovskite structure, and the introduction of Ni and Ru dopants led to an expansion in the unit cell. The exsolution of a bimetallic alloy nanoparticle from Ni and Ru co-doped $SrFeO_{3-\delta}$ was analysed through various characterisation techniques such as XRD, XPS, and TEM. The exsolution process resulted in the formation of

Ni-Ru alloy well-dispersed on brownmillerite structure ($Sr_2Fe_2O_5$). The active Ni-Ru species formed from $SrFe_{0.9}Ni_{0.05}Ru_{0.05}O_{3-\delta}$ catalyst exhibit better catalytic performance in the hydrogenation of furfural, a biomass model component. The uniform distribution of Ni-Ru species on oxygen deficient perovskite support facilitates the conversion of furfural (99%) with 91% furfuryl alcohol selectivity.

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Computational Investigation of Strong Ferromagnetic Coupling between Metal and Odd Electron (Anti)aromatic Radicals

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Researchers have long been fascinated by the challenge of designing and understanding innovative magnetic molecules applicable across diverse practical domains such as spintronics, quantum information science, and organic electronics. Unlike aromatic systems, antiaromatic molecules exhibit characteristics of having (4n) π-electrons within planar, cyclic, and conjugated organic frameworks. Numerous investigations have been dedicated to unravelling the significance of aromaticity and antiaromaticity concepts in understanding organic compounds, particularly regarding their stability and reactivity. However, the odd electron systems are still questionable about their aromatic and antiaromatic behaviour.

In this work we aim to understand the interaction between the odd electron aromatic or antiaromatic radicals with cobalt to understand the magnetic interaction between them. We have used density functional theory-based methods to calculate the magnetic exchange coupling constant between the molecules and metals. The Yamaguchi formulae has been used to calculate the magnetic interaction. Our findings indicate that all the metal radical complexes show strong ferromagnetic interaction. Frequency analysis reveals that the one of our radical undergoes a transition state structure in the absence of Co metal but becomes stabilized upon the addition of Co metal atom. We have also investigated the non-covalent interaction between the metal and the radical molecules.

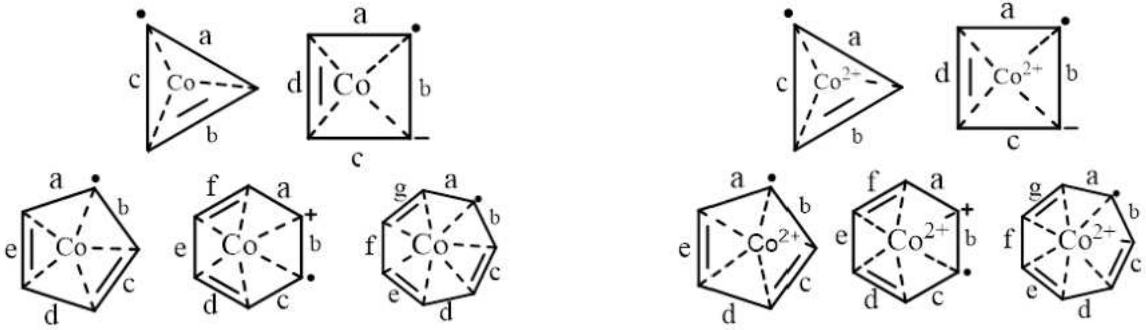

Figure. The structure of the radical complexes with neutral and charged Cobalt atom.

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Eco-friendly Single component white light emissive trivalent Europium complex: combined experimental and theoretical study

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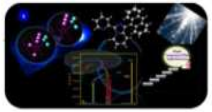
Abstract:

Eco-friendly white light emitting diodes (including solid state lightings) are highly in demand and especially single-component white-light emissive luminogens are an economical and simplistic selection for phosphor-converted white light emitting diodes (pc-WLEDs)[1]. In this context, purposefully designed ligand (structurally characterised) and metalated with trivalent europium ions along with energy harvesters (TTA & DBM). The photophysical study reveals these complexes showed white light emission in the solid as well as solution state (CIE x = , y = , and x = , y = , respectively). DFT and TD-DFT calculations were utilised to understand the energy transfer processes from complexes to the ligands. Taking advantage of this emission behaviour we have fabricated white LEDs as well as studied the thermometer applications. The fabricated LEDs showed excellent performance ("eye-friendly"). The detailed photophysical properties will be discussed.

Figure



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Chirality Generation in a Nickel(II) Square Planar Complex Supported by a Dipyrromethane-based Tetradentate Ligand

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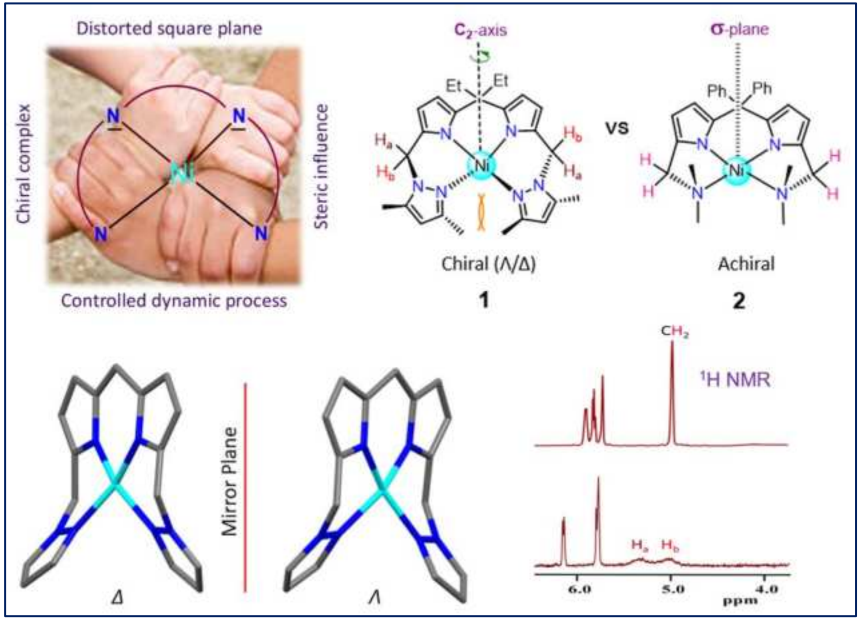
Square planar complexes are normally achiral owing to the existence of a plane of symmetry (σ) through their square planes. However, if the planes are somehow distorted by any means the complexes become chiral. Here, we present two nickel(II) square planar complexes supported by two similar dipyrromethene-based tetradentate ligands [1,2] containing the same donor atoms. The complexes are synthesized and characterized by spectroscopic as well as crystallographic techniques. The steric demand of the bulkier 3,5-dimethylpyrazole groups in one ligand distorts the nickel square plane so as to result in helical stereoisomers (Δ and Λ), while the smaller dimethylamine groups in another ligand offer achiral complex. Their solution behaviours are consistent with the solid-state structures as monitored by ^{1}H NMR spectroscopy. The complex **1** displays a broad AB quartet type signal for the methylene protons whereas complex **2** shows a single resonance for the same.



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An Extended Rudolph Diagram: B_3H_5 and $B_3H_6^+$ relate 3D-, 2D-boron allotropes and boranes

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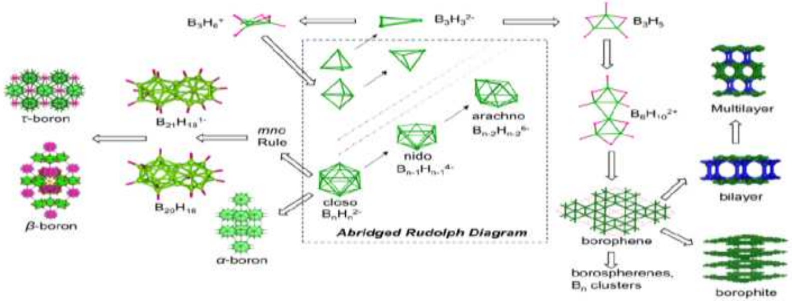
Abstract: After 155 years of the Periodic Table of Elements, one would imagine that the structural principles that explain the relationship between the elements and their compounds are well known. While this is true for most elements, boron remains as a difficult exception. I have been searching for an understanding of the structures of boron 3D allotropes, and 2D allotropes (borophenes) and compounds of boron for more than 50 years. Partial answers to these questions were found after 30 years of unrelenting efforts when a relationship between polyhedral boranes and beta-rhombohedral boron could be established.[1] Another 20 years of resolute search has brought us an understanding of 2D-boron such as borophenes and the idea of Extended Rudolph Diagram that relates both the 3D- and 2D-boron allotropes to polyhedral boranes.[2-5] Details of these finding will be presented. SERB-DST is acknowledged for funding through the Year of Science Chair Professorship.



Extended Rudolph Diagram

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Structural Phase Transition and Interesting Magnetism of Ni Intercalated NbS_2 ($0 \leq x \leq 0.5$)

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Layered materials, particularly, layered transition metal dichalcogenides (TMDs) have generated huge research interest due to their exotic two-dimensional physical properties and structural diversity. The layered TMDs have hexagonal layered structure in which a layer of metal atoms covalently bonded to two layers of chalcogens (X-M-X, X = S, Se, and Te, M = Any Metal atom). In this work, we intercalated Ni in the NbS_2 system ($0 \leq x \leq 0.5$) at 1000 °C, in which guest species Ni accommodates octahedral vacancies of the van der Wall gap. Intercalation on NbS_2 noticed significant changes in the structural, magnetic properties compare with pristine NbS_2. The 2H phase is obtained in the composition range of ($0.15 \leq x \leq 0.5$), while pristine NbS_2 forming 3R phase. From Ni_xNbS_2 magnetic studies with different intercalant compositions noticed peculiar types of magnetic behaviour. Moreover, Ni_xNbS_2 ($x = 0.1$) exhibited superconductivity with T_c 7.9 K which is higher than reported pristine NbS_2 T_c 5.7 K, while $Ni_{0.2}NbS_2$ showing the Anti-Ferromagnetic behaviour with transition temperature of 78.5 K (Neel temperature). From Raman spectroscopy studies detected new stretching vibration peak of Ni-S at 284.6 cm^{-1} which means Ni strongly interacted with the host NbS_2 layer. XPS studies confirmed corresponding elements oxidation states.

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Temperature Programmed Reduction: A Method for Stabilisation of Inorganic Framework Materials

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Zeolites are prominent catalysts in sustainable processes like reforming, cracking, and isomerization within the petrochemical and biomass conversion sectors [1,2]. Notably, large-pore zeolites, exemplified by the ultrastable, rare earth-incorporated Faujasite type Zeolite-Y, are extensively utilized in fluid catalytic cracking processes within petrochemical industries [3]. However, materials like SAPO-37, which share a similar pore architecture and moderate acidity akin to Zeolite-Y, face limitations due to their poor structural stability in template-free form [3]. In this study, we propose a method to enhance the stability of the Faujasite framework in SAPO-37 through temperature-programmed reduction. To retain the Fajuasite framework, instead of removing the template by calcination, we use it as a carbon source to make metal carbides when different heteroelements, such as molybdenum, tungsten, and zirconium, are present. This approach yields a functional material exhibiting improved structural stability and catalytic activity. According to our findings and evidence from powder XRD and SEM analysis, the Faujasite framework of SAPO-37 remains intact even after treating at temperatures as high as 550 °C. The nitrogen sorption isotherm observed is a type I in nature and is

characteristic of the microporous zeolite framework. The resultant molybdenum (oxy) carbide loaded SAPO-37 was found to be the potential for the synthesis of methyl tertiary butyl ether with a yield of 83% under ambient conditions. The catalytic activity and faujasite framework remain intact for several catalytic cycles. This method can be extended to stabilise non-stable inorganic frameworks.

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Self-Assembly of a Water-Soluble Pd_{16} Square Bicupola Architecture and its Use in Aerobic Oxidation in Aqueous Media

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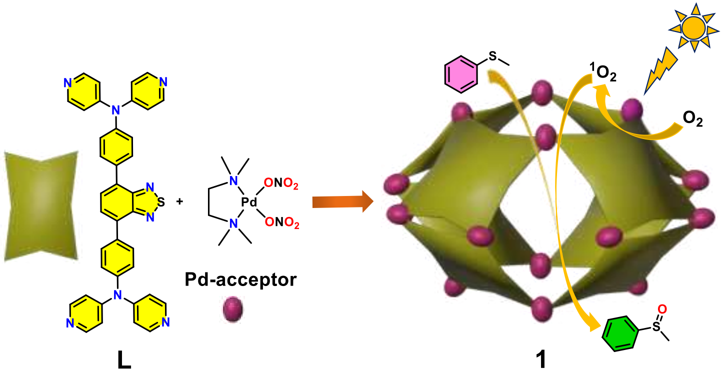
Designing supramolecular architectures with uncommon geometries has always been a key goal in the field of metal-ligand coordination-driven self-assembly. It acquires added significance if functional building units are employed in constructing such architectures for fruitful applications. In this report we address both these aspects by developing a water-soluble $Pd_{16}L_8$ coordination cage **1** with a unique square orthobicupola geometry, which was used for selective aerobic oxidation of aryl-sulphides. Self-assembly of a benzothiadiazole-based tetra-pyridyl donor **L** with a ditopic cis-[(tmeda)Pd$(NO_3)_2$] acceptor [tmeda=N,N,N′,N′-tetramethylethane-1,2-diamine] produced **1** and the geometry was determined by single crystal X-ray diffraction study. Unlike the typically observed tri- or tetra-facial barrel, the present $Pd_{16}L_8$ coordination assembly features a distinctive structural topology and is a unique example of a water-soluble molecular architecture with square-orthobicupola geometry. Efficient and selective aerobic oxidation of sulphides to sulfoxides is an important challenge as conventional oxidation generally leads to the formation of sulfoxide along with toxic sulfone. Cage **1**, designed with a ligand containing benzothiadiazole moiety, demonstrates an ability to photo generate reactive oxygen species (ROS) in water, thus enabling it to serve as a potential photocatalyst. The

cage showed excellent catalytic efficiency for highly selective conversion of alkyl and aryl-sulphides to their corresponding sulfoxides, therefore without the formation of toxic sulfones and other byproducts, under visible light in aqueous.



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Silver Catalysed Direct Benzylic sp^3 C-H Bond Oxidation: A facile Synthesis of Aldehyde

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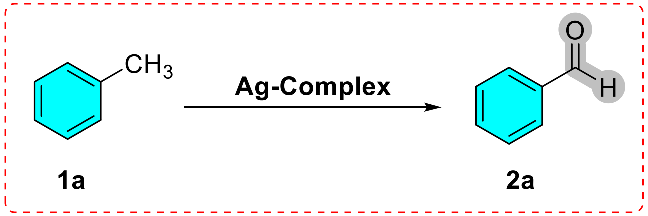
An efficient silver catalysed method was developed for the direct oxidation of benzylic C_{sp3}-H bond under open condition. High chemo- and regio-selectivities were observed for the desired products including highly challenging strong electron-withdrawing functionalities. Method was applicable for the oxidation of toluenes to aldehydes.



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SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL ACTIVITY OF ACETOPHENONE DERIVED SCHIFF BASE AND ITS Fe(III) COMPLEX

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Schiff bases are adaptable substances that may be used to create ternary complexes. A test was conducted to create an entirely novel Fe(III) compound. In this instance, L-valine served as the secondary ligand and the primary ligand or Schiff base was created by a condensation reaction between 4-methyl acetophenone and hydroxylamine hydrochloride. Condensation of primary and secondary ligands with iron salt produced a significant complex. The traditional reflux technique was used to carry out the reaction. The newly created ligand has strong antibacterial efficacy against particular bacterial and fungal species. Researchers may have a big chance here, and one special area of study that will receive future attention is the utilization of biological applications of new molecules that have been synthesized.The medical and pharmaceutical industries benefit greatly from the biological variety of acetophenone derivatives. Valine amino acids also have antibacterial and antifungal properties in addition to these molecules. Elemental analysis, molecular weight estimation, magnetic moment measurement, melting point estimation, spectrum analysis (IR, UV-Vis, 1H NMR, Mass, etc.), and X-ray diffraction were used to characterize the synthesized ligand and complex. The complex that was created was non-electrolytic and paramagnetic. The octahedral geometry of the complexes is suggested by the UV-Vis, FTIR, NMR, and mass spectra. Further testing of the synthesized chemicals in biological research against certain bacterial and fungal strains was done. According to research,most complexes have been shown to have stronger antibacterial action than ligands.

Keywords: 4-methyl acetophenone, Schiff bases, Hydroxylamine hydrochloride, L-valine, Antibacterial, Antifungal

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Cavity-Shape Dependent Divergent Chemical Reaction Inside Aqueous Pd_6L_4 Cages

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The structure of a molecule plays a key role in determining its property. For example, the catalytic properties of enzymes depend heavily on its three-dimensional structure. Molecular hosts are often termed as the artificial analogue of such enzymes as they can catalyze reactions with similar efficiency as shown by enzymes. The most well studied of such hosts are the ones formed by metal-ligand based self-assembly. Although many such reactions are known, the use of such cages toward the divergent synthesis of non-isomeric products have not been well explored. Divergent synthesis is a technique of forming two or more distinct products from the same reagents by changing the catalyst or reaction conditions. Changing the shape of the cage can also change the nature and magnitude of the host–guest interactions. Thus, is it possible for such changes to cause differences in the reaction pathways leading to formation of non-isomeric products? Herein, we report a divergent chemical transformation of anthrone [anthracen-9(10*H*)-one] inside different water-soluble $\mathbf{M_6L_4}$ cages. When anthrone was encapsulated

inside a newly synthesized **M_6L_4** octahedral cage **1**, it dimerized to form dianthrone [9,9′-bianthracen-10,10′(9*H*,9′*H*)-dione]. In contrast, when the same chemical reaction was performed inside a **M_6L_4** double-square shaped cage **2**, it was oxidized to form anthraquinone [anthracene-9,10-dione]. The present report demonstrates a unique example of different outcomes/results of a reaction depending on the shape of the molecular container, which was driven by the host–guest interactions and the preorganization of the substrates.[1]

Figure 1. Divergent synthesis using the different structural analogues of M_6L_4 cages.

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Spectroscopic characterization, reactivity of a Cu(III) species supported by a proline-based pseudo peptide and effect of Lewis acid

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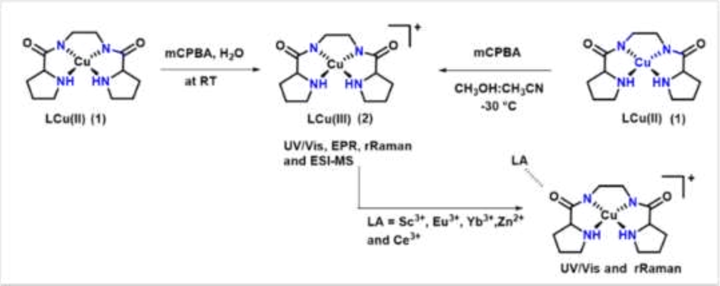
Inspired by the copper-based metalloenzymes, we intend to incorporate amino acids into our ligand system that enable us to have active copper intermediates, that serve as a structural and functional model for the enzymes. Herein, we discuss the synthesis of a C_2 symmetric proline-based pseudo peptide LH_2 (N,N'-(ethane-1,2-diyl)bis(pyrrolidine-2-carboxamide)) that supports the formation of LCu(III) *via* a (L)Cu(III)-OH intermediate in MeOH:CH_3CN (1:20) at -30 ˚C. From the comparative studies with the pyridine analog Cu(II) complex, it was manifested that incorporation of amino acid in the ligand framework reduces the Cu(III)/Cu(II) redox potential significantly, to react readily with *m*CPBA (Scheme 1). The generated LCu(III) is characterized by various spectroscopic techniques like UV/Vis, EPR, NMR and ESI-MS.[1] Since most of the functional activity of these metalloenzymes in nature takes place in water, wee tried to generate the species in water and succeeded in these effort. The generated LCu(III) can perform hydrogen atom transfer and electron transfer reactions. We further explored the effect of redox inactive Lewis acids like Sc^{3+}, Eu^{3+}, Yb^{3+} and Zn^{2+} on the stability and the reactivity of LCu(III) species. In the presence of LA the redox potential of Cu(III)/Cu(II) increased by 0.4 V. Remarkably, addition of redox active Ce^{3+} causes the decay of Cu(III), to form a distinctive



dimeric Cu(II) species. The binding of LA to the amide oxygen of pseudo peptide was confirmed by the UV/Vis and resonance Raman spectroscopy where the band of C=O vibration shifted upon LA addition. It is noteworthy to mention that the species discussed here is one of the active intermediates proposed in catalytic cycles of the Dopamine β monooxygenase (DβM) and Peptidylglycine alpha-hydroxylating monooxygenase (PHM) enzymatic.[2,3]

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Synthesis, Characterization, and Application Studies of Anionic Dithiolene Radical Ligand-based Metal Complexes

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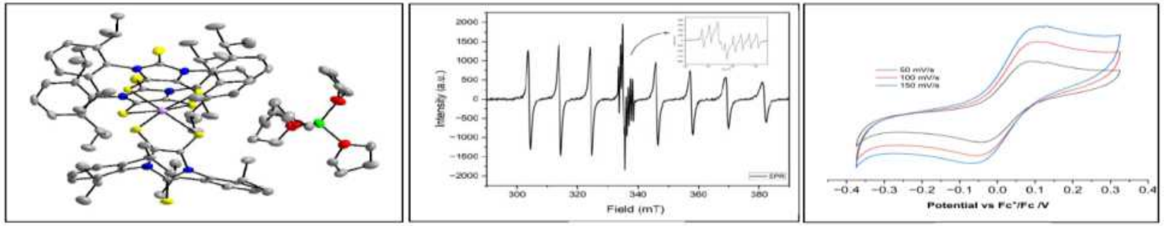
Abstract:

This work digs into the multifaceted properties of novel air and moisture sensitive transition metal complexes with anionic dithiolene radical ligand[1]. This focuses on the synthesis and characterization of the metal complexes, utilizing techniques such as SC-XRD, IR, EPR, CV, and UV. Due to their radical nature they exhibit significant redox property[2] as well. They show attractive cyclic voltammetry highlighting its redox reactivity, which can be harnessed for catalytic and sensing applications. Anticipated outcomes foresee significant contributions to fields such as single molecule magnets (SMMs)[3] and polymerization catalysis, marking a substantial advancement in the utilization of dithiolene radical ligand chemistry.



(a) (b) (c)

Figure 1: (a) Single crystal X-ray diffraction picture of the complex [Li(THF)$_4$][VL$_3$]. **(b)** EPR spectra of [Li(THF)$_4$][VL$_3$] at room temperature. **(c)** Cyclic voltammogram of the complex. [L= Anionic dithiolene radical ligand]

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Proton-assisted activation of a Mn^{III}−OOH for aromatic C−H hydroxylation through a putative [Mn^{V}=O] species

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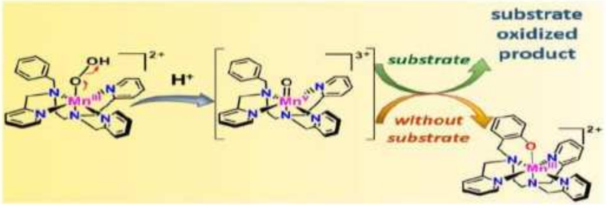
Abstract:

Nature has primarily employed transition metals, particularly 3d metals, in the metalloenzymes as they are relatively abundant, biocompatible, and redox-active.[1] Among all 3d metals, iron and manganese exhibit versatile oxidation states, which nature exploits in biological catalysis to achieve many vital chemical transformations.[2] These include Cytochrome P450, Bleomycin, manganese superoxide dismutase (MnSOD), and catalase, to name a few.[3] Inspired by such fascinating metalloenzymes, synthetic models involving M-peroxo, M-hydroperoxo, M-oxo, etc are being developed. Synthetic nonheme, both low spin and high spin Fe^{III}-OOH complexes are well explored in the literature as sluggish oxidants.[4] Unlike iron, however, Mn^{III}-OOH hydroperoxo species have not been much explored. In the present work, adding $HClO_4$ to the $[(BnTPEN)Mn^{III}\text{-}OO]^+$ in MeOH generates a short-lived Mn^{III}-OOH species, which converts to a putative Mn^{V}=O species. The potent Mn^{V}=O species in MeCN oxidizes the pendant phenyl ring of the ligand in an intramolecular fashion. The addition of benzene causes the formation of (BnTPEN)Mn(III)-phenolate. These findings suggest that high valent Mn species have the potential to catalyze challenging aromatic hydroxylation reactions.



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Immobilized Enzyme on Metal Organic Framework for Leather Applications

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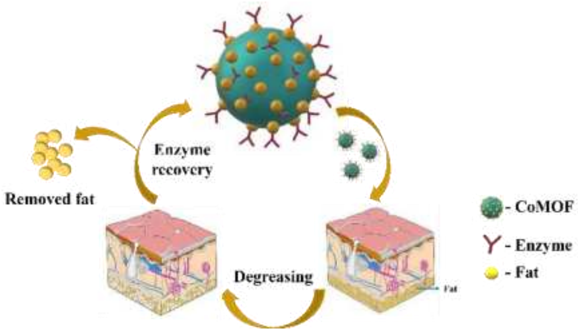
Leather processing involves multiple stages, with enzyme-based methods increasingly replacing chemical processes to mitigate environmental impact.[1] In the degreasing stage, lipase enzymes are utilized to remove fatty substances under alkaline conditions, enhancing hide flexibility. However, challenges arise as enzymes cannot be recovered post-process and can cause grain damage due to uncontrolled reactivity. Enzyme immobilization on solid substrates enhances enzyme stability, better recovery, and reusability of enzymes, for which, zeolites, activated carbon, mesoporous silica, nanoparticles and metal organic frameworks (MOF) are used as solid supports for enzyme immobilization.[2] MOF is porous crystalline structure consisting of metal cations and multidentate organic linkers. Here, alkaline stable Co_3O_4@CoMOF (CoMOF) were prepared as a solid support for lipase immobilization, and studied for its efficiency and recyclability over degreasing application. The prepared CoMOF and enzyme immobilized CoMOF were characterized using different spectroscopic and microscopic techniques. The degreasing application of the CoMOF-Enz were analysed. The fat removal efficiency was estimated using Soxhlet method and the CoMOF-Enz was effective up to four recycles with supplementary addition. From this it can be inferred that the application of enzyme immobilized MOF acts as a sustainable approach for leather applications.



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Novel Heterogeneous Magnetic Pd-NHC Catalyst for Sustainable Nitroarene Reduction and Buchwald-Hartwig Amination

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The development of efficient synthetic protocols for arylamines has always been a quest for several industries, as they are widely used structural motifs in medicines, agrochemicals, and high-performance materials. The traditional synthetic routes often rely on multi-step procedures and harsh reaction conditions and generate significant waste, raising serious concerns about environmental impact and cost-effectiveness. Palladium catalysts have emerged as powerful tools for constructing C-N bonds, particularly in the context of Buchwald-Hartwig amination.[1] The advent of Pd-NHC (N-Heterocyclic Carbene) complexes supported on magnetic nanoparticles opened a new window for a wide range of organic transformations due to their ease of handling, reusability, and recyclability.[2,3] Herein, we present the successful synthesis of a novel eco-friendly magnetic palladium catalyst incorporated on NHC functionalized Fe_3O_4@MCM-41 nanoparticles. The NHC ligand precursor and nanocatalyst were characterized by FT-IR, LC-MS, NMR, SEM-EDX, XRD, and XPS techniques. The thermal stability and surface area were studied using TG-DTA and BET analysis. This work demonstrates the unique properties of the catalyst to facilitate both nitroarene reduction and Buchwald-Hartwig amination effectively. The excellent yield of the product, broad substrate scope and functional group tolerance highlight the catalyst's

potential to enhance the sustainability and efficiency of arylamine synthesis. The facile magnetic separation and reusability of the catalyst, coupled with the use of environmentally benign solvents, underscores the sustainable nature of this work, aligning with the principles of green chemistry.

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Group VIII Metal Decorated Inorganic Framework Materials: A Potential Catalysts for Hydrotreating of Biomass Model Components

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Hydrotreating biomass to reduce the oxygen content and convert it into fuel additives and value-added products is a green route to sustainable development in society. Inorganic framework materials, like zeolites, have three-dimensional pore structures, large surface area and uniform distribution of active sites, which have the potential for petroleum, petrochemical and biomass refineries and catalytic transformation of biomass molecules.1,2 The catalyst stability and the reactivity were enhanced by the introduction of group VIII metal ions.1,2 Among the Group VIII metals, ruthenium and nickel facilitate hydrogen spillover due to the suitable electronic and geometric factors. In this regard, nickel and ruthenium species are loaded into various supports, viz., layered zeolite like ITQ-2, large pore zeolites like zeolite-b, MCM-22.1,2 This work focuses on the development of less expensive nickel and ruthenium decorated ITQ-2, Zeolite-b, MCM-22, etc., on hydrotreating of biomass model component, *m*-cresol to value-added chemicals. The deoxygenation/decarboxylation of heavier carboxylic acid has also been studied using developed materials. The representative results are tabulated in Table 1. In summary, group VIII metal-decorated zeolites are demonstrated as the potential for the conversion of biomass to platform chemicals.

Table 1 Results for conversion of biomass model compounds over developed catalysts

Hydrotreating of *m*-cresol to methyl cyclohexane			
Catalyst	Reaction conditions	Con. (%)	Sel. (%)
5 wt% Ru loaded Zeolite-β	170 °C/ 10 bar H_2 for 8 h in IPA	100	100
20 wt% Ni loaded ITQ-2	170 °C/ 20 bar H_2 for 6 h in dodecane	100	100
Deoxygenation of heavier carboxylic acid to hydrocarbon			
Catalyst	Reaction conditions	Con. (%)	Sel. (%)
5 wt% Ru loaded Zeolite-β	200 °C/ 13 bar H_2 for 24 h in octane	59	95
5 wt% Ru loaded MCM-22	200 °C/ 13 bar H_2 for 24 h in octane	100	60

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Synthesis, characterization, antimicrobial and anticancerous studies of Mn(II) & Hg(II) bridging complexes

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Morpholine, a six membered heterocyclic ring with both amine and ether functional groups is viewed as good building block in medicinal Chemistry. The oxygen atom present in its structure is the main reason behind its bioactivity and interactions as a donor acceptor molecule through which it forms strong complexes with its targets.The reactions has synthesized new transition metal complexes Mn[$C_{10}H_{16}O_2N_2S_4$]. Hg[$C_{10}H_{16}O_2N_2S_4$] of sodium morpholine dithiocarbamate ligand and characterized by FTIR , UV-Visible, $_1$HNMR, $_{13}$C-NMR Physiochemical Techniques. Finally the synthesized metal Complexes were examined for antibacterial, antifungal, and also received attention in search for a novel anticancer drug. On the basis of spectral studies results indicate that dithiocarbamate ion allows the formation of strong bridging complexes with Mn(II) and Hg(II) ions with reduced tendency to dative π bond formation from metal to sulphur atom. The complexes under investigations have shown good Biocidal properties as well as complexes are promising Chemotherapeutic alternatives in the search of anticancer agents.

Acknowledgement Authors are thankful to the Department of higher Education UP Government Lucknow, India for financial Support under R & D Scheme.

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Dimethyl sulfoxide promoted quinazolinone synthesis

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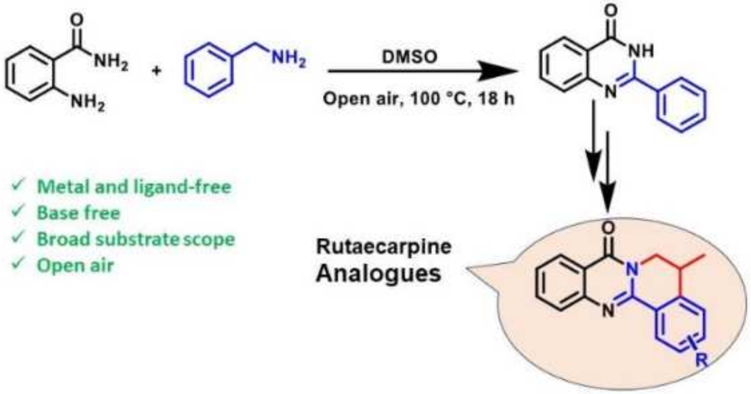
We report a highly efficient method of synthesizing quinazolinone derivatives in dimethyl sulfoxide (DMSO) using 2-aminobenzamide and benzylamine through aerobic oxidation in open-air conditions, affording good-to-excellent yields. A simple pathway, broad substrate scope, no additional catalysts and bases, and environment-friendly mild reaction conditions are the main attributes of this synthesis. The synthesized quinazolinone derivatives were then used to produce pharmaceutically active rutaecarpine analogs using a two-step reaction: N-alkylation followed by intramolecular cyclization.



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A Metal-Free, Amination of 1,2-Diaza-1,3-dienes Using Hydrazine Hydrate through *N-N* bond cleavage

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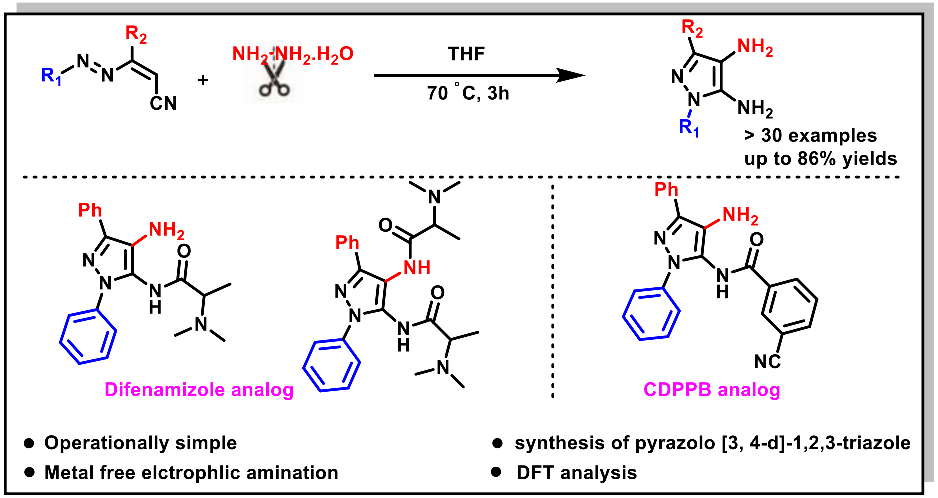
Herein, we have developed a metal-free, atom-economical, intrinsically sustainable approach for synthesizing unprotected 4,5-diamino pyrazoles from readily available 1,2-diaza-1,3-dienes. This approach utilizes inexpensive hydrazine hydrate as the aminating source. Further, we have explored the reactivity of 4,5-diamino pyrazole to synthesize fused pyrazolo[3,4-*d*]-1,2,3-triazole heterocyclic compounds. We have also successfully demonstrated the synthetic utility of this methodology in synthesizing two drug analogs: analgesic difenamizole and anti-psychotic CDPPB. With the aid of control experiments and density functional theory (DFT) computational studies, we elucidated the role of the phenyl ring in 3-substituted-1,2-diaza-1,3-diene.



- Operationally simple
- Metal free elctrophlic amination
- synthesis of pyrazolo [3, 4-d]-1,2,3-triazole
- DFT analysis

Scheme: Synthesis of unprotected 4,5-diamino pyrazoles from 1,2-diaza-1,3-dienes.

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Halogen-free oxidation of aryl ketones and benzyl nitrile derivatives to corresponding carboxylic acids by using NaOH/ TBHP in aqueous medium

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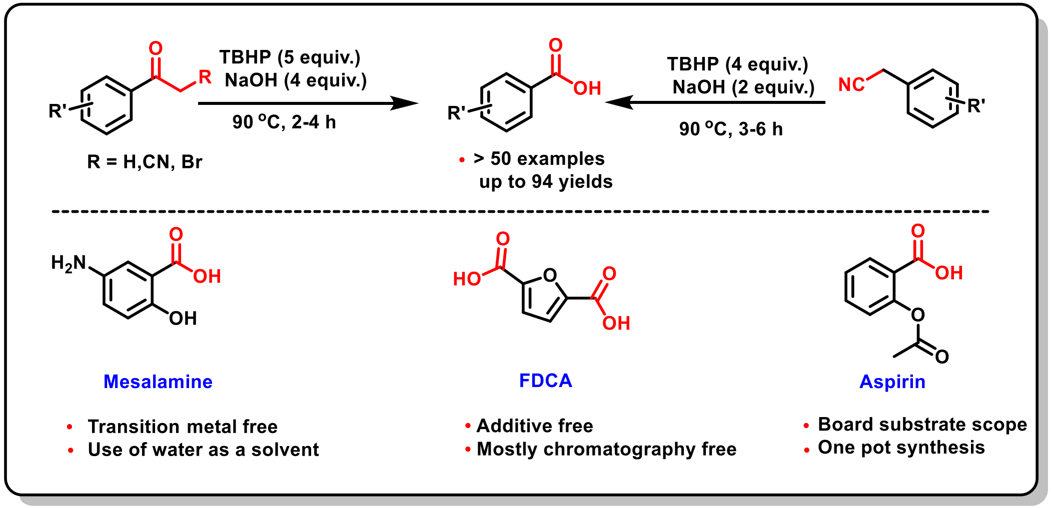
Using inexpensive NaOH as the base and aq. TBHP (70 %) as the oxidant, we have developed an efficient oxidative methodology for converting aryl ketones and benzyl nitrile derivatives to their corresponding acids in good yields. During the reaction, it was revealed that base is essential for the oxidation to corresponding acids. Control experiments and the mechanistic investigation suggested radical mechanisms operating for oxidation. Broad substrate scope and graceful scaling up are additional features of this economical, additive-free, metal-free method that uses green solvent. Salicylic acid, 5-nitrosalicylic acid, anthranilic acid, aspirin terephthalic acid, and furan dicarboxylic acid (FDCA) are a few significant acid derivatives that can be accessed using this approach for industrial and pharmacological purposes.



Scheme: Synthesis of benzoic acid derivatives from aryl ketones and benzyl nitriles.

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Isoxazole as a Nitrile Synthon: *En Routes* to the *Ortho*-Alkenylated Isoxazole and Benzonitrile with Allyl Sulfone Catalyzed by Ru(II)

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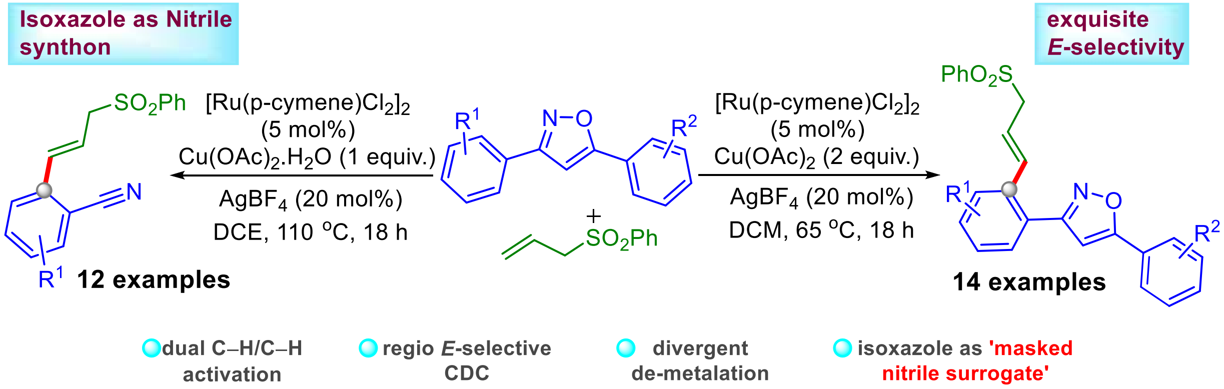
A Ru(II) catalyzed regioselective Heck-type C–H olefination of isoxazole with unactivated allyl phenyl sulfone is revealed. The solvent DCM offers dual sp^2–sp^2 C–H activation *via* an *N*-directed strategy, leading to *ortho*-olefinated isoxazoles with exclusive *E*-selectivity. On the other hand, in DCE solvent, isoxazole serves as the nitrile synthon and leads to *o*-olefinated benzonitrile. At a higher temperature (110 °C) in DCE, after the *ortho*-olefination Ru(II) mediated cleavage of isoxazoles delivered the nitrile functionality. Both the products were formed with good yield. In both conditions, reactions took place smoothly at 1 mmol scale. A plausible reaction mechanism involving *N*-directed *ortho* C−H activation was proposed which is supported by control experiments.



Figure/Scheme: A Ru(II) catalyzed solvent-switched divergent de-metalation divulges *E*-selective *o*-olefinated isoxazoles and *o*-olefinated benzonitriles from isoxazoles and unactivated allyl phenyl sulfones.

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Synthesis of Quinazolinone Scaffolds *via* Zinc(II) Stabilized Amidyl Radical Promoted Deaminative Approach

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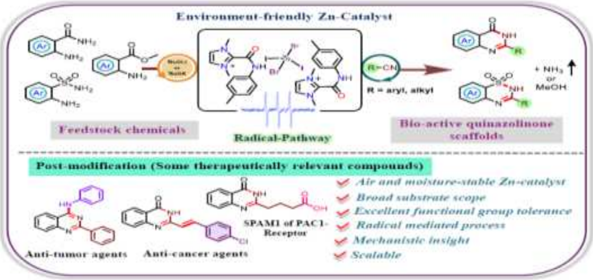
Abstract:

The C-N bond is one of the most important and prevalent bonds in nature, hence, development of better ways to generate C-N bonds has become one of the vital research objectives in synthetic chemistry.[1] In this context, N-heterocyclic scaffolds like quinazolinone indeed hold a significant position due to their versatile presence in several fields such as agrochemicals, pharmaceuticals, natural products etc.[2] In this line, herein, we report a solely ligand-based redox controlled effective deaminative protocol for the coupling of *o*-amino amides/esters with nitriles to afford quinazolin-4(3*H*)-ones, for the first time, utilizing C2-amidated imidazolium salt supported Zn-compound.[3] This readily scalable solvent-free protocol works proficiently under low catalyst loading for a broad range of *o*-amino amides including sulfonamides and nitriles, ranging from benzonitrile to benzyl cyanide and also the aliphatic nitriles, with high level of functional group tolerance to provide the desired products possessing medicinally relevant scaffold in high yields Importantly, detailed mechanistic probes established the reaction pathway that proceeds *via* aminyl radical formation. Further, the synthetic utility of the obtained products was showcased by their post-modification to access therapeutically relevant complex organic molecules.



Schematic representation of the present work

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Visible-Light-Mediated Difluoroalkoxylation of Imidazo[1,2-*a*]pyridines

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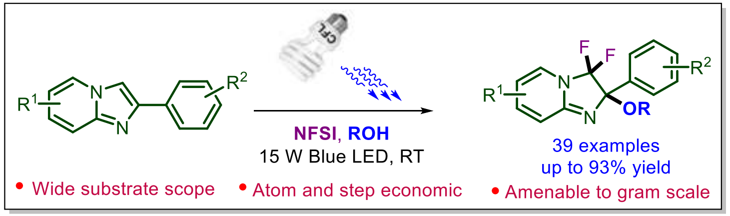
Imidazo[1,2-*a*]pyridine is an interesting fused *N*-heterocyclic moiety with significant applications in medicinal chemistry.[1] This moiety is found in several marketed drugs such as Necopidem and Saripidem (treat anxiety and insomnia), Zolpidem, Alpidem (sedative and hypnotic), Minodronic acid (for the treatment of osteoporosis), Olprinone and GSK812397 (CXCR4 receptor antagonist).[2] Because of their wide range of applicability, their site-specific mono-functionalization has attracted considerable interest of organic chemists, but the difunctionalization of imidazo[1,2-*a*]pyridine nucleus remains less explored. On the other hand, organofluorine compounds play vital roles in pharmaceuticals, pharmacology, agrochemistry, materials science, and electrochemistry. Incorporating fluorine atom into an organic compound can significantly improve their pKa, lipophilicity, membrane permeability, metabolic stability, bioavailablity, and protein-ligand interactions.[3] A wide range of electrophilic, nucleophilic and radical-based fluorinating agents including Selectfluor, NFSI, DAST, Dexo-Fluor^{TM}, TBAF etc. have been used for the mono-fluorination of organic compounds[4] but geminal difluorination is very less explored.

With our interest in the functionalization of imidazo[1,2-*a*]pyridines,[5] we have developed a metal-free visible light-promoted site-selective difluoroalkoxylation of imidazo[1,2-*a*]pyridines using *N*-fluorobenzenesulfonimide (NFSI) as a fluorinating agent (Scheme 1). This practical reaction has a wide range of substrate scope for both imidazo[1,2-*a*]pyridines and alcohols to give 3,3-difluoro-2-alkoxy-2-arylimidazo[1,2-*a*]pyridines in good to excellent yields. The reaction proceeds at room temperature, showed high functional group tolerance and was amenable for scale-up. Details of the protocol will be presented in the poster.



Scheme 1. Geminal-difluoroalkoxylation of imidazo[1,2-*a*]pyridines using NFSI.

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Direct Access to Trifluoromethylated Benzo[*d*]oxepines from *o*-Alkynylaryl Aldehydes and Trifluorodiazoethane

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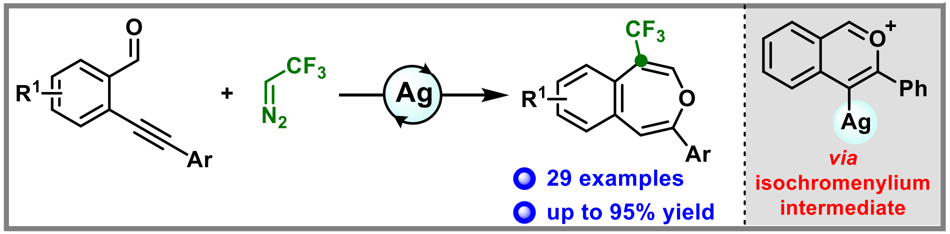
Trifluoromethylated scaffolds are ubiquitous in pharmaceutics and agrochemicals as the presence of trifluoromethyl group can significantly improve the physicochemical and biological properties of the organic molecule.[1] In this regard, trifluorodiazoethane (CF_3CHN_2) has emerged as an expeditious reagent for the swift construction of vital CF_3-containing subunits.[2] Consequently, our efforts in harnessing the reactivity of CF_3CHN_2 led to the synthesis of various relevant trifluoromethylated heterocycles such as 3-trifluoromethyl 1,2,3-triazolines, 3-trifluoromethylpyrazoles, and 4-trifluoromethylquinolinones.[3] Although considerable research has been devoted to the exploration of trifluorodiazoethane in the construction of trifluoromethylated five- and six-membered rings, practical approaches for the construction of medium-sized rings utilizing trifluorodiazoethane remain obscure. We developed a silver-catalyzed reaction between *o*-alkynylaryl aldehydes and trifluorodiazoethane to enable straightforward access to trifluoromethylated benzo[*d*]oxepines. The reaction proceeds via a silver-promoted 6-endo-dig cyclization of *o*-alkynylbenzaldehydes followed by ring-expansive addition of trifluorodiazoethane to deliver a novel class of trifluoromethylated benzoxepine frameworks.[4]



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Amine Functionalized Bifunctional Co^{III}-NHC Complexes: Highly Effective Phosphine-Free Catalysts for the α-Alkylation of Nitriles

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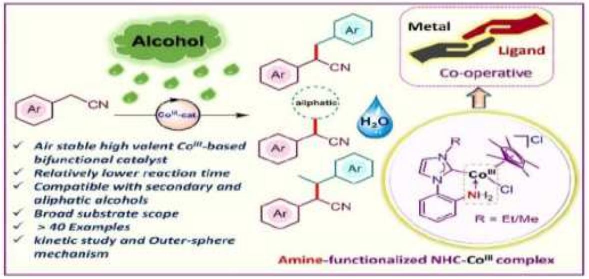
Abstract:

α-Alkylated nitriles find various applications in synthetic organic chemistry e.g. readily convertible into diverse functional groups (amines, amides, carboxylic acids etc.) that are used as key synthons for making various drug molecules and biologically active compounds.[1] Herein, we reported a highly effective protocol for the alkylation of nitriles using a plethora of alcohols, ranging from aliphatic to aromatic and intriguingly, both primary and secondary *via* a robust bifunctional Co^{III}-catalyst system utilizing amine functionalized NHC ligand is presented.[2] Further, comparison of the activity of these cobalt-NHC systems in the α-alkylation of nitriles with alcohols uncovered extremely high activity of the bifunctional complexes, whereas the non-bifunctional analogues were found to be essentially inactive for secondary alcohols. Moreover, an array of control experiments including the deuterium labelling one established the present catalytic cycle, following a "Borrowing Hydrogen" protocol, that proceeds *via* an outer sphere bifunctional reaction mechanism. Finally, the kinetic studies revealed that the reaction is first order with respect to nitrile and catalyst.



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One-pot synthesis of triarylamine using a sequential Pd-catalyzed C-N cross-coupling

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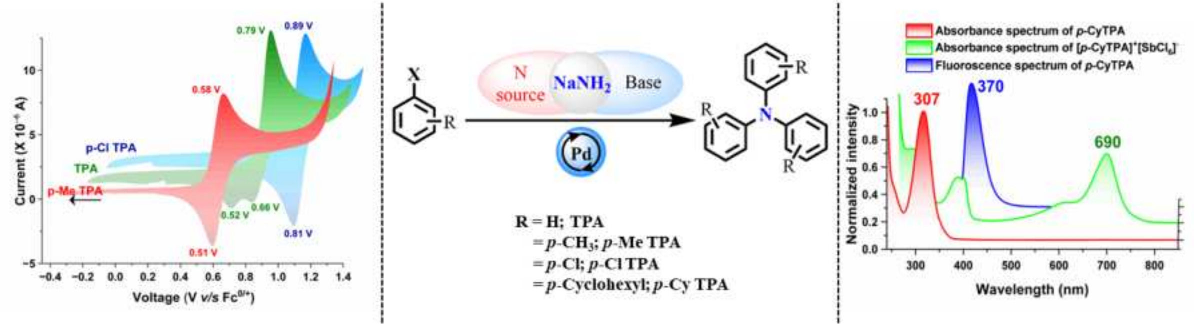
Triarylamines (TAAs) are core structures for various functional materials in the field of photocatalysts, redox mediators, polymers, solar cells, and supramolecular chemistry[1]. The well-explored method is transition metal-catalyzed C–N cross-coupling between aryl halide and 1° or 2° amines using an additional base. However, it needs the pre-designed 1° or 2° amines and a base, NaO^{t}Bu. The C–N coupling of aryl halides with NH_3 or $LiNH_2$ was studied to the extent of 1° and 2° amine synthesis[2]. One-pot synthesis of these triarylamines from feedstock materials is inevitable. The $NaNH_2$, which can act as a nitrogen source and base simultaneously, could be a better alternative for NH_3/$LiNH_2$ because of its cost-effectiveness and handling. The Pd_2dba_3/Xantphos catalytic system exclusively furnishes triarylamine from aryl bromides and $NaNH_2$ under optimized conditions. The *para-substituted* or *meta-*

substituted aryl bromides give triarylamine products, resulting in moderate to excellent yield. At the same time, *ortho*-substituted aryl bromides lead to only diarylamine products. The mechanistic investigation and control reaction suggest that triarylamine products are formed by three sequential C–N coupling reactions between aryl bromide with $NaNH_2$, *in-situ* formed 1° amine and 2° amine. The post-synthetic modification allows the synthesis of functionalizable synthetic intermediates and further photophysical and electrochemical studies that showed substitution-based patterns in optical and redox properties[3].



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(Benz)imidazo[1,2-a]quinolinium Salts: Access *via* Unprecedented Regiospecific non-AAIPEX Strategy and Study of Their Tunable Properties

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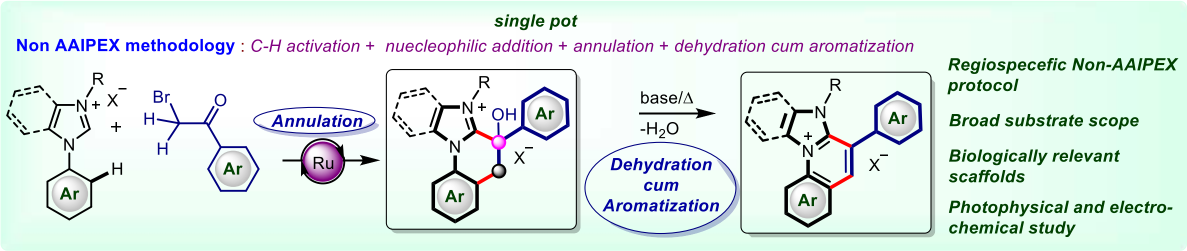
Recently, the π-extended polycyclic heteroaromatic compounds (PHACs) including the azolium fused heterocycles have greatly attracted the attention of synthetic chemists for their broad applications in optoelectronics and DNA intercalation. Such derivatives are generally synthesized following the well-established annulative alkyne-insertion π-extension (AAIPEX) strategy.[1-2] An unprecedented non-AAIPEX protocol has been developed to access diverse monosubstituted cationic poly heteroaromatic compounds (cPHACs) from the readily available azolium salts and phenacyl bromides *via* Ru(II)-catalyzed tandem annulation cum aromatization. This atom-economic protocol executes a range of intermediate steps e.g. double C-H activation, nucleophilic addition, annulation, and dehydration cum aromatization in one-pot manner under the generation of H_2O as the sole byproduct.[3] Moreover, the systematic tunability of photo-physical and electrochemical properties of these new class of cPHACs can be authenticated from the DFT calculated frontier molecular orbital energies that might be beneficial for their potential applications in optoelectronics and DNA intercalation.



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Room-Temperature Phosphorescence Triggered by Surface Coating in Flexible Organic Crystals for Futuristic Applications

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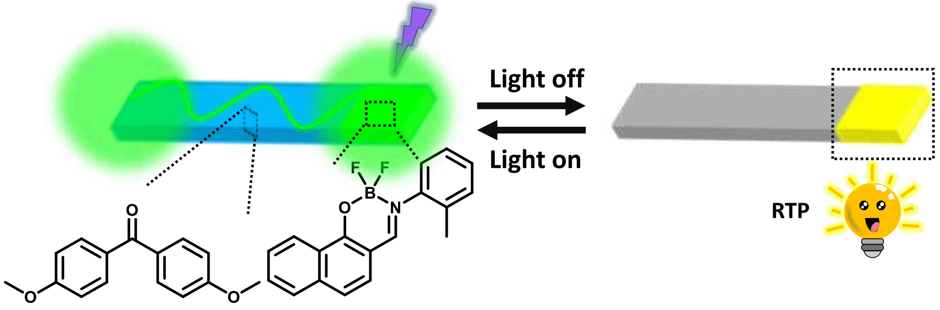
Phosphorescent materials play a pivotal role in a myriad of display technologies. In contrast to their inorganic counterparts, organic phosphorescent materials offer distinct advantages stemming from facile synthetic routes, customizable emission spectra via functionalization, and higher energy efficiency.[1] Because of their unique optical and mechanical properties, flexible, room-temperature phosphorescent (RTP) organic single crystals will be beneficial in fabricating flexible electronic devices. Recently, host-guest doping or halogenation has been reported to impart RTP in single crystals.[2] However, the incorporation of heavy metals is potentially toxic, and halogenated compounds are typically prone to photobleaching. Thus, developing heavy atom and metal-free RTP flexible organic crystals is highly desired. Herein, we present a strategy based on surface coating for obtaining RTP. Detailed investigations revealed that energy transfer was crucial in the RTP process. Furthermore, a combination of RTP and flexible mechanical properties resulted in tuneable optical waveguide properties. Finally, using these properties, flexible single crystals were utilized for anti-counterfeiting applications with multi-level safety features. Combining

unique features such as mechanical flexibility, RTP, and optical waveguiding in a single system makes these crystals ideal for future advanced optical security devices.



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Accessing axial chiral formamides from amino acid derivatives through radical decarboxylative coupling

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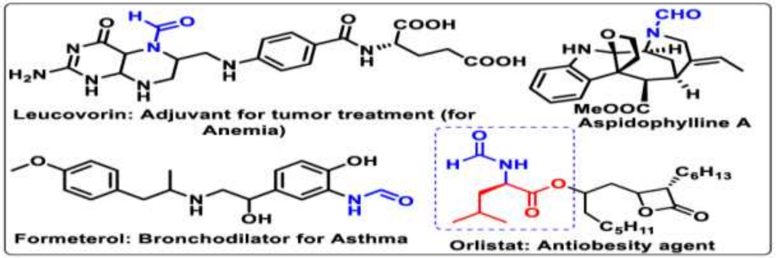
Abstract: Amides are basic structural blocks in biological system, and they are backbone of all natural peptides and proteins. Out of the thirty-seven new drugs approved by the FDA in 2022, eleven small molecules contains ***at least one amide bond*** and nineteen large molecules approved as new drugs, with peptide structures. ***Formamides*** are ubiquitous and important structural motifs that widely exist in natural products, pharmaceuticals as well as functions as key intermediates for the synthesis of heterocycles with antibiotics and cancer chemotherapeutic agents such as orlistat, leucovorin, and formoterol. Moreover, ***axially chiral amides*** are good ligands for asymmetric synthesis. Herein, we have accomplished a simple, transition metal free and efficient methodology for N-formylation of amino acids with glyoxylic acid by H_2O_2 mediated decarboxylative coupling in excellent yields. Notably, N-Formylated leucine moiety is found in Orlistat, a clinically running drug for the treatment of obesity. The reaction worked well for different ferrocenyl protected amino acid derivatives which could function as hybrid material for medicinal and electrochemical applications.



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A Synthetic Route to Polyheterocyclic *spiro*-Oxindoles via Friedel-Craft type *C*-3 Alkylation/Pictet-Spengler Reactions of Indoles with *spiro*-Epoxy oxindoles/ Aldehydes, and Study of their *three*-Photon Absorption *non*Linear Properties

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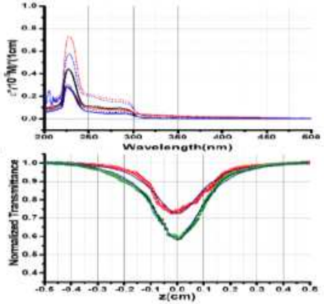
Abstract: One-Pot two-step synthetic route to polyheterocyclic *spiro*-oxindoles by Lewis-acid catalyzed Friedel-Craft type C-3 alkylation of Indoles via nucleophilic ring-opening of *spiro*-epoxy oxindoles in a regioselective fashion, followed by *p*-TSA catalyzed Pictet-Spengler reaction in *6-endo-trig* fashion with aldehydes has been reported. A study of their *three*-photon absorption *non*linear properties has been reported. To the best of our knowledge, we are the first going to demonstrate that two diastereomeric pair may have different *three*-Photon Absorption *non*Linear Properties. The scope and generality of our protocol have been demonstrated by the synthesis of 19 diastereomeric pairs and the study of their *three*-photon absorption *non*linear properties.



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Rh(III)-Catalyzed Controlled Amidation of Primary Amides Using Dioxazolones: En Route Synthesis of *Ortho*-Amidated Arylamides

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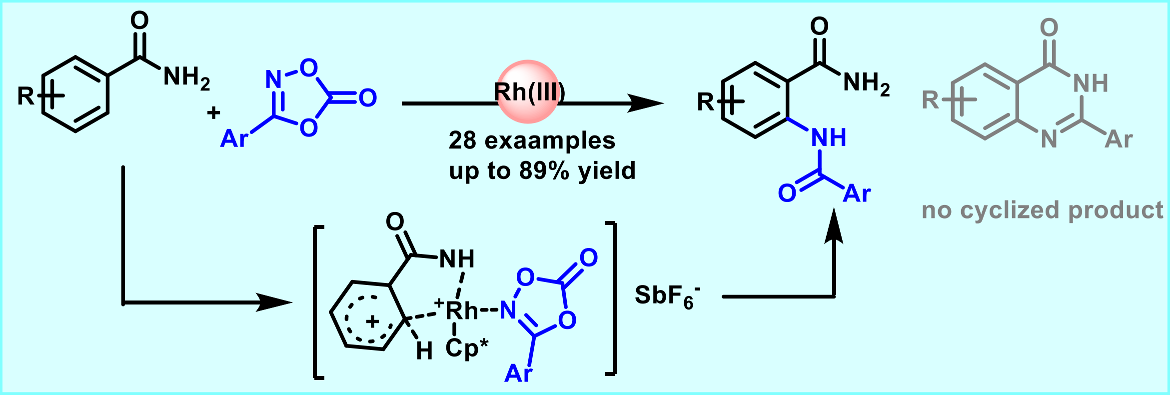
The *ortho*-amido-substituted arylamide derivatives belong to the important class of organic molecules as they serve as an important structural unit in several natural products, bioactive molecules, and key intermediates in numerous active pharmaceutical ingredients. Owing to their usefulness, their synthesis *via* a faster and more economical route was desired. Hence, we hereby developed a synthetic process for the controlled introduction of amide units at the *ortho*-position of an electron-deficient arylamide system without affording any cyclized products utilizing user-friendly dioxazolone as an amidating reagent in the presence of Rh(III)-catalyst. This is the first report where native primary amide has been utilized as a weakly coordinating group for site-selective C-N bond formation, leading to the synthesis of desired *ortho*-amido-substituted arylamide. The developed protocol works under external auxiliary-free conditions with a wide substrate scope. Some of the appealing features of this protocol include the controlled introduction of amide motifs, scale-up synthesis, useful synthetic transformation, and no cyclized product formation.



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Visible light mediated selective synthesis of Allyl-Aryl Sulphoxides

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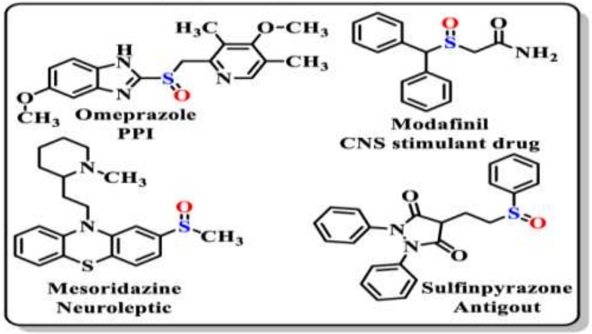
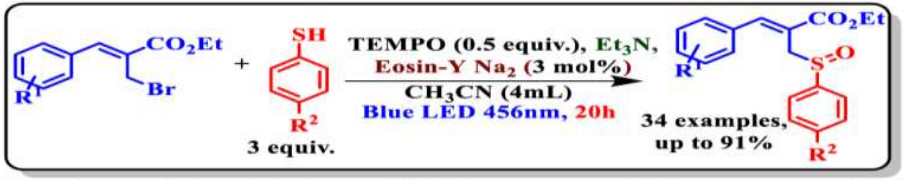


Sulphoxides are major class organosulfur compounds used as chiral auxiliaries and important intermediates in organic transformations. Also, sulfoxide plays a significant role in medicinal chemistry especially, medicinally important drugs for proton pump inhibitors (Omeprazole, Pantoprazole), Anti-psychotics (Modafanil), anti-inflammatory (Sulindec) contain sulfoxide as a functional group. Many sulfur containing drugs get metabolized by converting to sulfoxides in the first step of the metabolism pathway. Among them, allylic sulfinyls or sulfones, display widespread distributions in biologically active molecules and received increasing attention in the past few years. Herein, we have accomplished a simple visible light mediated protocol for the synthesis of allyl sulfinyls in excellent to moderate yields from Morita–Baylis–Hillman (MBH) adducts and thiols under mild conditions which proceeds through a controlled oxidation of the initially formed allyl aryl sulphide. Eosin Y disodium salt is used as a photocatalyst, and TEMPO used as oxidizing agent. A plausible mechanism is proposed to rationalize the radical sulfinylation.



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Organophosphine-Promoted Cascade Ring Opening/Recyclization of Cyclopropyl Ketones

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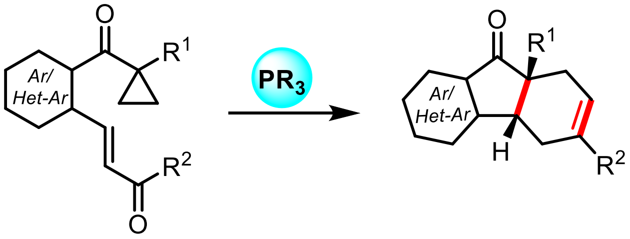
The ring-reorganizing transformations of activated cyclopropanes are typically achieved under acidic conditions or transition metal catalysis.[1] Here, we report the first acid-free and Lewis base-mediated cascade ring opening/recyclization of designed cyclopropyl ketones to access tetrahydrofluorenones[2]. We rationally merged the nucleophilic features of phosphines with the electronically biased cyclopropanes to synthesize several new classes of hydrofluorenones. We have also demonstrated the synthetic utility of the products in accessing highly functionalized molecular scaffolds.



First Lewis base-promoted ring opening of cyclopropyl ketones
one pot homoconjugate/Michael/Wittig reaction cascade
Several post-synthetic modifications to natural product-like structures

Scheme 1. Phosphine-promoted ring opening/recyclization of designed cyclopropyl ketones

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Photodecarboxylative Radical Cascade Involving *N*-(acyloxy)pthalimides: Synthesis of Pyrazolones

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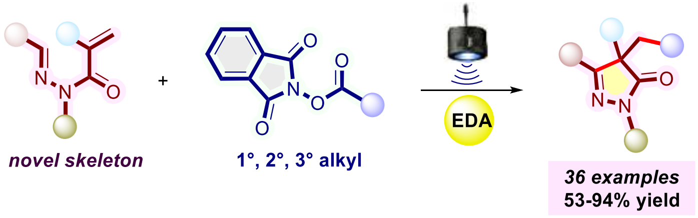
Pyrazolones belong to the class of *N*-heterocycles with high medicinal importance as well as building blocks of various pharmacophores.[1] Although various methods have been devised for synthesizing 2-pyrazoline-5-ones, traditional methods often require harsh reaction conditions, expensive toxic additives, and precious metal catalysts.[2-3] Therefore, the development of a facile and environmentally benign protocol in this realm needs to be addressed. On the other hand, *N*-(acyloxy)phthalimides, which can be easily synthesized from feedstock carboxylic acids, have been used predominantly as an effective alkylating source for direct functionalization as well as the construction of various heterocycles.[4-6] Accordingly, we have designed a novel scaffold and put forth a well-curated radical cascade strategy for synthesizing alkylated Pyrazolones employing *N*-acyloxypthalimides as alkyl radical precursors under photoinduced conditions.[7] This reaction unveils a mild and efficient pathway for synthesizing a diverse array of alkylated pyrazolones armed with various functionalities incorporating drugs and natural products.



▪ robust and mild condition ▪ broad scope and scalable

▪ transition metal free ▪ applicable on drugs and natural products

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Palladium Catalysis Enabled Sequential C(sp^3)−H/C−C Activation: Access to Vinyl *γ*-Lactams

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A Pd(II)-catalyzed tandem reaction of aliphatic amides with vinylcyclopropanes has been accomplished by merging C(sp^3)−H and C−C activation. The reaction of VCP revealed alkenylation/cyclization followed by ring opening *via* C−C cleavage, delivering vinyl *γ*-lactams with (*E*)-selectivity. The role of ligands, site-selectivity, functional group diversity, mechanistic insight, and synthetic utilities are important practical features.

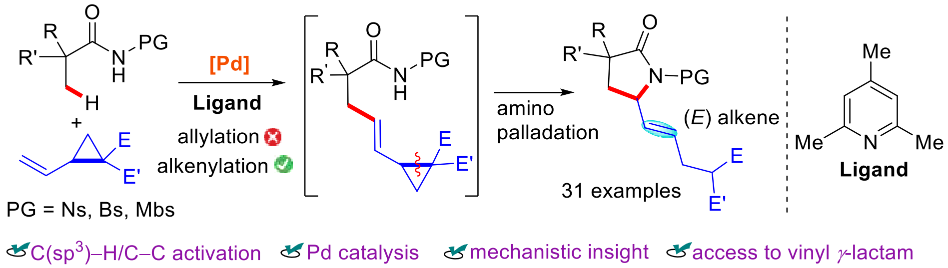

Figure: Merging C(sp^3)−H/C−C Activation with VCP

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Barman, M.; Mishra, M.; Mandal, S.; Punniyamurthy, T. ***Org. Lett.*, 2024**, DOI: 10.1021/acs.orglett.4c00710.

Photochemical Decarboxylative Formylation of Indoles with Aqueous Glyoxylic Acid Under Basic Condition

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Abstract:

Several formylation reactions of aromatic or heteroaromatic compounds have been reported in recent decades, owing to their usage in natural products and in drug discovery. The indole C-3 formylation is a significant reaction in synthetic chemistry as the carbonyl groups can easily perform the C–C and C–N coupling reactions as well as oxidation and reduction reactions. Herein, we execute a transition-metal-free and oxidant-free photo-chemical decarboxylative formylation of indoles with 50% aqueous glyoxylic acid as a formyl synthon, which proceeds in good to moderate yields. A simple visible light mediated protocol with Eosin Y disodium salt is used as a photocatalyst under basic condition. A possible decarboxylative formylation mechanism with radical pathway was proposed.

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Regioselective Annulation and Hydroarylation of Allenylphosphine Oxides with Ruthenium and Cobalt Catalysts

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Organophosphorus compounds are fundamental in bioactive molecules, drug candidates, and functionalized materials.[1] Consequently, their efficient synthesis remains in the focus of general interest.[2] We have leveraged the innate reactivity of allenylphosphine oxides in ruthenium and cobalt catalyzed C–H bond activation reactions of aromatic compounds. Under ruthenium(II)-catalysis, allenylphosphine oxides were coupled with aryl hydroxamic acid esters in the form of (4+2) annulation to forge NH-free isoquinolinones in high yields.[3] By exploiting cobalt(III)-catalysis, we have accomplished the reversed regioselectivity in the insertion step, offering C-7 and C-2 functionalized indolines and indoles, respectively, where a mechanistically distinct metal-π-allyl pathway is operating. The details of this orthogonal reactivity will be presented at the conference.

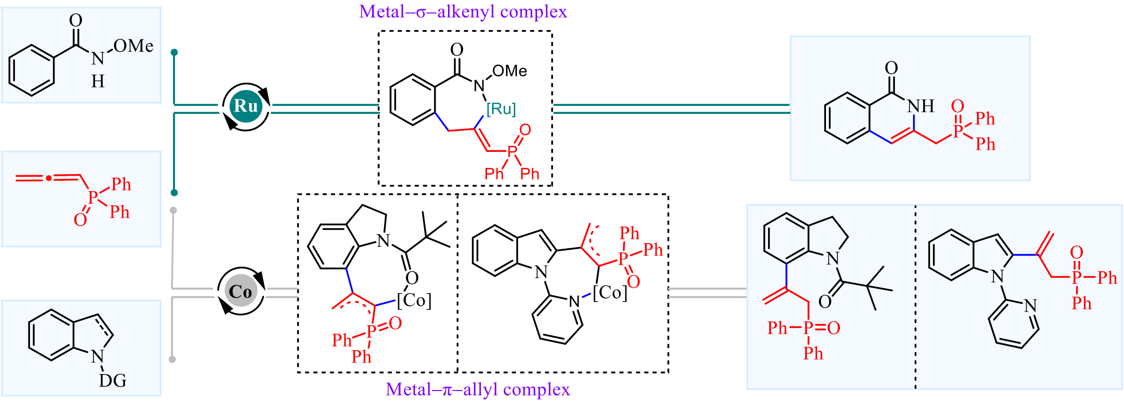

Figure 1: Taming of allenylphosphine oxides with ruthenium and cobalt catalysts.

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One-pot synthesis of *N*-(α-aryl/ α-phosphonyl/*O*-silyl)alkyl sulfoximines/sulfonimidamides

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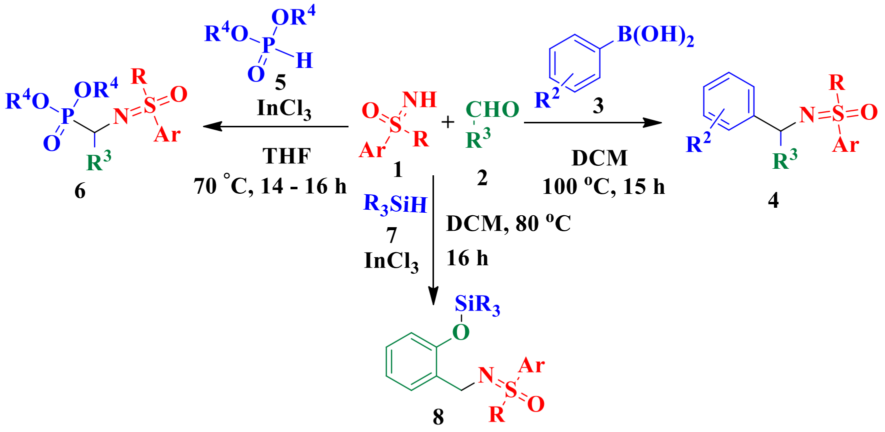
Sulfoximines, the aza-analogue of sulfones, with a S(VI) (stereo)centre, received tremendous attention in the field of synthetic and medicinal chemistry for quite long time due to the unique functionality and bio-activities. Especially, *N*-alkyl sulfoximines were used in many bio-active molecules as the nitrogen substituents led to the modification of significant properties, such as molecular dimensions, acidity and H-bonding capabilities. Consequently, several methods were developed to derive *N*-alkyl sulfoximines. Which involved the use of strong bases and phase transfer catalysts to enhance the nucleophilicity of the imino group of sulfoximines. Additionally, none of the methods discussed the preparation of *N*-(α-substituted)alkyl sulfoximines, which are commonly very difficult to synthesize, as introduction of an α-substituent at the *N*-alkyl group may need harsh reaction conditions. We discovered a metal-/oxidant-free Petasis reaction of aryl boronic acids, ortho-hydroxyarylaldehydes and sulfoximines to synthesize *N*-(α-substituted)alkyl sulfoximines[1] (Scheme 1, Right side), synthesis of hitherto unknown *α*-sulfoximinophosphonate *via* the Kabachnik–Fields reaction of aldehyde, dialkylphosphite and sulfoximine in the presence of indium(III)[2] (Scheme 1, Left side) and $InCl_3$ catalyzed simultaneous *O*-silylation and reductive sulfoximination for synthesis of Silyloxy Benzylsulfoximine. (Scheme 1, below)



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Redox-neutral zinc-catalyzed cascade [1,4]-H shift/annulation of diaziridines with donor-acceptor aziridines

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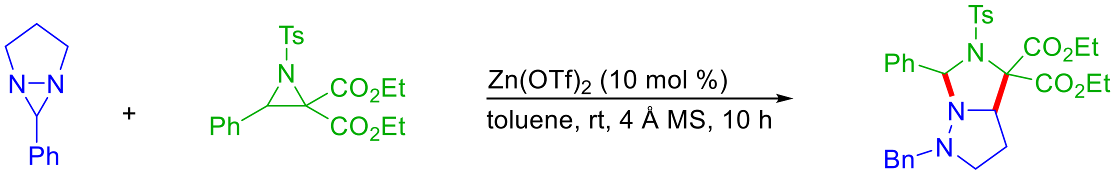
Expeditious access to Imidazopyrazole scaffold *via* 1,4-Hydride shift triggered C(sp^3)-H bond functionalization/ cyclization of diaziridines with donor-acceptor aziridines has been developed in presence of Zn-catalysis. The *in situ* generated pyrazoline intermediate was successfully isolated to showcase the unusual (2+n) reactivity of diaziridine. Notably, this methodology facile to construct the corresponding fused heterocycles from moderate to good yields and can be easily expanded to gram scale under mild condition. In addition, natural product mutation and a late stage *in silico* molecular docking study are the significant features.



✓ Broad substrate scope

✓ Fused heterocycles

✓ Mild reaction conditions

✓ Molecular docking study

Scheme: Zn-catalyzed (3+2)-annulation of diaziridine with donor-acceptor aziridine

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Divergent Synthesis of Unsymmetrical Bis-heteroaryl Ketones via Base-promoted Cascade Reactions of 1,2-Alkynedione-derived *N*-propargylic β-enaminones

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Bis-heteroaryl ketones are versatile compounds that serve as components of pharmacophores and bioactive natural products. Despite their potential importance, the straightforward synthesis of bis-heteroaryl ketones, specifically unsymmetrical bis-heteroaryl ketones is limited.[1] We have developed a transition-metal-free strategy to access bis-heteroaryl ketones from heteroaryl ynediones following base-mediated cascade reactions of ynedione-derived *N*-propargylic β-enaminones in one pot.[2] The use of a variety of alcohols as solvents led to the formation of the 2-alkoxylated pyridine scaffolds involving base-promoted *7-exo-dig* enamine oxacyclization and subsequent cascade processes. However, changing the solvent to DMSO resulted in the formation of pyrroles involving a base-promoted carbonyl-allene metathesis pathway. The established strategy is operationally simple and accompanied by a wide substrate scope as well as various post-synthetic transformations.

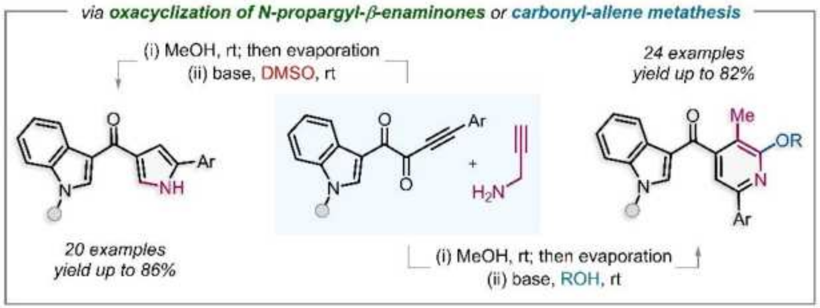

Figure: Divergent Synthesis of Unsymmetrical Bis-heteroaryl Ketones from Ynediones

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Copper(II) Complex: Catalyst for Enantioselective Synthesis of Propargylamines

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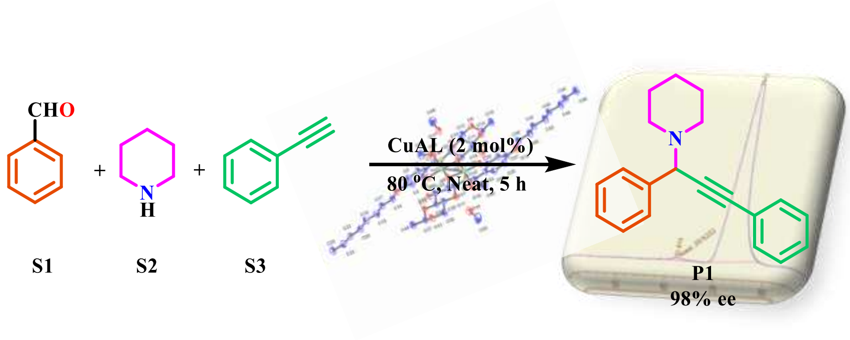
Development of catalytic systems using nontoxic natural precursors is the need of the era, and along this line, we have synthesized a new D-glucose derived ligand (4,6-*O*-ethylidene-*N*-(2-hydroxy-4-(octyloxy)benzylidene)-β-D-glucopyranosylamine) and its dinuclear copper(II) complex. The molecular structure of the complex has been established by single-crystal X-ray diffraction studies. Further, the complex has been used as catalyst in the synthesis of propargylamines *via* aldehyde-amine-acetylene (A^3) coupling reaction under solvent-free condition (**Scheme 1**).



Scheme 1. Catalytic synthesis of propargylamine

Under optimized reaction conditions, twenty enantioselective (87-99% ee) propargylamine derivatives have been synthesized in good to excellent yield (82-95%) including six new ones. The formation of aminal intermediate during the reaction has been confirmed by ^{1}H-NMR and single-crystal X-ray diffraction studies.

SYNTHESIS, CHARACTERIZATION AND *in silico* MOLECULAR DOCKING OF SOME PYRIMIDO-PYRAZOLO-PHTHALAZINE DERIVATIVES

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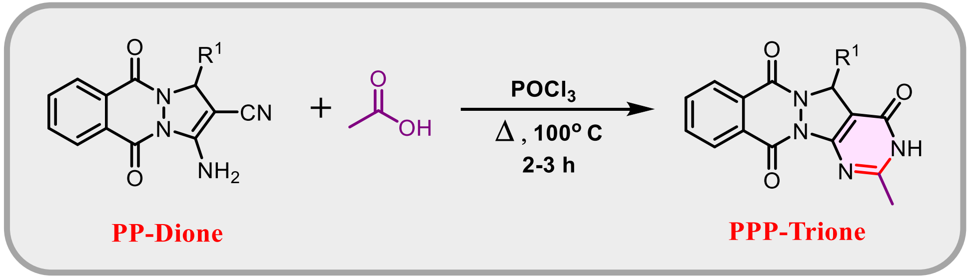
Pyrazole, phthalazine and pyrimidine derivatives, either alone or as fused rings, are extremely important in organic chemistry as well as biological science because of their significant biological actions viz., anticancer, antitubercular, anti-HCV, antiviral, antifungal, anti-inflammatory, antibacterial, and antipyretic properties. Due to these significant characteristics, our research group has been interested in creating such heterocycles and investigating their synthetic methodologies. Thus, these new pyrimido-pyrazolo-phthalazine-trione (PPP-Trione) derivatives were synthesized by reacting pyrazolo- phthalazine-dione (PP-Dione) with acetic acid in the presence of well-known chlorinating agent $POCl_3$ under the reflux condition. Previously limited derivatives were synthesized by Hosseininasab et al. [1]. Herein, we report additional derivatives of PPP-Trione. The starting materials PP-Dione were prepared according to the literature reports [2]. A Tandem intramolecular Pinner-Dimroth rearrangement-based process was also suggested as a plausible mechanism for the synthesis of PPP-Trione derivatives [3]. In addition to that, we also carried out the *in silico* docking study of the PPP-Trione derivatives. The scheme of the reaction is given below:



Scheme: Synthesis of the Pyrimido-pyrazolo-phthalazine derivatives

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A one-pot bimetallic telescopic assembly of benzo[*b*]carbazoles en route towards a room-temperature nematic liquid crystal

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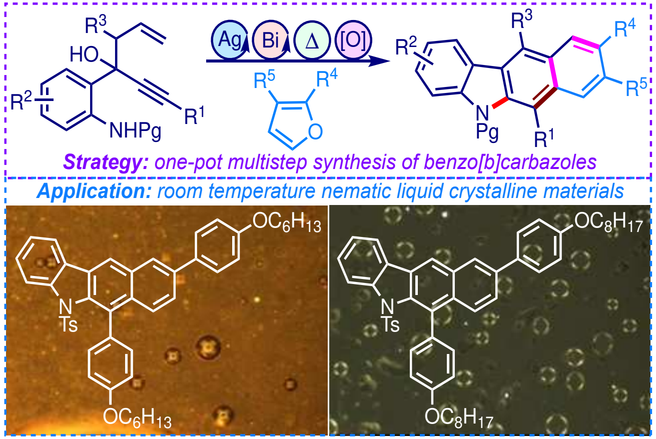
Arene- and heteroarene-fused carbazoles are an important class of nitrogen-containing heterocycles that attracted considerable attention in the recent past due to their widespread applications in medicinal chemistry and materials sciences.[1] In particular, the benzo[*b*]carbazole scaffold is the part structure of several pharmaceutically relevant compounds and photoactive materials. Here we described a diversity-oriented stitching of benzo[*b*]carbazole *via* a one-pot telescopic methodology where naphthannulation of indoles has been used as a key step, enabled by an intramolecular furan-olefin Diels-Alder reaction. With its efficiency spanning across a wide range of substrates, this methodology was employed to achieve and duly characterize the first examples of benzo[*b*]carbazole-based liquid crystals. The unique molecular design, with the help of peripheral alkyl chains, ascertained a rare room-temperature nematic mesophase.[2]



Scheme 1: One-pot telescopic synthesis of benzo[*b*]carbazoles and their liquid crystalline nature

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Syntheses and Exploration of the Catalytic Activities of Organotin(IV) Compounds

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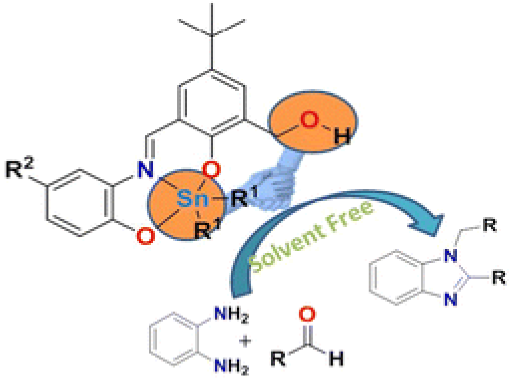
Six organotin(IV) compounds, $HLSnR_2$ (**1**, R = Ph; **2**, R = *t*-Bu; **3**, R = *n*-Bu) and L^1SnR_2 (**4**, R = Ph; **5**, R = *t*-Bu; **6**, R = *n* -Bu) have been synthesized by reaction of the polydentate pro-ligands, $\mathbf{H_3L}$ and $\mathbf{H_2L^1}$, respectively, with the corresponding diorganotin chlorides. All compounds were characterized by FT-IR spectroscopy, ^1H, $^{13}C\{^1H\}$, ^{119}Sn (^1H) NMR spectroscopy, HRMS spectrometry, and single-crystal X-ray diffraction. The solid-state structures show that all compounds are monomeric (except compound **3**) and contain a penta-coordinated tin atom. Compound **3** is a dimer with two hexa-coordinated tin atoms. Compounds **1**-**3** contain a non-coordinated hydroxymethyl group. All compounds have been screened for their catalytic efficacy in the synthesis of 1,2 disubstituted benzimidazole using *o*-phenyldiammine and aldehyde derivatives. It has been observed that both Lewis acidic Sn(IV) centre and hydroxymethyl group (hydrogen bond donor) catalyse the reactions with a yield of product up to 92%.



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Silver-Catalyzed Asymmetric Double Desymmetrization via Vinylogous Michael Addition of Prochiral α,α-Dicyanoalkenes to Cyclopentendiones

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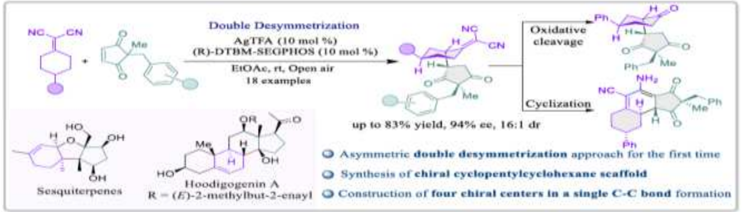
Abstract:

Asymmetric desymmetrization of prochiral compounds containing a pre-installed quaternary carbon (or other desired substitution) is a promising strategy for synthesizing complex structural frameworks.[1] The last decade has witnessed significant growth in the development of catalytic asymmetric desymmetrization strategies delivering optically active compounds with intricate structures.[2] To the best of our knowledge, all the known asymmetric strategies till date involve desymmetrization of only one of the reaction partners. One can access the next level of molecular complexity with more than one reaction partner undergoing desymmetrization, but interestingly, this task is yet to be accomplished. In this work, we have developed an asymmetric double desymmetrization methodology for synthesizing densely functionalized chiral cyclopentylcyclohexane scaffolds.[3] The salient feature of this protocol is the construction of four chiral centers, including an all-carbon quaternary stereocenter in a single C-C bond formation event. This vinylogous Michael addition reaction of prochiral α,α-dicyanocyclohexane to 2,2-disubstituted cyclopentene-1,3-dione is catalyzed by a chiral Ag-(*R*)-DTBM-SEGPHOS catalyst and has high functional-group tolerance and delivers a broad range of enantioenriched products (**18 examples** with up to **94 % ee**). The utility of the obtained products was demonstrated by performing an oxidative cleavage reaction and intramolecular base-promoted cyclization.



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Visible-Light-Mediated Triplet Carbene Catalyzed *Cis* to *Trans* Isomerization

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Abstract:

Alkenes are ubiquitous in biologically active molecules and serve as one of the most valuable functional groups in synthetic organic chemistry. Although a wide variety of methods have been established for the preparation of alkenes, these protocols have always suffered from poor *E/Z* selectivity. The stereochemistry of the alkenes, namely the *E*- or *Z*-isomeric form, not only governs the properties of the molecule but also determines the stereochemical outcome of chemical reactions. Therefore, stereoselective access of either isomer in alkene synthesis is highly desired. At the same time, numerous beneficial synthetic transformations have been conducted using carbenes generated from corresponding diazo compounds under light irradiation. However, catalytic chemical transformations utilizing the diradical character of triplet carbenes have not been investigated until now. Although *contra*-thermodynamic isomerization of *E* to *Z* is well known by photochemical activation via a sensitizer, the organo-photocatalyzed isomerization of *Z* to *E* remains relatively unexplored under milder conditions. The current study confirms that the *"downhill"* process of *Z* to *E* isomerization is indeed achievable through the reactivity of triplet carbene in a catalytic amount.

In this poster, we will present the selective synthesis of the *E* alkene under metal-free, strong acid-free conditions, marking the pioneering use of triplet carbenes as an organo-photocatalyst.

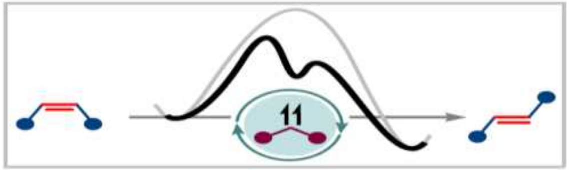

Figure 1: Photochemical *Cis* to *Trans* Isomerization

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Palladium-Catalyzed Weak Chelation-Assisted Site-Selective C-H Arylation of *N*-Aryl Pyridones *via* 2-fold C-H Activation

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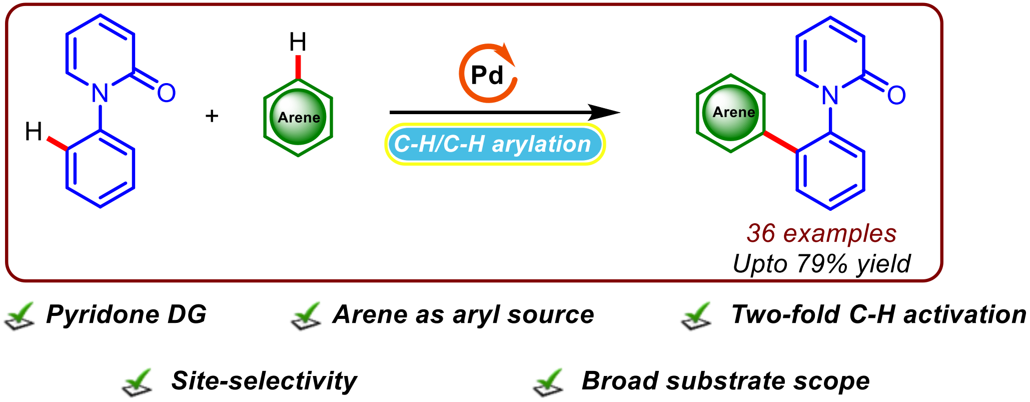
The development of efficient synthetic methodologies for the diversification of pyridone and related heterocycles holds immense synthetic interest as their existence in various natural products and pharmaceuticals. Unlike the structural diversification of the pyridone heterocycle, the method demonstrated here is the arylation of aromatic ring of *N*-aryl pyridone. Accessing the arene C–H bond of *N*-aryl pyridone in the presence of potentially reactive sites on the pyridone ring imposes a formidable synthetic challenge. Herein, we report a Pd-catalyzed site-selective C–H arylation of the *N*-aryl ring with arenes as the aryl source *via* the cross-dehydrogenative coupling utilizing weak chelating pyridone as the directing group.[1] The procedure offers an opportunity to utilize arenes as the coupling partner, obviating the need for prefunctionalized arylation source. The significant features of the method include the use of medicinally important pyridone as the intrinsic directing group, two-fold C-H activation, substrate scope, and late-stage diversification of medicinally important compounds.



Scheme 1. Pyridone directed C-H arylation of *N*-aryl pyridone

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New NNE Pincer Palladium (II) Complexes: Synthesis, Structure and Catalytic Application for Decarboxylative Heteroarylation of Coumarins

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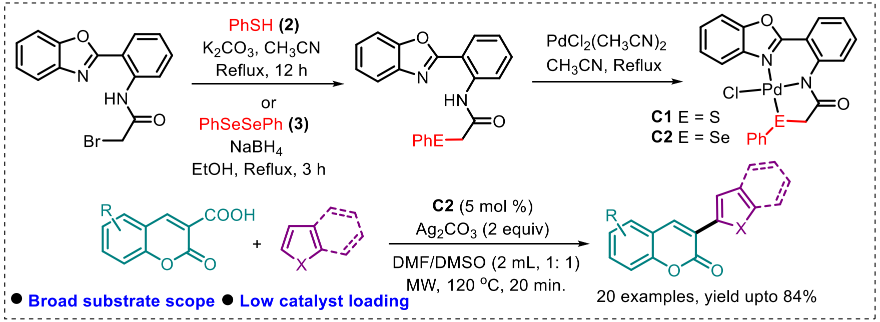
The transition metal-catalyzed C–H bond functionalization strategy represents a paradigm shift for constructing C–C and C–heteroatom bonds in organic synthesis. Direct functionalization of the C–H bond provides an atom- or step-economical, cost-effective, and environmentally friendly synthesis of important building blocks, natural products, and medicinally relevant molecules.[1] However, the typical catalysts employed in these transformations suffer from thermal stability and selectivity issues.[2] Pincer ligands show tight coordination ability with metal because of tridentate coordination, resulting in their high thermal stability. This peculiarity thus makes pincer ligands attractive auxiliaries for organometallic chemistry and homogeneous catalysis.[3] Considering the importance of pincer ligands and our interest in the catalytic application of pincer complexes,[4] we have designed and synthesized new NNE (E = S, Se) pincer ligands and prepared their palladium complexes. Both the ligands and complexes have been fully characterized by using NMR (^{1}H and ^{13}C) spectroscopy, XPS data, and single-crystal X-ray crystallography. The thermal stability of the complexes was also confirmed by TGA. Further, the catalytic application of the palladium NNE pincer complex was evaluated. Interestingly, the Pd-complex have been found to exhibit interesting catalytic activity for the C-H functionalization of N-heterocycles *via* decarboxylative coupling with various acids under microwave irradiation (Scheme 1).

Details of the catalyst and decarboxylative coupling protocol will be presented in the poster.



Scheme 1: Synthesis of NNE pincer Pd(II) complex and their catalytic application

Key words: Palladium. pincer complex, homogenous catalysis, decarboxylative coupling.

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CsF-Mediated Reaction of Trifluorodiazoethane with 3-Nitroindoles Enables Access to Trifluoromethylpyrazolo[4,3-*b*]indoles

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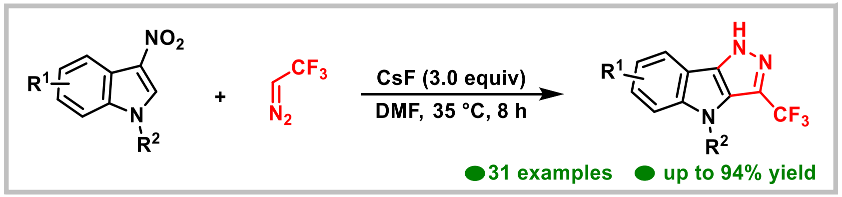
Indole-fused heterocyclic compounds are prevalent in various natural products, including alkaloids.[1] Among these, pyrazoloindoles stand out as prominent nitrogen-containing heteroarenes.[2] Meanwhile, heterocyclic compounds with a trifluoromethyl group are highly significant due to their ability to enhance the pharmacological properties of the parent molecule, such as increasing bioavailability, metabolic stability, and lipophilicity. In this regard, trifluorodiazoethane has emerged as a rapid reagent for constructing various three-, five-, six-, and seven-membered heterocycles, including aziridine, pyrazoline, pyrazole, triazole, tetrazole, triazine, pyridazine, benzoxepine, and benzazepine, by reacting with suitable partners. Although trifluorodiazoethane has been utilized in synthesizing diverse trifluoromethylated aza-heterocycles, practical methods for constructing fused aza-heterocycles using trifluorodiazoethane remain unexplored.[3] Herein, we report a mild and metal-free strategy for constructing trifluoromethylated pyrazolo[4,3-*b*]indoles through the reaction of *N*-substituted 3-nitroindoles with trifluorodiazoethane. This straightforward transformation involves a [3 + 2] cycloaddition of trifluorodiazoethane with 3-nitroindole, followed by the elimination of the nitro group to access pyrazole-fused indoles. The synthetic utility of this method is further demonstrated by applying it to other heterocycles, such as 3 nitrobenzothiophene and 2-nitrobenzofuran.[4]



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Tetrahydroisoquinoline (THIQ) Based Hydroxamate Derivatives as HDAC6 Inhibitors for Cancer Therapy

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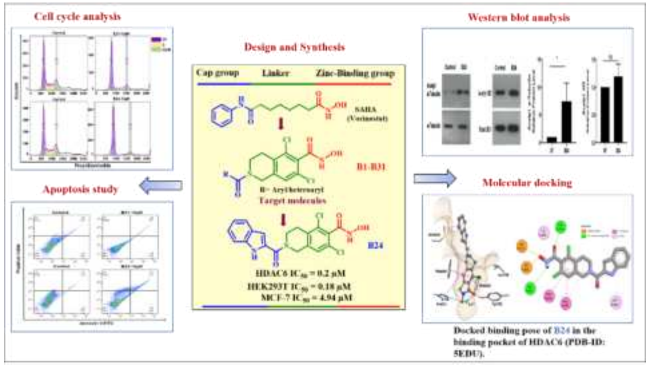
Tetrahydroisoquinoline (THIQ) compounds were synthesized and assessed for their ability to inhibit histone deacetylase 6 (HDAC6). These compounds were strategically designed, incorporating different aromatic groups as cap groups, utilizing tetrahydroisoquinoline as a linker, and employing hydroxamic acid as a metal-binding group. Thirty-one novel THIQ analogues (**B1-B31**) were designed and synthesized. The structures of these synthesized compounds were validated through various analytical techniques including ^{1}H NMR, ^{13}C NMR, LC-MS, and elemental analysis. These characterized compounds were then evaluated for their inhibitory activity against Class I HDAC8, Class IIa HDAC4, and Class IIb HDAC6. Several of these compounds exhibited potent antiproliferative activities in multiple tumor cell lines. Among the **B24** was found to be most potent selective inhibitor of HDAC6 with IC_{50} value of 0.2 µM. **B21** and **B24** remarkably blocked colony formation in MCF-7 cancer cells. Inhibition of cancer cell proliferation by **B21** and **B24** involved cell cycle arrest in G1 phase and apoptotic death of the cancer cells.



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β-Carboline-based light and pH dual stimuli-responsive ion transporters induce cancer cell death

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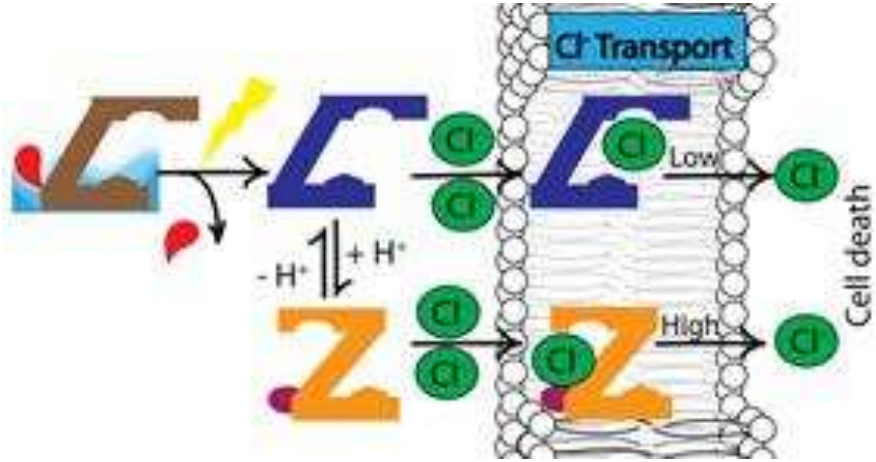
Responsive ion carriers that can be triggered specifically within cancer cells have shown promise as anticancer agents by disrupting the balance of ions and prompting cell demise. Dual-responsive carriers sensitive to both light and pH offer enhanced utility due to their adjustability and low toxicity. In this study, we present active ionophores based on β-carboline with thiourea, and proionophores consisting of thiourea-linked β-carboline and 4-methyl-3-nitro benzoic acid. These compounds facilitate controlled chloride transport across membranes. The potent compound demonstrates effective H+/Cl– transport activity across model and cell membranes. Cellular experiments reveal that its chloride transport capability induces apoptotic and autophagic cancer cell death. The inclusion of a photolinker, 4-methyl-3-nitro benzoic acid, in the β-carboline structure is crucial for generating inactive proionophores and improving solubility. Photoinduced conversion of proionophores to active ionophores leads to significant chloride transport across membranes, resulting in cancer cell death.

Graphical abstract:



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H_2S-Releasing Peptides: A Multifaceted Therapeutic Approach to Alzheimer's

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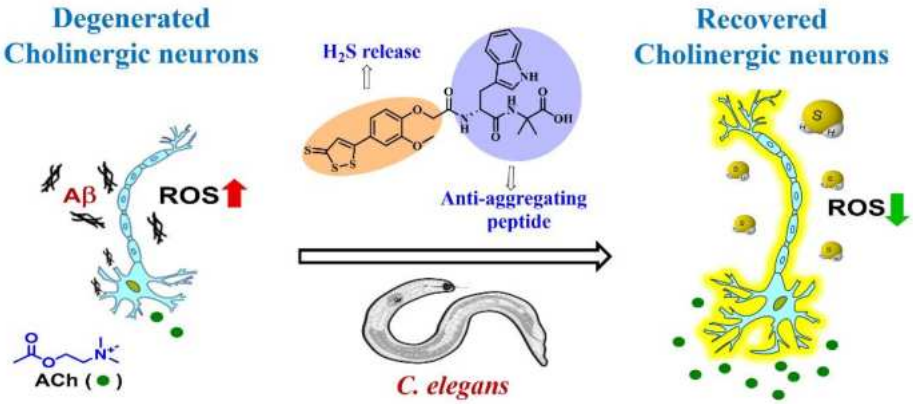
Alzheimer's disease (AD) is a progressive neurodegenerative condition that leads to cognitive decline. Several factors, such as Aβ plaque accumulation, oxidative stress, neuronal inflammation, and reduced acetylcholine (ACh) levels, are responsible for its onset and progression. This complexity presents a significant challenge, with current treatments only alleviating symptoms rather than addressing the root causes or halting disease progression. Given this urgency, novel therapeutic strategies are essential, aiming to target the underlying disease pathways instead of just offering symptomatic relief. Hydrogen sulfide (H_2S), once considered toxic, now stands out for its antioxidant, neuroprotective, and neuromodulatory properties as an endogenous signaling molecule. However, its exogenous delivery for therapeutic purposes is limited because of its gaseous nature and shorter half-life. Our efforts have resulted in the successful development of peptide frameworks capable of gradually and precisely releasing H_2S. These peptides form unique nanostructures in aqueous solutions, facilitating effective H_2S delivery in the model organism *Caenorhabditis elegans* (*C. elegans*). They demonstrate efficacy in reducing oxidative stress, impeding Aβ aggregation, and elevating ACh levels within a transgenic *C. elegans* model expressing human Aβ. This innovative class of peptide conjugates targets multiple facets of AD pathology, offering promise for the development of new therapeutics against this debilitating condition.



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Investigation of Serotonin-Receptor Interactions, Stability, and Signal Transduction Pathways via Molecular Dynamics Simulations

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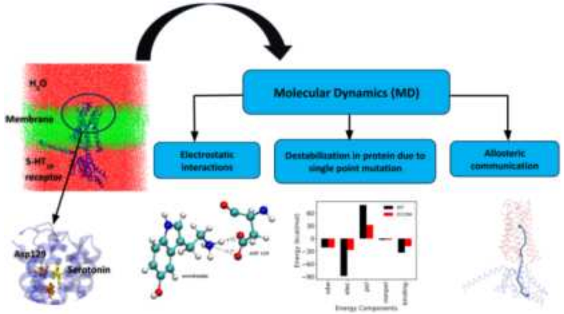
Serotonin-receptor binding is the key to several neurological and biological processes, including mood, sleep, hunger, cognition, learning, and memory. In this article, we performed a molecular dynamics simulation to examine the key residues that play an essential role in the serotonin binding to the G-protein-coupled 5-HT$_{1B}$ receptor (5-HT$_{1B}$ R) via electrostatic interactions. An end-point free energy calculation method (MM-PBSA) determines the stability of the 5-HT$_{1B}$ R due to serotonin binding. The single-point mutation of the polar or charged amino acid residues (Asp129, Thr134) on the binding sites and the binding free energy calculation validate the importance of these residues in the serotonin-receptor complex's stability. Principal component analysis indicates that the serotonin-bound 5-HT$_{1B}$R is more stabilized than the apo-receptor in dynamic changes. The difference dynamic cross-correlations map shows the correlation between the transmembranes and mini-Go, indicating signal transduction between mini-Go and the receptor. Allosteric communication reveals the key nodes for signal transduction in 5-HT$_{1B}$R. These results provide valuable insights into the study of signal transduction pathways and mutagenesis to regulate the functionality of the complex. The developed protocols can be applied to study local non-covalent interactions and long-range allosteric communications in any protein-ligand system for computer-aided drug design.



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Access of a small protein to the restricted biomimetic dicopper active-site installed in MOF pores compromises the oxidase nanozyme selectivity

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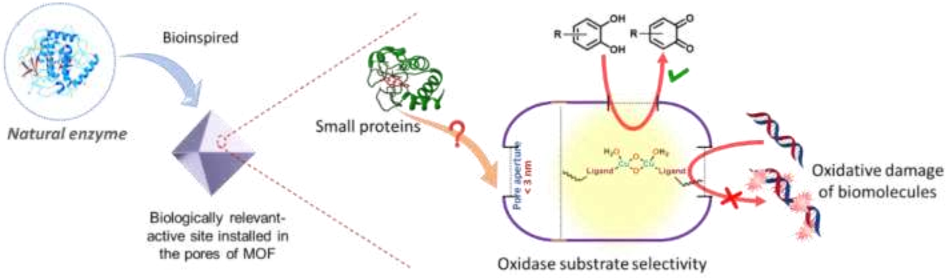
In recent years nanozymes have made significant advances in several domains. However, the nanozymes field is still in its infancy due to several limitations, particularly selectivity, specificity, and low catalytic activity at physiological pH. Repetitive efforts only lead to known examples of enzyme mimetics without reaction selectivity and acting as multi-enzyme mimetics. While nanozymes hold promise for therapeutic applications, their multienzyme mimetic activities can compromise their intended use.[1] This work aims to emphasize a flexible approach to designing nanozymes using metal organic frameworks (MOF) with several structural features having nanoconfined active sites and their pores to regulate reaction selectivity and, single enzyme mimetic activity. In this work, we demonstrate the biologically relevant dicopper active site installed in the pores of MOF-808 for selectively mimicking oxidase.[2] This oxidase mimetic with a small pore-aperture, similar to the enzyme binding pockets, projects a tight control over the reactivity of substrates, making it distinct from the general oxidase nanozymes. The design and the well-regulated activity of this nanozyme effectively prevent the oxidative damage of biomolecules. Crucially, we also show that the selectivity of the oxidase mimetic is compromised by small proteins, having dimensions larger than the pore aperture of MOF-808. These

unintended side reactivities necessitate careful attention as they can perturb various cellular energy pathways. Our study provides insight into developing next-generation artificial enzymes with improved selectivity and catalytic efficiency, addressing a long-standing challenge.



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Advancements in Superhydrophobic Coatings for Biomedical and Pharmaceutical Applications: Insights and real-world applications

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Biomimetics is an expanding field of study that seeks to replicate biological processes in order to develop nanomaterials, nanodevices, and processes with desirable characteristics. Superhydrophobic surfaces have garnered considerable attention in both research and industrial applications due to their exceptional wettability and versatility. These surfaces exhibit high mechanical durability, thermal stability, and chemical stability, making them highly promising for applications in sectors such as aerospace, food industries, and biomedicine. Superhydrophobic surfaces are highly effective in repelling water and find utility in various industries such as marine, biomedical, and energy sectors. Nevertheless, the limited suitability of superhydrophobic coatings for biomedical applications can be attributed to the inherent hazards associated with synthetic chemicals. During the COVID-19 pandemic, superhydrophobic materials (SHM) are essential for addressing biofouling problems in medical equipment and are utilized in personal protective equipment kits. Superhydrophobic materials hold an enormous potential in sectors as important as aerospace, food industries or biomedicine.

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QSAR and Molecular Docking Studies on Uracil-Based Benzoic Acid and Ester Derivatives to Explore Novel Dipeptidyl Peptidase-4 Inhibitors

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Today, diabetes mellitus (DM) is considered a major global health problem and especially diabetes mellitus type-2 (T2DM), which accounts for 90-95% of all diabetes cases. Among the novel glucose-lowering agents, dipeptidyl peptidase-4 (DPP-4) inhibitors have been extensively studied in recent years. This paper integrates a Quantitative Structure-Activity Relationship (QSAR) study and docking analysis of a series of uracil-based benzoic acid and ester derivatives as novel DPP-4 inhibitors. The correlation of chemical structure with the biological activity in Combinatorial Protocol in Multiple Linear Regression (CP-MLR) led to the detection of eleven descriptors from various classes of Dragon descriptors for modeling the activity. The resulting QSAR model has been validated internally and externally using CP-MLR and Partial Least Squares (PLS). Further, the Applicability Domain (AD) analysis revealed the acceptable predictivity of highest significant model. The best QSAR model displays the r^2_{Test} value of 0.715, Q^2_{LOO} value of 0.797 and Q^2_{L5O} value of 0.809. Further docking study was executed using Autodock 4.2 against DPP-4 protein (PDB ID: 2RGU). From the results, four new congeners have been predicted and validated with good inhibitory activity against DPP-4.

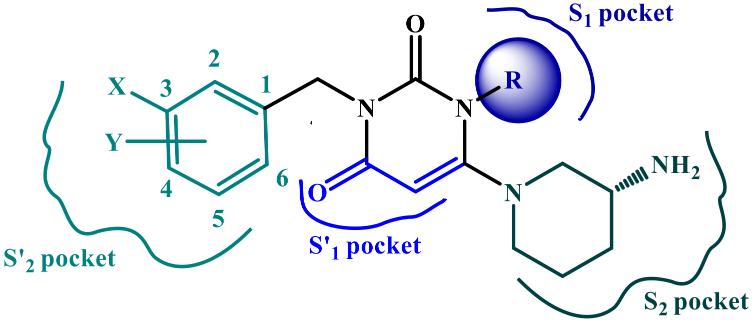

Figure: The uracil-based benzoic acid and ester derivatives interacting at DPP-4 receptor site.

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Guanidine-modified cellulose enhances capturing and recovery of phosphates from wastewater

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The recovery of dwindling materials from wastewater could be helpful in resolving the rising need for resources for society. Phosphate, an essential nutrient for all living organisms, plays a crucial role in maintaining human food security.[1]However, the depletion of global phosphate rock reserves poses a significant threat to our future. In order to address this issue, a novel biopolymer was synthesized by incorporating a guanidine functional group onto a cellulose-based matrix, coordinated with Zn(II) ions. The polymer exhibited a remarkable and rapid phosphate removal efficiency, demonstrating a maximum adsorption capacity of 310 $mg.g^{-1}$ at pH 7.0. It is worth noting that the phosphate that has been sequestered can be easily recovered, and the biopolymer can be conveniently recycled by adjusting the pH of the solution to around 11. Additional investigations unveiled that the inclusion of guanidinium moieties played a crucial role in its dispersion in water and its ability to combat both Gram-negative and Gram-positive bacteria. This study aims to enhance the design of water-insoluble biopolymers for more effective extraction and recovery of phosphate from wastewater. By doing so, it can help mitigate the negative impact of water eutrophication.

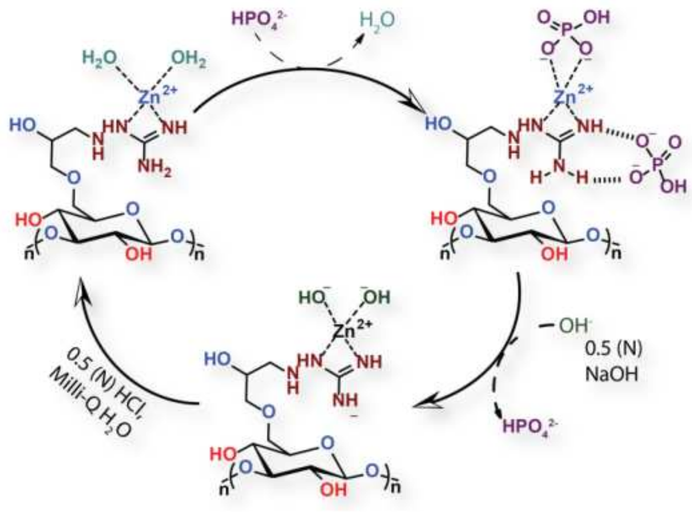

Figure. Possible mechanistic pathways for phosphate adsorption and desorption process.

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Evaluation of mode of indoleamine 2,3-dioxygenase 1 inhibition by 4,7-dichloroquinolines

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Herein, we report the development of synthetically simpler analogs of 4,7-dichloroquinoline (DCQ) as apo-indoleamine 2,3-dioxygenase 1(IDO1) protein targeting ligand to inhibit the activity of IDO1 enzyme. Derivatization of the DCQ moiety improved the IDO1 inhibitory activity both against purified enzyme and the cellular environment without any significant cytotoxicity, leading to the identification of piperazine containing DCQ derivative DCQ4 as a potent IDO1 inhibitor. A series of biophysical studies, including UV–Vis spectroscopy of the Soret band, docking, as well as protoporphyrin IX binding studies, suggested that the IDO1 inhibitory activity of potent compound could be due to its direct binding to apo-IDO1 protein and formation of DCQ4-heme complex. This simple strategy of developing apo-IDO1 targeting molecules having DCQ, piperazine, and amino acid moieties as potent IDO1 inhibitors could be useful in fighting against immune-related diseases.

Graphical abstract:

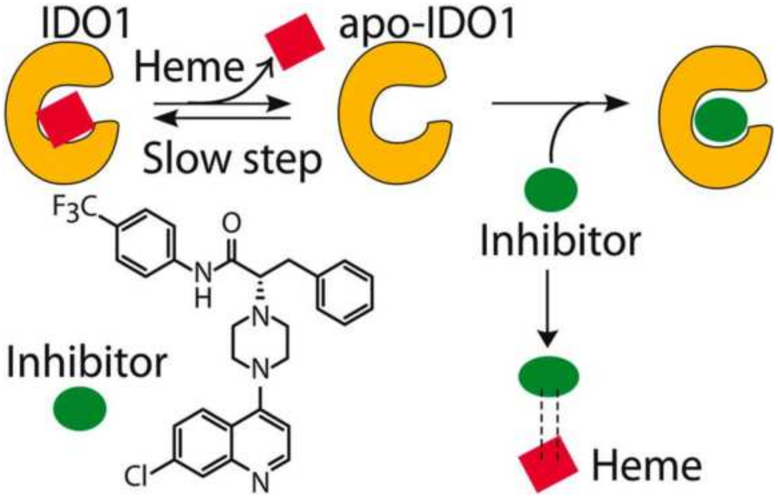

Figure. Schematic diagram depicting the duel mode of action for **DCQ4.**

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Ru atomic cluster hotspots on Co-Co_2B nanocatalyst boost hydrogen production by effectively preventing product inhibition in a unique way

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Product inhibition is a significant issue in catalysis that negatively impacts reaction rates and selectivity, resulting in substantial economic losses in industrial applications.[1] This problem is especially severe in sustainable hydrogen production from solid state chemical hydrogen storage sources, where byproduct, ammonium tetramethoxyborate (AMB)-induced inhibition often hampers catalytic efficiency. Herein, we have designed a unique catalyst comprising Ru atomic clusters (ACs) as hotspots installed on Co-Co_2B (10% RuACs/Co-Co_2B) that effectively combats product inhibition by AMB during hydrogen production from ammonia borane (AB), while sustaining the catalyst's efficacy in hydrogen production throughout the cycle.[2] The hydrogen generation proceeds with a superior rate (26559.14 ± 169.67 mL min^{-1} g_{cat}^{-1}) and an excellent turnover frequency (TOF) (1032.2 ± 114.6 mol_{H2} mol_{Ru}^{-1} min^{-1}), dehydrogenating AB in just 9 sec. Through a comprehensive analysis combining detailed experiments, computational studies, and successive half-life analyses, we unravel that significant charge reorganization between the Ru atomic clusters and the Co-Co_2B support facilitates rapid kinetics and promotes the removal of the byproduct (AMB), from the catalyst's surface. This unique ability to combat product inhibition while maintaining high rates and TOF sets the 10% RuACs/Co-Co_2B catalyst apart from others reported in the literature.

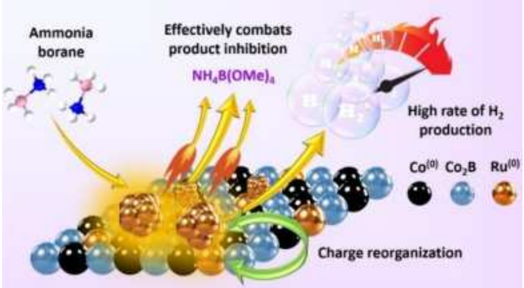

Figure: Prevention of product inhibition by 10% RuACs/Co-Co_2B during AB dehydrogenation.

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Exploring the impact of trifluoromethyl (-CF_3) functional group on the anti-cancer activity of isoxazole-based molecules.

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With readily available α,β-unsaturated carbonyl compounds, we revealed a metal-free, cascade regio- and stereoselective trifluormethyloximation, cyclization, and elimination strategy that can access a wide range of pharmaceutically potential heteroaromatics, i.e., 4-(trifluoromethyl)isoxazoles. based on the structure of an isoxazole based anticancer agent, we designed and synthesised a series of 4-(trifluoromethyl)isoxazoles including the trifluoromethyl analogue of the anticancer agent. We assessed the anti-cancer activity of the synthesized compounds against MCF-7, 4T1, and PC-3 cell lines. The trifluoromethylated analogue **2g** (IC_{50} = 2.63 μM) of the anti-cancer agent (**14**) is found to be eight times more active than the parent compound **14** (IC_{50} of 19.72 μM) against MCF-7 cell line. This indicates that the 'CF_3' moiety plays a crucial role in enhancing the anti-cancer activity of **14**. Nuclear labelling, apoptosis induction, and cell cycle analysis supports the apoptotic cell death process. Studies on molecular docking further supported the influence of –CF_3 moiety in enhancing the anti-cancer activity of isoxazoles.

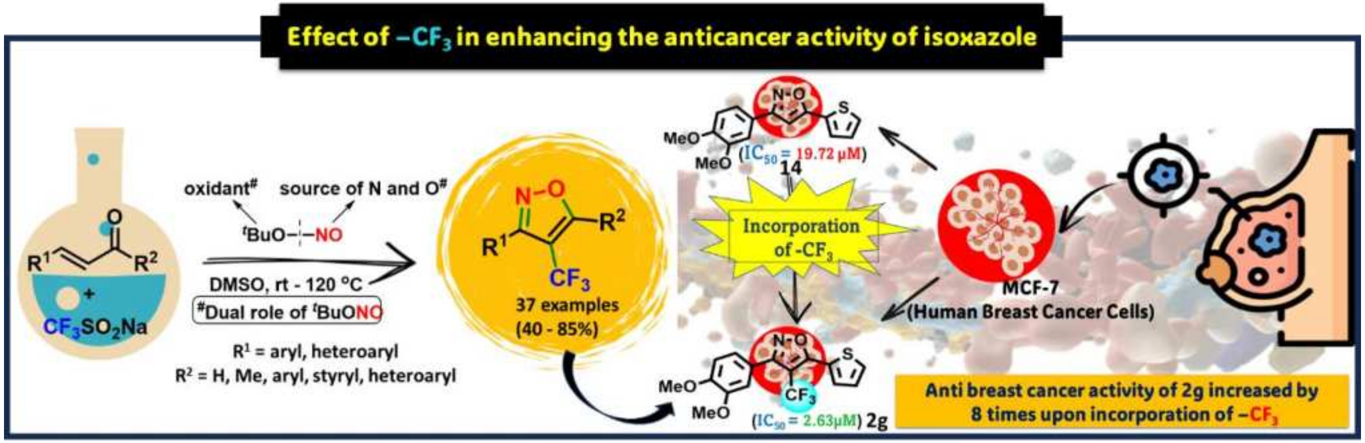

Figure: Synthesis of 4-(trifluoromethyl)isoxazoles and evalution of anticancer activity.

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Stimuli-responsive assembly and disassembly of anionic suprasomes with tunable antibacterial activity

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Host–guest complexation-based suprasomes successfully deliver benzimidazolium amphiphiles. β-CD and Zn^{2+} or an acidic environment act as the stimuli for the assembly and disassembly of suprasomes. We developed host–guest complexation-based suprasomes to deliver cationic amphiphiles and antibiotics. The β-CD-mediated formation of suprasomes with negative surface potential from the mixed micelles of cationic and anionic amphiphile could also release the encapsulated cargos in a stimuli-responsive manner in the presence of Zn^{2+} or an acidic environment. The superior activity of tetracycline-encapsulated suprasomes in the presence of Zn^{2+} ions could be due to the combined effect of cationic amphiphile, tetracycline, and Zn^{2+} ions against Gram-positive *S. aureus* bacterial cells. The hemolytic assays showed that the selected formulation has lower toxicity against RBCs. Therefore, the multi-stimuli regulated step-wise transition of micelles suprasomes-other aggregates is of great interest in drug delivery. In addition, facile functionalization and stimuli-responsiveness could provide suprasomes as the next-generation drug delivery systems to combat bacterial infections, cancer, and other diseases.

Graphical abstract:

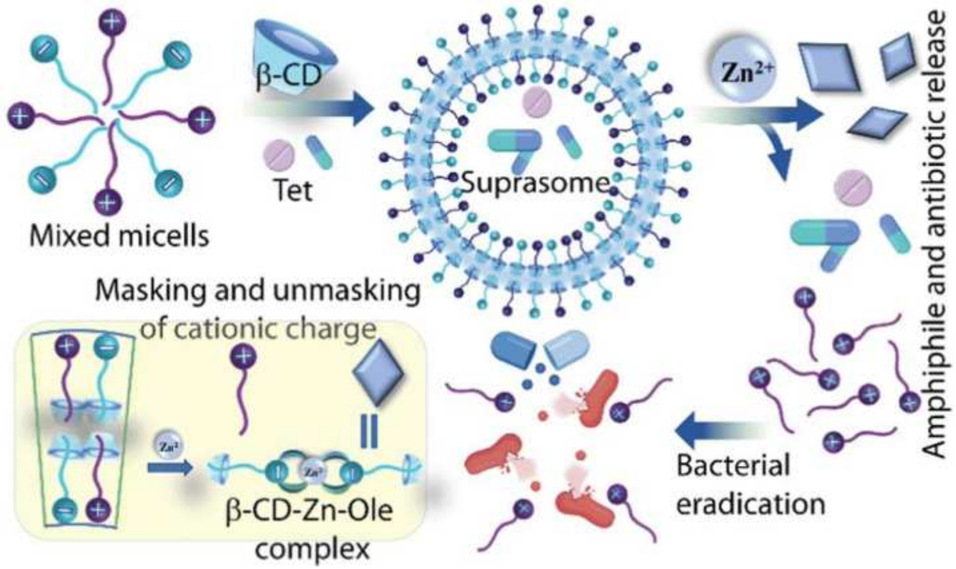

Figure 1. Schematic representation of the stimuli-regulated assembly and disassembly of suprasomes and their antibacterial activity.

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Stimuli-responsive release of active anionophore from RGD-peptide-linked proanionophore

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Integrin-mediated cellular delivery was attempted to optimize practical applications of hydrophobic ionophores. The potent ionophore preferentially transports H^+/Cl^- across the lipid bilayers following a symport mechanism. The RGD-peptide-appended tag was stimulated by glutathione to generate the active ionophore, prompting the transport of Cl^- under the cellular environment. We developed a thiourea-based synthetic ion carrier that transports H^+/Cl^- across the lipid bilayer following a symport mechanism. The RGD-appended proionophore features effectual stimulation of transmembrane ion transport due to the cleavage of its GSH-responsive tag. Additionally, the RGD-peptide-appended proionophore showed higher cytotoxicity against A375 cells than HEK293T cells, possibly due to its preferential internalization via the integrin-mediated pathway. The potential to enhance the selectivity of synthetic ionophores for cancer cells over normal healthy cells by tuning the cancer cell targeting ligand of the appended stimuli-responsive linker unit makes them exciting new proionophore scaffolds for transmembrane transport of ions.

Graphical abstract:

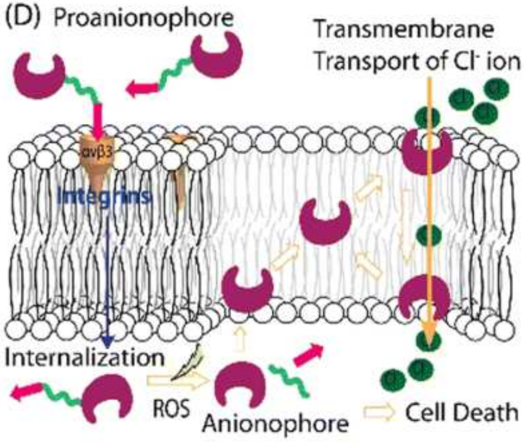

Figure 1. Schematic representation demonstrating the internalization, stimuli-mediated generation of active ionophore, and Cl^- transport-mediated cell death.

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Sustainable Development of Graphene Quantum Dots as high specific Nanoenzyme to Inhibit Neuronal Cell Damage

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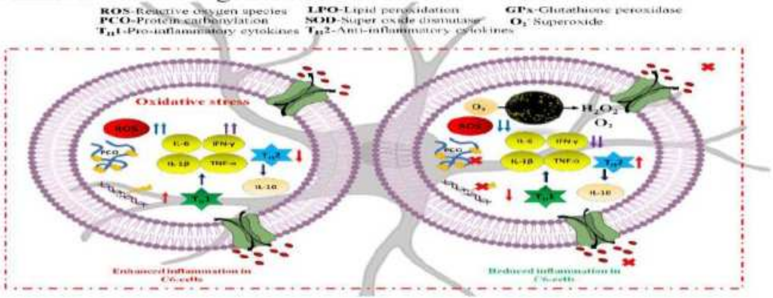
Abstract:

The disintegration of waste coal (WC) for scalable production of distinct nanozymes relies on the fate of its hydrothermal assisted breakdown. Herein, for the first time, we have shown a novel economic and scalable strategy to prepare yellow luminescent graphene quantum dots (YGQDs) having specific superoxide dismutase (SOD) like nanozyme activity using in-situ "anionic-radical" based bond cleavage in water. The presence of introduced surface-oriented defects like C=O, C-O-C, C=C, and O-H groups in the YGQDs acted as prominent stabilizers of radicals, presenting a prominent anti-oxidative property that were later determined to be linked to its specific SOD like activity [15 μM YGQDs equalling the activity of 1U of natural SOD (bSOD)]. Moreover, having shown its excellent thermodynamic stability and binding affinity towards superoxide ($O_2^{\bullet-}$) with Kd ~586 nM along with high biocompatibility towards human cells these YGQDs were used to counter oxidative stress mediated neuronal damage under ex-vivo condition. Optimal results indicate YGQDs rescue C6-cells from severe ROS (~90% reversal) through hydrogen bond donation and crystal plane stabilization. Further, the anti-apoptotic mechanism verified from the cytokine release pattern indicated complete normalization of Th1 and Th2 cytokines levels with only 5 μM treatment dose of YGQDs alongside showing its time dependent cytosolic and nuclear internalization. These outcomes further emphasize a strategy to remediate WC to produce GQDs based nanomedicines that can act as high specific SOD mimics and can be supplemented for treatment of wide variety of oxidative stress inflicted neurodegenerative diseases.



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Dicopper(II)-μ_2-Phenoxido bridge complex as a potential enzyme mimic with catecholase activity

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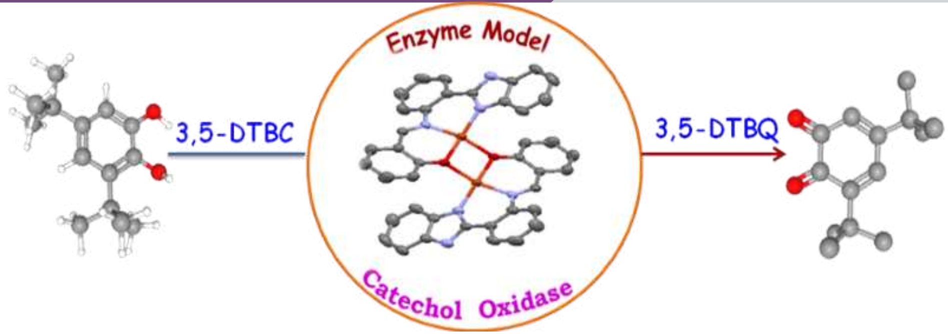
In an effort to model the active sites of numerous metalloenzymes and host small molecules in catalysis, efforts have been undertaken to synthesize dinuclear copper complexes that can hold two proximal copper ions. Enzyme designs containing a binuclear copper center that is antiferromagnetically coupled have been developed for type-3 copper active sites, such as catechol oxidase, which oxidizes catechols. It has been demonstrated that some of them exhibit catecholase activity. Thus, in order to explore a possible structural and functional model for the catecholase activity of the dicopper(II) site, we produced a novel dicopper(II)-μ_2-Phenoxido complex, {{$[Cu(L)(H_2O)]_2(ClO_4)_2$, H(L) is Schiff base). The X-ray structure reveals that (i) each of the two Cu(II) centres adopts distorted square pyramidal geometries, (ii) two μ-phenoxido bridged dimer of binuclear copper(II) units (ii) O-Cu-O angle (78.5°) is small, (iii) Cu-O-Cu bridge angle (101.5°) is large and, (iv) the Cu···Cu separation is 2.999 Å. Magnetic measurements show that the complex is strongly antiferromagnetically coupled with J = -524 cm^{-1}. It shows (a) a broad band with low absorptivity (b) axial EPR with the trend $g_{\|} > g_{\perp} > 2.0023$ and $d_{x^2-y^2}$ ground state and, (c) two Cu^{II}/Cu^{I} redox couples. While the highest catalytic activity in buffer solution at the optimum pH level is indicated by a value of 10^6, which is identical to the value measured for the catechol oxidase enzyme, the k_{cat} value in MeOH is in the order of 10^3. With a k_{cat} of around suitable, the complex is an outstanding proximity for the dicopper active site seen in catecholase enzymes.



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4′-*C*-ACETAMIDOMETHYL-2′-*O*-METHOXYETHYL NUCLEIC ACID MODIFICATIONS IMPROVE THERMAL STABILITY, NUCLEASE RESISTANCE, POTENCY, AND hAGO2 BINDING OF SMALL INTERFERING RNAs

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Over the past two decades, researchers have gained a deeper understanding of RNAi as a natural mechanism of post-transcriptional gene silencing through which small interfering RNAs (siRNAs) silence any gene of interest in a sequence-specific manner.[1] Chemically modified siRNAs, such as 2′-modifications including 2′-F, 2′-*O*-Me, and glycol nucleic acid (GNA), have improved siRNA activity, reduced off-target effects induced toxicity, and suppressed siRNA-mediated innate immune response.[1] Recently, numerous 2′,4′ and 2′,5′-sugar modifications were reported in siRNAs, tuning sugar conformation precisely to C2′-*endo*/C3′-*endo*, imparting better nuclease resistance, and achieving efficient gene silencing through a synergistic effect.[1]

In this study, we designed the 4′-*C*-acetamidomethyl-2′-*O*-methoxyethyl (4′-*C*-ACM-2′-*O*-MOE) uridine and thymidine modifications, which aims to test into small interfering RNAs.[2] Thermal melting studies revealed that incorporating a single 4′-*C*-ACM-2′-*O*-MOE modification in the DNA duplex reduced thermal stability. In contrast, an increase in thermal stability was observed when modification was introduced in DNA:RNA hybrid and in siRNAs. A single 4′-*C*-ACM-2′-*O*-MOE thymidine modification at the penultimate position at 3′-end of dT_{20} oligonucleotides in the presence of 3′-specific exonucleases, snake venom phosphodiesterase (SVPD) demonstrated significant stability as compared to monomer modified ONs including 2′-*O*-Me, 2′-*O*-MOE, and 2′-F. In gene silencing studies, we found that the 4′-*C*-ACM-2′-*O*-MOE uridine or thymidine modifications at 3′-overhang in the passenger strand in combination with two 2′-F modifications exhibited superior RNAi activity. The results suggest that dual modification is well tolerated at the 3′-end of the passenger strand, which reflects better siRNA stability and silencing activity. The computational model concluded that introducing the dual modification at the 3′-end of the siRNA guide strand anchors the strand within the PAZ domain of the hAgo2 protein. The overall results indicate that the 4′-*C*-ACM-2′-*O*-MOE uridine and thymidine modifications are promising modifications to improve the stability, potency, and hAgo2 binding of siRNAs.

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Au(I)-NHC Complexes as Thioredoxin Reductase (TrxR)-Inhibitors for Anticancer Therapy

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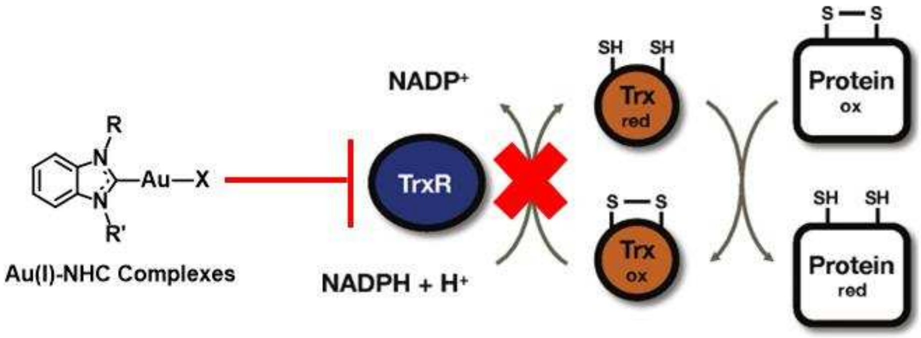
The key goal of this work is to develop novel metal complexes as TrxR-inhibitor with potent anticancer properties. TrxR is a homodimeric protein consisting of N-terminal catalytic site C59/C64 (dithiol/disulfide motif from Cys residues) and the C-terminal catalytic site C497/U498 (selenolthiol/selenenylsulfide motif from Cys and Sec residues). This enzyme plays an important role in maintaining cellular redox equilibrium by reducing oxidised thioredoxin through utilisation of electrons from NADPH.[1]

TrxR/Trx has been increasingly recognised as a critical modulator of tumor development. Increased oxidative stress in highly proliferating, metabolically active cancer cells causes them to overexpress antioxidant enzymes in an attempt to counteract the increased reactive oxygen species and prevent irreversible damage and cell death; TrxR has also been found to be overexpressed in cancer cells and is crucial for the cells to activate pro-survival pathways, suggests targeting TrxR is therapeutically potential approach to prevent tumor progression.[2,3] In our study, we synthesized novel Au(I)-NHC complexes and evaluated their potency to induce cell death in TrxR-overexpressed cancerous cell lines. We found some of the potent Au(I)-NHC complexes inducing cancer cell death with lower IC_{50} values. In future, we will be underlying the molecular mechanism by which these complexes exhibits anticancerous activity.



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Harnessing the Power of π-System and β-Sheet Formation in Collagen Model Peptide for Collagen Mimicry

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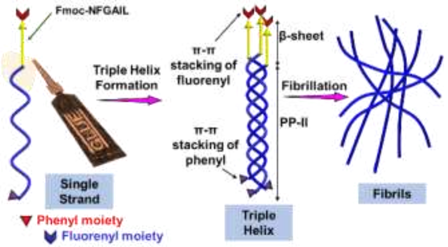
Collagen model peptide (CMP)-based fibrils are a suitable substitute for collagen in producing biomaterials for tissue regeneration.[1, 2] However, the reported CMPs do not form fibril networks like collagen, and their sequences are lengthy, making large-scale applications challenging.[2, 3] We have strategically designed and synthesized a minimalistic CMP by fusing a hydrogel-forming, Fmoc-functionalized ultrashort peptide(NFGAIL) at the N-terminus and phenylalanine at the C-terminus of a short $(GPO)_5$ (Fmoc-NFGAIL-$(GPO)_5$-F-COOH, FmP-GPO). FmP-GPO forms a strong triple helix in aqueous buffer with a denaturation temperature of 35 °C. The fluorenyl motif stabilises the triple helix through π-π interactions, as without it, the triple helix fails to form. NFGAIL also stabilises the triple helix through intermolecular hydrogen bonding and hydrophobic interactions. FmP-GPO further self-assemble into entangled fibrils of micrometre length and 13.2±2.8 nm diameter, promoting cell viability. The NFGAIL region, which produces a β-sheet, is important for fibrillation. Without it, no fibrils were detected, yet a less stable triple helix was produced. The formation of triple helix and fibrils in such a short CMP sequence is extremely challenging, and the implications in tissue engineering are vast. The present approach emphasizes the possibility of generating unique CMP sequences by altering fusion peptides and GPO repeats.



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Eco-friendly Single component white light emissive trivalent Europium complex: combined experimental and theoretical study

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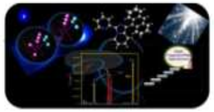
Abstract:

Eco-friendly white light emitting diodes (including solid state lightings) are highly in demand and especially single-component white-light emissive luminogens are an economical and simplistic selection for phosphor-converted white light emitting diodes (pc-WLEDs)[1]. In this context, purposefully designed ligand (structurally characterised) and metalated with trivalent europium ions along with energy harvesters (TTA & DBM). The photophysical study reveals these complexes showed white light emission in the solid as well as solution state (CIE x = , y = , and x = , y = , respectively). DFT and TD-DFT calculations were utilised to understand the energy transfer processes from complexes to the ligands. Taking advantage of this emission behaviour we have fabricated white LEDs as well as studied the thermometer applications. The fabricated LEDs showed excellent performance ("eye-friendly"). The detailed photophysical properties will be discussed.

Figure



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Hydrogen Bonding Dominance over Aromatic π-π Interactions in Enhancing the Efficiency of Peptide Hydrogelator in Forming 3D Supramolecular Soft Gels: Asparagine as a Key Factor

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Peptide-based supramolecular hydrogels formed through self-assembled peptides have garnered substantial interest due to their inherent bioactivity, biocompatibility and design flexibility. These peptide assemblies are typically stabilized by intermolecular non-covalent interactions arising from amino acid side chains, in addition to the primary hydrogen bonding between peptide backbone amide groups[1]. Previous studies have demonstrated the importance of aromatic π-π interactions as a major driving force for self-assembly, whereas the impact of side-chain hydrogen bonding was less pronounced. Herein, we explored the role of side-chain hydrogen bonding interaction on hydrogelation efficiency using an amino acid mutation strategy. To elucidate this, we investigated the hydrogelation efficiency of two sets of Synuclein and islet amyloid peptide fragments [Fmoc-NVGGAVVT and Fmoc-NFGAIL], wherein asparagine was substituted with phenylalanine, alanine, and glutamine, representing aromatic π-system, aliphatic, and hydrogen bonding effects with varying chain lengths, respectively. Our results reveal that the efficiency of asparagine and glutamine containing hydrogelators was drastically increased by several folds compared to others. This indicates that side-chain hydrogen bonding takes precedence over aromatic π-π interactions, a phenomenon currently considered crucial

for efficient gelation in peptide hydrogelation processes. Given the dependence of supramolecular gel properties on gelator concentrations, we propose that point mutation of asparagine/glutamine in short peptide gelators presents an opportunity to tailor their properties for targeted applications.

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Tailoring efficacious interventions against ER-positive cancer by targeting aromatase to constrain oestrogen production

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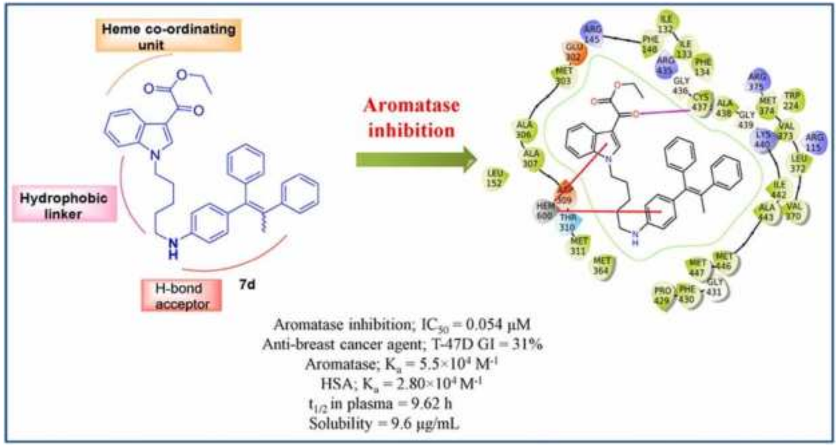
Aromatase inhibitors (AIs) are main stay therapeutics for treating hormone dependent breast cancer in postmenopausal women. However, rising resistance to widely utilised aromatase inhibitors such as letrozole, exmestane, and anastrazole, as well as off-target effects, demand the development of new aromatase inhibitors with superior pharmacological profiles. To improve the efficacy of the AIs, a series of compounds were developed on the basis of the structure of A4 and mechanism of aromatase. Among all the synthesised compounds 7d demonstrated exceptional potency within the series with IC_{50} 54.0 nM for aromatase. Significant tumor growth inhibitory activities of these compounds were also observed against breast cancer cell lines. Overall, the experiment results suggest that these compounds could give new insight to develop novel breast cancer drug.



Aromatase inhibition; $IC_{50} = 0.054\ \mu M$
Anti-breast cancer agent; T-47D GI = 31%
Aromatase; $K_a = 5.5\times10^4\ M^{-1}$
HSA; $K_a = 2.80\times10^4\ M^{-1}$
$t_{1/2}$ in plasma = 9.62 h
Solubility = 9.6 µg/mL

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Impact of surfactants in modulating the viscoelastic properties of Fmoc-Phe hydrogels

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Supramolecular gels, arising from the self-assembly of low molecular weight (LMW) gelators, have garnered significant interest in various fields including biosensors, drug delivery systems, optical sensors, and tissue engineering. These hydrogels are formed through non-covalent interactions between self-assembled molecular networks. In this study, we investigated the impact of different surfactants - sodium dodecyl sulphate (SDS), Cetyltrimethylammonium bromide (CTAB), and Triton-X-100 - on the viscoelastic properties of hydrogels composed of Fluorenylmethoxycarbonyl group conjugated Phenylalanine (Fmoc-Phe). By varying the surfactant concentration relative to its critical micelle concentration (CMC), we explored its influence on Fmoc-Phe self-assembly and viscoelastic behavior. Rheological analysis indicated that the viscoelastic property of the Fmoc-Phe hydrogel was significantly modulated in the present of different surfactants. Morphological analysis revealed that surfactant nanoparticles were embedded

within the fibrils of Fmoc-Phe hydrogels. Biophysical techniques such as UV-visible spectroscopy, circular dichroism (CD), Fourier-transform infrared spectroscopy (FT-IR), and fluorescence measurements provided insights into the interaction between surfactants and Fmoc-Phe, influencing viscoelastic properties. The development of hydrogel-surfactant composite gel materials holds promise for diverse biomedical applications, particularly in drug delivery and tissue engineering contexts.

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Functional models of ascorbate, amine, and catechol oxidases: Impressive catalytic promiscuity of monocopper(II) complexes

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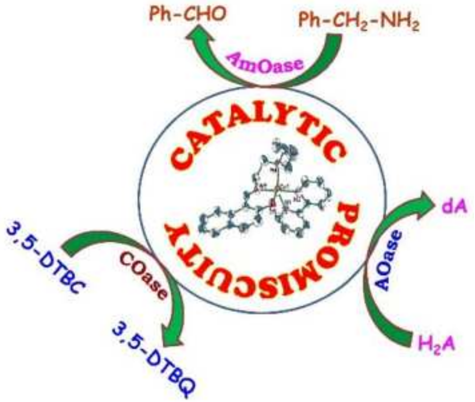
Copper metalloenzymes ascorbate oxidase (AOase), amine oxidase (AmOase), and catechol oxidase (COase) possess copper(II) sites of coordination which are trimeric, homodimeric, and dimeric, respectively. Two, $[Cu(L)(bpy)](ClO_4)$ (**1**) and $[Cu(L)(phen)](ClO_4)$ (**2**) [H(L), Schiff base], are newly synthesized monocopper(II) complexes. The distorted square pyramidal copper(II) complexes were confirmed by their UV-visible studies. EPR spectra determined axial spectral characteristics typical of monocopper(II) species with a distorted square pyramidal geometry around copper(II) ion. A positive $Cu^{II/I}$ redox potential indicates the stable switching between Cu^{II} and Cu^{I} redox states. One of the active model complexes displays a distorted square pyramidal geometry in its X-ray crystal structure. In spite of the monomeric origin, both homogeneous catalysts found to convert three distinct effective chemical transformations as a single active site in MeOH like ascorbic acid (H_2A) to dehydroascorbic acid (dA), benzylamine ($Ph-CH_2-NH_2$) to benzaldehyde (Ph-CHO), and 3,5-di-*tert*-butylcatechol (3,5-DTBC) to 3,5-di-*tert*-butylquinone (3,5-DTBQ) [k_{cat}: AOase, 9.6 (**1**) or 2.0×10^6 h^{-1} (**2**); AmOase, 13.4 (**1**) or 9.4×10^6 h^{-1} (**2**); COase, 2.0 (**1**) or 1.9×10^3 h^{-1} (**2**)]. In comparison to the AOase (2.45×10^6-3.1×10^7 h^{-1}) enzyme, the k_{cat} values of the complexes displayed the highest AOase activity. On the other hand, the k_{cat} values for COase activity in buffer solution [5.93×10^5 (**1**) or 2.95×10^5 h^{-1} (**2**)] are one order lower than those of the enzymes from *Ipomoea batatas* (8.25×10^6 h^{-1}), and the same as those of the COase from *Lycopus europaeus* (5.7×10^5 h^{-1}). This is due to the



following factors: (a) the labile nature of the coordinated donor; (b) the flexibility of the ligand; (c) the simplicity of the catalyst-substrate interaction; and (d) the positive $Cu^{II}/^{I}$ redox potential. Interestingly, catalysis is observed to be effective and even better than with other mono- and dicopper(II) complexes

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Iodine-mediated, chalcogen-chalcogen bond formation in water: Sustainable synthesis of carbamo(dithioperoxo)thioates, carbamo(selenothioperoxo)thioates, carbono(dithioperoxo)thioates, and carbono(selenothioperoxo)

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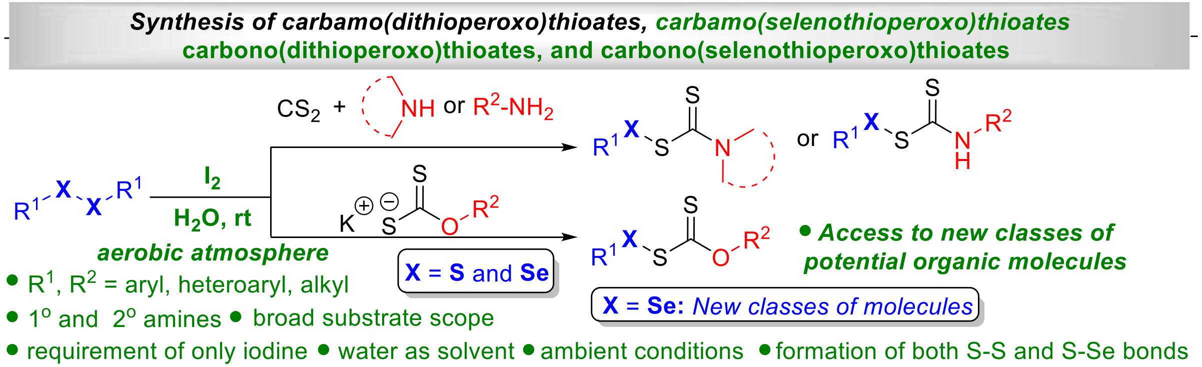
Herein, we disclose an iodine-mediated, three-component versatile synthetic strategy for the sustainable synthesis of a wide variety of biologically active carbamo(dithioperoxo)thioates and new classes of highly potential carbamo(selenothioperoxo)thioates, carbono(dithioperoxo)thioates, and carbono(selenothioperoxo)thioates by using readily available amines/alcohols, CS_2, and diorganyl disulfides/diselenides *via* chalcogen-chalcogen bond (S-S and S-Se) formation in water at room temperature under aerobic atmosphere. This strategy required only sub-stoichiometric iodine (0.5 equiv) and proceeded through the *in-situ* formation of corresponding chalcogenyl iodides followed by nucleophilic substitution at the chalcogen center by the *in situ* generated dithiocarbamates or xanthates. Two synthetically challenging, however, highly potential classes of molecules, *i.e.*, carbamo(selenothioperoxo)thioates and carbono(selenothioperoxo)thioates, have been synthesized in a sustainable manner in water at room temperature *via* the formation of a challenging S-Se bond.



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Color Tunable TADF Emitters: Design, Synthesis and Photophysical Study

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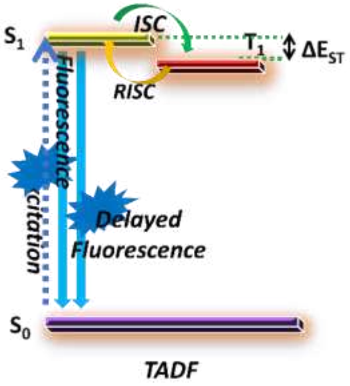
Thermally activated delayed fluorescence (TADF) based emitters are efficient and could harvest the dark triplet excitons in the OLEDs [1]. Development of highly efficient red and, specifically, blue TADF OLEDs has not proceeded as promptly. An efficient/ideal strategy to construct TADF-emissive metal-free luminophores is to combine an electron donor (D) and acceptor (A) moieties with a large torsion angle between them to construct D-A, D-A-D or A-D-A types of molecules with smaller energy gap between S_1 and T_1 states. The HOMO of the TADF emitter is determined by the donor moiety and the LUMO by the acceptor moiety. In this context, the acceptor core based on benzene substituted with CN, and two methyl (twisting nature) groups were integrated with different donors (carbazole, phenothiazine, phenoxazine and acridine). We performed the theoretical investigation to find the electronic nature of the designed emitters and found that these molecules show color tenability. The detailed synthesis, photophysical and electrochemical properties will be presented and discussed.



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Small Peptides Targeting BACE-1, AChE, and Aβ: A Novel Approach to Alzheimer's Treatment

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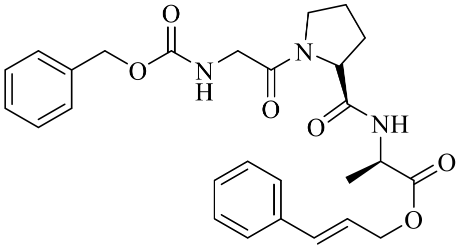
The abnormal activity of AChE/BACE-1 enzymes and the aggregation of Aβ are key factors in Alzheimer's disease. Inhibiting these enzymes is crucial to reduce plaque formation. Therefore, the molecules were designed that target the catalytic triad and diad of AChE and BACE-1 enzymes. The designed molecules were subject to some in vitro and In vivo studies and they showed significant inhibition of AChE, BACE-1 and Aβ aggregation motif. Also, all the compounds displayed good efficacy in animal studies. Among all the synthesized compounds, the following compound emerged as the most potent in enzyme immunoassay and in animal studies.



Potent Compound

IC_{50} (BACE-1) = 0.02 μM

IC_{50} (AChE) = 1.2 μM

% A-beta 1-42 aggregation inhibition = 54%

P_e (permeability value from PAMPA assay = $17.8*10^{-6}$

Shows only 4 % degradation in human blood plasma for 12h.

Shows similar effect as standard drug Donepezil in In vivo mice model studies.

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Extensive Polymerization of Atomically Precise Alloy Metal Clusters During Solid State Reactions

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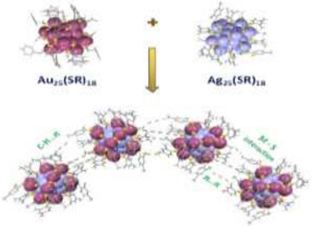
Abstract:

Exploring the reactions between atomically precise metal clusters and their applications has been an exciting field of research during the last decade. Initial studies in the area were on reactions between clusters in the solution phase, which proceed through the formation of dimers of reacting clusters. In the present work, we examine the interaction between two atomically precise clusters, $[Au_{25}(PET)_{18}]^-$ and $[Ag_{25}(DMBT)_{18}]^-$ in the solid state, where PET and DMBT are 2-phenylethanethiol and 2,4-dimethylbenzenethiol, respectively. The experiments were performed using different ratios of these two clusters, and it was inferred that the kinetics of the reactions were faster compared to reactions in solution. Metal exchange between these two clusters, due to their interaction in the solid state, leads to the formation of dimers, trimers, tetramers and polymers of atomically precise alloy metal clusters. We observed polymer entities up to hexamers, which were observed for the first time. Control experiments revealed that metal exchange is the key factor leading to polymerization. Our work points to a new approach for synthesizing polymers of atomically precise alloy metal clusters.



Scheme. Representation of the formation of polymers through intercluster reaction.

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