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Fabrication of Mn-NiOOH/BiVO₄ Photoanode for Efficient

Photoelectrocatalytic Water Oxidation

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Abstract:

Photoelectrocatalytic (PEC) water splitting is a promising technique for hydrogen production in a renewable way. In which the semiconductor electrodes absorb sunlight, and generate the electron-hole pairs, which undergo a redox reaction with the evolution of oxygen (photoanode) and hydrogen (photocathode). Recently bismuth vanadate (BiVO₄) has gained much attention as a photoanode in PEC water splitting, due to its narrow band-gap (2.4 eV), suitable valance band maximum for water oxidation, high stability, low cost, ease of synthesis, and non-toxicity. However, the efficiency of the pristine BiVO₄ is affected by the high charge recombination process and indolent water oxidation kinetics. These issues are effectively overcome by introducing the oxygen evolution catalyst as a co-catalyst on the surface of the BiVO₄, which can improve the water oxidation kinetics and reduce the charge recombination via improving the hole injection ability at the electrode/electrolyte interface. With these criteria, in this study, Mn-doped NiOOH was used as a co-catalyst for enhancing the PEC performance of pristine BiVO₄. Initially, the BiVO₄ was fabricated by facile electrodeposition method and Mn-doped NiOOH co-catalyst was loaded on the BiVO4 via hydrothermal growth. Then the fabricated electrodes were characterized by suitable analytical techniques such as XRD, Raman, UV-vis, PL, XPS, FESEM, and HRTEM, and the PEC performance and the influence of Mndoped NiOOH on the charge transfer process and water oxidation kinetics at the interface was investigated using linear sweep voltammetry and electrochemical impedance spectroscopy techniques under AM 1.5G (100 mW cm⁻²) illumination. The results show that the Mn-NiOOH co-catalysed BiVO₄ photoanode exhibited an enhanced PEC activity than the pristine BiVO₄, due to the rapid charge transfer across electrode/electrolyte interface, which minimizes the electron-hole recombination rate.

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Dual ESIPT based Schiff base for the detection of hypochlorite (ClO⁻) ion in aqueous system

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Abstract:

HOCl/ClO- is a physiologically important component of reactive oxygen species (ROS) and is important for human immunological function^{1, 2}. HOCl/ClO- can destroy invading germs and pathogens at low concentrations, mediate the body's physiological equilibrium, and cause oxidation of biomolecules like proteins, lipids, and nucleic acid in biological cells, resulting in a range of illnesses³⁻⁵. As a result, it's crucial to know how much HOCl/ClO- is present in organisms. We developed benzothiazole- amino salicyaldehyde Schiff base probe **1**, a ratiometric and colorimetric fluorescent probe for the detection of ClO- using the imine bond as the fluorophore unit, in this study. Probe **1** has a high selectivity and sensitivity for detecting ClO-. With the addition of ClO- ions, the emission maximum of probe **1** showed quenching with a small red shift in the emission band. Probe **1**'s lowest detection limit for the detection of ClO- ion was discovered to be 5.5 μ M. After adding ClO- ions, the colour of probe **1** also changes from green to colourless. Probe **1** was also successfully used for biological imaging with minimal harm.



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Efficient Charge Transfer from Organometal Lead Halide Perovskite Nanocrystals (PNCs) to Free Base *Meso*-Tetraphenylporphyrins

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Abstract: The efficient charge transfers from methylammonium lead halide, MAPbX₃ (X = Br, I) perovskite nanocrystals (PNCs) and 5, 10, 15, 20-tetraphenylporphyrin (TPP) molecules are investigated in detail. Hydrophobically-capped MAPbX₃ PNCs exhibited bright fluorescence in the solution state. However, in the presence of TPP, fluorescence intensity was quenched Which is ascribed to the electron transfer from PNCs to TPP. Photoluminescence (PL) spectroscopy was used to evaluate fluorescence quenching in turn quenching efficiency. The quenching of fluorescence intensity is not attributed to the change in a lifetime as investigated by time-correlated single-photon counting (TCSPC) measurement, suggesting static electron transfer from PNCs to TPP molecules. Such static fluorescence quenching corresponds to the adsorption of hydrophobic PNCs onto the surface of TPP and is examined via Transmission Electron Microscopy (TEM). The cyclic voltammetry (CV) studies were used to compare PNCs and PNCs @TPP nanocomposites revealing that the electron transfer process occurs from the PNC to the organic acceptor TPP molecules.



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Chemically Bonded, Lead-free, Tungsten based Polymer Composites for Shielding Diagnostic X-rays

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Abstract:

Ionizing radiations are harmful to humans when overexposed. The radiation shielding aprons, gonad shield, thyroid shield, etc., are used to protect the operating personnel and patients from ionizing radiations. Conventionally, lead and lead-based composite are used as protective apparel.[1] But lead is toxic, cancer causing and heavyweight, hence its usage is discouraged.[2] Therefore, lead-free metal-polymer composite based protective apparels are a better alternative due to their lightweight, flexibility, and less toxicity.[3] The conventional metal-polymer composites used for shielding material suffer from the drawback of the nonuniform distribution of metal in the polymer matrix.[4] In this work, efforts were made to address these drawbacks by developing a lead-free, chemically bonded, non-toxic metalpolymer composite. The WO₃ with different wt. % was incorporated in the blend of polyvinyl alcohol and polyvinyl pyrrolidone by dissolution technique rather than simple dispersion. The XRD and SEM analysis revealed the formation of sodium tungstate and its uniform distribution in the polymer matrix, respectively. FTIR and XPS data revealed the establishment of a coordinate bond between the polymer matrix and the W-based filler resulting in uniform distribution. The X-ray attenuation properties were determined from 60 kV to 140 kV. The optimum samples with 2.35 mm thickness possess the attenuation equivalent to 0.25 mm lead at 100kV. Tensile strength of the sample was also determined which is suitable for the fabrication of wearable apparel.

Key words: Polymer composite, ionizing radiation, radiation shielding Aprons, linear attenuation coefficient

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Pyrene – N-phenylparaphenylene Diamine-Based Imine Conjugate as a Chemodosimeter for the Detection of Trace Amounts of Water in Organic Solvents

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Abstract:

Pyrene based fluorescent PET sensor have been synthesised by a single step condensation reaction in the presence of green solvent EtOH. The probe (PNPD) was utilised to detect water content in organic solvents via fluorescence titration studies. Water in solvents, even in trace concentrations, is a cause for concern since it could cause quenching of reactive intermediates, especially in organometallic chemistry, could reduce the yield of reaction by inhibiting the reaction mechanism, and it could even cause catastrophic failures like fires and explosion owing to the reagents' exceptional reactivity.



Pyrene moiety exhibited intense blue fluorescence with high quantum efficiency in dilute solution characteristic of its highly conjugated aromatic structure. The extended conjugation in N-phenyl-paraphenylenediamine further facilitates electron transportation throughout the molecule. The photoelectron transfer mechanism (PET) was found to operate in the transfer of electrons from the nitrogen lone pair to the pyrene moiety. PNPD showed a cyan-blue emission in the presence of water content due to chemodosimetric cleavage of imine bond in the presence of water, causing PET OFF. The findings revealed that PNPD can detect water in polar, non-polar, protic, and aprotic solvents, with detection limit and quantitation limit preferring polar aprotic solvent acetonitrile and dioxane in both higher and lower water content. Also, we have developed a method for quantitative detection of water content in organic solvents by fluorescence studies in which acetonitrile evidenced the least error percentage detection of $x\pm 0.226$ %. Using honey as an example, the capacity of PNPD to detect water content quantitatively in real-life samples has been demonstrated and found a detection limit of 0.206 v/v% and quantitation limit of 0.624 v/v%. The relative water percentage in different brands of honey was also found out.

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Transition-metal free C-C cross-coupling reaction via single electron transfer from insitu generated anions

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Abstract:



The synthesis of biaryls bears great importance in organic chemistry, as the unit is seen in a large number of core structural motifs that are found in molecules having tremendous medicinal, agrochemical, and harmaceutical importance. Henceforth, there is a strong interest in furnishing C–C bonds in biaryls by easily accessible routes. Thus, direct C–H arylation of arenes has gained tremendous attention as it can bypass double preactivation for both participating substrates. In the domain of single electron transfer catalysis, simple organic additives in conjunction with KO'Bu are very effective for facile electron transfer. Profound understanding of the initiation pathway reveals multiple initiator species to be responsible for aryl radical generation via single electron transfer. This protocol has been explored successfully in carrying out coupling reactions with various arene partners.

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Conversion of Non-Perovskites (SnBr₄(DMSO)₂) phase into Vacancy ordered Double Halide Perovskites (MA₂SnBr₆) phase using Cu(I and II) and study of the Humidochromic behavior of the converted system.

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Abstract:

Lead based organic halide perovskites have taken the solar cell industry by storm due to low cost, easy solution based processing and exceptional optoelectronic features¹. But lead is toxic and has been replaced with Sn from the same group 14 family². MABr:SnBr₂ (1:1) in DMSO solvent under nitrogen atmosphere results in MASnBr₃ (a 3D perovskites), whereas the same in ambient condition results in a biphasic system, SnBr₄(DMSO)₂ and MABr (i.e. a non-perovskite phase and the precursor salt). Herein, we convert this non-perovskite phase into MA₂SnBr₆ (vacancy ordered double halide perovskites) phase using the species Cu (I and II). Also, originally MA₂SnBr₆ being transparent in the visible range starts absorbing around 510 nm after introduction of Cu(I and II). Further, this converted system is humidochromic and transits reversibly from lavender colored film at lower humidity to colorless transparent films at higher humidity, providing a prospect for use of the same in humidochromic windows.



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Phenazine based supramolecular photosensitizing assemblies: A 'smart' control on catalytic activity of Pd(II) nanoparticles

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Abstract:

Palladium catalysed Suzuki cross-coupling reaction is a powerful tool for the preparation of various pharmaceuticals, advanced functional materials, and natural products.¹ Though Pd Nanoparticles (NPs) based heterogeneous catalysts are preferred due to their high efficiency, easy recovery and recycling in comparison with homogeneous catalysts but need of tedious methods for achieving desired purity of target derivatives limit their further applications. So selection of support for the preparation of Pd NPs becomes very important step in achieving the desired catalyst recovery. Recently, Zeng et al. reported an interesting heterogeneous catalyst that actually catalyses the Suzuki cross-coupling reaction via homogeneous mode through the leached palladium ions in the solution.² The reaction conditions require an additional oxidising agent to amplify the aerial re-oxidation of leached Pd⁰ to facilitate the recycling of the catalyst. This study inspired us to develop the phenazine based photosensitizing supramolecular assemblies **PPA** showing strong affinity towards Pd²⁺ ions to generate Pd²⁺ centred supramolecular ensemble **PPA@Pd** NPs. The **PPA@Pd** NPs have dual advantages of homogeneous as well as heterogeneous catalysts to facilitate the Suzuki crosscoupling reactions under mild conditions (aerial conditions, aqueous media and visible light irradiations). Various studies confirm that the electron rich supramolecular **PPA** assemblies not only facilitate the oxidative addition step by photoinduced electron transfer to Pd²⁺ ions, but also bring the reactant closer to catalytic centre by selective interacting with aryl halide in presence of arylboronic acid under visible light.



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Synthetic study towards the Angucyclinones natural products

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Abstract: An efficient and collective synthetic approach towards the various angucyclinone natural products has been described. The key synthetic steps involved a sequential enyne metathesis/Diels-Alder approach to construct the tetra-cyclic framework of the natural products. The enyne precursor has been derived from commercially available geraniol by utilising asymmetric Sharpless epoxidation followed by regioselective epoxide ring opening as key steps.



(3S)-2,3-Dihydro-3-hydroxy-8-methoxy-3methylbenz[a]anthracene-1,4,7,12-tetrone

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Process development for lignocellulosic biomass conversion to 5hydroxymethylfurfural and furfural and their further value addition

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Abstract:

The sugarcane bagasse, corn stover, rice and wheat straws are ever-increasing global challenges for the modern civilization in agro waste refinery. In past, numerous approaches have been built-up for 2G-ethanol production. However, the comprehensive exploitation of these waste materials into furan based value added products to cover the area of textile, laminate, resin, nitro-furan based drug, medicinal and bio-polymer industry is still lacking.¹

Our research group have been dedicatedly involved in this field of biomass conversion to 5hydroxymethylfurfural (5-HMF) and furfural production, and their further value addition to other furanic compounds.^{2,3} We have developed a scalable, economical, energy efficient and highly specific process for 5-HMF and furfural production by utilizing sugarcane bagasse, corncob and cellulose as initial feedstocks.¹ The crucial role of oxalic acid dihydrate in biomass softening, delignification and fractionation to individual biopolymer under reaction conditions was found to be the main cause of conversion. In addition, the synergistic effect of AlCl₃, HCl, oxalic acid and activated charcoal for further biopolymer conversion to 5-HMF and furfural was also explored in our study. The process resulted 5-HMF and furfural in 55 and 47% yields respectively from sugarcane bagasse while 40 and 78% respectively from corncob biomass. The process was tested successfully in 500-gram scale as well in our existing scale up facility. Also, in case of structurally more complicated rice straw biomass, we utilized liquid nitrogen as effective grinding media for biomass preparation using mechanochemistry principals, and then proved the loosening or weakening of inter- or intramolecular interactions happened within or among biopolymers by using IR, SEM, TEM, TGA and DSC analytical studies.⁴ The fractionated biomass then under acidic system performed well and resulted furfural and 5-HMF in 57 and 14 % yields respectively along with lignin (165 g/Kg) and bio-char (660 g/Kg) as additional products. In our next phase development, we have invented sustainable, recyclable and cost effective heterogeneous catalytic systems for diformylfuran, furan dicarboxylic methyl ester and methyl 5-(hydroxymethyl)-2-furoate synthesis as versatile polymer building blocks, and biologically potent molecules.

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Supported bimetallic Pd-Au as catalyst development and its applications for carbonylative synthesis of S-methylthioesters and bis(indolyl)methanes

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Abstract:

Bimetallic catalysis is a rapidly emerging area owed to numerous opportunities for achieving new catalysts with enhanced activity, selectivity, recyclability and stability compared to parent monometallic catalysts. Specifically, for supported Pd-Au bimetallic catalysts (BMCs) it could be attributed to excellent ligand and ensemble effects between Pd and Au metals as well as role of applied support and method selection for their preparation.¹ Alongside, carbonylation reactions have been turned out as vital tool for insertion of carbonyl group into the targeted substrate. Since, CO gas is colourless, odourless, tasteless and highly toxic in nature and requires sophisticated equipment for its handling. Therefore, herein we are focusing on application of oxalic acid as solid and viable CO source along with polystyrene (PS) supported Pd-Au BMC for carbonylative transformations.²⁻⁴ The prepared Pd-Au@PS BMC with equimolar Pd/Au ratio was well characterized through HR-TEM, TEM-EDX, P-XRD, XPS and ICP-AES techniques. This Pd-Au@PS BMC is very easy to handle, air/moisture stable, recyclable and easily separable from reaction mixture. Thioesters exhibits enhanced reactivity in comparison to ordinary esters and have been well implemented in vast range of synthetic organic routes, foods, pharmaceuticals, and agrochemicals. The Pd-Au@PS BMC efficiently catalysed S-methylthioesterification of aryl iodides, where oxalic acid and DMSO have been applied as CO and -SCH₃ sources respectively.⁴ The Pd-Au BMC has shown appreciable activity and poisoning resistance under CO and CH₃SH environment during the course of reaction than respective monometallic Pd@PS catalyst. Furthermore, bis(indolyl)methanes (BIMs) which are 3-substituted indoles have numerous applications in pharmaceuticals, biologically active natural products and agrochemicals sector as anticancer, antimicrobial, antifungal, anti-inflammatory drugs and HIV-1 integrase inhibitor. Considering the importance of BIMs, a carbonylative approach also have been introduced from aryl iodides and indoles as starting material which superiorly catalysed by Pd-Au BMC using oxalic acid as CO source. The protocol for synthesis of BIMs found to be applicable for vast range of substrates either for aryl iodides or for indoles with moderate to excellent yields.

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Recyclable Polymer Anchored Pyridine: Utilization in Cascade Synthesis of Dihydrobenzofurans

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Abstract:

Polymer-supported catalysts and reagents have received considerable attention in regard to the synthesis of many organic molecules. It has become an essential approach in the green chemistry process of organic synthesis. These supported analogs have found many advantages, such as simplified product purifications, reusability, reduction of side products, less waste generation, sustainable, economic process, etc.

During the last few decades, dihydrobenzofurans have been considered to be highly privileged scaffolds that are found in many natural and bioactive compounds. In our continuous efforts to develop novel and sustainable approaches to construct structurally interesting and biologically applicable organic molecules. We present our recent research outcome on the highly stereoselective synthesis of, 2,3-disubstituted-2,3-dihydrobenzofurans *via* cascade 1,4-conjugate addition followed by intramolecular substitution reactions utilizing newly synthesized polymer anchored pyridines. This cascade approach relies on the in-situ generations of supported pyridinium ylides. The polymer anchored pyridines have been reused for multiple cycles without losing efficiency.



Scheme: Cascade cyclization reaction for the synthesis of 2,3-dihydrobenzofurans.

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Ruthenium(II)-Catalyzed functionalization of Arylamide *via* Weakly Coordinating Primary amide as Directing Group

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Abstract:



Considering the high importance of functionalized arene derivatives across the field of science, including pharmaceuticals, material science, and agrochemical industry, we aim herein to design and develop a new synthetic strategy for the synthesis of alkenylated and alkynylatedarenes *via* C-H bond activation using commonly occurring functional group such as primary amide as a directing group. In this context, a robust and general method for *ortho*-olefination and alkynylation of benzamide and hetero-arylamide has been established using a ruthenium catalyst. A major advantage of the developed method lies in the usage of a simple primary amide motif (-NH₂) as a desired directing group which eventually circumvents the installation and removal of extra auxiliary and less expensive ruthenium(II) salt as a catalyst. This newly developed protocol is simple, efficient, and has broad substrate scope and functional group tolerance.

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A Metal-free Four-component Sulfonylation, Geise cyclization, Selenylation Cascade via Insertion of Sulfur Dioxide

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Abstract:

Alkynyl Cyclohexadienones have emerged as imaginative synthons to rapidly access complex cyclic cores in a single operation via cascade cyclizations.¹ The presence of two reactive \Box -systems *viz* alkyne and enone leads to various diversely functionalized dihydrobenzofuranone and dihydrochromenone derivatives. The synthesis of monofunctionalized derivatives from cyclohexadienones² is well documented but corresponding difunctionalizations are synthetically more challenging and intriguing and therefore less explored.³



We have developed a highly regio- and diastereoselective arylsulfonylation-radical cyclization-selenylation cascade of alkynyl cyclohexadienones to access highly functionalized dihydrochromenones in good to excellent yields.⁴ The protocol utilizes aryldiazonium salts as aryl partners and DABSO as a benign SO₂ source and also as a redox mediator. The reaction tolerates a wide range of functionalities and is scalable. The products could be further modified and mechanistic studies were carried out to probe the reaction mechanism. Additionally, we also developed a visible light mediated protocol wherein diaryliodonium salts were used as the aryl partners at room temperature.

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Inhibitory effect of nucleotides on Acetylcholinesterase activity and its microflow based actuation in Blood Plasma

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Abstract:

In human body adenosine acts as an inhibitory neurotransmitter in the brain and involves in various path of signalling by forming Adenosine diphosphate, triphosphate (ATP) and cyclic Adenosine monophosphate. As far as the importance of biomolecules are concerned, it became curious to know how the acetylcholinesterase activity can be affected by them. The catalytic study of the enzyme has been performed in presence of Adenosine monophosphate, diphosphates, triphosphates, cyclic Adenosine monophosphate and Beta NADP in buffer as well as in human plasma.

Whatever can change the enzymatic activity it can also change the flow induced by substrate catalysis. Moving from this simple system of enzyme, an enzyme powered micropump was constructed with the help of layer-by-layer assembly of enzyme. This lab-on-chip (LOC) is the device for forthcoming generation where one can monitor the changes in the system without help of any external sources. The layer-by-layer assembly approach is independent of substrate, cost effective, enzyme multilayers can be developed with specific dimension and has wide applications in sensing, drug delivery etc. This makes enzyme micropump more useful in order to detect minimal amount of analyte in short duration.

Also, herein we have immobilized human Plasma i.e., biological fluid which is more complex system (a mixture of different enzymes) with the help of layer-by-layer assembly approach. The Plasma itself contained the enzyme acetylcholinesterase along with other enzymes that makes system more complex and more interesting. In this way various inhibitors and toxins can be detected in biological fluids. Also, this flow-based actuation Plasma system will open new doors in immobilizing real-life media and in modulation of different essential biomolecules in our body.

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Investigation of various nano-conductive additives on electrochemical performance of Na₂Ti₃O₇ anode in hybrid lithium-ion batteries

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Abstract:

Na₂Ti₃O₇ (Sodium titanate) is a promising anode material for Li-ion and Na-ion batteries. Its wide direct band gap of 3.07 eV leads to poor performance and high capacity fading after prolonged cycling, limiting the mobility of lithium ions between vacant sites of the structure, which results in low intrinsic electrical conductivity across the material. In this work, we explore the enhancement in electrochemical performance of Na₂Ti₃O₇ (NTO) as an active material admixed with multiwalled carbon nanotubes (MWCNT) as a nano-conductive additive along with carbon black (CB) for its application in Li-ion batteries. Various electrochemical measurements- EIS, CV, galvanostatic cycling, etc were carried out in the CR2016 half-cell configuration. The charge-discharge profile has been comparatively analyzed with the effect of CB and CB +MWCNT at different C-rates to investigate performance and capacity retention. The discharge capacity of the NTO/(CB+MWCNT) half-cell was improved to 123.33 mAh/g compared to NTO/CB half-cells with 96mAh/g at a 0.1 C-rate. Also, there is a significant reduction of 21% in internal resistance in the NTO/(CB+MWCNT) half-cell when recorded between 10 mHz to 100 kHz. Cyclic voltammetry study shows an increase in the maximum peak current leading to high diffusivity (D_{Li}⁺) in the case of NTO/(CB+MWCNT) compared to NTO/CB. Thus, our study concludes that the cumulative addition of MWCNT and conventional CB in NTO provides better 'inter-particle connectivity' attributed to the longrange electron pathway leading to enhancement in discharge capacity and overall capacity retention of the cell. Also, various Ex-situ characterization techniques like FESEM, AFM, etc were recorded to analyze the morphology and subsequent roughness of the electrode before and after cycling. Moreover, the percolation threshold from the power-law equation was evaluated and discussed.

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PHYSICAL CHEMISTRY

Kinetic and Mechanistic Investigation of oxidation between sulfanilic acid and HCF(III) in alkaline medium.

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Abstract:

The Kinetic investigation between Sulfanilic acid and Hexacyanoferrate [III] in alkaline medium have been performed. The overall reaction is second order *viz*. first order with respect to each reactant. The rate of reaction increases with the concentration of alkali. The thermodynamic parameters are evaluated and plausible reaction mechanism has been suggested. Accounting these observations probable reaction mechanism has been suggested and the derived rate law by equation 1.

$$\frac{d[Fe(CN)6]^{3-}}{dt} = \mathbf{k} \frac{[SA][Fe(CN)6]^{3-}[OH]^{-}[M^{n+}]}{[Fe(CN)6]^{4-}}$$
(1)

Activation parameter such as energy of activation and entropy of activation have also been calculated to be (29.57 ± 0.1) kJmol⁻¹ and (-162.9 ± 0.53) JK⁻¹mol⁻¹ respectively by employing Erying equation.

Keywords: Kinetics; Oxidation; Mechanism; Sulfanilic Acid; Hexacyanoferrate [III].

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Recyclable Luminescent Metal-Organic Probes for Real-Time Fast and Selective Detection of 2,4,6-Trinitrophenol in Aqueous Media

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Abstract:

Nitroaromatic compounds are frequently used as ingredients of explosive devices, such as bombs, grenades, and mine fillings.¹ Their excessive use in fireworks and leather industries has also led to water and soil contamination, which in turn has resulted in several human health hazards.² In the past two decades, a variety of materials organic and metal-organic probes has been developed by many research groups including ours to demonstrate ultrafast, selective and efficient detection of such nitroaromatic compounds, specifically 2,4,6-trinitrophenol (TNP).³ In this work, we extend our efforts to this important issue by utilizing the green emission property, established by fluorescence spectroscopy, of a series of Zn(II) and Cd(II) based metal-organic probes, namely $\{[Zn(mbhna)(bpma)]\}_n$ (1), $\{[Cd(mbhna)(bpma)], DMF\}_n$ (2), $\{[Zn(mbhna)(bpea)]\}_n$ (3), ${[Cd(mbhna)(bpea)]}_n$ (4), ${[Zn(mbhna)(bpta)]}_n$ (5), ${[Cd(mbhna)(bpta)(CH_3OH)]}_n$ (6), {[Zn(mbhna)(bpba)][·]CH₃OH H_2O_n (7), and $\{ [Cd(mbhna)(bpba)] \}_n$ (8), where $H_2(mbhna) = 4,4$ '-methylene-bis[3-hydroxy-2-naphthalene carboxylic acid], and bpma, bpea, bpta, and bpba are tridentate polypyridyl ancillary ligands.⁴⁻ ⁵ These probes are found to detect the presence of TNP in aqueous media in 20 secs with high efficiency and selectivity (detection limit as low as 0.24 ppm). With the help paper strip detection tests, it has been confirmed that these recyclable probes can be utilized for real time applications.

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Naphthalimide-gold-based nanocomposite for the ratiometric detection of okadaic acid in shellfish

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Abstract:

Okadaic acid (OA) is one of the known marine biotoxins produced by various dinoflagellates and exists in seafood such as shellfish. The consumption of contaminated shellfish with OA leads to diarrheic shellfish poisoning (DSP), which results in the inhibition of protein phosphatase enzymes in humans. This poisoning can cause immunotoxicity and tumor promotion due to the accumulation of okadaic acid in more than the allowed limit in bivalve molluscs. The reported methods for the detection of okadaic acid include mouse bioassays, immunoassays, chromatography coupled with spectroscopic techniques, electrochemical sensors and immunosensors. We have developed a naphthalimide-gold-based nanocomposite for the detection of okadaic acid. Individually, the organic nanoparticles (ONPs) of synthesized naphthalimide-based receptors and gold-coated ONPs are less sensitive for detection. However, fabrication of the composite of Au@ONPs and ONPs enhance the sensing properties and selectivity. The composite shows a ratiometric response in the UV-Vis absorption spectrum and quenching in the fluorescence profile for OA in aqueous medium. In cyclic voltammetry, a shift was observed in the cathodic peak as well as in the anodic peak with the addition of okadaic acid. To study the quick binding of the composite with OA, a time response experiment was performed. Also, the developed sensor retains its sensing ability in the wide pH range and in high salt conditions. This developed composite can be used for the detection of OA in real applications.

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Synthesis and characterization of Cs₄CuSb₂Cl₁₂ layered double perovskites: Effect of surface capping ligand on charge carrier dynamics mediated by trap states

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Abstract:

Perovskite solar cells have recently emerged as one of the most promising photovoltaics technology. Over a decade, the efficiency of perovskite solar cells has enhanced from a meagre 3.8% to over 25.5%. These solar cells offer facile synthesis methods, a tunable bandgap and demonstrate enormous potential to be used instead of or in tandem with silicon solar cells. In this regard, lead halide perovskites, particularly MAPbI₃, bring forth the most promising results. Despite unparalleled progress, lead halide perovskites encounter several stability issues upon exposure to heat, oxygen and moisture and are toxic as they contain lead. This has prompted researchers to explore other non-toxic and more stable substituents to lead halide perovskites for perovskite solar cells.

The introduction of double perovskites (DPs) ushered in new possibilities for the development of stable and lead-free perovskites. In this respect, a new class of DPs namely Cs₄CuSb₂Cl₁₂ (CCSC) has been reported. CCSC has evolved to offer high photo- and thermal stability and is tolerant towards moisture. However, the most pressing concern about CCSC is the presence of abundant surface traps which are detrimental to the stability and efficiency of the solar device. Here, to address this issue, we have passivated surface traps using oleic acid (OA), and oleylamine (OAm) surface capping ligands. We have used the UPS technique to determine hole trap states in CCSC. Further, we have studied the excited dynamics of CCSC microcrystals (MCs) with and without capping ligands using femtosecond transient absorption spectroscopy.

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Title of the Poster Ring Expansion of Isatins *via* 1,2-Phospha-Brook Rearrangement: A Convenient Synthesis of 2-quinolinone derived *p*-quinone methide.

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Abstract:



A Lewis acid-mediated one-pot two-step one-carbon homologation approach is efficiently carried out and the *para*-Quinone Methides embedded 2-quinolinone cores are established. The spirocyclopropane formed *in situ* from isatin and traditional *p*-QMs *via* [1,2]phospha-Brook rearrangement¹ was expanded with Lewis acid to afford the intended product. A wide range of *p*-QMs embedded 2-quinolinone cores are synthesized with yield up to 92 % with high regioselectivity. Also, post synthetic modifications such as C-P, C-S, and C-C bond formation have been elegantly demonstrated as well as substituted 3,4-dihydroquinilinone-2 cores are formed.

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Electrochemical Determination of Triclosan on Self Assembled Aromatic and Heterocyclic Thiol amines via Surface Reactions

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Abstract:

The abundance of triclosan in the natural environment is attributed to its extensive use in commercial products and healthcare. Significant concerns regarding usage of triclosan have been raised as it is known to have detrimental effects on aquatic and marine life, disrupts hormonal and reproductive functioning in animals and is responsible for asthma, skin allergies, photo-allergic dermatitis, increase in body mass index, etc¹. The present work is intended towards the development of a fast, simple and reliable method for the detection of triclosan. Self-assembly of two thiols, 4-aminothiophenol (ATP) and 5-amino-2-mercaptobenzimidazole (AMB), was achieved on gold electrodes and was electrochemically characterized using Cyclic Voltammetry (CV) and Electrochemical impedance spectroscopy (EIS). The amine groups of these thiols were further subjected to diazotization which allowed the detection of triclosan in aqueous media². The proposed sensors based on Au-AMB-diazo-TCS and Au-ATP-diazo-TCS exhibited sensitivity towards triclosan in the concentration range of $1.0 \times 10^{-12} \text{ M} - 1.0 \times 10^{-4}$ M and 1.0×10^{-10} M - 1.0×10^{-2} M respectively. A good selectivity was observed in the presence of diverse metal ions (Na⁺, K⁺, Ca²⁺, Mg²⁺, Cu²⁺, Fe³⁺, Zn²⁺, Co²⁺) and surfactants (SDS, Triton X100, Triton X114). The estimation of triclosan in real samples has been achieved using the proposed sensors.

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Scanning Tunnelling Microscope – A tool to study materials at atomic level

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Abstract:

Scanning tunnelling microscope (STM) is an instrument of paramount importance to study surfaces and atoms or molecules adsorbed on surfaces. STM can be used as a tool for not merely imaging but various electronic and mechanical studies to test the strength of modern nanomaterials. STM is based on the concept of quantum tunnelling. When the tip is brought very near to the surface to be examined, a bias (voltage difference) applied between the two can allow electrons to tunnel through the vacuum between them. The resulting tunnelling current is a function of tip-sample distance, applied voltage, and the local density of states (LDOS) of the sample. Information is acquired by monitoring the current as the tip's position scans across the surface, and is usually displayed in image form. The experiments were intended to perform on Si (111), Ag (111) and Au (111) in UHV (ultra-high vacuum) conditions. The sample was repeatedly sputtered with argon ions and annealed to induce the formation of terraces and smooth top layer. Organic molecule - phthalocyanine were sublimated on the Ag (111) surface using an e-beam evaporator. Then, the sample was imaged to find how phthalocyanines are adsorbed and the conditions for molecule deposition are optimized. Better resolution images were obtained at low temperature. Mono/few layered WS2/MoS₂ was deposited onto Silicon using Chemical Vapor Deposition (CVD) technique. The grown WS2/MoS₂ was then confirmed with Raman Spectroscopy and imaged using Optical Microscope and Atomic Force Microscope. The interactions between WS2/MoS2 and Phthalocyanines will be studied with STM.



Figure 1 (left) STM image of MoS2 on Si (111), (middle) STM image on Phthalocyanine monolayer on Ag (111) and (right) individual phthalocyanine molecules on Ag (111)

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Single-Droplet Vibrational Raman Spectroscopy Illuminates the Inner Workings of Phase-Separated Biomolecular Condensates

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Eukaryotic cells contain a host of non-canonical membrane-less organelles that are formed via liquid-liquid phase separation (LLPS) of intrinsically disordered proteins/regions (IDPs/IDRs) along with nucleic acids and other biomolecules. These biomolecular condensates are involved in a myriad of critical cellular functions and neurodegenerative diseases. Unmasking the role of intrinsic disorder and conformational heterogeneity of IDPs/IDRs in promoting promiscuous and ephemeral interactions resulting in liquid-like behavior of these condensates is crucial to understand the molecular drivers of LLPS. While a host of existing microscopic and spectroscopic tools are immensely useful to study LLPS, most of these methodologies are inadequate in illuminating the conformational heterogeneity and distribution within individual droplets. In order to overcome these limitations, we have developed and adapted a novel, highly sensitive, single-droplet structural tool involving dispersive laser Raman spectroscopy in a microscopy format that offers a wealth of fundamental molecular information within the mesoscopic liquid condensed phase. This design allows us to focus the laser beam into the protein-rich dense phase of individual droplets to capture Raman scattering bands associated with a range of molecular vibrational modes from protein-rich single droplets. Using our studies, we have been able to capture unique conformational characteristics that govern LLPS of an intrinsically disordered pathological stop codon variant of the prion protein namely, Y145Stop that is associated with Gerstmann-Sträussler-Scheinker syndrome and familial cerebral amyloid angiopathy. These single-droplet vibrations studies illuminate the conformational disorder, heterogeneity, and distribution in Y145Stop liquid droplets and their maturation into ordered, β-rich, autocatalytic, amyloid-like aggregates formed via liquid-tosolid phase transitions. I will also discuss new results from our ongoing Raman spectroscopic investigation on the phase transition of FUS that is modulated by the RNA-protein stoichiometry.

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Chemically Functionalized MoS₂ Nanosheets for Lubrication Enhancement

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Abstract:

Excellent mechanical properties, low shear strength, high thermal stability, and large surface area make MoS₂ a promising material for the enhancement of lubrication properties. Interlamellar weak van der Waals interaction between adjacent molecular lamellae of MoS₂ facilitates shearing under the sliding stress, which reduces the friction. The dangling sulfur atoms of MoS₂ show good adhesion with iron-based substrates under the tribo-stress and form a protecting thin film to extend antiwear properties. However, the poor dispersibility of MoS₂ nanosheets in liquid lubricants has been a major challenge for real-time lubricant applications. Present work addresses a bottom-up single-step approach to prepare long alkyl chains grafted MoS₂ nanosheets through a hydrothermal approach. Chemical, structural, and morphological features of chemically-grafted MoS₂ nanosheets are evaluated by XPS, FTIR, Raman, HRETM, and XRD measurements. The chemical functionalization extended the dispersion stability of MoS₂ nanosheets, which is crucial for their utilization in liquid lubricant applications. The chemically-functionalized MoS₂ as an additive to 10W40 engine oil decreased the coefficient of friction and wear scar diameter of steel tribo pair. Detailed microscopic and spectroscopic results of worn scars will be discussed during the presentation to emphasize the role of chemically-functionalized MoS₂ in the enhancement of lubrication properties.

Immobilized Enzyme on Metal Organic Framework for Leather Applications

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Abstract:

Enzymes are widely used in leather industries in certain processes such as unhairing, bating and degreasing. In the bating process, the enzyme lipase is used to remove protein-based inter fibrillary materials to make hides pliable for further leather processing.¹ The downside is that the enzyme cannot be recovered at the end of the process. Immobilization of enzyme on solid substrates has been known to have several advantages such as good enzyme stability, short digestion time, easy recovery and reusability of enzymes.² Herein we have synthesized Co₃O₄@CoMOF composite using pervlene-3,4,9,10-tetracarboxylic dianhydride as the ligand. The prepared Co₃O₄@CoMOF (CMF) and enzyme immobilized Co₃O₄@CoMOF (CMF-L) was confirmed by using Fourier transform infrared spectroscopy (FTIR) and powder XRD. The activity and concentration of lipase was confirmed using UV-visible spectrophotometer. The size and morphology of the MOF was analysed using dynamic light scattering (DLS) and scanning electron microscope (SEM). The lipase activity of CMF-L at varied pH and temperature were analysed and confirmed by XRD and FTIR. CMF-L lipase activity at repeated cycles were analysed to determine the recycling efficiency at pH 8.5 (37 °C). The results obtained here suggest that lipase activity diminished slightly but conserved in the enzyme immobilized CMF-L. In addition, CMF-L can be recovered and reused in the activity assay. Further, the prepared CMF-L can be used potentially in the leather industry for enzyme recovery and reusability.



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Synthesis of Non-anomeric Spiro-Fused Bicyclic Sugar derivatives *via* Light Mediated Intramolecular Hydrogen Atom Transfer (HAT) Process

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Carbohydrates, an important class of biomolecules, play vital roles in all living systems and are essential components of many natural products and pharmaceuticals. However, selective modifications in the sugar scaffold containing multiple hydroxyl groups remains an abiding challenge in synthetic organic chemistry. Importantly, the incorporation of functionalized heterocyclic units to the carbohydrate skeleton have found large applications in medicinal and pharmaceutical industry. In this context, the modified spiro-fused bicyclic sugars have emerged as an important class of carbohydrates with wide biological and synthetic utility. We, herein, demonstrate a mild synthetic strategy for the construction of complex spiro-fused bicyclic sugar derivatives from easily synthesizable glycosyl 6-trichloroacetimidates via visible light mediated intramolecular hydrogen atom transfer process. The efficient C-H functionalization initiates via *in situ* generation of N centered radicals under metal-free conditions using NaI and hypervalent iodine PIDA as the reagents. Taken together, mild reaction conditions, green source of energy, broad substrate scope encompassing both armed and disarmed hexoses and high yields of conformationally constrained products makes this strategy a novel tool for facilitating advances in the field of glycosciences.

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Photochemistry of Benzothiazole and 2-iodobenzothiazole in cryogenic conditions in inert gas matrices

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Abstract:

Thiazole is a biologically and pharmaceutically important heterocyclic moiety. The generation and catalysis of bio-inspired *N*-heterocyclic carbene based on thiamine molecule are well known in the literature.[1] However, the formation and reactivity aspects of simpler dehydro-radical derivatives of the thiazole have not been experimentally explored yet. Based on our group's earlier computational investigations on various thiazole radicals, the electronic structure, stability, and unimolecular decomposition channels, several insights, and properties of them have been investigated.[2] In particular, the kinetic stability of these radicals was found to be low. Apparently, matrix isolation and photo-fragmentation studies on thiazole by Miyazaki J. et al. revealed that C-S in thiazole can be cleaved easily, which can lead to multiple photoproducts.[3]

To limit the multiple photochemical ring-opening channels, we have utilized a benzene fused benzothiazole. Besides this, we have also considered the 2-iodobenzothiazole, as an additional precursor, whereas the iodo precursors are known for the generation of radicals. With these two precursor molecules, we intended to explore the competition between C-I vs C-S bond cleavages under photochemical conditions. Interestingly, we observed that under photochemical conditions, the C-S bond was more prone to cleavage than the C-I bond ending up with ring-opened and rearrangement products. The photochemistry of 2-iodobenzothiazole and benzothiazole, and characterization of various photoproducts have been carried out using matrix isolation infrared spectroscopy in combination with computations. The preliminary results of this investigation are reported in this contribution (**Scheme 1**).



Scheme1. Photochemistry of 2-iodobenzothiazole and benzothiazole

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Azobenzene-based ligands exhibiting high Z-stability and Supramolecular Assembly

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Abstract:

The reversible photoisomerization of azobenzene is a remarkable phenomenon, which can be utilized in supramolecular chemistry for making self-assembly materials, smart switches, gels, light responsive liquid crystals, etc. The photoisomerization behaviour of azobenzene may be affected by various factors such as temperature, mode of excitation, radiation wavelength, solvents, the substituent effects, etc.¹⁻³ Furthermore, the reversibility of photoisomerization is found to be very useful to control the supramolecular assembly of azobenzene within the polymer structure. The systematic studies of the effect of various substitution at different position of azobenzene on supramolecular assembly have not been carried out so far in detail.

In this regard, we attempted to design systems with mono, di and tetra substituted azobenzene core appended with triazole-amide linkers and terminal groups with benzene, *ortho*, *meta* and *para* substituted pyridine. Through this, we have successfully synthesized a series of 15 compounds that exhibit different aggregation behaviour. We have explored their photoisomerization behaviour, thermal Z-isomer stability, activation parameters associated with the thermal reverse isomerization steps, etc., by means of UV-Vis and NMR spectroscopy. Also, using systematic variations in the designs, we successfully achieved supramolecular hydrogels with excellent water holding capacity. All these results are presented in this contribution.



Figure: Sol-gel behavior of azobenzene based ligand upon photoisomerization

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. Photophysics of N-ButylcarbazoleBODIPYs: A Comparative study

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Abstract:

Fluorescent probes have been extensively used for understanding the environment around the probe molecule at nanoscopic/microscopic levels. BODIPY dyes are considered to be potential compounds for functional fluorescent probe development because of their relatively high photostability, neutral total charge, high fluorescence quantum yield, and sharp absorption and emission spectra. The photophysical behaviour of these molecules has drawn huge attention in different light-harvesting-material and imaging applications[1]. In addition, linking of efficient donor-acceptor moieties at suitable orientations may make them active to sense the alteration of micro-environment with all six different fluorescence parameters like emission intensity, wavelength, anisotropy and their corresponding time dependent parameters.Substitution of carbazole at the meso-position of BODIPY core has shown to alter its photophysical properties significantly[2]. In this study, we explore the photophysics of two conjugates, N-butylcarbazoleBODIPY carbazole-BODIPY and N-butylcarbazolebis-BODIPY, with a specific objective of doing a comparative study. The dyes were synthesized using previously reported procedures[3,4].

The absorption and emission spectra of the dyes were recorded in different solvents with varying polarity. The longest wavelength absorption was observed in the range 494 - 498 nm. Bis-BODIPY shows absorbance as twice as its monomer due to the presence of two BODIPY chromophores. The red-shifting of emission maxima and decrease in intensity with solvent polarity is predominant in N-butylcarbazoleBODIPY. The Lippert-Mataga plot shows that the magnitude of Stoke's shift is more in mono-BODIPY dye. The fluorescence lifetime values show that the extent of ICT emission is more in N-butylcarbazoleBODIPY than the dimer in most of the solvents. The DFT calculations show that the charge transfer occurs from carbazole unit to the BODIPY core. The temperature study confirms that the charge transfer is due to TICT in both the molecules. The potential energy curves plotted as a function of twisted angle obtained from theoretical calculations confirm TICT behavior of the dyes. The fluorescence anisotropy (r) values were found to be significant in both the molecules. The high 'r' values suggest that their S₀ \leftrightarrow S₁ transition dipoles are nearly parallel in viscous medium.

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Effective degradation of organic molecules and increased antibacterial activity by bandgap tuning of ZnS

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Abstract:

Metal chalcogenides have received widespread attention for their application in phosphors, electroluminescence devices, light-emitting displays, and optical sensors. Among many metal chalcogenides, zinc sulfide (ZnS) is studied extensively by researchers for versatile applications. To realize the suitable property for various applications, we have produced ZnS (sf-ZnS) and metal-doped ZnS nanoflakes (sf-m-ZnS; where m = Cu, Ni, Cd, Bi, or Mn) and correlated their activity with bandgap variation. We obtained all these materials via hexamethyldisilazane (HMDS)-assisted synthetic method without using any surfactants, polymers, or template molecules to enhance the activity providing free active surface and characterized them thoroughly using various techniques. Photocatalytic, as well as antibacterial, activities of these materials showed their bifunctional utility. We have demonstrated the effect of doping and consequent extension of absorption band to the visible region and resultant improved photocatalytic activity under sunlight. Among all materials produced, sf-Cd-ZnS provided superior results as a photocatalyst while degrading two organic pollutants-rhodamine B (RhB) and methylene blue (MB) in water. The antibacterial activity of sf-ZnS and sf-m-ZnS against Gram-positive bacteria, i.e., Staphylococcus aureus (S. aureus), was examined by the zone of inhibition method, wherein sf-Ni-ZnS showed maximum activity. The enhanced activity of these ZnS materials can be attributed to the free surface of nanoparticles without any capping by organic molecules, which provided an intimate interaction of inorganic semiconductor material with organic and biomolecules. Thus, we have demonstrated modification of properties both by bandgap tuning of materials and providing the opportunity for intimate interaction of materials with substrates. These results illustrate that the nanoparticles synthesized using HMDS are promising materials for water purification and environmental remediation.

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Abstract:

The increasing utilisation and depletion of non-renewable resources is the major concern of the present world which needs an alternative and efficient way to overcome the problems of energy supply.¹⁻² Hydrogen is regarded as sustainable fuel for the future and plays a crucial role in diminishing CO₂ emission and problems caused by the usage of non-renewable resources.³ Highly efficient conversion of glycerol to hydrogen gas (1.59 equiv.) and lactic acid (70% yield) over ruthenium nanoparticle catalyst (~2.7 nm) was achieved in water at 90-120 °C. The synthesized ruthenium nanoparticle catalyst was characterized by PXRD, FE-SEM, TEM, and XPS analysis techniques. It was revealed that the size of ruthenium nanoparticles formed was approximately 2.7 nm calculated using TEM analysis and shows the high activity for the hydrogen production and synthesis of sodium lactate from biomass-derived glycerol. Moreover, hydrogen production from glycerol (6.84 mmol) and water solution produces 6.37 mmol (156 mL) of H₂ gas with 83% selectivity of sodium lactate under the catalytic reaction condition. Furthermore, the temperature effect, catalyst loading, dilution effect, and effect of different bases (NaOH, KOH, K^tOBu, and Na₂CO₃) were investigated in detail. The activation energy for hydrogen production over ruthenium nanoparticles catalyst was estimated as 77 kJ/mol.

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Photophysical Studies Extended π-Conjugated Azopyrazole and Azoisoxazole derivatives

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Abstract:



Azobenzene photoswitches are favoured since the discovery of azobenzene for their robust photoswitching ability and wide array of applications. Azoheteroarenes represent a relatively new class of azobezene, which are less explored, where one of the aryl rings from the conventional azobenzene has been replaced with a five-membered heteroaromatic ring. Considering their increasing importance in a variety of fields, tuning and understanding the structure-property relationships of them are quite useful.

In this regard, we synthesized 23 extended π -conjugated azopyrazole and azoisoxazole derivatives appended with diverse functionalities phenyl, phenyl acetylyne, styrene, pyrene and tetraphenylethene styrene. To achieve this, various cross-coupling reactions, especially Heck, Suzuki, and Sonogashira reactions have been considered. The aims of this study include the effect of π -conjugation at different position of azopyrazole and azoisoxazole derivatives on the photoswitching, and the thermal stability of their *cis*-isomers. Through systematic studies, a comparison has been made and the results are presented in this contribution.

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Architectural influence on the nano-aggregates of randomly decorated amphiphilic polymers

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Abstract: Self-assembly of polymers into diverse nanoscale morphologies such as micelles, vesicles, rods, and cylinders, is well established in the polymer world for many decades¹. These intriguing self-assembled structures exhibit essential applications in various fields, including multi-stimuli responsive materials, drug delivery, optical materials, etc. The self-assembled morphologies are generally derived from multiple non-covalent interactions, such as hydrogen bonding, $\pi - \pi$ stacking, and solvophobic interactions.

Among the whole library of polymers such as linear, branched, star, dendritic etc. Hyperbranched polymers are highly branched 3D macromolecules and peoples are attracted owing to topological structure and unique properties like high solubility, lower viscosity, intramolecular cavities and plenty of terminal functional groups¹. Hyperbranched polymers are well known to be able to from unimolecular micelles² due to their globular structure whereas linear are not. In contrast, nano aggregates of these polymers are multimolecular micelles.

Herein, we have demonstrated the synthesis of randomly grafted amphiphilic hyperbranched copolymers and their equivalent linear analog consisting of two chemically distinct segments, hydrophilic and hydrophobic. The present studies have been explicitly focused on the self-assembly behavior of these polymers; the effect of architecture linear vs. hyperbranched on the ease of reorganization to form some fascinating nano aggregates and their encapsulation efficiency in solution. Amphiphilic polymers with two distinct segments are known for segregation into unique Janus configurations³ and have potential to self assemble. Micelles were characterized by TEM and DLS data. Sensing of the microenvironment of core-shell structure was performed in two ways covalent and non covalent guest encapsulation studied using spectroscopic techniques. Both topologies revealed same results irrespective of the architecture although hyperbranched polymers are more responsive in few respects.



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Polymer Supported DMAP: Effective reusable catalyst for the construction of αpyrone via Michael addition/cyclization

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Abstract:

Polymer-supported catalysts have emerged as one of the efficient and cost-effective alternatives in organic synthetic chemistry. In recent years, considerable efforts have been driven for the use of supported catalysts, especially polystyrene-supported organocatalysts. Over the non-supported catalysts, supported analogues have found many advantages, such as, simplified product purifications, recyclability of the supported catalysts, minimized formation of side products, less waste, greener, sustainable and economic process etc.

5*H*-oxazol-4-one is one of the strategic pronucliophile for the installation of the hydroxy group at the α -position of carbonyls to construct α -alkyl- α -hydroxycarboxylic acid derivatives. Hearin, we have presented our recent finding on supported DMAP catalyzed synthesis of \Box -pyrone via cascade Michael addition/cyclization of 5*H*-oxazol-4-ones and $\Box \Box$ -unsaturated- \Box -ketoesters.



Scheme 1: Synthesis of α -pyrone via supported amines catalyzed cascade reactions.

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Role of Crystal Structure and Electrical Polarization in Bi-Fe-O system on their Electrocatalytic Oxygen Evolution performance

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Abstract:

Water electrolysis is dependable link for primary hydrogen and oxygen evolution reaction. Oxygen evolution reaction (OER) requires high overpotential owing to the four-electron transfer requirements. In order to overcome the high overpotential, various metal oxides/hydroxides have been developed and studied for OER [1]. The efficiency of electrocatalytic OER also depends on the various parameters of the catalyst such as electronic structure, crystal structure, phase structure, morphology, oxidation state etc. Crystalline arrangement of the inorganic materials influence the arrangement of atoms and their electronic structure affecting their catalytic performance [2]. In addition to the crystal structure, electrical polarization also influences water oxidation. Herein, we discuss the influence of crystal structure in Bi-Fe-O system and the effect of electric polarization on their performance towards electrochemical OER [3]. The three phases of Bi-Fe-O systems discussed are BiFeO₃, Bi₂Fe₄O₉ and Bi25FeO40. BiFeO3 (multiferroic oxide) crystallizes in perovskite structure, Bi2Fe4O9 possesses the mullite structure whereas Bi₂₅FeO₄₀ crystallizes in the sillenite structure. From their current density profiles, it was observed that orthorhombic Bi₂Fe₄O₉ exhibits better OER activity due to lowest charge transfer resistance and the highest double layer capacitance. After the electrical polarization of these three oxides, Bi25FeO40 was observed to show an enhancement of OER activity by 4-fold as compared to BiFeO3 and Bi2Fe4O9.

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Abstract:

Knoevenagel condensation is widely used in organic synthetic chemistry and several reaction conditions have been demonstrated. These reactions in a neutral medium are challenging. In this report, we present a sustainable and greener method for Knoevenagel condensation reaction between carbonyl compounds (both aldehydes and ketones) and active methylene compounds using rose bengal as a photosensitizer in an aqueous medium. This protocol works smoothly for aromatic aldehydes and ketones containing both electron-donating and electronwithdrawing substituents.

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In-vitro metabolite identification of beauvericin using liquid chromatography high resolution tandem mass spectrometry for biomonitoring studies

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Abstract:

Mycotoxin contamination of cereal crops is a global problem since about 35% of cereal crop products contain detectable levels of mycotoxins. Beauvericin (BEA) is one of the emerging mycotoxins having a cyclodepsipeptidic ring and is majorly produced by the Fusarium species and Beauveria bassiana as a toxic secondary metabolite. BEA is known for contaminating cereals and grains (wheat, maize). BEA has a variety of lethal activities in mammalian cell lines, which includes inducing apoptosis, a rise in cytoplasmic calcium concentration due to its ionophoric mechanism, and DNA fragmentation. Humans might be exposed to BEA through contaminated food. Biomonitoring is a method for measuring environmental and occupational exposures to a specific chemical for assessing the human health risk. In biomonitoring studies, the measurements of chemical biomarkers are used to quantify the exposure to a specific chemical. To assess the human's exposure to BEA, it is necessary to identify a specific and sensitive biomarker of BEA. So far, no chemical biomarkers of exposure are known for BEA. To identify such biomarkers, we investigated the *in-vitro* metabolism of BEA in rat liver microsomes (RLM) using LC-MS/MS and LC-HRMS technique. A total of 10 Phase-I metabolites were identified by HRMS based on retention times, theoretical and observed mass difference and fragmentation spectra. The main metabolites obtained were basically the product of mono-oxygenation, di-oxygenation, reduction and oxidative deamination to alcohol or ketone. Further, in-vivo studies are required to confirm the usefulness of identified BEA metabolites as chemical biomarkers of exposure.

Keywords: Beauvericin, mycotoxin, chemical biomarker, metabolite, high-resolution tandem mass spectrometry

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Hematite/Zinc-Iron Layered Double Hydroxides for Efficient

Photoelectrocatalytic Water Splitting

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Abstract:

The continuous degradation of ambient air quality in the urban centres of India demands effective measures to curb air pollution. Solar driven photoelectrocatalytic (PEC) water splitting has recently gained wide attention due to its pollution free green hydrogen production. The semiconductor photoelectrodes undergo redox reaction and covert incident solar energy into electrochemical energy. However, due to the rapid recombination of electron-hole pairs, poor catalytic activity, and electrode stability, PEC water oxidation is a difficult reaction in solar water splitting for the production of green hydrogen, to the existing global energy crisis. Hematite (α -Fe₂O₃) is a highly promising photoanode because of its narrow bandgap of 1.9-2.2 eV (> 400 nm), the higher theoretical solar to hydrogen conversion efficiency ($\approx 17\%$), ease of production, low cost, abundance, and non-toxicity. The greatest impediment to the stability and performance of a pristine hematite photoanode is charge recombination. Layered double hydroxides (LDHs), which have gained increasing attention due to their tunable chemical composition and multi-functionalities, have become an effective strategy for overcoming these obstacles. Transition metals containing LDHs, in particular, have demonstrated excellent catalytic performance in PEC water splitting and can be employed as co-catalysts in PEC water splitting. In the current work, the in-situ electrodeposition of Zn-Fe LDH was carried out over the α -Fe₂O₃ electrode. The physiochemical properties of the fabricated electrodes were analysed by XRD, FE-SEM, HR-TEM, UV-vis, PL, XPS, FT-IR, and Raman spectra and PEC performance was studied under the illumination of AM 1.5G (100 mW cm⁻²). The α -Fe₂O₃/Zn-Fe LDH exhibits remarkably enhanced PEC performance by improving electron-hole separation and hole injection efficiency than bare α -Fe₂O₃.

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Piperazine-Linked Covalent Organic Polymer as the Efficient Platform for the Removal of Toxic Mercury Ions from Wastewater

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Abstract:

A new piperazine-linked robust covalent organic polymer (COP), SMCOP-1 has been synthesized by a catalyst free method and characterized by FTIR, ¹³C CP/MAS, XPS and PXRD. There are very few reports where N-containing covalent organic polymers can effectively uptake Hg^{2+} from wastewater. This system has shown >97% Hg^{2+} removal as confirmed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) with an uptake value of 1329 mg/g which is even better than many S-containing covalent organic polymers classically used for Hg^{2+} removal. The high Hg^{2+} adsorption by the SMCOP-1 could be ascribed to the presence of strong non-covalent interaction between the Hg^{2+} ion and the binding sites of the covalent organic polymer, which is confirmed by the XPS analysis. The recyclability of the material was studied up to four consecutive cycle and it was observed that this material retains the high removal capacity without any change in the structure and morphology as confirmed by FTIR and FE-SEM.



A case study of the structural transformation for colloidal Ruddlesden-Popper Iodide Perovskite Nanoplates: Effect of the UV light and moisture

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Abstract:

Quantum confined two-dimensional (2D) Ruddlesden-Popper (RP) lead halide perovskite (LHP) materials are recently a rising star with their three-dimensional (3D) family. When significant research is already started for their crystal growth, commercialization in the field of optoelectronics, a limited study is observed on their phase pure colloidal version. Here, we have synthesized and characterized phase pure, colloidal and orange emitting oleylammonium iodide-based RP perovskite nanoplate (NPl), (C₁₈H₃₅NH₃)₂(CH₃NH₃PbI₃)₂PbI₄ having a photoluminescence quantum yield (PLQY) of 40% and the thickness of lead iodide octahedral layer (n) is 3. Then we had systematically studied the fate of the UV light irradiation on this NPl and a crucial role of the moisture is revealed. The continuous UV exposure in presence of the atmosphere transformed the 2D RP NPl structure into bulk 3D methylammonium lead iodide (CH₃NH₃PbI₃) nanorods (NR) ($n = \infty$) having a PLQY of 65% whereas in presence of the inert atmosphere, the RP structure gets collapsed. The mechanism of this structural transformation is explained by a ligand desorption followed by the structural association Further, we have studied the colloidal stability of the 2D NPl and 3D MAPbI₃ NR solution where so-called vulnerable MAPbI₃ nanostructure shows an excellent colloidal and tetragonal phase stability. We hypothesize that UV light irradiation may reduce the intrinsic defect states of the MAPbI₃ and provides an excellent phase stability. This study provides a significant understanding about the interaction of the colloidal alkylammonium based RP NPl with UV light, moisture and in future the path of defect suppression by UV light will be explored.

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Conformational transition derived phase segregation of polypeptide-based hybrid di-block copolymer

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Abstract:

Synthetic di-block copolymers containing polypeptide as one of the blocks are known as hybrid block copolymers. With the ability to mimic biological systems, the polypeptide-based hybrid block copolymers have a broad range of applications in biomedicine, biosensing, and cell engineering.¹ Polypeptides are known to form various secondary structures like a-helix, ß-sheet in solution. Due to a combination of well-defined secondary structure (from polypeptide block) and the random coil structure (from synthetic polymer block) in a hybrid block copolymer, they have a high tendency for microphase separation at nano-dimensions. Among various homopolypeptides, polyproline is unique in terms of their secondary structure formations. For

example, depending on the geometry of the amide bonds (cis or trans), it can adopt into two different helical conformations (PPI and PPII) with mutually opposite helical sense. The importance of such PPI and PPII structures in the biological context is well explored. However, the impact of the PPI and PPII helix in the hybrid block copolymers particularly for microphase separation, where the chemical incompatibility between the constituent blocks results in the phase-



Phase-segregated lamellar morphology in Nano-dimension

segregated structures has not explored yet.

Herein we have synthesized a hybrid di-block copolymer {polystyrene-*block*-polyproline (**PS**_n*b*-**PLP**_n)} with the help of atom transfer radical polymerization (ATRP) of styrene and ringopening polymerization (ROP) of NCA proline. The synthesized homopolymer and block copolymer were characterized by NMR and SEC. The propensity of PPI and PPII helix of polyproline in the block copolymer was confirmed by FT-IR. Phase segregation was confirmed by SAXS and WAXS studies. The combined WAXS and SAXS shows that the trans (PPII) hybrid di-block copolymer (**PS**₈₀-*b*-**PLP**₈₀) have a lamellar morphology in solid state whereas the cis (PPI) hybrid di-block copolymer did not have any phase-segregated morphology.

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A Paper-Based *Turn-on* Photoluminescent Protocol for the Naked-Eye Detection of Hydrogen Peroxide

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Abstract:

Hydrogen peroxide (H₂O₂), a versatile molecule, is extensively used in industry and household purposes.¹ Interestingly, this small molecule has also been found to exist *in vivo*, controlling crucial biological functions when present in a regulated concentration. Its aberrant level has been implicated in various disease conditions such as cardiovascular disease, Alzheimer, Parkinson's disease, etc.^{2,3} Besides, H₂O₂ has been known to be associated with peroxide-based explosives, either as a starting material or a decomposition compound. Such a broad involvement makes the detection of H_2O_2 imperative. We have developed a turn-on terbium (Tb³⁺) photoluminescent protocol, based on a supramolecular approach of lanthanide sensitization,^{4,5} to detect hydrogen peroxide in solution. We designed a *pro*-sensitizer molecule 2 which releases Tb^{3+} sensitizer 1 upon reaction with hydrogen peroxide, resulting in a turn-on luminescence response. The mechanism of sensitization and analyte triggered emission enhancement were investigated using spectroscopic and HPLC analysis. A paper-based platform makes the sensing process user-friendly and allows naked-eye detection without any sophisticated instrumentation. Practical utility of this protocol was successfully demonstrated by testing commercial hand sanitizers, indicating potential adaptability of this sensor, especially in resource-limited areas, for quality control purposes or other applications.⁶



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A light(er) approach for the selective HMF hydrogenation to BHMF without external H₂: Nothing to sacrifice

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Abstract:

The selective upconversion of **5-hydroxymethyfurfural** (**HMF**), a biomass derived platform molecule to value added chemicals can ease the burden on petroleum based fine chemical synthesis.¹⁻⁴ The active contribution of renewable energy sources along with low cost, environment friendly and simple reaction systems must be adopted for better sustainability. In this context, photocatalytic selective hydrogenation of HMF to **2,5-bis(hydroxymethyl)furan** (**BHMF**) is achieved over **P25 Titania nanoparticles** without chemical squander. Simultaneously the photo-oxidation of **p-methoxybenzyl alcohol** (**MeOBA**) to **p-methoxybenzaldehyde** (**MeOBaL**) is carried out abolishing the need of additional redox reagents. This system put forwards the competent employment of photogenerated excitons for the valorization of lignocellulosic biomass to fine chemicals which is an urgent requirement for sustainable chemical synthesis.

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Pd(II)-Schiff base complex covalently anchored on modified mesoporous MCM-41: An efficient and reusable catalyst for heck reaction

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Abstract:

Mesoporous MCM-41 (member of M41S family) has attracted considerable attention as catalyst support and adsorbent in recent years because of its unique properties such as tunable pore size, extremely high surface area, thermal stability and rich silanol groups in the inner walls [1-2]. In this work, we have fabricated an efficient and recyclable heterogeneous catalyst by immobilizing palladium (II) Schiff base complex on the surface of MCM-41using post-synthesis functionalization techniques. The surface of MCM-41 initially modified with 3-chloropropyltriethoxysilane (CPTES), followed by the Schiff base ligand (PAL) which on reacting with PdCl₂ resulted in the formation of MCM@CP@PAL@Pd complex. It was characterized by a number of techniques such as FT-IR, TGA, Low angle Powder XRD, SEM, TEM, MP-AES, XPS and N₂ sorption and used for heck reactions. Good to high product yields, low catalyst loading, reusability at least up to seven runs, stability toward air and short reaction times are the main advantages of synthesized heterogeneous catalyst.

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Palladium-catalysed C-H functionalization of pyrene scaffolds

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Abstract:

Functionalized pyrene moiety is a versatile chromophore for designing luminescent materials, organic light emitting diodes, organic electronics etc. The 2- and 7- position of pyrene are known as 'nodal plane positions and uncommon or inaccessible sites'. These are relatively rigid to functionalise. We report the synthesis of diverse class of pyrene derivatives palladium catalysed C-H bond functionalization strategy using 2-picolinic acid as directing group. The strategy affords access to a broad scope of 1,2-disubstitued pyrene derivatives. The removal of directing group were also carried out after functionalization of pyrene moiety.



DG : Directing group FG : Functional group

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Kinetic and Mechanistic investigation of Ruthenium (III) Chloride Catalyzed Oxidation of Sulfanilic Acid by Thallium (III) in Acid Perchlorate Medium

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Abstract

The kinetics and mechanism of oxidation of sulfanilic acid by thallium (III) in acid perchlorate medium have been studied. The reaction exhibits first order with respect to oxidant whereas order with respect to sulfanilic acid is complex. The rate is retarded by hydrogen ion concentration. Accounting for all such observations, a plausible reaction mechanism has been suggested corresponding to the rate law (1)

$$(k'_{cat} - k''_{un}) = \frac{k'K'K''K_{h}[SA]}{[H^{+}] + K_{h} + KK_{h}[SA]}$$
(1)

The activation parameters such as energy and entropy of activation have also been calculated to be (37.61 ± 0.3) kJ mol⁻¹ and (-157.9 ± 1.6) JK⁻¹mol⁻¹ respectively employing Eyring equation.

Keywords: Kinetics; Mechanism; Ruthenium (III) Chloride; Oxidation; Sulfanilic Acid; Thallium (III).

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Effect of donor-acceptor substituents on the photophysics of 4-ethynyl[c] 2,1,5 benzothiadiazole molecular Systems

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Abstract:

Fluorescent compounds have found widespread use in scientific and technological areas, especially as organic light-emitting diodes (OLEDs)¹. Among these fluorophores, benzothiadiazoles are one of the most important classes due to their relatively high reduction potential, electron affinity, large planar structure, electron rich nature, less optical band gap and fairly nice quantum yield². For 4-aryl substituted benzothiadiazole, the introduction of ethynyl linkages leads to more planar geometries, exhibit more delocalized orbitals³ and thus, a significant red-shift in their absorption spectra. Here the fluorophores based on benzothiadiazole and phenyl acetylene were synthetized through Sonogashira cross coupling reaction and the effects of electron donor/acceptor substituents on the solvatochromic properties were studied. The fluorescence emission spectra of the fluorophores were studied using solvents of different polarities, and the influence of specific solvent solute interactions over emission properties was investigated through Lipperte-Mataga and $E_T(30)$ model. The coupled fluorophore presented absorption maxima ranging from ca. 356 to 430 nm with remarkably high extinction coefficient values $(2.0-3.0 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1})$. Regarding the emission, compounds are fluorescent in solution with emission maxima ranging from 481 to 530 nm having LE (locally excited) and ICT (intramolecular charge transfer) emisions. The compounds show a large Stokes shifts indicating a larger dipole moment change in the excited state and it was also calculated by using Lipperte-Mataga correlation. The quantum yields of fluorescence (φ_f) ranged from 0.36 to 0.91 in different solvents and, were dependent on the terminal substituent of the phenyl ring in the compounds. The geometry and electronic transitions were analysed by DFT and TD-DFT, and the results are consistent with the experimental observations.

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Thiazetidin-2-ylidenes as four membered N-heterocyclic carbenes

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Abstract:

Thiazetidin-2-ylidenes have been identified as new four membered *N*-heterocyclic carbenes (NHCs) using quantum chemical studies. These species are smaller analogs of thiazol-2-ylidenes as they have same type of heteroatoms in the ring. They exhibit high singlet stability and large nucleophilicity. Quantum chemical analysis reveals that the thiazetidin-2-ylidene NHC has a good donor ability as a ligand (TEP: 2174 cm⁻¹) which is comparable to the thiazol-2-ylidene NHC (TEP: 2165 cm⁻¹). The possible existence of these carbenes has been established by synthesizing and crystalizing a library of compounds with NHC \rightarrow N⁺ \leftarrow (thiazetidin-2-ylidene) dative bond known as nitreones. These thiazetidin-2-ylidenes are also expected to form complexes with transition metals and main group elements because of their high nucleophilicity.



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Application of Aqueous Biphasic System Containing Ammonium-based Ionic Liquid and Phosphate Buffer in DNA partitioning

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Abstract:

Aqueous biphasic system (ABS) is a biocompatible alternative to traditional liquid-liquid extraction as both the phases are aqueous and the phase formation occurs due to the nature of the different solutes present in it. The aqueous environment provides stability to biologically active substances and ABS is proved to be an effective separation method for recovering and purifying biomolecules, including DNA and proteins¹. A novel ABS is developed here constituting ammonium-based ionic liquids (ILs) and phosphate buffer (K₂HPO₄-KH₂PO₄) for the partitioning of DNA at 298.15 K and atmospheric pressure. A number of ammonium cation based ILs were synthesised which differ in their functional groups so that the influence of the functional groups in ABS formation as well as DNA partitioning can be studied. The influence of alkyl chain length, hydroxyl group and aromatic group of the IL cation on the phase splitting agree with the previous studies². Among studied systems, [BTBA]Cl/K₂HPO₄-KH₂PO₄-KH₂PO₄(1.82:1.00)/water system showed a maximum efficiency of 99% for the partitioning. Further, the partitioning was optimized in terms of the concentration of [BTBA]Cl and buffer. The partition was driven by the IL-DNA interaction which was investigated through techniques such as FT-IR and circular dichroism spectra³.

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Effect of carbon number in diol intercalation on nickel hydroxide structure and their effect on supercapacitor electrodes

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Abstract:

The layered structure seems to be the most promising electrode materials for supercapacitor applications which helps in easy intercalation/de-intercalation of electrolytic ions in between the layers during rapid charge-discharge.¹ The Ni(OH)₂ is a high performance electrode active materials due to its multi crystal phase (α - and β - phase), layered structure and high electrochemical redox activity.² The effect of carbon number in diols i.e., 1,2-Ethanediol (ED) and 1,4-Butanediol (BD), on the synthesis and electrochemical properties of layered Ni(OH)₂ is investigated. Controlled solvothermal approach has been developed to synthesize single phase (α -) and mixed (α - and β -) phase Ni(OH)₂ in the presence of ED and BD, respectively. These are confirmed from XRD and FTIR studies. The Ni(OH)₂ synthesized with BD exhibited higher specific capacitance of 758 F g⁻¹ in comparison to ED (529 F g⁻¹) at 1.5 A g⁻¹ owing to its multi-crystal phase and increased interlayer distance. This is attributed to intercalation of diol with more linear carbon of 1,4-Butanediol, facilitating enhanced charge storage phenomenon. The layered structure of Ni(OH)₂ is confirmed from the flaky FESEM and HRTEM images which facilitates the charge transport process. The symmetric device of the best performing electrode i.e., [Ni(OH)₂]_{BD}//[Ni(OH)₂]_{BD} is also fabricated by connecting two as-designed symmetric supercapacitor device in series increases the output voltage to 1.5 V, which lit red light. The corresponding energy and power density is found to be 15 W h Kg⁻¹ and 3375 W Kg⁻¹.

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"Nature-to-New" in discovery of anticancer agents: Organocatalyzed Umpolung Addition in the synthesis of Privileged Heterocyclic Scaffold

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Abstract:

A strategy of "Nature-to-new" with iterative scaffold-hopping was considered for investigation of privileged ring/functional motif-elaborated analogs of natural aurones as potential anticancer agents. An organocatalyzed umpolung chemistry based method was established for moleculardiversity feasible synthesis of title class of heterocyclic-fused arylidene-imidazolones. Various biophysical experiments indicated their important biological properties. The analogs showed characteristic anticancer activities with efficiency more than an anticancer drug. The compounds induced apoptosis with arrest in the S phase of the cell cycle regulation. The compounds' significant effect in up/down-regulation of various apoptotic proteins, an apoptosis cascade, and the inhibition of topoisomerases-mediated DNA relaxation process was identified. The distinctive medicinal molecule-to-properties of the investigated chemotypes have been explored.



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Ligand-assisted nickel catalysis enabling sp³ C–H alkylation of 9H-fluorene with alcohols via Hydrogen Atom Transfer (HAT) Pathway

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Abstract:

Herein we report a nickel-catalyzed sp³ C–H alkylation protocol of 9*H*-fluorene using cheap and abundant alcohols as the source of alkyl groups. The described method covers a variety of primary, secondary, aliphatic and alicyclic alcohols as the alkylating partner and exhibits chemoselectivity during alkylation.¹⁻⁵ Our catalyst system furnishes the fluorene alkylated products in moderate to high yields. One of the important intermediates during this alkylation reaction is 9-alkylidenefluorene which undergoes hydrogenation to yield the final product. This intermediate has been synthesized separately and hydrogenated to elucidate the reaction mechanism. The process relies on ligand-mediated redox and follows a radical pathway which is significantly different from all conventional approaches to alkylate fluorene.

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Spectroscopically deciphering the formation of a fleeting Ni(III) bisphenoxyl diradical complex

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Abstract:

Nature's extremely vital metalloenzymes, *i.e.*, Cytochrome P450s and Galactose Oxidases exploit non-innocent ligands to form reactive high valent intermediates for oxidation reactions.¹ This strategy works well for the late 3d metals where accessing high valent states is rather challenging.² In this regard, Ni^{II}(salen) complexes have been one of the most promising avenues for those aiming to generate high valent Ni species.^{3, 4} The present work is a result of one such inquisitiveness where a Ni^{II}(salen) [salen = N,N'-bis(3,5-di-*tert*-butyl-salicylidene)-1,2- cyclohexane-(1R,2R)-diamine)] was treated with *m*CPBA to form a novel Ni(III) bisphenoxyl diradical species, formally analogous to a high valent Ni(V) species. Electrochemical and spectroscopic analyses using UV-Vis and EPR further revealed oxidation events on the ligand as well as on the metal centre to yield a Ni(III) bisphenoxyl diradical species, Ni^{III}(L^{••}).

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Recovery of metals from used Lithium-ion battery cathode materials using deep eutectic solvents

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Abstract:

The rapid technology changes and the short life span of electronic devices create an abrupt accumulation of electrical and electronic waste (WEEE). The heterogeneity of constituents in e-waste and the presence of hazardous materials arise complexity in the e-waste treatment¹. Even though the cost and the high concentration of metals grab greater attention than the other constituents of e-waste like plastics, organics. Nowadays, the contribution of lithium battery wastes rises a severe threat to the sustainable ecosystem. Therefore, the regeneration of valuable metals from lithium-ion batteries has received significant attention. The regeneration process involves the leaching of Co and Li from the waste cathode material (LiCoO₂) of the lithium-ion battery, followed by separate precipitation². The global e-waste technique for metals consumes highly corrosive substances for the leaching process, which negatively impacts the environment. Here we have designed a novel Choline Chloride-Carboxylic acid deep eutectic solvent (DES) as an alternative to the conventional leaching acids for the leaching of LiCoO₂. DES are the low-melting mixtures prepared by mixing carboxylic acid as hydrogen bond donor (HBD) and choline chloride as hydrogen bond acceptor (HBA)³. Differential Scanning Calorimetry (DSC) curves provide information on the eutectic composition. The mechanism involves the destruction of the crystal structure of LiCoO₂ followed by the reduction of Co^{3+} to Co^{2+} . The high chloride concentration provided by DES stabilizes the reduced Co²⁺ by forming a blue color Cobalt-chloro complex, which was proved by UV-Vis spectroscopy⁴.

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Bioinspired radical-mediated transition-metal-free dehydrogenation of heteroarene towards N-heterocycles

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Abstract:

The active redox cofactor 2,4,5-trihydroxyphenylalanine quinone or topaquinone (TPQ) found in the amine oxidase class of enzymes oxidises primary amines via a 2e-/2H+ reversible redox cycle. Inspire by this, we set out to develop a metal-free oxidative dehydrogenation of saturated heterocycles using the homogeneous catalyst pyrene-iminoquinone (**PA**). The redox-active backbone mimics and perform efficient two-electron oxidation in a catalytic manner towards the dehydrogenation of saturated heterocycles, which are en route to value-added heterocycles such as quinoline, pyrimidine, benzimidazole, and their derivatives

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A General Method for a-Oxyacylation of Vinyl Ketones Using Koser's Reagent

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Abstract:



A direct general method for the preparation of α -oxyacylated vinyl ketones using Koser's hypervalent iodine reagent is reported. A variety of acyloxy groups from the long chain aliphatic, aromatic, α , β -unsaturated carboxylic acids have been installed efficiently for the first time. This method is suitable for functionalizing even the electron-deficient aryl- and aliphatic chain-substituted-vinyl ketones. The oxyacylated adducts were used for the preparation of densely-functionalized chiral δ -lactones and cyclopentenes using carbene organocatalysis. The cyclopentene could be converted to cyclopentenone, an advanced intermediate for the preparation of (+)-chamaecypanone.

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Quantum Chemical Exploration of the Mechanism of Robinson–Gabriel Reaction

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Abstract:

The Robinson-Gabriel reaction is used for generating N-heterocyclic compounds. This classical reaction is being employed in the generation of crucial, medicinally important heterocycles like oxazoles, imidazoles, and thiazoles.^{1–3} Not many studies have been done to find out the mechanistic paths of the reaction.⁴ Also, there has no investigation for the energetics associated with this reaction, the 3D structures of intermediates, and the transition state along the reaction path. The reaction mechanism follows the same path as described in the Paal-Knorr reaction.⁵ Quantum chemical studies demonstrated the energy profile and the mechanism of the Paal-Knorr reaction. Taking clues from these works, the mechanism of the reaction Robinson-Gabriel reaction in detail has been explored in this work using quantum chemical methods. The pathway suggested here are i) water-assisted tautomeric pathway, ii) hemiacetal pathway, iii) water-assisted hemiacetal pathway. The Robinson-Gabriel reaction to give oxazole and thiazole using tautomeric pathway is endergonic by 16 and 3 kcal/mol, whereas the same reaction is exothermic for imidazole by 7.1 kcal/mol, using B3LYP/6-311+G(2df,3pd) method. The cyclization step for the hemiacetal pathway is associated with a larger barrier (56 kcal/mol). However, participation of explicit water for the water-assisted tautomeric and hemiacetal pathways reduces the barrier by significantly requiring 33 and 35 kcal/mol energy respectively. The cyclization step becomes highly favourable in the presence of water for thiazole and imidazole as well. This quantum chemical study demonstrates the importance of water-mediated tautomeric and hemiacetal pathways in 1,3-azole synthesis. These findings need further experimental investigation.

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Base free aerial oxidation of 1,6-hexanediol to adipic acid over Pd/HAP catalyst

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Abstract:

Lignocellulosic biomass as a renewable, low cost, highly abundant, easily accessible and carbon rich source has a great potential to replace non-renewable fossil resources to produce high value-added chemicals and fuel components.^{1,2} Current industrial routes for the synthesis of fuels and chemicals are largely dependent on fossil and petroleum resource which needs to be replaced with sustainable resources. Lignocellulosic biomass derived furfural (FUR) and 5hydroxymethyl furfural (5-HMF), are the promising platform for the synthesis of chemically sustainable value-added chemicals and fuel components.³⁻⁵ Adipic acid, is one of such valueadded chemical which is an important precursor to produce nylon 6,6, polyurethanes and other polymers and can be synthesized from biomass derived 1,6 hexanediol (HDO). In this study, we explored Pd/hydroxyapatite (Pd/HAP) catalyst to selectively oxidise HDO to adipic acid at 70 °C in water under base-free conditions. Experiments with Pd on various supports (Rice husk ash (RHA), TiO₂, C, ZnO, Al₂O₃, La₂O₃, Mg(OH)₂, HAP) demonstrated that the basicity of the support is beneficial for efficient aerial oxidation of HDO and also avoids the need for any additional base additives and a neutralisation step at the end of the reaction. Moreover, gram scale oxidation of HDO to adipic acid can also be achieved over Pd/HAP catalyst. Structural and chemical identification of highly active Pd/HAP catalyst was established by P-XRD, SEM, BET, XPS, HR-TEM, EDS, elemental mapping, and ICP-AES analysis.

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Design and Synthesis of Turn-On Fluorescent Probe for Acidic pH in Aqueous Solution

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Abstract:

For the detection and monitoring of the target of the interests, the fluorescence approach is the most suitable methods. Fluorescence approach in combination with small molecular probes offers several benefits such as real-time detection, high sensitivity, and measurement in living cells with minimum interference to the physiological processes. Because of these benefits, the fluorescence approach is widely employed in pH monitoring, both in-vitro and in-vivo.ⁱ Recently, we have designed and synthesized a xanthene based probe which shows strong red-colored fluorescence due to change in pH value.ⁱⁱ A turn-on fluorescent Xanth-NPr, containing a xanthene moiety modified by the dipropyl aniline group, was designed as an efficient fluorescent probe for sensitive for pH detection regulated by the photoinduced electron transfer (PET) mechanism. There photophysical studies also recorded. This probe shows turn on/off fluorescence with change in acidic or basic medium. In the poster presentation, we will discuss the synthesis and photophysical properties of xanthene-based derivatives.

Figure/Scheme:



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Dual-Functional Propylene Carbonate Additive for High-performance Aqueous Zn-ion Batteries

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Abstract:

Aqueous rechargeable zinc-ion batteries are fascinating for large-scale energy storage applications. However, challenges such as the dendritic growth of zinc, structural degradation and dissolution of oxide cathodes, and poor coulombic efficiencies (CEs) limit their scope¹. To address these issues, various studies demonstrate the importance of organic co-solvents and additives at different concentration in Zn^{2+} -ion electrolytes. For instance, Z. Guo *et.al.* reported the use of 51.6 wt% of triethyl phosphate (TEP) to suppress the water derived parasitic reaction at the electrodes². However, overall efficiency of the battery performance is hindered due to the large amount requirements of these additives. This ultimately reduces the key electrolyte features such as electrical conductivity and thereby poor or limited performance or cycling stability.

In this line, we have studied the electrochemical properties of highly polar propylene carbonate as a dual functional co-solvent, which suppresses water-derived parasitic reactions occurring at both the Zn anode and the V₂O₅ cathode³. We have observed the significant enhancement in the battery characteristics such as high columbic efficiency and stable capacity, merely by tuning the solvation structure of the electrolyte. Upon a small addition of PC (≤ 20 wt.%) in 1M zinc triflate electrolyte, water molecules solvating Zn²⁺ ions are replaced by carbonate and triflate anions. This further electrochemically reduced to form a ZnF₂ rich solid electrolyte interphase, as demonstrated by post cycling XPS studies. The resultant zinc anode exhibits a prominent columbic efficiency of ~99.3% in Zn|Cu cells for 700 cycles. Moreover, the spectroscopy studies suggest the strong interaction of highly basic carbonyl oxygen of PC with water molecules which in turn suppresses the dissolution of the cathode, enabling exceptional capacities of ~300 mA h g⁻¹ over 900 cycles at 1 A g⁻¹. In this poster, the detailed understanding of the role of PC to supress the parasitic reaction at anode and dissolution of cathode will be discussed thoroughly.

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Synthesis of substituted 1,4- and 1,2-Napthoquinones using Eosin Y as Photoredox catalyst

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Abstract:

An efficient, one-step procedure for thiolation and arylation of substituted 1,4-Napthaquinones (1,4-NQ) was carried out in the presence of green LED light (30 watt, 530 nm) using Eosin Y (EY) as photoredox catalyst at room temperature. Generation of thiyl radical (RS', R = aryl, alkyl) *via* reductive quenching of ${}^{3}EY^{*}$ (triplet excited state of EY) was the rate determining step for thioloation and RS' was captured as TEMPO adduct in HR-MS. Similarly, aryl radical (Ar') was generated *via* oxidatiove quenching of ${}^{3}EY^{*}$ and TEMPO-Ar adduct was trapped in HR-MS. For thiolation, the photoredox cycle was completed by the formation of superoxide radical anion (O₂⁻) which was confirmed through HR-MS using 5,5-dimethyl-1-pyrroline N-oxide (DMPO), a selective scavenger for superoxide. However, involvement of O₂ was not found in the case of arylation where photoredox cycle was completed by the reaction between EY⁺⁺ and 1,4-NQ-aryl adduct. Both, the reaction was not inhibited by the addition of a singlet oxygen quencher like 1,4- diazabicyclo[2.2.2]octane (DABCO) which suggests that singlet oxygen is not necessary.



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Prototype large scale reactor for cost-effective H₂ production from water under natural sunlight

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Abstract:

Natural sunlight-driven H_2 production at large scale through artificial photosynthesis could solve two of the major challenges of current modern civilization: rapid fossil fuel depletion and global warming. Moreover, the solar energy is best possible renewable energy source having technical potential (1500-50000 EJ per year) much higher than the 2050 expected primary energy demand (1000 EJ per year).¹ Therefore, developing efficient visible light active photocatalysts becomes the need-of-the-hour research for the modern scientific community. In this regard, the carbon nitride (g-CN), a visible light active organic semiconductor has drawn the major scientific attention especially for H_2 production due to it's easy synthesis and appropriate band positions.²⁻⁴ Here, we have developed a large-scale prototype photocatalytic reactor which operates under natural sunlight.

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A Silver(I) Catalysed Stereoselective one pot synthesis of Bridged [2.2.2][3.3.1] Polycyclic Isochromans.

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Abstract:



A stereoselective silver catalysed one pot vinylogous aldol-michael addition followed by an oxa-aldol cyclization reaction of alkylidene pyrazolones to *in situ* generated isobenzopyrylium ions¹ has been developed under milder reaction conditions, which provides an unprecedented bridged bicyclo [2.2.2] [3.3.1] pentacyclic [5-6-6-6-6] isochromans consisting a pyran, isochroman and a diazole unit in one molecule with good to high yields in a single diastereomer.

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Two new NHC-Pd-PEPPSI complexes and their catalytic activity in Suzuki Miyaura Cross-coupling reaction.

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Abstract: PEPPSI-type Pd-NHC complexes have received significant attention during the past few years due to their unusual activity in cross-coupling reactions^[1]. The potentiality of these complexes for Suzuki Miyaura Cross-coupling reaction is relatively less explored. In this work we have synthesized two PEPPSI type Pd-NHC complexes of general formula [Pd (NHC_x)Br₂(Py)] by reacting PdCl₂ with NHC ligands [NHC_a: 3-benzyl-1-(4-methoxyphenyl)-1H-imidazolline-2-ylidiene, NHC_b:1-(4-methoxyphenyl)-3-(naphthalen-1-ylmethyl)-1Himidazolline-2-ylidiene] using pyridine as reaction media in presence of base (K₂CO₃) and excess KBr^[2,3]. Both complexes are characterized by ESI-MS, ¹H, and ¹³C NMR spectroscopy. The catalytic activities of these complexes are explored in the Suzuki Miyaura cross-coupling reaction with various aryl halides. Good to excellent yields of biaryl products were obtained with a range of representative aryl bromides/iodides under relatively mild conditions (35^oC, $C1 = [Pd (NHC_a) Br_2(Py)] = 0.5 mol\%, C2 = [Pd (NHC_b) Br_2(Py)] = 0.4 mol\%)$ in aqueous isopropanol. The aryl bromides/iodides having electron-donating groups (-OMe, -CH₃)/ electron-withdrawing group (-CHO,>C=O,-CN,-NO₂) gives excellent yield ranges from 80-96%. The yield of the products decreases gradually according to para, meta, and ortho substituents. In addition to it, the reaction with heterocyclic bromides results moderate, while aryl chlorides yield lower conversion to the biaryl products.



Scheme: Suzuki Miyaura Cross-coupling reaction by C1, C2 at the mild condition

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Microwave assisted metal free synthesis of quinazolin-4(3H)-one derivatives

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Abstract:

A novel bifunctional ionic liquid has been designed and explored for the first time as an efficient catalyst for the synthesis of medicinally important 2-phenylquinazolin-4(3H)-one derivatives starting from anthranilamide and benzyl alcohol derivatives under microwave irradiation. The newly developed ionic liquid was found to be a benchmark catalyst in this study which showed a breakthrough in catalytic performances, enabling the quantitative yield of the desired products under microwave irradiation. 2-phenylquinazolin-4(3H)-one was attained through one pot oxidative synthesis led by the ionic liquid. Metal/external acid-base/ ligand free protocol for oxidative synthesis of quinazolinones via in situ oxidation of benzyl alcohol derivatives using the designed ionic liquid adds a golden touch to the task-specificity of the ionic liquid.



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γ-Aminocyclopentenone Enables Divergent Access to Functionalized Indoles and Polycyclic Indole Derivatives

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Abstract:

The aza-piancatelly rearrangement represents an attractive strategy for accessing γ -amino functionalized cyclopentenones.¹We have developed aLewis acid promoted γ -amino displacement on such substrate with an array of nucleophiles, which was based-on a retro-aza-Piancatelli manifold.²While presence of C5-diaryl on cyclopentenone was crucial, with our further investigations, we have developed the β -functionalization or β , γ -annulation leading to various cyclopentanoidswithC-5 monosubstituted aminocyclopentenones. This reaction proceeded via *pseudo*cine substition.³Overall, thestrategy offers a means to construct elusive indole-based polycyclic architectures.



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Facile Construction of BiVO₄/Co₃O₄ p-n Junction Photoanode for Enhanced Photoelectrocatalytic Hydrogen Production

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Abstract:

The construction of the p-n junction is a promising way to enhance the charge transfer dynamics of the photoelectrodes in the photoelectrocatalytic water splitting process. During the formation of the p-n junction, at the interface the electrons on the n-type semiconductor are diffused to the surface of the p-type, similarly, the holes are diffused to the surface of the ntype from the p-type, which leads to the formation of positive and negative charge species on the surface of the n and p-type semiconductors, respectively. This electron-hole diffusion takes place until the Fermi level equilibrium is obtained. As a result, a charged region is created at the interface of the p-n junction, called an internal electric field (IEF). Upon light illumination, this IEF quickly drives electrons to the conduction band of n-type and holes to the valence band of p-type and thus the IEF effectively separates the electrons and holes. In the present work, we have constructed the BiVO₄/Co₃O₄ p-n junction photoanode via electrodeposition followed by pulsed laser deposition (PLD). The BiVO₄/Co₃O₄ p-n junction photoanode results in a higher current density of 4.66 mA cm⁻² at +1.23 V_{RHE} and applied bias photon-to-current efficiency (ABPE) of 0.78% under the illumination of AM 1.5G, which is ~7-folds higher than the BiVO₄. The enhanced PEC performance of the BiVO₄/Co₃O₄ electrode will be explained by means of (i) charge recombination, (ii) charge-transfer efficiency at the electrode/electrolyte interface (EEI), (iii) active sites, and (iv) facile water oxidation kinetics of the Co₃O₄. The formation p-n junction improves the lifetime of charge carriers, the BiVO₄/Co₃O₄ electrode has \sim 9- folds higher transient decay time than the BiVO₄ electrode. Nyquist and Bode phase analysis confirmed the rapid charge transfer process at EEI in the case of the BiVO₄/Co₃O₄ electrode compared to the BiVO₄ electrode. Deposition of Co₃O₄ over the BiVO₄ surface increases the reactive sites for water oxidation, which was confirmed by the double-layer capacitance (C_{dl}) measurements. The formation of the p-n junction boosts the water oxidation by enhancing the hole injection ability at the interface due to the electrocatalytic activity of the Co_3O_4 in the p-n junction electrode.

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Ruthenium(II)-Catalyzed Regioselective (4+2) Annulation of Aromatic Amides with Unactivated Olefins

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Abstract:



Transition-metal-catalyzed C–H bond activation and annulation represent an important manoeuvre to fabricate high-value carbocycles and heterocycles from simple building blocks.^{1a-b,e} In this realm, Ru(II)-catalysis has particularly received significant attention owing to its operational simplicity, cost effectiveness, and efficiency under the assistance of weak coordination.^{1c,d} Typically, annulation reactions of Ru(II)-catalysts have been accomplished with alkynes and activated olefins.^{2a,b} At present, such examples using unactivated olefins bearing an isolated C–C double bond are rare. Considering this synthetic space, we developed a ruthenium catalyzed (4+2) annulation reaction between aromatic hydroxamic acid esters and allylic amides, offering valuable aminomethyl isoquinolinones in good to excellent yields³. This annulation reaction. Synthetic applications were demonstrated through the production of natural product derivatives including amino acid scaffolds and late-stage derivatization of a steroid molecule.

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Brønsted acid-catalyzed reaction between *C*-alkynyl imine precursor and thiol: Access to highly enantioenriched propargyl amides

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Abstract:

The chiral propargyl amides are significant structural motifs in natural products and biologically active compounds.¹ The asymmetric approach^{2,3} to propargyl amide bearing *N*,*S*-acetals is exceptionally rare. In addition, the presence of isoindolinone core express important pharmacological properties.⁴ We have built a novel route via Brønsted acid-catalyzed highly enantioselective Mannich-type reaction of propargyl alcohol derived *C*-alkynyl imines and thiols resulting in a wide range of propargyl amides bearing important *N*,*S*-acetals in excellent yields (up to 99%) and excellent enantioselectivities (up to 99% ee). Further, various interesting transformations of the product are demonstrated.

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A Template-free Approach to Predict Secondary Structure of Proteins in Eight classes

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Abstract:

Proteins are biomacromolecules consisting of linear chain of amino acids connected by peptide bonds and they play an important role in many biological processes. Infact, inside every living organism proteins control almost every process within cells. The functional properties of protein directly depend on its three dimensional native structure and the structural information of a protein is encoded in its amino acid sequence. Hence protein structure prediction from its amino acid sequence is a very challenging and important problem in computational biophysics. In this work a template free procedure for prediction of secondary structure of proteins is developed. For prediction of secondary structure of individual residues in a given sequence the structural propensities of amino acid sequence segments are used. First, a set of more than 4000 globular protein sequences, each comprising single chain without any ligand as well as no modified residues and with X-ray crystallographic structures of resolution in between 0-3 Å are selected as training set from RCSB PDB database. Another set of proteins comprising of 200 proteins sequences are selected as test set. Then using DSSP program, eight-state secondary structures (G,H,I,E,B,S,T,C) of both training and test sets of proteins are assigned. Protein sequences of the training set are used to calculate the statistical scores and measure the favorability of an amino acid residue adopting a certain secondary structure. On the basis of calculated triplet propensities and the propensity distributions a method is developed to predict secondary structures of residues in a given amino acid sequence. The prediction accuracy of the developed method is measured using the 200 protein sequences of the test set and the results obtained from the developed method is found promising for α -helix and β -strand prediction.

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First Principles study on Structure and electronics dependent on thickness of traditional 2D layered II-VI semiconductor; growth and stability

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Abstract:

First-principles density-functional theory calculations on thickness-dependent structural and electronic properties of (0001) surface slabs of wurtzite MX compounds were used to demonstrate the existence of 2D layered materials from traditional semiconducting compounds of the II-VI group, which are widely used in numerous fields today.¹⁻³ The (0001) surface slabs of wurtzite ZnO and CdO compounds prefer to stabilise as sp² hybridised atomically thin graphitic layers, which are separated by van der Waals distances, as compared to their respective wurtzite slabs. In contrast, sp³ hybridised bilayers composed of an X-Zn (Cd)-Zn (Cd)-X structural arrangement are energetically stable until specific slab thicknesses for various ZnX and CdX (X = S, Se, Te) compounds surface slabs. Both 2D layered MX systems are electronically insulating nature. The band gap narrows as the number of layers in these systems grows because the energy bands are becoming wider. These 2D MX systems have the structural, elastic, and lattice dynamical stabilities, indicating their compatibility with optoelectronics and photovoltaic applications, as shown by their effective mass and mobility.

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Surfactant free-synthesis of cobalt–iron chalcogenides as bifunctional electrocatalyst for the water splitting reaction and Cr (VI) reduction

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Abstract:

This paper reports the synthesis of a pair of novel cobalt-iron chalcogenides [Co_{0.8}Fe_{0.2}S₂ and Co_{0.8}Fe_{0.2}Se₂] with heightened electro catalytic activities. These ternary metal chalcogenides were synthesized by a one-step template-free approach via a hexamethyldisilazane (HMDS)-assisted synthetic method. Transient photocurrent (TPC) studies and electrochemical impedance spectra (EIS) of these materials showed free electron mobility. Their bifunctional activities were verified in both the electrochemical



oxygen evolution reaction (OER) and in the electrochemical reduction of toxic inorganic heavy metal ions [Cr (VI)] in polluted water. The materials showed robust catalytic ability in the oxygen evolution reaction with minimum over potential (345 and 350 mV @ η_{10}) as determined by linear sweep voltammetry and the lower Tafel values (52.4 and 84.5 mV dec⁻¹) for Co_{0.8}Fe_{0.2}Se₂ and Co_{0.8}Fe_{0.2}S₂ respectively. Surprisingly, maximum current achieved for Co_{0.8}Fe_{0.2}S₂, a minimum value for the Limit of detection was obtained for Co_{0.8}Fe_{0.2}S₂ (0.159 mg L⁻¹) compared to Co_{0.8}Fe_{0.2}Se₂ (0.196 mg L⁻¹). Both catalysts presented outstanding electro catalytic activities for up to 1500 CV cycles and chronoamperometry studies also confirmed exceptional stability. Therefore, the surfactant free synthesis of these electro catalysts containing non-noble metal illustrates the practical approach to develop bifunctional electrocatalysis.

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Exploring reactivity of diazo-derived carbene: Sustainable photolytic synthesis of diverse bioactive small molecules

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Abstract:

My research work is based upon application of D-A (donor-acceptor) carbenes from aryl diazoesters (ADEs) in blue LED to generate novel organic building blocks with potential utility in medicinal chemistry and material science. We demonstrated an environmentally sustainable photolytic activation of an aryl diazoester by a blue LED to generate oxonium ylide with 1,4dioxane in aqueous medium. This ylide could be transformed to various biologically interesting poly-oxy heterocycles when treated with phthalimides, thiazolidinediones and hydantoins and heterocycles such as indoles and pyrroles. The same ylide also underwent a [1,2] shift in water to afford 1,4-dioxepane derivatives. Polyoxyphthalimides were deprotected in isopropanol to afford macrocyclic dioxyazanonane. The unique selling point is an efficient conversion of environmentally hazardous substances like 1,4-dioxane (an ecotoxic grade 2/3 hazardous compound) to interesting heterocycles in water with blue LED. DFT calculations and kinetic studies explained the mechanistic pathway of the transformation.¹ The reaction could be successfully scalable to multigram quantities. In continuation, instead of oxonium ylide we envisioned that pyridinium ylide could also be explored to develop new synthetic tool. With this objective, we went a step ahead and found a novel blue LED mediated solvent free multicomponent reaction involving a pyridinium ylide (prepared from pyridine and aryl diazoacetates) and N-alkyl maleimides to afford diversely substituted diastereo-selective itaconimide derivatives in good to excellent yields. Itaconimides displayed various therapeutic properties as anticancer and antibiotics. This is a low cost and sustainable strategy to synthesise such molecules. It requires zero collection, recycling or removal of solvents with lesser energy consumption than general organic reactions. The strategy could be scaled-up to multigram quantities. DFT study supported the proposed mechanism and the rationale behind the diastereo-selectivity.²

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Effect of Metal Ions on the Intrinsic Blue Fluorescence Property and Morphology of Aromatic Amino Acid Self-Assembly

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Abstract: The metal ions are known to strongly bind with different proteins and peptides, resulting in alteration of their different physicochemical properties. In this work, we investigate the effect of metal ions of different nuclear charges and sizes on the intrinsic blue luminescence of the self-assemblies formed by aromatic amino acids namely phenylalanine and tryptophan using spectroscopic and imaging techniques. The study reveals that the intrinsic blue fluorescence of amino acid assemblies is influenced by the metal ions and pH of the medium. The metal ions with a higher charge to radius ratio promote clusterization which results in the enhancement of the intrinsic fluorescence known as "clusteroluminescence" of the amino acids aggregates. The imaging study reveals that metal ions with a higher charge to size ratio inhibit the large fibrillation of aromatic amino acids by promoting the formation of small non-fibrillar aggregates through increased hydrophobicity in the medium. The nano-aggregates are assumed to be responsible for the enhancement in the blue "clusteroluminescence".

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Copper(II) and Copper(I) Complexes of Arylazopyrazole Incorporated Photoresponsive Ligands: Synthesis, Photochemistry, and Applications in Photoswitchable Catalysis

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Abstract:



Photo-responsive transition metal complexes are useful in different optomechanical devices, light-driven ligand-induced spin-crossover (LD-LISC), photoswitchable catalysis applications, logics and memories, photochromic materials, etc.^{1,2} These applications demand compounds to photoisomerize efficiently between different states with considerable stability for the photoswitched states. In this regard, we have prepared a few photoactive analogs of tri- and tetradentate azopyrazole-based ligands by modeling a ligand framework based on the wellknown pyridine-pyrazole chelating ligands.³ Phenylazo-3,5-dimethyl-pyrazole photoswitches were chosen because of their efficient forward and reverse photoisomerization, and also, due to their excellent thermal stability of the Z-isomeric states.⁴ We have investigated the complexation properties of these ligands with Cu(II) and Cu(I) ions. We have explored the photoswitching properties of these ligands and complexes in the solution phase and solid-state with the help of UV-Vis spectroscopy. We have also explored the kinetics of thermal reverse isomerization of the ligands and complexes in the solution state. The ligands and their copper (I) complexes showed efficient forward and reverse photoswitching and long thermal half-lives for the Z-isomeric states. Taking advantage of these properties, we have also explored their utility as photoswitchable catalysts. The results will be discussed through this contribution.

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Fishing out Hyaluronan, a Colon Cancer Biomarker from Extracellular Vesicles

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Abstract:

Extracellular Vesicles (EVs) are naturally occurring nanoparticles with unique structure, surface biochemistry, and mechanical characteristics. These distinct nanometer-sized bioparticles are secreted from the surfaces of normal and cancer cells and are of potential interest as cancer biomarkers [1]. We use high-resolution Atomic Force Microscopy (AFM) to show single-vesicle quantitative differences between EVs derived from colon cancer cell HCT 116 and normal colon epithelial cell CCD-18CO. At the single-vesicle level, HCT 116 derived EVs exhibit significantly (P < 0.05) increased Hyaluronan surface densities compare to CCD-Co18. To our knowledge, it represents the first report detecting single-EV surface biomarker variations [2]. We also performed spectroscopic experiments including Fourier Transform Infrared Spectroscopy (FT-IR), Circular Dichroism (CD), and RAMAN spectroscopy to support the abundance of Hyaluronan coated vesicles derived from HCT116 compared to CCD-Co18. Additionally, high-resolution AFM imaging revealed discrete multi-vesicular bodies with EVs enclosed and our data also showed some distinct morphological features of the cancer EVs. We believe that this work would provide a quantitative single vesicle level biomolecular analysis milieu to realize a new colon cancer diagnostic in near future.

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Room Temperature Organic Ferroelectrics / A Synergy between HygrogenBonding and Charge Transfer Interaction

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Abstract:

Ferroelectrics are polar material, in which an external electric field can be used to reverse the spontaneous polarization of the bulk material. Ferroelectric (FE) materials have been widely explored due to their usage as non-volatile memory in electronic devices. In this context, unlike inorganic FE materials, organic materials are highly promising because of their flexibility, lightness, solution processibility and non-toxicity. As a result, PVDF (polyvinylidene fluoride) and some of its copolymer have been widely used to serve the purpose. However, necessity of high operating voltage (large coercive field PVDF 1200 kV/cm⁻¹, low coercive field BaTiO₃ 10 kV/cm⁻¹) limits their wide range application in electronic devices. Recently, as opposed to single-component system, multi-component system and their supramolecular assemble structure showed promising results to have both high polarity as well as low coercieve voltage. Research in this area indicated a noncentrosymmetric polar structure is prerequisite to have ferroelectric properties. In this regard, only a few supramolecular systems have been reported so far to have room temparture ferroelectric properties. For example, Tayi and coworkers reported a co-crystal of aromatic electron-rich and electron deficient specie shows a highly promising organic ferroelectric materials at room temperature. In this example, molecular dipoles originated from charge-transfer (C-T) complexation resides in a noncentrosymmetric environment of the crystal. Recently, self-assembly of 1,3,5-benzene tricarboximide (BTA) into a columnar structure has also been shown a very promising approach to serve the purpose. Herein, the polar amides in BTA-motifs are directed towards the growth of the 1-D supramolecular polymer resulting in a highly polar structure needed for ferroelectric properties.

In this context we have designed a new supramolecular system which not only have multiple polar segments at single molecular level but also has a strong propensity for supramolecular polymerizations. So, the main objective of our study was to direct all polar segments into the same direction and to have a material with appreciable ferroelectric properties. To this objective a few molecules are synthesized in which the BTA core and C-T motif are same but the distance between these are vary with different carbon spacer (C_2 , C_4 , C_6). In the C-T complexation studies we found that all molecules are showing very little charge transfer in chloroform. Insterestingly when a non solvent (methyl cylcohexane) was added, a remarkable change is observed and the intensity of the C-T band increase enormously which indicates that the co-localization of donor and acceptor molecules. All these molecules are showing the supramolecular assemblies in the solution state and C_6 -derivative easily formed an organo-gel after C-T complexation. Such observation indicates the role of spacer-length between BTA core and C-T motifs for supramolecular polymerizations. Ferroelctric properties of those supramolecular motifs has been measured before and C-T complexation and found good remanant polarization as well as less coercive field for the later.

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Molecular Picture of Effect of Cosolvent Crowding on Ligand Binding and Dispersed Solvation Dynamics in G-Quadruplex DNA

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Abstract:

DNA can form various non-canonical structures, such as G-quadruplex DNA (GqDNA) in several locations of genome and adopt various topologies which have been shown to be strongly affected by molecular crowding. However, it is unknown how such molecular crowding affects the dynamics of solvation within GqDNA. Here we studied the effect of cosolvent (acetonitrile) crowding on ligand (DAPI) binding and solvation dynamics in human telomeric antiparallel GqDNA through direct comparison of time-resolved fluorescence Stokes shift (TRFSS) experiments and molecular dynamics (MD) simulations results.¹ The dynamics of solvation probed by DAPI within groove of GqDNA showed dispersed dynamics from ~100 fs to 10 ns in absence and presence of 20% and 40% (v/v) ACN. The quantitative information of the origin of dispersed solvation dynamics in GqDNA are extracted from direct comparison of results of TRFSS experiments and large-scale atomistic MD simulations. Our data unravel a detailed molecular picture showing that though ACN crowding affects ligand binding affinity to GqDNA significantly, the dispersed solvation dynamics of ligand inside GqDNA groove remain similar in absence and presence of 20% ACN, but only a small effect of crowding on the faster dynamics is observed in presence of 40% ACN.¹ The origin of such subtle effect of crowding lies with the preferential solvation of the groove-bound ligand by ACN molecules which displace hydration water from near the ligand binding site within GqDNA.

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In vitro anticancer activities on human pancreatic cancer MIA-PaCa-2 cell using novel Ni(II) complexes bearing ONS donor ligands

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Abstract:

Cancer is major worldwide disease, spread abnormally cause significantly adverse effects on human health.¹ Metal based anticancer drugs must be less toxic, more-efficacious, target specific and preferably non-covalently bound anticancer drugs. Anticancer drugs exert their drug effects by interfering the DNA through apoptosis.^{2,3} Ni(II) play a significant role in biological systems and reported as promising anticancer and antimicrobial agents.^{4,5} Purpose of researches is to find the promising contenders to improve the efficacy of anticancer drug. The present work aims to provide a better anticancer drug that has high biocompatibility and causes apoptosis at lowest concentration. In this work, we have synthesized six ligands (L1-L6) by using different aldehyde with 2-aminothiophenol/2-(methylthio)anilines in good yield. The reactions of L1-L6 with $[Ni(OAc)_2 \cdot 4H_2O)]$ separately in methanol at 90°C have resulted in complexes 1-6. All ligands and their Ni(II) complexes have been characterized using elemental analysis (C, H, N, S), FTIR, NMR (¹H, ¹³C), ESI-MS and UV–visible spectroscopy. The molecular structure confirmed by single crystal XRD data of complexes 1 and 6. The anticancer activity of complexes 1-6 was investigated on human pancreatic cancer cell line MIA-PaCa-2 which revealed that the complex **4** and complex **6** were the most significantly effective in decreasing cell viability of cancer cells at the lowest dose. Additionally, computational studies of complex 1 were done to validate the solid state structure obtained from single crystal XRD.



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Design and Engineering of Dimeric Cholic Acid-Peptide (CAP) Conjugates to Target Vancomycin Resistant Bacteria.

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Abstract:

Bile acids are the naturally occurring steroids that are biosynthesized from cholesterol metabolism. The presence of steroidal backbone and hydroxyl groups make bile acids amphiphilic in nature, that mimic with naturally occurring antimicrobial peptides (AMPs). Cholic acid (CA) is a primary bile acid having three free hydroxyl groups and a free carboxylic acid, and chemical manipulation of CA functional groups can yield potent antimicrobial agents. We have earlier reported a series of glycine conjugated CA-derived cationic amphiphiles (CAA) with varying alkyl chains at the C24 position of CA. An amphiphile armed with a hexyl alkyl chain was found to be potent against gram-positive and negative pathogens. We have also engineered twenty CAP (cholic acid peptide) molecules. Among the series, glycine-valine tethered molecule can interact with the lipopolysaccharide (LPS) and displayed potent membrane disruptive properties. However, toxicity profile of these CA-derivatives is a major concern. Based on these findings, we designed and synthesised a series of eight membrane-targeting CA dimers to increase the therapeutic index. For Dimers 1 to 4, we installed 3 glycine moieties at the hydroxyl groups and terminal alkyne moiety at C24 position. Next, we dimerized the molecule with different alkyl diazides via click chemistry. In case of Dimers 5 to 8, we tethered glycine-valine group at hydroxyl positions of CA. Among the dimers, dimer 5 was found to be selective against Vancomycin-Resistant Enterococcus (VRE) and less toxic towards mammalian cells, and possesses strong bacterial membrane-disrupting properties. In addition, Dimer 5 displayed potent therapeutic potential in a murine wound infection model. In my poster, I will explain the design, synthesis, and biological evaluation of CA-derived dimers.

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Abstract

The tricompartmental ligands tris(H₂ONO) [H₆L¹⁻³ (**I**–**III**)] having *C*₃ symmetry, obtained from the condensation of benzene-1,3,5-tricarbohydrazide and 3-acetyl-2-hydroxy-6-methyl-4H-pyran-4-one (**I**), 3-acetyl-4-hydroxy-2H-chromene-2-one (**II**) and 3-hydroxy-5-(hydroxymethyl)-2-methylpyridine-4-carbaldehyde (**III**) react with [Mo^{VI}O₂(acac)₂] in refluxing methanol to give tris-{*cis*-[MoO₂]²⁺} complexes [{Mo^{VI}O₂(H₂O)}₃L¹] (**1**), [{Mo^{VI}O₂(H₂O)₃}L²] (**2**), and [{Mo^{VI}O₂(H₂O)₃}L³] (**3**), respectively. These complexes show potential catalytic activity towards the one-pot three-components [alkyl acetoacetate, benzaldehyde (or its derivatives) and urea] synthesis of biologically active 3,4dihydropyrimidine (DHMP) based molecules via Biginelli reaction under mild and solvent free condition.



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Systematic structural modification in electrophilic molecules possessing 1,3-Allylic-type strain for anticancer applications

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Cancer is the leading cause of mortality across the globe and the emergence of drug resistance for commercially used anticancer agents warrants new therapeutic modalities. Several unique strategies targeting cancer therapy are in the development, targeted protein inhibitors, small molecule-based proteolysis activating chimeras (PROTACs), chimeric antigen-directed T-cell (CAR-T cell) therapy, and antibody-drug conjugates amongst them. While the advanced technologies mark a huge success, a majority of them are in the clinical phase or personalized medicines. In the past couple of decades, covalent small molecules have emerged as powerful therapeutics to treat several cancers. Several of these small molecules including Afatinib, imatinib, and ibrutinib contain reactive electrophilic warheads and are directed to inhibit specific protein targets. Another property of these electrophilic molecules is that they disturb the Keap1-NRF2 interaction, thereby induce stress in the cells called electrophilic stress. The reactivity of electrophilic units is depending on the complexity associated with the scaffold it is tagged to, which could be controlled for dictating target specificity. Here, we show that the reactivity of chloroacetamide, a thiol-reactive electrophile could be controlled by introducing appropriate steric and electronic factors around the electrophile. We chose 2-aminobenzophenone as our starting scaffold, which is present in many existing therapeutics including the doxorubicin class of molecules. We introduced substitutions on the amine to break the flatness within the structure, and to create A^{1,3}-allylic-type strain to derive unique three-dimensional structures to prevent their random reactivity with many reactive proteins. From our thiol reactivity studies with N-acetyl cysteine (NAC), we established a clear link that the introduction of sterically hindered substituents prevents or reduce its reactivity with NAC. Then we directly assessed the small molecule library for their anticancer activity against lung cancer and osteosarcoma cells. Our careful design of molecules based on their thiol reactivity resulted in 30 unique electrophilic molecules. Among the library of 30 molecules, eight molecules were found to inhibit the cancer cell growth at nanomolar concentrations, which is better than commercially used anticancer drugs doxorubicin and staurosporine, thereby, highlighting an exciting class of molecules for pursuing their mechanism of action in cancer cells.



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Studies on Morphology and Magnetic properties of Cu²⁺ substituted CoFe₂O₄ Nanoparticles Synthesized via Glycolate Approach

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Abstract:

Substitution is an important tool for altering magnetic, optical, and electrical properties of host materials with incorporation of substituent ions [1, 2]. Cu^{2+} substituted CoFe₂O₄ nanoparticles are promising for applications in multilayer chip inductors, electromagnetic interference filters, switching, memory, and microwave devices [3, 4]. In the present study, Cu²⁺ substituted cobalt ferrite nanoparticles were synthesized using different Cu^{2+} concentrations (0.1 mmol to 0.3 mmol) [5]. First, Cu²⁺ substituted Co-Fe glycolates were prepared via an ethylene glycol mediated route followed by calcination at 500 °C. XRD studies indicate incorporation of Cu²⁺ ions in the Co-Fe glycolates, and Cu²⁺ substituted CoFe₂O₄ nanoparticles were obtained after calcination of the Cu²⁺ substituted Co-Fe glycolates. Rietveld refinement of XRD data indicates that when Cu²⁺ concentration is 0.10 mmol and 0.20 mmol, Co²⁺ ions in octahedral sites of $CoFe_2O_4$ are substituted by the Cu^{2+} ions. When Cu^{2+} concentration is increased to 0.3 mmol. substitution of Co²⁺ by Cu²⁺ occurs in tetrahedral sites in addition to the octahedral sites of CoFe₂O₄. SEM images demonstrate that the morphology of pure Co-Fe glycolate is hexagonal which converts to near micro-spherical particles in the Cu²⁺ substituted Co-Fe glycolates. TEM study shows that the CoFe₂O₄ hexagon and near micro-spherical particles of Cu²⁺ substituted CoFe₂O₄ are made up of small nanoparticles. Magnetic studies of Cu²⁺ substituted CoFe₂O₄ nanoparticles indicate soft ferromagnetic behavior at 300 K and hard ferromagnetic magnetic behavior at 15 K. At 300 K, the coercivity decreases on increasing the Cu²⁺ concentration. At 15 K, the coercivity of $Cu^{2+} [Cu^{2+}] = 0.10$ mmol) substituted CoFe₂O₄ nanoparticles exhibit higher coercivity as compared to pure CoFe₂O₄ nanoparticles. The saturation magnetization, remanent magnetization, and coercivity of Cu²⁺ substituted CoFe₂O₄ nanoparticles can be varied by varying the concentration of Cu^{2+} in the Cu^{2+} substituted CoFe₂O₄ nanoparticles. **References:**

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Abstract:

Emerging multiple drug resistance (MDR) is a major challenge to existing effective chemotherapeutics. Broadly MDR impacts multiple fatal diseases including infectious diseases and cancer, and is projected to be a major concern by 2050. One of the causes of MDR is the enhanced efflux of highly effective drugs by various membrane transporters. P-glycoprotein (P-gp), an integral membrane transport, plays an important role in governing bioavailability of various antitumor drugs. Highly upregulated overexpression of P-gp in cancer cell is one of the major causes of MDR, and therefore non-toxic P-gp inhibitors are urgently needed.



Nocardioazine A & Nocardioazine B are marine derived Tryptophan alkaloid natural products possessing P-gp inhibitory activity. Hence Nocardioazine B and its derivatives are potential anticancer leads. Here we have demonstrated the shortest total synthesis of Nocardioazine B and its analogues through 7 linear steps, each, in comparison to existing strategies. The pathway consists of stereo and regio selective indole C3-methylation strategy and a biomimetic C3'-normal prenylation strategy, followed by peptide bond formation and cyclization events. Our strategy mimics the enzymatic reactions of prenyltransferases and is scalable, short and achieved with minimal protecting group manipulations. Screening of libraries of prenylated and benzylated Nocardioazine analogues will be illustrated.

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Distinct interfacial ordering of liquid crystals observed by protein–lipid interactions that enabled the label-free sensing of cytoplasmic protein at the liquid crystal-aqueous interface¹

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Abstract:

Interfaces formed between a lipid decorated liquid crystal (LC) film and an aqueous phase can mimic the bimolecular membrane where interfacially occurring biological phenomena (e.g., lipid-protein interactions, protein adsorption) can be visually monitored by observing the surface-sensitive orientations of LCs.² The ordering behavior of LCs at different phospholipidbased LC interfaces (1,2-dilauroyl-sn-glycero-3-phosphocholine (DLPC) and lysophosphatidic acid (LPA)) were investigated to determine the sensing of an important cytoplasmic protein (juxtamembrane of epidermal growth factor receptor (JM-EGFR)). At both DLPC and LPA decorated interfaces, the LC adopts homeotropic ordering, causing a dark optical appearance under crossed polarizers. Interestingly, upon the introduction of JM-EGFR to these LCaqueous interfaces, the homeotropic orientation of the LC changed to planar (bright optical appearance), suggesting the potential of the designed system for JM-EGFR sensing. The use of different lipid decorated LC-aqueous interfaces results in the emergence of distinct optical patterns. For example, at a DLPC laden interface, elongated bright domains are observed, whereas a uniform bright texture is observed on an LPA laden interface. The DLPC decorated LC-aqueous interface is found to be highly selective for the sensing of JM-EGFR with a detection limit in the nanomolar concentration region (~ 50 nM). When compared to spectroscopic and other conventional techniques, the LC-based design is simpler, and it allows the simple and label-free optical sensing of JM-EGFR at fluidic interfaces.

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Abstract:

The kinetics of oxidation of sulfanilic acid by hexachloroiridate (IV) in aqueous acid medium has been studied. The reaction is second order viz. first order with respect to each reactant. However hydrogen ion concentration retards the rate of reaction. Various types of proposals are suggested to account for the reactivity of hexachloroiridate (IV).

The activation parameters such as energy and entropy of activation were calculated by employing Eyring equation to be (59.99 ± 0.93) kJ mol⁻¹ and (-106.44 ± 2.2) JK⁻¹ mol⁻¹ respectively. The oxidation product on the basis of spectral analysis, 2-keto-azoxy- benzene-4,4'disulfonic acid has been confirmed spectrally.

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Self-regulated micropatterning of Synergistically Interactive Enzyme and Nanoparticle-bound Nucleotides

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Abstract:

Non-equilibrium surface patterning of catalytically active soft matter or nano/microparticles is vital in diverse areas, namely- (bio)chemical analysis, from catalysis to plasmonic, and optoelectronics.¹ Commonly, surface-immobilized enzyme or specific protein-ligand binding affinity or nanoparticle organization using complementary DNA strand or DNA origami have been known for gradient and localized patterning by utilizing both non-template and templateassisted strategies.² Herein, we have used affinity between specific enzyme and its substrate, which is non-covalently bound to a nanoparticle surface, to prompt assembly of the overall ensemble in a spatiotemporally controllable way. Specifically, we used a cationic nanoparticle aggregation phenomenon which takes place in the concurrent presence of multivalent anionic nanoparticle binding adenosine-based nucleotide and enzyme, alkaline phosphatase. We further demonstrate that the spatial control in the aggregation pattern can be regulated simply by modulating the synergistic non-equilibrium interactivity of the nanoparticle, nucleotide, and enzyme in microfluidic conditions. Notably, the Marangoni effect generated due to the gradient of surface tension resulted in the migration of surfactant-bound nanoparticles more towards the zone of high enzyme concentration. Thus, it showed a counterintuitive phenomenon of enzyme-substrate binding and their migratory behavior when the substrate is rather bound in a nanoparticle surface in a zone of low surface tension. Overall, this work amalgamated both surface patterning of nanoparticles and enzyme in one platform, simply mediated by their assembly using a substrate here ATP, demonstrating a unique method for macroscale surface nanobiopatterning with potential application in controlled large area patterning with diverse cascade catalytic surface and multisensory-based application.³



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AITF (4-Acetamidophenyl triflimide) mediated racemization free synthesis of amides & peptides

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Abstract:

Herein, an efficient, one pot synthesis of amides and peptides employing 4-acetamidophenyl triflimide (AITF) as novel coupling reagent is delineated. AITF is crystalline, bench stable reagent. It is utilized in peptide segment condensation, as the coupling of peptides bearing C-terminal unit occurs without loss of configuration at the activated amino acid. Evidently no racemization is detected. Also, amidation of nitrogen containing two carbon atoms which was challenging is also achieved with good to excellent yields. Interestingly, the developed protocol is illustrated with broad substrate scope, functional group tolerance, and extremely mild conditions. The resulted amides and peptides are characterized by ¹H NMR, ¹³C NMR and LCMS. Some of their results will be presented.

Scheme:



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Multianalytes sensing of amphiphilic bis(benzimidazolyl)pyridine Derivative Incorporated in Liposomes and their application in β-glucosidase enzyme assay

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Abstract:

Liposome based nano sensor Lipo-1 for efficient detection of copper, cyanide (CN⁻) and ATP in pure aqueous medium has been described. Liposomes considered as an efficient tool as a sensor to detect various biological and environmental relevant analytes[1]. Liposomes based senor systems are effective to enhance the sensitivity of the analyte by increasing binding affinity. Lipo-1 shows fluorescence ON-OFF response with copper. However, Lipo-1.Cu (Lipo-1 and copper ensemble) used for the OFF-ON detection of ATP with nM and CN⁻ with □M detection level, lower than WHO permissible level for safe drinking. Lipo-1 has better and enhanced binding properties over the counter organic amphiphilic compound **Bzimpy-LC**, which is not soluble in water. The significant changes in the emission spectra in the presence of Cu²⁺, CN⁻ and ATP ions, as variable inputs, are used to construct INHIBIT and OR logic operations in a nano-scale environment. The fluorescent detection of CN⁻ ion with Lipo-1.Cu was used to develop an enzyme assay for β -glucosidase using amygdalin as substrate. β glucosidase enzymatic activity was monitored by emission OFF-ON signal of probe Lipo-1.Cu by CN⁻ detection. This approach could be an efficient method for developing a fluorescencebased β-glucosidase enzyme assay. Switch ON luminescence response, low detection limit, fast response, 100% aqueous solution, biocompatibility, multi-analyte detection, and improved sensitivity and selectivity of Bzimpy-LC in lipid bilayer membranes are main features of the nanoprobe Lipo-1. These properties give it a clear advantage for analytical applications [2, 3].



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Palladium-Catalyzed Aminocarbonylation of (Hetero)aryl Iodides with α-Amino Acid Esters as Nucleophiles

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Abstract:

We report palladium-catalyzed aminocarbonylation of (hetero)aryl iodides with α -amino acid esters as nucleophiles. The synthesized N-capped α -amino acids are biologically important building blocks. The mild conditions provide product with high enantioselectivity at 80 °C in 35 min. The reactions are performed under air in a sealed vessel using chloroform as *in situ* CO source. For the first time, regioselective carbonylation of histidine is also presented.



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Notes: Publication Date: June 3, 2022

Entropically favored Au³⁺⁻L-methionine induced dynamic transition of nanospheres to thermodynamically stable superhelix in aqueous media.

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Abstract: Natural systems transfer chiral information across multiple length scales through non-covalent interactions to accomplish smooth biological operation. Inspired by nature, several artificial supramolecular architectures have been developed, where controlling the supramolecular chirality is the key tool to completing specific tasks. However, recognition control over supramolecular chirality in aqueous media is challenging. Here, we designed and synthesized pyrazine based derivative **Pyra-Met** having L-methionine group as chiral handle. Due to the presence of flexible side chains in **Pyra-Met** building block, its interaction with the solvent molecules are restricted which leads to the generation of nanospheres in aqueous media. The **Pyra-Met** nanospheres selectively interact with Au³⁺ ions to generate dynamic helical fibers of **Pyra-Met:Au³⁺** ensemble with 'hidden' chirality. Finally, superhelix with desired helical sense is achieved in the presence of L/D-methionine *via* co-assembly process. This work not only presents a feasible strategy to achieve the desired handedness of supramolecular assembly for better understanding the chiral self-assembly process in supramolecular chemistry, but also facilities the development of 'smart' building block with controllable handedness in materials science.



Delineating the molecular mechanism of Age-related Hearing Loss (ARHL)

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Abstract:

Age-related hearing loss (**ARHL**) or **presbycusis** has become a significant concern in present-day society, especially with increasing life expectancy. As we grow older we tend to lose our sensitivity towards high-frequency sound more abruptly than low-frequency sound and finally a complete hearing loss. The origin of **ARHL** is multifactorial. However, one of the major causes in ARHL is the damage in the inner-ear. Cdh23 protein in tip-links that plays a crucial role in mechanotransduction process is identified as one of the ARHL (ahl1) loci in many inbred mice models.

Human patients suffering from hearing-loss diseases have been identified with Cdh23 variants. From that clinical and phenotypical study, two single-point mutations P240L and R301Q in Cdh23 have been shown to cause ARHL². To understand the molecular origin and mechanism of this disease, we investigate how these mutations alter the flexibility, stability, binding affinity (with Pcdh15 in tip-link complex), unfolding and folding kinetics using Molecular Dynamics (MD) simulation, Atomic Force Microscopy, Bio-Layer Interferometry (BLI) and Magnetic Tweezer.

Both of these variants shows higher conformational flexibility (from MD simulations) as well as lesser mechanical stability compared to WT. Atomic force microscopy based single-molecule force spectroscopy experiments have provided insight into the higher unfolding rates for the disease variants. Affinity based experiments using BLI has also shown that the mutant variants are less favoured as the binding partner for Pcdh15, breaking off the highly stable tip-link complex essential for carrying out normal hearing. We aim to investigate more biophysical characteristics using repetitive force pulse as an external stimulus, which will uncover new dimensions for investigating hearing loss problems and possibly point us to the direction for potential drug candidates for ARHL treatment.

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Boron-Catalyzed Hydroarylation of 1,3-Dienes with Arylamines

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Abstract:

Catalytic hydroarylation reactions of conjugated dienes are achieved using tris(pentafluorophenyl)borane as a Lewis acid catalyst under mild reaction conditions. This new protocol shows broad substrate scope for the highly regioselective functionalization of sterically hindered aniline derivatives. Experimental and extensive DFT mechanistic studies show that the complex of residual water and $B(C_6F_5)_3$ plays a crucial role in the aryl-assisted protonation of conjugated dienes, forming allyl cation intermediates that induce facile electrophilic aromatic substitution of aniline substrates.



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Abstract:

The multicomponent reactions (MCRs) involving at least three reactants are the most common and effective to date, resulting in the formation of multiple bonds in a single step with high molecular complexity and structural diversity. MCRs are based on green chemistry those have been shown to be extremely efficient in terms of atom economy, convergence, and environmentally friendly manner.^{1,2}



Figure 1: Biologically active organic molecules

An eco-friendly, inexpensive, and efficient taurine-catalyzed green multicomponent approach has been described for the synthesis of therapeutic core 1,4-dihydropyrano[2,3-*c*]pyrazoles containing isonicotinamide, spirooxindole, and indole moieties..³ Further, this strategy was applied under sonication conditions for the synthesis of medicinally important 3,3'-bis(indolyl)methanes (BIMs) and their derivatives via an electrophilic substitution reaction of indole with structurally divergent aldehydes.⁴ Detailed *in silico* analysis of the synthesized analogues of 1,4-dihydropyrano[2,3-*c*]pyrazoles and BIMs revealed their potential to bind wild-type antibiotic-resistant variants of dihydrofolate reductase and a principal drug target enzyme for emerging antibiotic-resistant pathogenic *Staphylococcus aureus* strains respectively.^{3,4} In addition, we have also developed the green multicomponent approach for the synthesis of bioactive heterocycles such as fused 2,3-dihydrofuran derivatives and, highly functionalized trans-2,3-dihydrofuro[3,2-*c*]coumarins using imidazole and water as a green catalyst and solvent, respectively, under mild conditions.

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Synthesis of dibenzobicyclo[3.2.1]octadienones, spiro[4.4]nonanes from 2keto-1,3-indandiones

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Abstract:

Synthetically challenging dibenzobicyclo[3.2.1]octadienone (1) and spiro[4.4]nonane (2) scaffolds have been prepared from various 2-keto-1,3-Indandiones. The novel methodologies availed 2-keto-1,3-indandiones as an intriguing key substrate because of their diverse reactivity sites within the molecule. Aryne intermediate owing to its highly strained triple bond has been utilized for the construction of dibenzobicyclo[3.2.1]octadienone core.^[1] The reaction of dimethyl acetylene dicarboxylate with 2-keto-1,3-indandiones afforded strenuous all-carbon quaternary spiro[4.4]nonane compounds, which have been present in an antibiotic natural product fredericamycin A.^[2] These products were well characterized by extensive NMR studies, DEPT, COSY, HMQC, NOESY, and single-crystal X-ray analysis.



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Recycled Zinc Manganese oxides as cathode material for aqueous rechargeable zinc ion batteries

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Abstract:

Latter-day, recycling used batteries to extract high-value minerals or refurbishing the same has picked up a research interest of it among the battery researchers due to the present-day energy storage demands and the limited supply chain of the raw materials. On the other hand, the safety issues prevailing in non-aqueous lithium-ion batteries have made researchers work on aqueous batteries for large grid storage and in electric vehicles. With this motivation, we attempted to give a second life to the dead alkaline Zinc-Manganese dioxide batteries for rechargeable aqueous Zinc ion batteries (AZIB). The black powdered cathode mixture of the dead batteries was analysed with the XRD, XRF and other physical characterization for understanding its phase and composition. The obtained material was tested as cathode material for AZIB in the aqueous electrolyte of 2M ZnSO₄ with 0.2M MnSO₄ additive and cycled between the 1.75 V - 0.8V vs Zn/Zn²⁺. The cathode delivered a specific capacity of 214 mAh/g at 100 mA/g current density, which faded below 130 mAh/g after 90 cycles. The fading of the capacity phase impurity and structure degradation is addressed with the material characterizations.

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Highly efficient metal/solvent-free chemical fixation of CO₂ at atmospheric pressure conditions using functionalized porous covalent organic frameworks

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Abstract:

The significant rise in CO₂ levels in the atmosphere has resulted in various environmental issues such as global warming, ocean acidification, extreme weather, etc.¹ Thus, there is an urgent requirement to mitigate the increasing concentration of CO₂ by utilizing it as a C1-feedstock for the synthesis of high-value chemicals and fuels.² In this direction, the cycloaddition of CO₂ with epoxides to afford cyclic carbonates (CCs) has gained special interest owing to the potential applications of CCs as commodity chemicals for polymers and pharmaceuticals.³ Most of the reported catalysts require high temperature, and/or high-pressure conditions for high yield generation of CO₂ at eco-friendly mild conditions.⁴ In this regard, we are working on developing functionalized covalent organic frameworks (COFs) for selective capture and fixation of CO₂ into value-added chemicals. The synthesis, characterization, and catalytic investigation of the COFs for selective capture and conversion of CO₂ into value-added chemicals.⁵



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Functionalized Triphyrin(2.1.1)s and their Coordination Chemistry

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Abstract:

Triphyrin(2.1.1)s are contracted porphyrinoids containing three pyrrole rings connected via four *meso* carbons. They are $14\Box$ aromatic macrocycles but contain one pyrrole less than 18 aromatic porphyrins and possess almost similar physico-chemical and coordination properties. A series of mono β -substituted triphyrin(2.1.1)s were synthesized by coupling mono β -bromo triphyrin(2.1.1) with appropriate boronic acid in THF/toluene/water (1:1:1) in the presence of catalytic amount of $Pd(PPh_3)_4$ in 17-67% yields.¹ Different boronic acids such as methyl, phenyl, p-tolyl, p-anisyl, p-fluorophenyl, p-chlorophenyl, 3-thienyl, 3-pyridyl, 4pyridyl, *p*-biphenyl, 4-formylphenyl boronic acids were used. The \Box -formylphenyl triphyrin(2.1.1) was further treated with excess pyrrole under acid catalyzed conditions in CH_2Cl_2 to afford dipyrramethanyl triphyrin(2.1.1), which was subjected to oxidation by treating it with DDQ to afford the desired ligand, \Box -dipyrrinyl triphyrin(2.1.1). The dipyrrinyl unit of triphyrin(2.1.1) can act as bidentate ligand to form interesting coordination complexes. Thus, the dipyrrinyl triphyrin(2.1.1) ligand was treated with BF_3 (OEt)₂ as well as metal salts such as [Ru(p-cymene)Cl₂]₂, Pd(acac)₂ and Zn(CH₃COO)₂ and afforded BODIPYtriphyrin(2.1.1), Pd(II)dipyrrin-triphyrin(2.1.1), Ru(II)-dipyrrin-triphyrin(2.1.1) and bis(Zn dipyrrin)-triphyrin(2.1.1) conjugates in good yields.² The ligand and all four conjugates were thoroughly characterized and studied by HR-MS, 1D & 2D NMR spectroscopy, absorption, cyclic voltammetry and DFT/TD-DFT studies. The optimized structures indicated that the triphyrin(2.1.1) and BODIPY/metal dipyrrin units in conjugates were oriented w.r.t each other with an angle in the range of 25.18°-77.55°. The spectral studies indicated that the two moieties in conjugates interact weakly and retain their individual characteristics whereas electrochemical studies revealed their electron deficient nature. The TD-DFT studies were in agreement with the experimental observations.



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Entropically Favoured 'Through Space Charge Transfer' Assemblies: Visible light promoted Photosensitizer for Regulated Oxidation of Alcohols and Aldehydes

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Abstract:

Visible light driven sensitized oxidation of organic compounds is a sustainable approach for preparation of synthetically important building blocks.¹⁻² Photosensitization enables activation of oxygen to generate reactive oxygen species (ROS) which eventually act as the potent 'oxidants' in the oxidative organic transformations. Thus, we developed strong acceptor-weak acceptor **FN-TPy** which undergoes solvent dependent self-assembly in mixed aqueous media to generate through space intermolecular charge transfer assemblies. The as prepared entropically favoured assemblies of **FN-TPy** exhibit excellent photostability and photosensitizing properties in the assembled state to activate aerial oxygen for efficient generation of reactive oxygen species (ROS) through Type-I and Type-II pathways. The **FN-TPy** exhibits excellent potential for regulated oxidation of alcohols and aldehydes under mild reaction conditions (visible light irradiation, aqueous media, room temperature) using aerial oxygen as the 'oxidant'.³ The present study demonstrates the potential of **FN-TPy** assemblies to catalyse controlled oxidation of benzyl alcohol to benzoic acid.



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Dithiocarbazate based oxidomethoxidovanadium(V) and mixed-ligand oxidovanadium(IV) complexes: Study of solution behavior, DNA binding, and anticancer activity

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Abstract:

In this work, one oxidomethoxidovanadium(V) $[V^{V}O(L)(OMe)]$ (1) and two mixed-ligand oxidovanadium(IV) $[V^{IV}O(L)(phen)]$ (2), and $[V^{IV}O(L)(bipy)]$ (3) complexes have been synthesized using a tridentate bi-negative ONS donor dithiocarbazate as main ligand, H₂L [where, $H_2L = S$ -benzyl-3-(2-hydroxy-3-ethoxyphenyl)methylenedithiocarbazate] along with 1,10-phenanthroline (phen) (for 2) and 2,2'-bipyridine (bipy) (for 3) as co-ligands. The ligand and complexes have been characterised by FT-IR, UV-vis, NMR, and HR-ESI-MS techniques. Distorted square pyramidal for 1, and distorted octahedral geometry for 2 and 3 was confirmed by single crystal X-ray crystallography. The behavior of 1-3 in solution medium has been investigated through various physicochemical techniques.¹ It is observed that **1** completely and 2 - 3partially decomposes and converts into a penta-coordinated species. $[V^{IV}O(L)(DMSO/H_2O)]$ after the release of the methoxido group (1) or breaking of the diimine based co-ligands (2 and 3) in DMSO/aqueous solution. Interestingly, in DMSO/aqueous solution, **1** gets completely reduced and converted into the corresponding oxidovanadium(IV) species.² Interaction of 1-3 with calf thymus DNA (CT-DNA) was investigated¹ and the results show, complex 2 exhibited the maximum binding constants, $K_b = 7.12 \times 10^4 \text{ M}^{-1}$. The anticancer potential of 1-3 was evaluated^{1,3} by cell viability assay against human breast carcinoma cell, MCF-7, and noncancerous mouse embryonic cell, NIH-3T3 and 2 was found to be the most cytotoxic complex (IC₅₀ = 6.73 \pm 0.36 \Box M) in the series. In addition, 2 selectively inhibit colony formation compared to the rest complexes. Also, the cell cycle studies of the complexes were performed using flow cytometry analysis.³



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Physicochemical studies on the interfacial and aggregation behavior of imidazolium -cholate and -deoxycholate in aqueous medium

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Abstract:

Two bile salts sodium cholate (NaC) and sodium deoxycholate (NaDC) were converted into salt-free surface-active ionic liquids (SAILs), 1-butyl-3-methylimidazolium cholate ([bmim]C) and 1-butyl-3-methylimidazolium deoxycholate ([bmim]DC) by double decomposition technique. Synthesized SAILs were characterized by FTIR, ¹H-NMR, ¹³C-NMR, Thermogravimetric analysis-differential thermal analysis, and X-ray powder diffraction studies. Interfacial and aggregation behavior of synthesized surfactants were investigated by tensiometry, conductometry, fluorescence emission spectroscopy, dynamic light scattering, and isothermal titration calorimetry (ITC). Critical micelle concentration (CMC) was evaluated by tensiometry, conductometry, emission spectroscopy, and ITC methods. CMC of synthesized SAILs was lower compared with precursor surfactants; NaC > NaDC > [bmim]C > [bmim]DC. Lower surface excess values of SAILs were due to electrostatic interaction between IL cation and bile salts anion. Negative Gibbs free energy of micellization and a higher fraction of counter ion binding values further support the proposition. Aggregation number (n) and size $(d_{\rm h})$ of the micelles were determined by fluorescence quenching and dynamic light scattering studies respectively; both 'n' and ' d_h ' values were higher for SAILs than precursor surfactants ([bmim]DC > NaDC > [bmim]C > NaC). SAIL aggregates, although larger in size with a higher aggregation number, were more compact than NaC and NaDC micelles. Enthalpies of micellization, being exothermic in nature, were higher for SAILs although the micellization processes were entropically controlled. SAILs are considered to have dual advantages of surfactant and IL

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Interfacial Nanostructuring of δ-PVDF Nanoparticles with Giant Piezoelectricity and Piezoelectric Ink

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Abstract:

Piezo-, pyro-, ferro-electricity in carbon-fluoro polymers such as poly (vinylidene fluoride) (PVDF), its copolymers and their nanostructures are gaining remarkable technological interest in self-powered flexible electronics. However, achieving nanostructures of PVDF with the preferred electroactive phase and the enhanced piezoelectric coefficient still remains a challenge. In this regard, we have introduced a nanoprecipitation technique to machinate PVDF nanoparticles with the predominant piezoelectric delta (δ) phase (which is least studied till date) using the bi-solvent phase separation technique.^{1, 2} It is noteworthy that δ -phase of PVDF possesses excellent piezoelectric properties which are comparable to the β -phase, nevertheless, it has been rarely explored because of its ultra-high electric field (~MV/m) based processing conditions adopted so far.³ In this context, the solvent-based phase separation approach is most convenient and thus expected to be an industrially viable approach to scale up piezoelectric δ -PVDF nanoparticles which have enormous technological and commercial merits.¹ The piezoresponse force microscopy (PFM) study confirms the nanoscale piezo- and ferroelectricity in δ -PVDF nanoparticles that manifests the giant piezoelectric coefficient (d₃₃) of ~ -43 pm/V and optimum phase reversal ($\Delta \phi \approx 180^\circ$) behaviour under very low applied bias (i.e., at $\sim \pm 5$ V). Further, as prepared PVDF nanoparticles are functionalized with polydopamine and polyethylenimine (PDA:PEI) conjugates to ensure the well aqueous dispersion. Noteworthy to mention that, functionalized PVDF δ -PVDF nanoparticles have shown potential application as a piezoelectric ink. As a proof of concept, a flexible piezoelectric nanogenerator (f-PNG) was fabricated comprising of δ - PVDF nanoparticles. It generates promising electrical output with a power density of $2 \mu W/cm^{2}$.¹ Moreover, its ability to track physiological signal such as arterial pulse detection and aqueous dispersion indicates the potential utility of δ -PVDF nanoparticles based on self-powered sensors, actuators and piezoelectric ink.

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Significant Boost of the Stability and PLQY of CsPbBr3 NCs by Cu-BTC MOF

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Abstract:

Lead halide perovskites are very efficient materials for potential applications such as solar cell, light-emitting diodes (LEDs), lasers, and photodetectors. However, the environmental instability of perovskites straits their commercialization progress. To address the stability issue, We engaged perovskite NCs in Cu^{2+} ion-based metal-organic framework (MOF) Cu-BTC (BTC = 1,3,5-benzene tricarboxylate) by physical mixing of MOF with CsPbBr₃ NCs in toluene. MOF-protected perovskite NCs achieved high photoluminescence quantum yield (PLQY) 96.51% than pristine CsPbBr₃ NCs (51.66%). Along with the improvement in optical properties, the long-term stability of CsPbBr₃ NCs in the solution phase also increases considerably upon loading in Cu-BTC MOF.

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Zinc Chloride Promoted Inimitable Dissolution and Degradation of Polyethylene in a Deep Eutectic Solvent Under White Light

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Abstract:

The non-biodegradability and thus environmental pollution caused by Polyethylene (PE) is a

major concern in many countries.¹ Most of the processes available for degradation PE the of are cumbersome and involve chemically harsh conditions at elevated temperatures. Therefore, new dissolution methods for and degradation of PE should be devised.² The major challenge in the development of such processes is to adopt environmentally benign



conditions. Herein, we have prepared and utilized a ZnCl₂ and lactic acid (LA) based deep eutectic solvent (DES) (LA:ZnCl₂) for the dissolution and degradation of PE under white light at 60 °C. The dissolved PE has been regenerated using water as an antisolvent. The regenerated material has been characterized and compared with virgin PE for alteration in inherent structure employing Scanning electron microscopy (SEM), Thermogravimetric analysis (TGA) and X-ray diffraction (XRD). The structural aspects of regenerated material have been probed by Fourier-Transform Infrared spectroscopy (FTIR), ¹H and ¹³C Nuclear magnetic resonance (NMR), and X-Ray photoelectron (XPS) spectroscopy. The obtained results suggested that the dissolution of PE in DES is free-radical mediated. ZnCl₂ activates the C=O of LA, resulting in lowering of the bond energy of π -bond of C=O, which is compensated by the energy provided by white light and temperature, simultaneously. The recyclability of the DES and no alterations in the properties of regenerated material from recycled DES further adds to sustainable nature of the process. It is believed that the present work would not only provide basic understanding about the dissolution of PE but also prompt other researchers to develop new DESs for dissolution of hard to dissolve materials in a sustainable manner.

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Screen-printed carbon nanofiber/gold nanoparticles/mercaptopropionic acid/polyethylenimine based immunosensor for detection of colistin in chicken liver

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Abstract:

Colistin is a commonly used antibacterial peptide drug that has been banned for human consumption but is still being used in veterinary as well as a feed additive for feedstock. The current study intended to develop a new innovative amperometric immunosensor for detecting colistin presence in the liver of chicken. The immunosensor was fabricated using the CNF/AuNPs/MPA/PEI surface of the screen-printed electrode onto which the anti-colistin Abs were immobilized. The developed sensor detects the electrochemical response in the colistin spiked chicken liver. For the characterization of the electrode surface, the FTIR and FE-SEM techniques were used at every development step. The detection limit with R_2 of 0.995 was determined to be 0.072μ gKg⁻¹ using CV. Moreover, the validation of the developed immunosensor was done by testing the chicken liver available in the market and comparing it with results recorded via conventional methods. The developed immunosensor showed high specificity against colistin and stability for six months after fabrication with 11% initial CV current loss.

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Aminotroponatogallium Triflate Catalysed Cyanosilylation of Aldehydes and Ketones

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Abstract:

Cyanohydrins obtained from the cyanosilylation reaction of carbonyl compounds are essential intermediates that can be converted to medicinally active compounds, such as α -amino acids, α -hydroxy acids, α -hydroxy ketones, and β -amino acids.^{1,2} Though various main group compounds have catalyzed this reaction, a gallium compound is not yet used as a catalyst.³ In this regard, aminotroponate (AT) ligand stabilized Ga(III) compounds [{(*i*-Bu)AT}₂GaCl] (1) and [{(*i*-Bu)AT}₂GaOTf] (2) were isolated. The catalytic utility of compound 2 for the cyanosilylation of various aldehydes and ketones with trimethylsilyl cyanide (TMSCN) was checked and found useful; benzaldehyde took 1.66 h for more than 99% conversion and gave a TOF of 60 h⁻¹ (Scheme 1). Further information regarding the work will be presented in the poster.



Scheme 1: Cyanosilylation of aldehydes and ketones using **2** as catalyst.

Figure 1: Molecular structure of compound 2

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Stitching Triazoles to Arenes *via* Transition Metal-Free Aryne Diels-Alder/Bond Migration/Dehydrobromination Cascade

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Abstract:



 $\sqrt{}$ General protocol for accessing both polynuclei arenes and dihydroarenes

 $\sqrt{}$ Easily accessible materials $\sqrt{}$ Mild reaction conditions $\sqrt{}$ Wide and tunable substrate scope

The synthesis of 1,2,3-triazole containing compounds has become increasingly important in the recent past, as this privileged heterocycle engulfs a variety of therapeutically active molecules. Their pharmaceutical potency covers several human terminal diseases, along with tuberculosis, malaria, inflammation and other viral and bacterial diseases. An ascent in the number of their synthetic protocols is also fueled by their extensive use in agricultural as fungicide, and material science.

The 1,2,3-triazole-fused polyaromatic frameworks are traditionally obtained through transition metal-catalyzed C-H/C-X arylation of the pre-installed triazoles at a very high temperature. Herein, a transition metal-free direct synthesis via aryne Diels-Alder (ADA)/bond migration/dehydrobromination cascade is reported. This method gives access to triazole-fused ar-omatic as well as the corresponding dihydrocarbocycles under a mild reaction condition.

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Conformational Isomerism Involving Carboxylate Groups of a Linker in Metal Organic Frameworks and Its Distinctive Influence on the Detection of Ketones

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Abstract:

Now-a-days, environmental pollution is one of the major concerns which is posing threat on human heath as well as aquatic and wildlife. This has raised worldwide concerns. Several essential steps have been taken to minimize the use of hazardous and toxic chemicals leading to the deterioration of the ecosystem.¹ One category of such chemicals includes ketones such as acetone, acetylacetone, cyclohexanone, etc., whose exposure causes skin irritation, corneal and mucosal infections, and anesthesia in CNS.² In this work, we report two Zn-based metal frameworks containing a mixed pyridine-carboxylate ligand H₂bpaipa: organic $\{[Zn(bpaipa)] \cdot DMF \cdot 2H_2O\}_n$ (1) and $\{[Zn(bpaipa)] \cdot 5H_2O\}_n$ (2), where $H_2bpaipa = 5$ -(bis(pyridin-2-ylmethyl)amino)isophthalic acid.³⁻⁴ Compounds 1 and 2 are synthesized from $Zn(OAc)_2 \cdot 2H_2O$ and H_2 begins building units under solvothermal and ambient conditions, respectively. Evidently from their single crystal X-ray structures, **1** and **2** show conformational isomerism with respect to the carboxylate groups of the ligand. Interestingly, the structural variation of 1 and 2 have also influenced their luminescence properties in different solvents. Utilizing their luminescence behaviour, the selective and sensitive detection of various ketones, including acetone and cyclohexanone (for an indirect sensing of RDX), has been explored in three different solvents (protic as well as aprotic).

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Triazine-based photoswitchable C3 symmetric azobenzenes and their photoresponsive behaviour

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Abstract:

 C_3 symmetric star-shaped systems with multiple photoswitchable azobenzenes have been widely explored. Particularly, 'triazine' as a core unit based tripodal systems attract a great deal of attention and provide encouraging application in the field of liquid crystals,¹ hierarchical supramolecular assembly,² and organic light emitting diodes (OLEDs).³ In this regard, we have synthesized C_3 symmetric photoswitchable aminoazobenzene and azoheteroarenes such derivatives of triazine through a linker (-NH or -O) based on the position of azo group relative to the linker⁴ (*ortho, meta,* and *para*). We have investigated their photoresponsive behaviour through UV-Vis and NMR spectroscopic techniques. Furthermore, we also appraised the impact of design in obtaining solvatochromism, and hydrogen bond acceptor ability.

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Differentiating Conformationally Distinct Alzheimer's Aβ Oligomers Using Liquid Crystals

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Abstract:

Transiently populated oligomeric intermediates of amyloid β (A β) peptide are believed to be the toxic species in Alzheimer's disease. The soluble A β oligomers can be classified into two fundamentally distinct fibrillar and prefibrillar oligomers which can be categorized based on their reactivity towards conformation-specific antibodies. It has been suggested that the interaction of A β oligomers with the lipid membrane is one of the mechanisms by which the oligomers impart toxicity in Alzheimer's disease. Thin films of thermotropic nematic liquid crystals (LC) at aqueous interfaces serve as sensitive reporters of lipid-protein binding events. Our study uncovers the design of a LC-based system to study the membrane-induced aggregation of the two fundamentally distinct A β oligomers at nanomolar concentrations. The dynamics of LC re-orientation in response to the lipid-induced aggregation of the fibrillar A β oligomers is faster than the pre-fibrillar A β oligomers. Our results unmask the potential of LC to distinguish the soluble oligomers of amyloidogenic proteins and provide fresh approaches for exploring these dynamic interactions at physiologically relevant concentrations.

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Exploiting the Lewis Acidity of Diverse ZnO Nanostructures for the C-C and C-N Bond Forming Reactions

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Abstract:

Recently metal-oxide nanostructures have gained great interest due to their distinct properties connected to their shapes and sizes. These nanostructures provide enormous opportunities as semiconductors, gas sensors and photocatalysts.¹ Unquestionably, **ZnO** is one of the most important versatile smart semiconductor materials with key applications in photocatalysis, sensors, piezoelectric transducers, and transparent conductors.²⁻³ However, the use of **ZnO** nanostructures as chemical catalysts is limited. In addition to the unique physical and chemical properties, the catalytic activity of **ZnO** nanostructures is also correlated to the changes in the surface properties (such as surface defects). This work reports the utility of three ZnO nanostructures (ZnO 1, 3D microflower; ZnO 2, 3D polyhedron; and ZnO 3, 1D nanorod), obtained from the direct calcination of a Metal-organic Framework $\{[Zn_4(\square_3-OH)_2(D-2,4 CBS_{2}(H_{2}O_{4}) \cdot 5H_{2}O_{n}$, (where D-2,4-CBS = 2-((4-carboxybenzyl)amino)succinate) at three different temperatures,⁴⁻⁵ as Lewis acid catalysts for the two-component Knoevenagel condensation (C-C bond formation) and the three- component Strecker (C-N bond formation) reactions.⁶ Among the three nanostructures, **ZnO_3** was the best heterogeneous catalyst for the Knoevenagel condensation reaction with a remarkable efficiency (100% conversion in 15 min using only 2 mol% catalyst in methanol at 25 °C). Similarly, ZnO_3 was found to be better than the other two for the Strecker reaction in water. Their recyclability for three consecutive runs (without any notable change in the catalytic activity) and mechanism of action were established.

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Lambert Salt-Initiated Development of Friedel–Crafts Reaction on Isatin to Access Distinct Derivatives of Oxindoles

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J. Org. Chem. 2021, 86, 17833-17847

Abstract:

Herein, a mild metal-free and efficacious route for the synthesis of biologically important 3aryl oxindole derivatives is described. Using Lambert salt-initiated hydroarylation of isatin, a

diverse array of monoarylated products, symmetrical/unsymmetrical doublearylated products, and deoxygenated hydroarylated products could be synthesized from the single starting



substrate in good to excellent yields. A preliminary mechanistic study revealed that the reaction proceeds via a monoarylated product followed by a nucleophilic attack by another electron-rich arene nucleophile under mild conditions. The potential of newly synthesized symmetric/unsymmetric 3,3-disubstituted oxindole, 3-substituted 3-hydroxy oxindoles, 3,3-di(indolyl)indolin-2-ones, and α -aryl oxindoles as valuable building blocks is further illustrated.

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Solvent dependence on cooperative vibrational strong coupling and cavity catalysis

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Abstract: Strong light-matter coupling has been a topic of interest for chemists and physicists due to its intriguing properties. In the strong coupling regime, a molecular transition and a resonant cavity mode exchange energy faster than any other dissipation process resulting in the formation of polaritonic states comprising the properties of both matter and photon.¹ The idea of coupling a fundamental vibrational transition to a Fabry-Perot (FP) cavity mode is popularly called vibrational strong coupling (VSC). It has been demonstrated that VSC can control chemical reactivity at the molecular level.^{2–4} In the current study, we try to understand the solvent effect on a trans-esterification reaction by coupling the reactant and the solvent molecules collectively to a cavity mode.⁵ Interestingly, different solvent systems behave differently under cooperative VSC conditions and show resonance effect at different temperatures. Thermodynamic studies were carried out for all the combinations and found that $\Box G^{\neq}$ changes up to 4 kJ/mol at ON-resonance condition. Cavity detuning and other control experiments suggest cooperative VSC of the solvent plays a crucial role in modifying the transition state energy of the reaction.

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Solubilization Studies of Hydrophobic Drugs in Pluronics and Pluronic-Labrasol Mixed micelles

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Abstract:

Owing to the hydrophobic nature of drugs, there is utmost requirement of an efficient system associated with adequate solubilization and thus superior oral drug delivery in order to achieve required pharmacological response [1]. In the present work, Pluronics (P84, F127, F68) have been employed to study the solubilization of hydrophobic drugs QCT and CUR. From UV-Visible studies, it was confirmed that solubility, drug loading efficiency, partition coefficient (P), standard free energy (ΔG°) associated with the solubilization of QCT and CUR were found to be higher in Pluronic P84 and P84-Labrasol mixed micelles [2]. Differential pulse voltammetry (DPV) measurements also revealed that the interactions between QCT and Pluronic P84 (P84-Labrasol) lead to a decrease in the peak current along with shifting of peak to higher potential. While in CUR, appearance of an additional peak at lower potential was observed. On the other hand, enhanced fluorescence intensity of the studied drugs in case of Pluronic P84 and Pluronic-Labrasol mixed micellar solution was observed. Both DPV and Fluorescence studies revealed better solubilization of QCT and CUR in P84 and P84-Labrasol mixed micelle. In vitro release of Pluronic and Pluronic-Labrasol mixed micellar formulations exhibited the continuous release of both QCT and CUR. Dynamic light scattering (DLS) results also supported the inferences obtained from electrochemical and spectroscopic measurements. Because of their small size and excellent encapsulation efficiency, the Labrasol mixed micelles carry the potential in controlled and targeted drug delivery.

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Experimental and Computational Study of Umpolung N-Bromoamines: Organocatalytic Bromination of Olefins

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Abstract: N-bromoamines are the results of quick exchange between the cationic bromine souce (NBS) and amines. An unprecedented study of change in polarity (umpolung) of Br from NBS to N-bromoamines were supported by both experimental and computational data. Further, its application has been extended towards the bromination of various substituted olefins. This organocatalytic bromination protocol, was found to be relatively efficient as compared to other conventional methodologies in terms of stereoselectivity, use of non-toxic reagents. Moreover the concept of "Umpolung" for the Br+ organocatalytically are not reported to the best of our knowledge and hopefully can be used for other reactions.



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A Bee-Line Approach to Access Organocatalysts:

Chemoselective & Time Driven O-functionalization of Prolinol

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Abstract:

Herein, a successful chemo-selective either functionalization of the nucleophilic sites of prolinol has been reported, by exploiting the relative acidity difference and inverted nucleophilicity of the corresponding conjugate bases with a suitable base. Failing to re-enact the former protocols, a mechanistic investigation was initiated which revealed that the rudimentary steps can be controlled by: a) A requisite base to distinguish the differently acidic sites (NH and OH) for the formation of the conjugate base reacting to the electrophile **b**) The disparity in nucleophilicity of the completely formed conjugate basic sites. As an example, functionalization of prolinol for the exclusive synthesis mono-Boc of either NBoc/OBoc/Oxazolidinone derivatives is reported. Never-reported-before O-Boc prolinol has been synthesized in 85% yield and other known derivatives (NBoc and oxazolidinone derivatives) have been synthesized in good to excellent yields. This protocol has proven to be successful with various other substrates which might prove to be applicatory as suitable organocatalysts in asymmetric reactions.



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Spectroscopic Investigation of Hemoglobin Interacting with DBU Based Novel Protic IL Media

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Abstract:

Various additives were experimented with protein molecules and, Ionic Liquids (ILs) had proven to be a wise choice considering the special features of ILs including higher thermalchemical stabilities, negligible vapour pressure, and mainly the ability to reuse [1,2]. Moreover, thermal stability, self-life and stronger enzymatic activities are the reason behind the selection of different ILs in many of the biological applications including protein separation, extraction, preservation, sensing of biomolecules, and so on. It is interesting to note that, the behavior of each protein is specific to the nature of the ionic liquids and the same IL can act as a stabilizer as well as a denaturing agent depending upon the protein molecule to which it is interacting with [3,4]. DBU (1,8-diazabicyclo[5,4.0]undec-7-ene), a tertiary amine with double heterocyclic structure, when combined with another main base molecules such as Imidazole, Morpholine, and Triazole, there formed an exciting series of stable ILs. Here in this study, these protic ILs are introduced in the field of protein studies and compared with a common protic DBU IL having a triflate anion, through spectroscopic analysis including uvvisible, fluorescence, DLS and lifetime techniques to find out the various interactions prevailing in the medium. Sometimes the ions present in the ionic liquid may coordinate well with the protein moiety and leads to the dissolution of the molecule in that IL whereas another scenario occurs where the disruption of the interactions due to the ILs were also observed. It was found that, among the ILs, [DBU][Tz] can be chosen as the most reactive medium towards hemoglobin like protein molecules. Even under very dilute concentrations of the [DBU][Tz], the protein molecules are effectively interacting to the medium and offers an affirmative to the possible choice of an IL additive to the protein molecule for preservation and stability in an economic way.

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Production of Xylitol from Spent Aromatic Biomass Derived D-Xylose as Renewable feedstock

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Abstract

Xylitol is an important sugar alcohol that occurs naturally as minor constituent in plums, strawberries, cauliflower, and pumpkin. In humans and many other animals, it is produced in trace amounts during carbohydrate metabolism. In recent years, it is used increasingly as a sugar substitute in drugs, dietary supplements, confections, toothpaste and chewing gum. A comparative high added value and growing market for xylitol has fostered extensive research on its dietary and technological properties. It can be produced by either chemical or biotechnological methods, wherein, D-xylose is used as a feed stock.¹ The chemical process via catalytic hydrogenation of D-xylose suffers from numerous disadvantages, e.g., non-eco-friendly nature, formation of by-products, necessity of high purity D-xylose as a substrate, costly down-streaming for product recovery, etc.² Therefore, the present research is being carried out with explicit objective of D-xylose recovery from spent waste in high purity and yield followed by its solvent free chemical conversion to xylitol.

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Unlocking the Chemistry of Bile Acids to Engineer Hydrogels for Sustained Drug Delivery.

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Abstract:

Delivery of antibiotics, anticancer drugs, and anti-inflammatory drugs is highly challenging due to their poor solubility, undesirable toxic effects caused by uncontrolled release of these drugs, and their accumulation in undesired organs. Numerous attempts have led to the development of biomaterials to minimize the systemic toxicity and enhance bioavailability of drugs at the desired site. Therefore, localized drug delivery systems and recent advances in engineering of hydrogels have gained popularity due to effective entrapment of drugs while maintaining the sustained and localized release of drugs. Therefore, we used self-assembled properties of bile acids to form supramolecular aggregates, and developed non-immunogenic and biocompatible bile acid-derived hydrogelators. Bile acids, lithocholic acid and cholic acid, were conjugated with a dipeptide sequence and screened for their hydrogelation property and rheological characteristics. Interestingly, Cholic Acid-Glycine-Glycine (CA-GG) showed low gel strength, high elasticity, and high spreadability making it ideal for the topical delivery of antibiotic (ciprofloxacin) and steroidal drug (betamethasone) for combating bacterial infection and psoriasis, respectively. Lithocholic acid-Glycine-Glycine (LCA-GG) showed high gel strength, high elasticity, and can maintain sustained release of combination of anticancer and anti-tuberculosis drugs in mice for ~20 days after implantation, and can help in mitigation of tumor progression and mycobacterial load in lungs. In my poster, I will present our recent attempts to engineer bile acid-derived hydrogels, their physicochemical properties, and biomedical applications.

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Mining the medicinal plant, *Trichopus zeylanicus* (Arogyapacha), using genome and high-resolution metabolome characterizations.

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Abstract:

Trichopus zeylanicus (Arogyapacha) is a treasure trove of bioactive natural products indigenous to Indian terrain. The concoctions of the plant as a wholesome medicinal agent have been medicinally valuable for several hundreds of years. Pharmacological studies on *T. zeylanicus* extracts point out its activities as antifatigue, antioxidant, anti-stress, antimicrobial, antitumor, antiulcer, antidiabetic agents, and their immunomodulatory, hepatoprotective, and aphrodisiac properties.^{1,2} Yet, the vital pharmacological agents exerting these activities are not identified from the plant.^{3,4} A recent advent from the Department of Computational Biology and Bioinformatics, University of Kerala, India, generated the first whole genome draft of Arogyapacha.⁵ Functional annotation have predicted some of the genes enriched towards secondary metabolite pathways that include bioactive molecules like aminoglycosides, isoquinoline alkaloids, peptidoglycans, macrolides, aminocoumarins, and lactams.

Our study characterizes these specialized bioactive moieties using HPLC purification and compound characterization by High-Resolution Mass Spectrometry and 1D and 2D NMR analysis. Redundancy is reduced through genomic characterizations. Metabolite specific solvent extraction strategies are optimized and employed prior to the HPLC separation. This helped in the concentration and isolation of low-yielding metabolites, which otherwise are unidentifiable by conventional methods. We summarise our initiative to identify crucial enzymes that generate specific chemical backbones. This includes an extensive bioinformatics analysis employing various BLAST and HMM analysis, prodding for a catalytic domain based search. Supplemented with multiple sequence alignment and phylogenetic tree construction, the bioinformatic analysis helps draw out putative enzyme homologs in the plant system. These efforts vastly improve the accuracy of mapping the biosynthetic pathways towards the isolated metabolites.

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Aminal link Covalent organic framework as a heterogenous catalyst.

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Abstract:

Here we have synthesized an aminal linked crystalline microporous covalent organic framework. The aminal linked COF formation is a great challenge because during the condensation process, the sp² carbon of the carbonyl group transformed into the sp³ carbon of aminal group (rearrange the sentence). The synthesized COF acts as an efficient catalyst. COF materials have porous structure so this COF matrial showing the gas sorption property.

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An asymmetric supercapacitor with prussian blue-coated carbon composite Electrodes

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Abstract:

Irrational use of fossil fuels led to global warming and pollution. Therefore, to combat climate change, the newer technologies should be sustainable and eco-friendly without compromising electrochemical performance. In this context, supercapacitors (SCs) are demonstrated with carbon materials derived from natural biomaterials. Although SCs exhibit high power density, they are not considered a primary energy source due to their poor energy density. This work is on escalating the energy density of SCs.

In the present work, asymmetric SC is developed by combining a porous 3D cubical shaped Prussian blue (PB) decorated carbon derived from tamarind seeds $(ACTS-800)^1$ (PB@ACTS-800)² as a positive electrode with ACTS-800 negative electrode with 3 M aqueous KNO₃ electrolyte. The resultant ACTS-800//PB@ACTS-800 (1:2) asymmetric SC demonstrated a broad electrochemical stable voltage window of 2.2 V in the aqueous medium. The high energy density of 60 Wh/kg @551 W/kg of the asymmetric device is much superior to most of the carbon/carbon SCs operated in an aqueous medium.

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A Computational Study of Mechanisms and Kinetics of Reaction of 4-Hydroxy-2-Pentanone (4H2P) with OH radicals

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Abstract:

The mechanistic, thermochemical, and kinetic study of the reaction of 4-hydroxy-2-pentanone (4H2P) with OH radicals is performed by employing quantum theoretical calculations. 4-hydroxy-2-pentanone (4H2P) is a biomass-derived compound produced in a significant amount.¹ For five possible reaction pathways, the potential energy diagram was evaluated at the CCSD(T)/cc-pVTZ//BH&HLYP/cc-pVTZ level of theory. The thermodynamic properties such as reaction enthalpies and Gibbs free energy are calculated at the BH&HLYP/cc-pVTZ level of theory.



Figure 1: Potential energy diagram of the 4H2P + OH reaction at CCSD(T)/cc-pVTZ//BH&HLYP/cc-pVTZ level of theory.

Theoretical rate coefficients of five abstraction pathways are calculated by the dual-level direct dynamics method using the canonical variational transition state theory $(CVT)^{2,3}$ in conjunction with small-curvature tunneling (SCT) over the 210-350 K temperature range. The overall rate coefficients and branching ratios have also been computed using the CVT/SCT rate coefficients. Branching ratios identified hydrogen abstraction from the –CH group adjacent to the hydroxyl group in 4H2P as the major pathway. The subsequent degradation mechanisms of the primary oxidation alkyl radical (CH₃C(O)CH₂C[•](OH)CH₃) product are further studied in a NO-rich environment. This results in acetone, NO₂, and oxygen as the major final products.

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Investigation of the Nature of Intermolecular Interactions in Tetra(thiocyanato)corrolato-Ag(III) Complexes: Agostic or Hydrogen bonded?

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Tetra(thiocyanato)corrolato-Ag(III) complexes presented here constitute a new class of metallo-corrole complexes. The spectroscopic properties of these complexes are quite unusual and interesting. For example, the absorption spectra of these β -substituted corrolato-Ag(III) complexes are very different from the β -unsubstituted corrolato-Ag(III) derivatives. Singlecrystal XRD analysis of a representative tetra(thiocyanato)corrolato-Ag(III) derivative reveals C-H···Ag interactions. The C-H···Ag interactions are rarely demonstrated in the crystal lattice of a discrete coordination/organometallic compound^{.[1]} Optimization of the hydrogen positions of the crystal structure discloses the geometrical parameters of the said interaction as Ag...H distance of 2.597 Å and \angle C-H···Ag of 109.62°. The NBO analysis provides information about the donor-acceptor orbitals involved in the interactions and their interaction energies.^[2] It was observed that the σ_{C-H} orbital overlaps with the vacant d-orbital of Ag with an interaction energy of 17.93 kJ/mol. The filled d-orbital of Ag overlaps with the σ^*_{C-H} orbital with interaction energy of 4.79 kJ/mol. The highlights of this work are that the H…Ag distance is outside of the distance range for the typical agostic interaction but fitted with the weak H-bond distance. However, the $\angle C$ -H···Ag angle is within the range of the agostic interaction. Both crystallographic data and electronic structure calculations reveal that these kinds of intermolecular interactions in square-planar d⁸ Ag(III) complexes are intermediate in nature. Thus they can not be categorically called either hydrogen bonding or agostic interaction.

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Artificial Light-Harvesting FRET Antennae based on Perylenediimide and Aza-BODIPY: From acyclic triads to macrocycles

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Abstract: Inspired by the natural photosynthesis process, numerous artificial light-harvesting (LH) multichromophoric systems for energy and electron transfer have been extensively studied over the decades. In such artificial LH systems, multiple chromophores with complementary absorption have been employed either through covalent connections or through pre-programmed self-assembling strategies. The excitation energy transfer occurs such that the peripheral chromophores absorb light and funnel it to a central chromophore by excitation energy transfer (EET) either through Förster resonance energy transfer (FRET) (dipole–dipole interactions) or through Dexter energy transfer (through bond interactions). Perylenediimides (PDIs), with high fluorescence quantum yield and tunable absorption in the visible region, can serve as suitable energy donors in EET cassettes with NIR absorbing aza-BODIPY as an energy acceptor. Here in this study, multichromophoric LH antennae of PDI and aza-BODIPY triads connected in an acyclic fashion have been synthesized and EET has been investigated by various photophysical techniques and in further studies, the PDI and aza-BODIPY were covalently connected in a cyclic fashion in single macrocycle and EET has been investigated.

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Ruthenium (II) Catalyzed Regioselective C-2'-Alkenylation of 2-Phenylimidazo[1,2-a]pyridine-3-carbaldehydes

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Abstract:

Functionalization of 2-phenylimidazo[1,2-a]pyridine-3-carbaldehydes has been achieved through ruthenium (II) catalysed oxidative C-2'-alkenylation with acrylate ester, leading to the formation of regioselective monoalkenylated products. This may be attributed to the unrestricted rotation along the C-2-C-1' bond, which is originating due to the presence of C-3 aldehyde group. A few earlier workers considered this reaction to be directed by the imidazo[1,2-a]pyridine functional unit at the aromatic α -position.^{1, 2} The key features of this protocol involve the synthesis of monoalkenylated products selectively, without using base/activators (silver salts) and the reactions can be completed in a shorter interval (4-6 h) in comparison to earlier reported methods. Further, this reaction tolerates a wide range of substrates and the products were formed in 66–86% yields. This protocol can also be utilised for the alkenylation of various 2-phenylbenzo[*d*]oxazole and 2-phenylbenzo[*d*]thiazole derivatives. Mechanistic studies revealed that the formation of a five membered cyclic ruthenium complex facilitated the C-H activation. Further, the control experiments including deuterium labelling and 2D NMR suggested the selective aromatic C-2' activation over C-5/C-8 positions of 2-phenylbindazo[1,2-a]pyridine-3-carbaldehydes.



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Regioselective Diversification of Activated Pyridines: A Cogent Strategy towards gem-Difluorinated (-CF₂-) N-Heterocycles

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Abstract:



The presence of fluorine functionality in organic molecules often favourably alters the pharmacokinetics and physicochemical properties of parent compounds, which plays pivotal roles in the drug discovery arena.¹ However, the supply of fluorine-rich organic scaffolds from natural sources is scarce and thereby, largely depends on the man-made protocols. Herein, we have capitalized **the nucleophilic reactivity of** *a*,*a*-difluorinated *gem*-diols which efficiently generate high-value *gem*-difluoro enolates under mild conditions^{2,3} and explored regioselective diversification of activated pyridinium salts⁴ to access biologically relevant 1,4-dihydropyridines and 3,4-dihydro-2-pyridones adorned with the valuable *gem*-difluoromethylene motif.⁵ The protocol is scalable, high yielding, and accommodates a broad range of substrates and functional groups. Further advancements have been showcased in the synthesis of challenging *gem*-difluorinated oxa-azabicyclo[3.3.1]nonane frameworks.

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Copper-Catalyzed Aerobic Cross-Dehydrogenative Coupling of β-Oxime Ether Furan with Indole

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Abstract:



Heterobiaryls serve as relevant structural motifs in many fields of high applicative importance such as drugs, agrochemicals, organic functional materials etc.^{1a-c} Cross-dehydrogenative coupling involving direct oxidation of two C-H bonds to construct a C-C bond is actively being pursued as a more benign and 'greener' alternative for synthesizing Heterobiaryls.^{2a-c} Herein, we report a Cu(I)-catalysed cross dehydrogenative coupling of indoles and furans, two of the most important aromatic heterocycles using air as the terminal oxidant. The reaction proceeds with regio- and chemoselectivity to give the cross-coupled products in good to excellent yields generally. A broad substrate scope with respect to both the coupling partners has been demonstrated to prove the generality of this reaction. Some control experiments and DFT calculations of our substrates suggest the involvement of radical mechanism in reaction. This represents the hitherto unexplored cross-dehydrogenative coupling methodology to obtain an indole-furan biaryl motif.

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Oxygen Atom Transfer Promoted Nitrate to Nitric Oxide Transformation: A Step-wise Reduction of Nitrate → Nitrite → Nitric Oxide

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Abstract:

The mechanism of microbial four-step denitrification $\{NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2\}$, is still one of the most mysterious subjects, despite being explored in detail in both in-vivo and invitro systems.¹ Nitrate reductases (NRs) are molybdenum-based enzymes that reduce nitrate (NO_3^-) to nitrite (NO_2^-) via (Oxygen atom transfer reaction) OAT, which further produces nitric oxide (NO) either in acid-induced NO_2^- reduction or in the presence of nitrite reductases (NiRs).² NO works as a signaling molecule in the biological system and is involved in various

bio-physiological processes.³ Reduction of NO_3^- to NO using a single reagent is still a challenge to the scientific community as two different enzymes play the catalytic role in each step in the biological system. Herein, we report a new approach of VCl₃ (V³⁺) induced step-wise reduction of NO_3^- in Co^{II}-nitrato (2) complex to $\{Co(NO)\}^8$ (4).⁴ The VCl₃ induced reduction of NO_3^- to NO is believed to proceed in two consecutive OAT reactions, i.e., OAT-1 = $NO_3^- \rightarrow NO_2^-$ (r₁) and OAT-2 = $NO_2^- \rightarrow NO$ (r₂). In these OAT reactions, VCl₃ functions as



oxophillic species producing **4** and V^V-Oxo via Co^{II}-nitrito (**3**) intermediate. Further, in a controlled experiment, we explored the reaction of **3** with V³⁺ formation of **4** was observed with V^V-Oxo, validating our proposed reaction sequences of OAT reactions. We ensured and characterized **3** using VCl₃ as a limiting reagent, as the second-order rate constant of OAT-2 (k_2 [/]) is found to be ~ 1420 times faster than that of the OAT-1 (k_2) reaction. Mechanistic investigations of these reactions using Co-¹⁵NO₃⁻ and Co-¹⁵NO₂⁻ revealed that the N-atom in the {Co(NO)}⁸ is derived from NO₃⁻ ligand. In nature, both the reduction process needs two different enzymes for converting NO₃⁻ to NO; hence, the proposed OAT reagent (VCl₃), which is capable of doing the same in a one-shot, has border significance with respect to biological as well as environmental systems.⁴

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Deep Eutectic Solvents based Biorefining of Value-added Chemicals from the Diatom *Thalassiosira andamanica* at Room Temperature

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Abstract:

The extraction and biorefining of value-added chemicals from bioresources using green solvents are among the key agenda of the circular bioeconomy. Herein we have developed a deep eutectic solvent (DES) based biorefining approach for clean separation and purification of value-added Fucoxanthin, Chlorophyll, and Biosilica from a diatom microalgae, Thalassiosira andamanica. Several hydrophilic/hydrophobic (DESs) based on quaternary ammonium salt as hydrogen bond acceptor and organic acids and alcohols as hydrogen bond donors were synthesized and tested for microalgae biomass dissolution and biorefining via phase partitioning method. Hydrophilic DES were able to extract 19.93 mg/g of Fucoxanthin via phase partitioning, with an increase in yield by 53 % and selectivity by 81 % compared to the conventional solvents. Subsequently, a hydrophobic DES was added to extract remaining Chlorophyll and Biosilica from hydrophilic DES layer and residual biomass. Chlorophyll extracted in the hydrophobic DES phase exhibited excellent photostability (6 folds greater than conventional solvent) indicating the efficacy of DESs as photoprotector for light-sensitive pigments. Additionally, extracted *Biosilica* showed an excellent adsorption capacity of 224.71 mg/g for the removal of methylene blue (MB) dye from water (94.3% up to 88.8 % after 4th consecutive steps). Complete utilization of biomass was achieved using non-toxic DESs. This is the first report wherein besides an extractant DES also acted as a good photostabilizer. Furthermore, we have replaced the acid-based purification method for *Biosilica* with non-toxic DESs.

"On-On" Approach for detection of Creatinine in Human Blood Serum using AIEE Active Supramolecular Metallic Ensemble

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Abstract:

Till date, the estimation of creatinine levels in blood/urine samples by Jaffe's method is the only reliable and economic clinical test to determine the kidney performance¹. The problem of this method is utilization of very toxic and environmentally hazardous picric acid as probe in the detection process. In this context, we have developed an ecofriendly supramolecular metallic ensemble (**3**-Fe²⁺) which exhibited highly sensitive 'on-on' response towards creatinine in human blood serum with detection limit in picomolar level. The present system demonstrates the real time application for the detection of creatinine and the results are found to be comparable to Jaffe's protocol. We also estimated the tentative cost of 10 mg of the probe which comes out to be 0.72 US Dollar (50.07 Indian Rupee). Thus, the system being reported in this manuscript is cost effective².



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Synthesis of Zn_xCo_{1-x}Fe₂O₄ nanoparticles via thermal decomposition method and their application as photocatalyst

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Abstract:

Doping of Zn²⁺ in CoFe₂O₄ nanoparticles can enhance their physicochemical properties and doped CoFe₂O₄ nanoparticles are useful in photodegradation of dyes [1]. Doping enhances electrical, optical, structural and magnetic properties of the host [2]. CoFe₂O₄ has an inverse spinel structure but when it is doped with Zn^{2+} , it changes its structure to normal spinel [3]. $CoFe_2O_4$ is a hard magnet and its hardness is reduced by the substitution of Zn^{2+} . $Zn_xCo_{1-x}Fe_2O_4$ being a soft magnet has high coercivity with good chemical stability [4,5]. In the current study, synthesis of Zn^{2+} substituted cobalt ferrite nanoparticles ([Zn^{2+}] = 0.10 mmol, 0.20 mmol, and 0.30 mmol) was done via a novel thermal decomposition approach [6]. First, ethylene glycol mediated route was used for the synthesis of Zn²⁺ doped Co-Fe glycolates followed by calcination at 500 °C in air. The substitution of Zn²⁺ in Co-Fe glycolates was confirmed by various analytical techniques. XRD results indicate substitution of Zn²⁺ in CoFe₂O₄ nanoparticles obtained after calcination of the Zn²⁺ substituted Co-Fe glycolates. FT-IR results indicate a shift in M–O stretching towards lower frequency in the Zn_xCo_{1-x}Fe₂O₄ nanoparticles. SEM images show hexagonal morphology for pure Co-Fe glycolate which converts into particles on substitution of Zn^{2+} in Co-Fe glycolates. TEM analysis of pure CoFe₂O₄ and Zn_xCo_{1-x}Fe₂O₄ reveals hexagon made up of small nanoparticles and nanoparticles with irregular morphology, respectively. Magnetic studies of the Zn^{2+} substituted CoFe₂O₄ nanoparticles indicate superparamagnetic behaviour at 300 K and hard ferromagnetic behavior at 15 K. The coercivity at 15 K decreases on increasing the Zn²⁺ concentration as compared to pure CoFe₂O₄ nanoparticles. The Zn_xCo_{1-x}Fe₂O₄ nanoparticles were explored as catalyst for the photocatalytic degradation of congored in an aqueous solution. The Zn_xCo_{1-x}Fe₂O₄ nanoparticles act as better catalyst for the photodegradation of congored as compared to pure CoFe₂O₄ nanoparticles.

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Bridging the Bays, Both Ways: A Janus Butterfly-shaped Intense NIR-Emitting Terrylene Diimide

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Abstract: Near Infrared (NIR) emitting molecules are in demand for their utility in night vision detectors and biological imaging.¹ Even though various NIR absorbing molecular classes are reported, intense NIR emitting molecules are less explored. Longer rylene diimides such as terrylene diimides (TDIs) are important class of molecules having intense absorption and emission in the NIR range.² However, these larger polyaromatics are less explored due to the challenges associated with their synthesis, isolation and characterization.

Herein, we present an exciting strategy to make novel Janus butterfly-shaped TDIcarbazole derivatives, obtained by bridging the bay positions of the terrylene core. These new molecules have intense absorption and emission in the range of 720 nm – 897 nm. The emission quantum yields observed are some of the highest among this class of molecules (up to **93%**).³ We also present the serendipitously obtained two-tiered TDI derivative (**TDI-Cbz4**) having emission maxima at 897 nm. This work highlights the utility of precise electronic and structural tuning necessary to achieve intense NIR absorbing and emitting molecules for modern applications.



Schematic representation of NIR emitting Terrylene Diimides

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Tuned assembly of asarylaldehyde treated type-I collagen: Potential application for next generation tissue engineering

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Abstract: Collagen monomer has triple helical structure and its supramolecular self-assembly forms fibril (fibrillogenesis), which is the main constitute of bone tissue, cartilage tissue, cornea, skin ECM etc¹. *In vitro* fibrillogenesis take place at physiological environment, but the reconstituted fibrils are much thicker with less packing density in comparison to the *in vivo*

fibrillogenesis process². To make it tunable to the desired properties, we have introduced a small molecule, asaryldehyde into the fibrillogenesis process. This small molecule, asarylaldehyde (2, 4, 5 trimethoxybenzaldehyde) found in carrot has unique cell proliferation property³. We tuned the self-assembly of collagen with the help of molecular interactions aldehyde with group present in various asarylaldehyde and active functional groups present in collagen



polyproline-II chain. Circular Dichroism spectra of native collagen and collagen treated asarylaldehyde at various ratios reveal that asarylaldehyde treated collagen is not changing its characteristic triple helical structure. From kinetic study it is clear that *in vitro* the reconstituted fibril formation rate is more compared to native collagen. Asarylaldehyde is showing fluorescence quenching in the mixture of collagen, while increasing the ratio of asarylaldehyde, the quenching is high, from that study it is clear that the asarylaldehyde molecule interacting with collagen on molecular level. The quenching property of asarylaldehyde treated collagen we observed that the cells are sustainable at various asaryldehyde concentration. This tuned and self-assembled fibrillar system creates a better understanding of various forces modulating its structure-function relationship. This will further aid these cross-linked scaffolds to act as templates, which will favour the growth and viability of specific cells for tissue engineering applications.

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Dual Responsive Fluorescent Probe for Detection of Cyanide and Hydrogen Sulfide: Real Time Application in Strip Test, Live Cells, and Identification of Food Spoilage

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Abstract:

Cyanide and hydrogen sulfide are highly reactive nucleophiles and small noxious analytes which pose a major impact on environment and human life^{1,2}. Colorimetric and fluorescent probes have received a lot of attention for detecting lethal analytes in realistic systems and in living things. Herein, a dual approachable Benzo-hemicyanine-based red-emitting fluorescent probe **PBiSMe** for the distinct and instantaneous detection of CN⁻ and HS⁻ was synthesised. The nucleophilic addition of CN⁻/HS⁻ via two different reaction sites alters the conjugation of system, resulting in two significant fluorescence emission maxima and a colour change from yellow to colourless in daylight. Other nucleophilic reagents, such as reactive sulphur species (RSS) and anions, have no interaction or interference with the probe, it has a particular approach to only with CN⁻ and HS⁻ over a wide pH range. The detection limits for CN⁻ and HS⁻ ions were calculated and found to be 0.43 μ M and 0.22 μ M, respectively, lower than the World Health Organization's (WHO) acceptable limits for these ions in drinking water. We confirmed 1:1 stoichiometry ratio by Job's plot and observed good quantum yield for both analytes. The paper strips immersed in probe solution was used to detect H₂S gas produced by food spoilage (such as eggs, raw meat, and fish) by an eye catching visible response. Moreover, fluorescence bioimaging studies of living cells was done to confirm the probe's potential by monitoring the presence of CN⁻ and HS⁻ in a living system.



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Structural and computational analysis of organic fluorine mediated interactions in controlling the crystal packing of tetrafluorinated secondary amides in the presence of weak C–H····O=C hydrogen bonds

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Abstract:

The structural and computational analysis of small organic compounds containing four fluorine atoms is studied. A library containing a secondary amide (-CONAr₂) group has been synthesized and structurally characterized to understand the influence of multiple C-F bonds in building various supramolecular synthons. This allows for the possibility of C-H···O-C and C-H···O=C hydrogen bonds in the molecules. Introduction of four C-F bonds in each molecule has resulted into a variety of fluorine mediated weak hydrogen bonded synthons and a few C-F...F-C contact mediated molecular dimers. These molecules offer the possibility of exploring the wide variation in crystal structures resulting out of different types of weak interactions offered by organic fluorine (C-F group) connected to an aromatic ring. Herein, we have observed 13 different synthons that help in the formation of C-H···F-C hydrogen bonded dimers and more than 50% of these interactions fall in the region of strong hydrogen bonds as per the definition by Desiraju and Steiner. In addition to the stabilization offered by C-H···F-C, C-H···O-C, and C-H···O=C hydrogen bonds, a variety of C-F···F-C interactions have also been found to provide stability to these structures. The stabilization energy offered by C–F···F–C interactions range between -0.2 and -9.0 kcal mol⁻¹. Herein, we intend to demonstrate the significance of those interactions using structural and computational methods.



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A Coumarin based fluorescent probe for hydrazine detection

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Abstract:



Hydrazine is utilized extensively in numerous sectors. During storage, transit, and sewage disposal, this exacerbated environmental degradation. Hydrazine classified as a group 2B toxin, also poses a concern to human health due to its water solubility and its ability to enter the human body through the skin and lungs. Its exposure might cause irreparable body damage. Hence, it is important to develop strategies to recognize it selectively. A benzo coumarin-based probe for the selective detection of N₂H₄ based on substitution-cyclization and elimination sequence was developed in this study. The probe 4-methyl-2-oxo-2H-benzo[h]chromen-8-yl 4-bromobutanoate in DMSO/H₂O (1:1) fluoresced green with an emission maximum at 528 nm when treated with N₂H₄. Other common ions, amine-containing species, and amino acids had no effect on the probe's ability to detect hydrazine. This probe can quantitatively detect N₂H₄ with a low detection limit of 2.74 μ M. The sensing mechanism was further verified by ¹H NMR titration. The probe could also detect hydrazine in different soil samples, indicating its practical applicability. Furthermore, the lack of a buffer would make real-time sample sensing considerably simpler and easier.

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Understanding the Effect of Monovalent Metal Salts on the Gelation Behaviour of Sodium Deoxycholate

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Abstract

Bile salts (BSs) have been extensively studied due to their physiological importance. They are natural-occurring surfactants that solubilize dietary lipids, fats, cholesterol, fatty acids, and phospholipids in the intestinal tract and in bile.¹ In contrast to other surfactants BSs is unusual because of the facial polarity. The concave side of the molecule is hydrophilic whereas the convex side is hydrophobic.² As a result, BSs form different aggregates above critical aggregation concentration. Depending upon the BSs concentration they form primary, secondary, and higher micellar aggregates. Additionally, the salt-induced gelation study of BSs was reported for NaCl salt.² The main objective of this work is to study the salt-induced gelation of BSs with a series of monovalent salts. Further, our objective is to understand the effect of ionic strength of the medium and the size of the cation in such a gelation process. We have used various techniques including fluorescence spectroscopy, light scattering, differential scanning calorimetry (DSC), and dynamic light scattering (DLS) to investigate the salt-induced gelation of BSs. It was observed that the fluorescence anisotropy of 1,6-diphenylhexatriene (DPH) increases with increasing monovalent salt concentration which suggests the increase in the viscosity due to the gelation process in BSs. After a certain salt concentration, the anisotropy decreases significantly which could be due to a decrease in the viscosity because of the competition between the gelation and precipitation process. We observed that the salt concentration required to induce the precipitation process depends on the size of the cation. DSC study shows a gel to sol phase transition in BSs. Further, the DSC results were supported by the DLS experiments.

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Phosphine triggered synthesis of 3-Hydroxyquinolone under neutral condition

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Abstract:

3-Hydroxyquinolone-4(1*H*)-one (3HQs) persists as an important structural motif in many biologically active natural products.¹ The pre-existing protocols for the synthesis of 3-Hydroxyquinolone-4(1*H*)-one (3HQs) require strong acidic or basic conditions, which draw its limitation with respect to its generality and practicability. Herein, we developed phosphine-mediated transformation to 3HQs from 1-(2-nitrophenyl)-3-phenylprop-2-yn-1-one. The method culminates a new approach in the synthesis of 3HQs under neutral condition. Furthermore, the synthetic utility was extended to the total synthesis of Japonine and its analogues.

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Studies on Aggregation Behaviour of *Cetyltrimethylammonium bromide* by Varing Polarity of Water-Dioxane Mixed Solvent System

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Abstract:

Cetyltrimethylammonium bromide (CTAB), a cationic surfactant, plays important roles in biology, material science and petroleum recovery. Interfacial and aggregation behavior of surfactants are noticeably different in different solvents. The present work intends to study aggregation behaviour of CTAB in water (Wa)-dioxane (DO, a non-polar, aprotic, cyclic ether) mixed solvent system, where the polarity was varied by varying the Wa/DO ratio. Critical micellization concentration (CMC) increases with increasing proportion of dioxane. DO, which can stable in two isomeric forms (either boat or chair), also can provide a lower dielectric medium and this would solvate more surfactant monomer than pure water. Thus solvophobicity of surfactant decreases, micelle formation becomes less favourable so CMC is increases with increasing proportion of DO in Wa-DO mixed solvent systems. Different physicochemical parameters were evaluated by using conductometry, surface tensiometry (by ring detachment method), fluorimetry (spectra, quenching and lifetime) and isothermal titration calorimetry. And all these results are correlated with respect to the composition of the mixed solvent system.

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Electronically Unsaturated Aluminum hydride Cation for Catalytic Hydroboration of Imines and Alkynes and Mechanistic Insights Thereof

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Abstract:

In the pursuit of environmentally benign and sustainable catalyst, Lewis acids relying on main group elements have been considered as new alternatives.^[1] The arena of Lewis acids mediated catalysts have been extended to the boron, silicon, phosphorus and other heavy main group elements. However, the Lewis acids capitalizing on aluminum are of great interest and have remain the heart of numerous important organic reactions.^[2]

The dawn of 21st century witnessed the emergence of aluminum complexes as potential catalyst for the reduction of unsaturated molecules *via* hydroelementation approach.^[2] In this regard, the low coordinated cationic aluminum complexes which exhibits enhanced Lewis acidity are expected to provide more competent catalytic system. Henceforth, we examined the electronically unsaturated low coordinated cationic aluminum hydride for hydroboration of alkynes and imines.

The present work emphasises on the syntheses of monomeric three-coordinated aluminum cations $[LAlH]^+[B(C_6F_5)_4]^-$ using weekly coordinating anion, and $LH = [\{(2,6-iPr_2C_6H_3N)P(Ph_2)\}_2N]H$.^[3] The quantitative estimation of Lewis acidity by Gutmann–Beckett method revealed $[LAlH]^+[HB(C_6F_5)_3]^-$ to be a better Lewis acid than $B(C_6F_5)_3$ and $AlCl_3$. This aluminum hydride complex is used for hydroboration of alkynes and imines using HBpin. The pioneering work of Roesky and Stephan have established neutral aluminum complexes as efficient catalysts for alkyne hydroboration and independently sketched out an acetylide and hydroalumination mediated pathway, respectively.^[4] In contrast to these reports, the current Al catalyst involves Lewis acid pathway for imine hydroboration and aluminum alkenyl complex as the active species for alkyne hydroboration.



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Room temperature phosphorescence and long-lived fluorescence in a supramolecular hydrogel matrix

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Abstract:

Room temperature organic phosphorescence (RTOP) is difficult to achieve, due to the quenching of the triplet state by surrounding media. Various strategies that have been developed to achieve RTOP include the 'heavy atom effect',¹ 'host-guest doping',² 'Crystal engineering',³ and 'polymer dispersion'.⁴ A rigid environment is required to avoid the triplet state quenching via molecular vibration and rotation through nonradiative transitions. There are very few reports available in the literature which report RTOP in aqueous media. We have developed a system exhibiting organic molecular phosphorescence at room temperature in a supramolecular hydrogel matrix. We have also shown subsequent energy transfer to several organic chromophores, resulting in long lifetimes with enhanced quantum yields. This result helps to provide a novel strategy to achieve RTP supplemented with long-lived fluorescence from organic chromophore in a hydrogel matrix.

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A Prismatic Nano cage for encapsulation and stabilization of radical initiators

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Abstract:

Coordination-driven self-assembly has been well recognised as an efficient strategy for the construction of a vast range of metallo-supramolecular architectures.¹ Palladium(II) driven self-assembled coordination cages are constructed by combination of a suitable mono/polydentate pyridine appended ligand, L with either cis-protected palladium(II) component i.e. [PdL'] (where L' stands for cis-protecting group) or simple palladium(II) component. The resulting assemblies can be formulated as [PdxL'x(L)y] and [PdmLn] respectively.² Metallo supramolecular cages have attracted increased attention due to their potential application in the field of catalysis, drug delivery, selective guest recognition, and stabilizing reactive species. Among various solvents used for complexation, water is an inexpensive green solvent and eco-friendly, thus can be preferred over other solvents. Here we have synthesized a new template free water-soluble Pd₆L'₆L₃ cage by co-ordination driven selfassembly, where a tetradentate ligand L reacts with cis-protected $Pd(tmeda)(NO_3)_2$ in 1:2 molar ratio in H₂O:CH₃CN(4:1) mixture. The ¹H NMR, ESI-MS, and single crystal XRD data analysis revealed formation of a discrete cage with prismatic shape. The cage was found to encapsulate medium size guest molecules including radical initiators. The encapsulated radical found to be stable inside the cage.



Scheme: Cartoon representation for synthesis of Pd₆L'₆L₃, prismatic cage 1.

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Complexes from Earth-Abundant Elements Magnesium and Aluminium as Catalysts for Selective Hydroboration of Amides and Alkynes

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Abstract:

In the view of the atom-economy, catalytic hydroelementation reactions such as hydroboration and hydrosilylation are key transformations in homogeneous catalysis for the reduction of different unsaturated functionalities and produce various value-added chemicals.^[1] Although for decades precious transition-metals have played an important role to serve this purpose, the use of more earth-abundant elements has attracted substantial attention in recent years. In this context, being more earth-abundant and non-toxic, magnesium and aluminium have captured immense limelight however, their applications in this direction are still in their infancy.

The work in the poster will demonstrate the catalytic efficacy of Mg-homoleptic (\mathbf{L})₂Mg (\mathbf{L} H = (2,6-^{*i*}Pr₂C₆H₃N)P(Ph₂)(N'Bu)H) and cationic aluminium complex [^{DIPP}NacNacAlMe]⁺[B(C₆F₅)₄]⁻ for the hydroboration of more taxing functionalities such amides and alkynes. Among the different carbonyl functionalities (aldehyde, ketones, esters), amide reduction is indeed a challenging task that owes to their thermodynamic stability.^[2] The precise control over the cleavage of two bonds, C-O and C-N, during the course of catalysis is another difficulty possessed by amides. Similarly, it is challenging to accomplish the selective semi reduction of alkynes, which usually leads to the formation of overly reduced alkyl boranes. Pleasingly, the presented catalysts showed a remarkable catalytic activity for the selective deoxygenation of tertiary, secondary, & primary amides and semi-reduction was studied *via* different controlled experiments. The obtained results for (\mathbf{L})₂Mg catalyst support the formation of *bis*-Mg-amidate complex as an active species which generated *via* rapid switching of the amide NH proton to the metal-bounded anionic ligand (\mathbf{L}). However, aluminium cation assists the reaction *via* Lewis acid activation pathway.



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Green Bismuth based upconversion nanomaterial for bioimaging of cells

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Abstract:

Upconversion materials have attracted considerable research interest for their application in bioimaging due to their unique anti-Stokes optical properties. Optimal concentration of codopents is an important determining criterion to achieve high upconversion efficiency and luminescence performance of the nanoparticle. In this study we propose NaBiF₄ as a host material for upconversion which is based on environmental friendly and cost effective bismuth. The synthesis of host material co-doped with Yb³⁺/Tm³⁺ have not been reported earlier through novel non-aqueous quaternary reverse micelle route. We report efficient Yb³⁺-Tm³⁺ doped NaBiF₄ based upconversion nanoparticles which exhibit photostable, wide upconversion emission range (NIR-to-NIR and VIS) under NIR-I (980 nm) excitation, *in-vitro* non-cytotoxic uptake by mammalian cancer cell lines as well as bacterial cells with high signal to background ratio. Here, we functionally validate these nanoparticles as viable alternatives to the currently available upconversion nanomaterials and highlight their potential as luminescent nanoprobes for bioimaging.

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Organocatalysed asymmetric synthesis of barbituric acid substituted axially chiral styrene via *in situ* generated VQM from 2- (phenyl acetylene) naphthol

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Abstract:



Barbituric acid-containing compounds, used as a major building block in organic synthesis. Barbituric acid belongs to the class of biologically active *N*-Heterocycles which find application in medicinal and pharmaceutical chemistry.¹ Furthermore Styrene is well-known as one of the most common and important feedstocks. This makes them both a great starting point for chemical synthesis. Herein, we have developed an enantioselective organocatalytic method for the synthesis of barbituric acid substituted axially chiral styrene from 2-(phenylacetylene) naphthols. Various successive compounds incorporating barbituric acid and an axially chiral styrene unit were prepared with excellent enantioselectivity (up to 99% ee) and yield (up to 99%). This approach provides an efficient methodology to synthesise wide range of substrates under moderate reaction conditions.

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'Lighted' Assemblies of a PBI Derivative: Activation of Aerial Oxygen *via* Combined Charge and Energy Transfer Processes for Photocatalytic Oxidative Hydroxylation of Boronic Acids

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Abstract:

The donor-acceptor 'lighted' assemblies of **PBI-TPY** have been developed which exhibit strong absorption in the visible region, have high photostability, excellent electron transportation ability and high potential to activate aerial oxygen to generate reactive oxygen species such as singlet oxygen, superoxide anion radical and hydroxide ions.¹ Empowered by excellent photosensitizing properties, assemblies of **PBI-TPY** exhibit high photocatalytic efficiency in visible light mediated oxidative hydroxylation of aromatic/aliphatic boronic acids through combined charge/energy transfer processes in the presence of weak electron donor (NEt₃) and air as the 'oxidant' in mixed aqueous media. The work being presented in this manuscript also reveales the potential of **PBI-TPY** assemblies for gram-scale preparation of phenol and recyclability of upto six catalytic cycles in the oxidative hydroxylation reaction.



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Transfer hydrogenation of carbonyls and imines with ⁱPrOH catalyzed by Ir(BICAAC)Cl(COD)

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Abstract:

Transfer hydrogenation (TH) methodology is widely accepted as a powerful greener alternative in place of the traditional reductive methods which include stoichiometric amount of reducing agents (LiAlH₄, NaBH₄, NaBH₃CN etc.) and the use of molecular hydrogen (H₂).¹ TH process involves metal-assisted abstraction of hydride from hydrogen donor solvent (oxidation step), which is subsequently inserted into the unsaturated acceptor substrates (reduction step). In the last few years, TH method has been exploited for the development of a substantial number of transition metal (Ru, Rh, Ir, Pd, Os, Ni, Co, etc.) based catalysts for reduction of C=O, C=C, and C=N bonds using various hydrogen sources (MeOH, EtOH, glycerol, H₂O, ⁱPrOH etc).²

The work presented in this poster mainly deals with the synthesis of a robust Ir(I) complex outfitted with bicyclic (alkyl)(amino)carbene (BICAAC) ligand and explored as a highly efficient catalyst for transfer hydrogenation of carbonyls (aldehyde and ketones) and imines (aldimines) using isopropanol as hydrogen delivery agent. A wide array of substrates functionalized with electron-withdrawing and -donating substituents have been surveyed and afforded their reduced products in good to excellent yields. Notably, the more challenging heteroaromatic substrates and potentially reducible cyano and nitro groups are well tolerated. No decomposition of the BICAAC unit from the metal center was observed upon prolonged refluxing of Ir(BICAAC)Cl(COD) which evidenced the high thermal stability of the catalyst. The results of deuterium labelling and other control experiments support the Ir-hydride as the key intermediate of the proposed catalytic cycle.



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A modular approach to synthesized Inorganic Macrocycles based on Main Group Elements

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Abstract:

In contrast of organic macrocycle such as crown ether, the design of robust molecular analogous inorganic frameworks are far less investigated and still represents a major synthetic challenge due to low bond energy of carbon-element covalent bond results in greater kinetic lability, bond polarity and the variable oxidation states leads to multiple product affecting their synthesis, reactivity, yield and purification.¹ Phosph(III)azane dimers of the type [ClP(μ -NR)]₂ are excellent building blocks for the formation of a range of inorganic macrocycles. Herein, we have synthesized dimeric macrocyclic [{P(μ -N^tBu)}₂{O(CH₂)₂N(Me)(CH₂)₂O}]₂ (1) having P^{III} center assembled by condensation with the quenching of HCl molecule. Further to enhanced the air and moisture stability of macrocycle (1) the P^{III} centers are oxidized to P^V with chalcogens (O, S and Se and BH₃) afforded [{(O=)P(μ -N^tBu)}₂{O(CH₂)₂N(Me)(CH₂)₂O}]₂ (2), [{(S=)P(μ -N^tBu)}₂{O(CH₂)₂N(Me)(CH₂)₂O}]₂ (4) and [{(BH₃)P(μ -N^tBu</sub>)₂{O(CH₂)₂N(BH₃)(Me)(CH₂)₂O}]₂ (5) respectively. All the new compounds have been fully characterized using multinuclear NMR, HRMS and by single crystal X-ray diffraction and also supported by DFT calculations.



Fig:1 Synthesis of macrocycle (1) and its stable derivatives.

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A 'self-activating' Bi₃TaO₇-Bi₄TaO₈Br photocatalyst and its use in the sustainable production of pro-fluorophoric Rhodamine-110

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Abstract: We counter two common notions that (i) photocatalysts are likely to degrade during use with barely any strategy to counter and (ii) Rhodamine-B (RhB) photo-degradation lacks any useful or commercial prospect even after 53 years of its discovery by developing a photocatalyst that continues to improve its activity for ~300 h due to a leaching induced 'selfactivation' process. Rhodamine-110 (Rh110) is a widely used pro-fluorophore in biological studies. However, its commercial production is highly challenging due to the formation of various side-products originating from the very presence of the two labile amino side-groups that induce the pro-fluorophore activity, leading to purification difficulties, low yield, and unusually high costs. Herein, we demonstrate a facile strategy to produce pure Rh110 using extremely inexpensive RhB and Bi₃TaO₇-Bi₄TaO₈Br heterostructures as a catalyst in sunlight. The catalyst is not just stable over 30 catalytic cycles but also gets activated continuously in successive cycles to produce a reaction yield as high as 88%. The role of heterostructure, the origin of surface activation, and the RhB-Rh110 transformation mechanism have been established. Based on 150 days of sunlight experiments, the large-scale production prospects (~4000 times scale-up) and isolation of Rh110 have also been realized, paving a novel way for its production by anyone, inexpensive biological essaying, and device fabrication. Continuously improving catalysts are unknown and compensatory leaching of metal atoms from the catalyst surface may pave the way to realize them.

Acceptor Interlocked Molecular Design for Solution-Processed Stable Deep-Blue TADF and Hyper Fluorescence Organic LED Enabling High-efficiency

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Abstract:

Solution processed deep-blue OLEDs with high external quantum efficiency and a long operational lifetime are constrained. In this context, we synthesized two TADF emitters utilizing new design strategy of twisted interlocked acceptor core integrated with carbazole (KCCz) and tert. butyl-carbazole (KCTBC) as donors for solution processed deep-blue TADF OLEDs. Twisting of acceptor core by two methyl groups resulted in complete separation of HOMO and LUMO along with cyanide group facilitate in generating low-lying triplet exited states as suggested by theoretical simulation. Combined effect of both resulted in tuning of emission in ultra-deep blue region through the efficient population of triplet excitons and concurrently RISC to produce highly efficient devices. A doped device based on KCTBC showed EQE_{max} of 9.0% along with low Efficiency roll-off with long operational device half lifetime of 72 minutes at initial brightness of 1,000 cd m⁻², and CIE coordinates of (0.17, 0.13). In addition, with 12.5 wt% of 4CzFCN as assistant dopant/co-host to enhanced the performance of the KCTBC based device with an EQE_{max} of 13.9% and CIE coordinates of (0.18, 0.13). Further, a high-efficiency warm white OLED adopting the TADF hybrid approach is realized with EQE_{max} of 9.0 %.

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Julolidine based red emitting ESIPT/AIE active material showing luminescence beyond excimer emission: A sensitive fluorescent detection of Cu²⁺

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Abstract:

A new julolidine-fluorene based excited state intramolecular proton transfer (ESIPT)/aggregate induced emission (AIE) active Schiff-base (JDF) has been synthesized and evaluated for its photophysical properties in solution and aggregated/solid states. The correlation between the emission behavior and the solid state crystal packing structure revealed the interplay of ESIPT coupled excimer reaction occurring in the solid state, which is one of the rare examples reported so far. For a comprehensive comparison, we synthesized a non-ESIPT methyl derivative (JDF-Me) of JDF capable of showing excimer emission only in the solid state. Further, JDF exhibits normal as well as keto emission in solution, upon addition of water, its poor solvent, that promotes aggregation, the fluorescence emission shows the preponderance of the excimer band in the low energy region. It was also interesting to note that in the solid state (thin films), JDF shows emission beyond the excimer emission, which is wavelength dependent. This is attributed to the formation of diverse clusters leading to the extended delocalization beyond excimers, and represents a clustering-triggered emission ascribing bright red color to the solid JDF. Such mélange of emission characteristics of JDF are responsible for the multicolor emission covering a broad range of electromagnetic spectrum, which is demonstrated by the confocal microscopy images of the JDF recorded in different states. Further, in its aggregated state, JDF recognized Cu²⁺ ions, selectively, manifested in the form of emission quenching via the interaction of Cu^{2+} ions with the oxygen and nitrogen atoms of JDF inhibiting the excimer formation.

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Studies in the development of π -conjugated fluorescent materials for detection of small organic molecules.

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Abstract:

The ESIPT active perylene bisamide (PBI) based supramolecular assemblies have been synthesized which could selectively detect organochlorine pesticide 2,6-dichloro-4-nitroaniline (DCN) in aqueous medium. This derivative could efficiently detect DCN with detection limit in nanomolar range. The real time application of this derivative has also demonstrated in different agricultural products and this derivative can efficiently detect residues of pesticides for many days. Further, the biological applications of the synthesized derivative to detect DCN in blood serum, in MG-63 cell lines and their ability to restrict the DCN-induced cell death have been demonstrated.

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Exploration of unique reactivity of α-keto sulfoxonium ylide for the synthesis of heterocyclic-fused furan and dihydro-furan

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Abstract:

A (4+1)-annulation of arylidene heterocyclic-N-fused imidazolones, a skeleton of natural aurone-analoge, with an α -carbonyl sulfoxonium ylide has been developed. The developed reaction affords the preparation of heterocyclic-fused furans and heterocyclic-fused dihydrofurans and an opportunity of installing a secondary hydroxyl or a ketone functionality into the product scaffold. In addition, solvent and temperature-guided intermediate-halt in the tandem process afforded product scaffold diversity. The α -ketosulfoxonium ylide plays triple roles; nucleophilic 1,1-dipolar one-carbon synthon, a source of DMSO, and the ylide itself facilitating the tandem transformations. The distinctive stereo-electronic property of the scaffolds, arylidene pyridine/pyrimidine-N-fused imidazolones has been identified. The characteristic chemical properties of the arylidene-imidazolones and the ylide have potential for application to synthetic organic chemistry. The product-skeletons are important for medicinal chemistry research.



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Synthesis and Characterization of Porphyrin-MWCNT Nanoconjugate and its

Utilization as Antimicrobial Agent against S. aureus

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Abstract:

In general, the over dose of antibiotic drugs, the pathogen have grown resistance against several antibiotic drugs. The development of multi-resistance organism increases because of not available of effective drugs presently which is a sign of big problem for all biotic component as well as for food industries.¹ Herein we report a nanoconjugate of acid functionalized Multi-wall Carbon Nanotubes (MWCNT-COOH) and *p*-amino Porphyrin.² The nanoconjugate was characterized by various characterization techniques such as UV-Vis., Fluorescence, FTIR, XRD, TGA, SEM, TEM and Raman etc. We have checked antimicrobial activity of nanoconjugate against *S. aureus* bacteria and used for photodynamic therapy in the presence of visible light. Antimicrobial studies of nanoconjugate shows that when we increase concentration of nanoconjugate then survival percentage rate of bacteria was decrease. To check the photodynamic therapy, we fixed the minimum concentration of nanoconjugate and increase the exposer time of light as 10, 30, 60 and 90 minutes, shows inhibition of bacterial colonies. From the above results, we could conclude that the small amount of nanoconjugate is enough for antibacterial activity.



Fig. (a) UV-Vis spectra (b) Nanoconjugate (c) survival percentage of *S. aureus* when treated with nanoconjugate.

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A ruthenium nitrosyl-functionalized nanoscale vesicles for NO release: Control of NO release by membrane fluidity and Anti-bacterial assay

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Abstract:

Nitric Oxide (NO) is the smallest structurally known pharmaceutical molecule and the first known and well-studied gaseous signaling molecule. Low concentration of NO promotes tumor cell growth, while high concentrations cause apoptosis or bacterial cell death due to nitrosative/oxidative stresses induced.¹ Over the past decade, several photo-responsive NO donors based nanoplatforms have been reported.^{2,3} A new amphiphilic ruthenium nitrosyl complex (**L.Ru-NO**) was synthesized and incorporated in the lipid bilayers to form **L.Ru-NO@Lip**. The NO-releasing amphiphilic **L.Ru-NO** was embedded with phospholipids to form vesicles and selective NO release in aqueous medium was achieved by irradiating the liposomes solution with blue light. The nanoscale vesicles are bio-compatible and NO releasing ability in pure aqueous medium has been confirmed by Greiss and DAF assay. The phospholipids (DOPC, DSPC, DPPC and DMPC) used for vesicle preparation varied in alkyl chain lengths and saturation. NO release studies reveal that, half-lives and rate of NO release could be effectively altered by varying lipid fludity. The effect of temperature and pH on NO release was also studied from **L.Ru-NO@Lip** upon blue light irradiation. The complex **L.Ru-NO** was assayed as an anti-bacterial agent against the strains of bacteria *E. coli* ATCC 25922.



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Design of Molecular Triads by Bandgap Engineering based on Donor-Acceptor small molecules for Optoelectronic Applications

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Abstract:

We have synthesized three non-fused novel acceptor-donor-acceptor-donor-acceptor (A-D-A'-D-A) types conjugated small molecules based on bithiophene (TT), isatin, and benzothiadiazole (BTz) intended for efficient photoinduced electron transfer and their possible applications toward organic photovoltaics (OPVs).¹ Bithiophene has been used as an electron donor because of its electronically rich, deep-lying HOMO levels, high hole mobilities as well as high power conversion efficiencies (PCEs) in organic photovoltaics.² On the other hand, isatin and BTz have been widely used as strong electron-deficient characters for enhancing the charge carrier transport properties in optoelectronic applications.^{3,4} In this contribution, BT-IT1, BT-IBT2, and BT2F-IBT3 were fully characterized and exhibited completely planar geometry as confirmed by density function theory (B3LYP/6-31G (d, p). The resulting materials have been showing a broad absorption range at 350 to 600 nm in solution, and in the thin film, materials show bathochromic shift (range 350 to 700 nm) due to π - π interaction. The materials have illustrated a low HOMO-LUMO energy gap of 1.80 eV, HOMO was localized at -5.50 eV while LUMO was delocalized at -3.68 eV. The electron mobility of the resultant compounds BT-IBT2, and BT2F-IBT3 are 3.44×10^{-3} and 1.12×10^{-3} respectively which are determined by Space-charge-limited current (SCLC) measurements.

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All MXene Heterointerface for Efficient Energy Storage Device with Super Long Life

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Abstract:

The global market for sustainable energy storage systems was dramatically increasing driven by unmet energy desires and the introduction of advanced electronic technologies. Headed toward this goal, energy storage devices, including supercapacitors, are nowadays fascinating intensive research efforts. The realization of emerging green technologies requires high power energy storage systems such as supercapacitors. Supercapacitors have appealed to extensive demand in current years because of their high-power density, fast charge-discharge cycles, comparing energy density, and long life. Electrochemical double layer capacitors, pseudocapacitors, and hybrid capacitors are the three major classification of supercapacitor based on their charge storage mechanism. A potential prospect to advanced supercapacitors, MXene, discovered in 2011 has emerged to be unassailable 2D structures with layered morphology with higher electronics conductivity, probed pseudocapacitance, hydrophilicity, and accompanying mechanical and surface functionalities. In particular, MXene obtained from Mn+1AXn phase, where n=1, 2, or 3, etc., M is an early transition metal, A is mostly group 13 and 14 elements and X denoting C and/or N is majorly investigated as electrode material for supercapacitors. Subsequently, MXene possesses far-reaching capacitance compared to other conventional electrode materials, extracting novel MXene architectures and its structural optimization and enhancements for high performance electrodes are highly under consideration. In this report, an attempt made for a 2D/2D heterointerface formation with 2D Nb₂C and 2D Ti₃C₂ in-situly by one pot chemical etching method. This is the first reporting synthesis strategy of chemical etching both MXenes together and this approach enhances the electrochemical properties. In situ developed heterointerface were characterised through different techniques like XRD and HR-TEM and the obtained results clearly conform the successful formation of the desired compound. When Nb₂C/Ti₃C₂ heterointerface is employed as a supercapacitor electrode, it can deliver a maximum capacitance of 584 F/g with a remarkable potential window of 1.3 V and state-of-the-art energy density of 38.5 Wh/kg. The developed all-solid-state system demonstrates greater cycling stability of 98% even after 50k cycles.

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Rapid Access to Arylated and Allylated Cyclopropanes via Brønsted Acid-Catalyzed Dehydrative Coupling of Cyclopropylcarbinols

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J. Org. Chem. 2022, 87, 6886–6901

Abstract:

A regioselective protocol for the synthesis of cyclopropyl derivatives that relies on Brookhart acidcatalyzed dehydrative coupling over substituted cyclopropylcarbinols without rearrangement is reported herein. The reactions proceed promptly at 25 °C with only 2.0 mol



% catalyst loading and produce the cyclopropyl derivatives in excellent yields. This method is well tolerated with a vast range of cyclopropylcarbinols including aliphatic cyclopropylcarbinols, where no elimination product was obtained, demonstrating the protocol's utility. Further, the Hammett correlation suggested the formation of a cyclopropylcarbinyl cation followed by a coupling reaction. An extremely effective gram-scale reaction has also been demonstrated with a high turnover number.

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Biomimetic Oxidative Bromination by *cis*-Dioxidotungsten(VI) Complexes of salan type N,N'–Capped Linear Tetradentate Amino Bisphenol

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Abstract:

Reaction of $[W^{VI}O_2(acac)_2]$ (Hacac = acetylacetone) with salar type dibasic tetradentate ONNO donor Mannich bases derived from ethylenediamine, formaldehyde and 2,4-di-tertbutylphenol (H₂L¹), 2-*tert*-butyl-4-methylphenol (H₂L²), 2,4-di-methylphenol (H₂L³) and 2.4–di–chlorophenol (H_2L^4) in a 1:1 molar ratio in refluxing MeOH resulted into the formation of corresponding *cis*-dioxidotungsten(VI) complexes $[W^{VI}O_2L^1]$ (1), $[W^{VI}O_2L^2]$ (2), $[W^{VI}O_2L^3]$ (3) and $[W^{VI}O_2L^4]$ (4), respectively. Characterization by elemental analysis, various spectroscopic (FT-IR, UV/Vis, ¹H and ¹³C NMR) studies, DFT calculation and single-crystal X-ray analysis of 2 and 3 suggest six-coordinated octahedral α -cis (symmetric) isomeric form of the complexes where ligands coordinate through the two phenolate oxygen and two amine nitrogen atoms (in a cis- α type symmetric binding mode) with one of the N atoms of the ligand and one of the terminal O atoms of the *cis*-WO₂ group in the axial position. There complexes are potential catalyst precursors for the oxidative bromination of thymol and styrene. Thymol upon bromination gave three products, namely, 2-bromothymol, 4-bromothymol, and 2,4dibromothymol; 2,4-dibromothymol being the major product. Oxidative bromination of styrene resulted in 2-bromo-1-phenylethanol and 1-phenylethane-1,2-diol; the later one is the result of nucleophilic attack of water on the α as well as β carbons both of the initially form 1,2-dibromo-1-phenylethane.



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Mechanochemical Zinc-Mediated Hydroxyalkylation of Imidazo[1,2-*a*]pyridines under Ball Milling Conditions

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Abstract:

Imidazo[1,2-*a*]pyridine is a fused *N*-heterocyclic moiety which has received significant attention in recent years due to its applications in medicinal chemistry, organometallic chemistry and materials chemistry. Several commercially available drugs such as alpidem, zolpidem, olprinone, minodronic acid, zolimidine, necopidem, saripidem and GSK812397 have been derived from imidazo[1,2-*a*]pyridine nucleus. Thus, synthesis and functionalization of imidazo[1,2-*a*]pyridines remains to be a fascinating subject in organic synthesis due to their vast existence in biologically interesting systems, natural products, and drug-like molecules.¹ C3-hydroxyalkylated imidazo[1,2-*a*]pyridines are bioactive derivatives and important intermediate in the preparation unsymmetrical *bis*[imidazo[1,2-*a*]pyridinyl)methanes. Traditionally, hydroxyalkylation of imidazo[1,2-*a*]pyridines with carbonyl group. These methodologies require preformed nucleophiles or involve multiple steps. Thus, the development of simple and straightforward methodology is highly desirable for hydroxyalkylation of imidazo[1,2-*a*]pyridines.

On the other hand, synthetic transformation employing mechanochemical techniques like ballmilling has received significant attention over solution-based chemical methods in recent years.² In addition to its ability to mechanically activating the molecules, ball milling has several advantages such as shorter reaction times, use of no or very little solvent, access to new mechanistic pathways and selectivity, lower reaction temperatures, and, reduced sensitivity of reactions to oxygen or water. With our interest in functionalization of *N*-heterocycles and mechanochemistry,³ herein we developed a mechanochemical solvent free, zinc-mediated hydroxyalkylation of 2-imidazo[1,2-*a*]pyridines (Scheme 1). Details of the protocol will be presented in the poster.



Scheme 1: Mechanochemical hydroxyalkylation of 2-imidazo[1,2-a]pyridines

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Chemo-robust and bi-functional MOF with divergent open Co(II)-nodes for cooperative deacetalization-Knoevenagel condensation and mild-condition tandem CO₂ fixation

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Abstract:



To alleviate the problem of global climate destabilization, capture of carbon dioxide (CO₂) and its chemical conversion into value-added products is considered as most effective green route to sustainable development. However, post-combustion CO_2 capture is tricky¹ as it requires tailor-made adsorbents with molecule-specific interactions on their internal surface. Alternatively, CO₂ cycloaddition to cyclic carbonate demands backing of a catalyst due to chemical inertness of the gas. Metal-organic frameworks (MOFs) are proven to be efficient material for CO₂ capture, and extensively used as heterogeneous catalyst in sustainable organic reactions. Among several MOF-catalyzed organic transformations, cascade reactions are particularly important due to the obvious advantages like reduction in chemical usage, less energy consumption, short reaction time, and minimization of waste generation. Here, we synthesized a chemically robust, anionic Co-MOF CSMCRI-10, built from tricarboxylate ligand and N.N-donor linker. Some of the splendid structural attributes of the framework are (i) activation induced generation of high density unsaturated Co(II) centres, (ii) N-functionality actuated guest interaction site in the ligand, and (iii) suitably sized unidirectional pores, controlling entrance of substrates with specific molecular dimension. Benefitting from its bifunctional attribute, the activated framework (10a) performs as an acid-base cooperative catalyst in cascade Knoevenagel condensation, where pore-fitting induced size-selectivity is first-time realized.² Alongside its high CO₂ adsorption potential, **10a** acts as excellent heterogeneous catalyst in tandem CO₂ cycloaddition with styrene under solvent-free mild condition.³

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Ni(II)-Catalyzed Oxidative Deamination of Primary Amines by Water

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Abstract:

Deamination reaction is very useful in functional group interconversion for the syntheses of important synthons like carbonyl, acid, imine, amide etc¹. In the biological system, enzymatic oxidative deamination affords aldehydes from primary amines, occurred by amine dehydrogenases (ADHs) or copper amine oxidases (CuAOs)². Herein, pyridyl functionalized water-soluble Ni(II)-NHC catalyst was synthesized and utilized in oxidative deamination of primary amines in aqueous medium. Salient feature of the reaction is the water acts here as an oxidant with the liberation of H₂. It doesn't require external oxidant. Hemilabile behaviour of pyridyl arm³ accelerates the nucleophilic attack of water to the targeted molecule through hydrogen-bond interaction with the cooperation of metal. Different experiments were performed to establish the reaction pathway.

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Designing a Redox Noninnocent Phenalenyl-Based Copper(II) Complex: An Autotandem Catalyst for the Selective Oxidation of Polycyclic Aromatic Hydrocarbons (PAHs)

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Abstract:

The realization of the elusive resonating-valence-bond (RVB) ground state in phenalenyl (PLY) systems has employed it as a potential candidate for catalysing various lewis acid catalysed organic transformations.¹ The energetically accessible nonbonding molecular orbitals (NBMOs) in PLY ligands can readily accept electrons and transforms to a singly occupied molecular orbital (SOMO) without any compromises in the pi-electron delocalization energy.² The "redox-storage motif" based on the phenalenyl system on metal coordination acts as an electron reservoir,³ which helps in the delocalization of excess electronic charge, thereby preventing metal ions from indulging into any unfavourable oxidation state during the catalytic reactions. In this light, we have prepared a square-planar [Cu^{II}L] complex 1, based on the redox-active phenalenyl unit $LH_2 = 9.9'$ -(ethane-1.2-diylbis(azanediyl))bis(1H-phenalen-1one), and confirmed the structure using single-crystal X-ray diffraction analysis. The molecular structure of 1 reveals the presence of intriguing C-H...Cu intermolecular anagostic interactions. Utilizing the presence of anagostic interactions⁴ and the free nonbonding molecular orbitals (NBMOs) of the closed-shell phenalenyl unit in 1, the oxidation reactions of some industrially important polycyclic aromatic hydrocarbons (PAHs)⁵ in the presence of the [Cu^{II}L] complex under very mild conditions have been studied. The catalyst shows dual activity in some of the chemical transformations. Also, this is a first report for "single-step" catalytic transformation of pyrene-1-carbaldehyde to the synthetically difficult pyren-4-ol, a precursor for the synthesis of several novel fluorescent probes for cell imaging.



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Halogen and Chalcogen Side Chains in N-aryl Glycine Peptoid Foldamers For Facilitating Noncovalent interactions Nithin Kumara M R, Manasa Purushotham, Bishwajit Paul * Department of Studies in Chemistry, Jnana Bharathi Campus, Bangalore University, Bangalore-560056. Email: bishu.nyu@gmail.com

Abstract:

We report the inclusion of *ortho*-halogens {X=F, Cl, Br, and I}, and chalcogens {S, Se} for promoting noncovalent interactions (NCIs), including halogen bonding (X-bonding), $n \rightarrow \pi^*$ interactions, and chalcogen bonding (Ch-bonding) in *N*-aryl glycine peptoid foldamers. We deciphered that the NCIs emanates from the *ortho*-halogen interact with the backbone tertiary amide carbonyl group to facilitate the intramolecular $n \rightarrow \pi^*$ interaction and the intermolecular X-bonding. We established these interactions originating from Caryl-X---O=C- by computational modeling and X-ray crystallography. We also demonstrate that we can modulate the folding propensity by varying the distance between the donor (Caryl-X) and the acceptor (-C=O) to control the $n \rightarrow \pi^*$ interaction. These findings highlight the simultaneous presence of the $n \rightarrow \pi^*$ interaction and halogen bonding in the *N*-aryl glycine peptoid foldamers. As a future direction, we have now included *ortho*-chalcogens in the *N*-aryl glycine peptoid foldamers.

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Macrocyclic Distortion due to Core Protonation and Peripheral Substitutions

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Abstract: The redox properties of porphyrins can be modulated by protonation of the macrocyclic core. Free base porphyrins exhibit characteristic spectral and conformational features upon protonation and deprotonation in solution.¹ Herein, we report all possible deprotonated and protonated species of 2,3,5,10,12,13,15,20-octaphenylporphyrin (OPP) ring systems *viz.* planar and nonplanar macrocycles using spectral changes, electrochemical and DFT studies. Protonation leads to the crowding inner hydrogen atoms attached to the pyrrole nitrogen atoms of the porphyrin core which induces macrocyclic ring distortion.² This nonplanarity in macrocyclic ring is experimentally observed in a single step. The macrocycles display incrementally increasing nonplanarity with protonation which follows the order, OPP < OPPBr₄ < OPPBr₃NO₂. The formation of porphyrin dication in toluene was observed by titration of the neutral porphyrin with trifluoroacetic acid (TFA) while tetrabutylammonium hydroxide (TBAOH) was employed for deprotonation study.



The progress of the protonation was monitored by UV-Vis spectroscopy, which was also used to calculate $\log\beta$ for proton addition to the core nitrogen atoms of the macrocycle. Planar porphyrins such as OPP shows a greater red shift in the electronic spectral features and downfield of NH protons as compared to nonplanar porphyrins OPPBr₄, OPPBr₃NO₂ on protonation. This can be attributed to the planar porphyrin ring in OPP, which experienced greater distortion during the course of protonation as compared to already distorted macrocycle in case of OPPBr₄ and OPPBr₃NO₂. DFT results clearly indicate that protonation and deprotonation results in tilting of pyrrole ring from the mean porphyrin plane which is verified by the spectral results. In this presentation, we will explore the power of proton(s) in tuning macrocyclic conformation by various spectroscopic and DFT studies.

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Self-Templated Conversion of A Self-healing Metallogel into Active Photocatalyst: Nd/MF@Carbon Quasiaerogels Boosting Photocatalytic CO₂ Reduction by Water

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Abstract

Light assisted conversion of CO₂ into fuels and feedstocks in presence of water mimics the natural photosynthesis process. This is a clean and sustainable technique to alleviate the energy shortage, as well as global climate change. In this context, herein, a self-templated carbonization strategy for the synthesis of neodymium@nitrogen-doped-carbon-quasiaerogel (Nd@NCA) is manifested using a rationally designed precursor of self-healing metallogel with neodymium and nitrogen-rich gelators. The SEM micrograph of Nd@NCA displays foam type of structure, and TEM images revealed that Nd@NCA photocatalyst is composed of highly porous 2D sheets which are grown on top of each other adopting the 3D foam-type structure. The as-synthesized Nd@NCA photocatalyst shows excellent activity with high selectivity (87%) for CO₂ conversion into CO (23.99 μ molg⁻¹) as compared to CH₄ (2.17 μ molg⁻¹) and H₂ (0.85 μ molg⁻¹).



A Novel Synthetic Strategy to Heterobiaryl Sultams and Subsequent N-S Bond Cleavage to Access Biaryl Sulfonamides

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Abstract:

The transition-metal-catalyzed oxidative C–H coupling is a powerful variant of traditional cross-couplings or direct arylations enabling rapid C–C bond formation in biaryls with wide substrate scope. A palladium catalyzed intramolecular oxidative coupling involving double C(sp2)–H bonds in sulfonanilides, providing a workable access to biaryl sultams annulated into a six-membered ring that are otherwise difficult to obtain by literature methods has been demonstrated in our previous studies. Herein, we report a novel palladium-catalyzed intramolecular oxidative coupling involving double C(sp2)–H bonds in *N*-arylsulfonyl indoles to the synthesis of heterobiaryl sultams, which upon subsequent N–S bond cleavage with amines gives access to 2- arylindoles containing an *o*-sulfonamide group. The installation of sulfonamide pharmacophores on heterobiaryls has successfully been executed by a previously unknown palladium-catalyzed intramolecular oxidative coupling in *N*-arylsulfonyl heterocycles followed by novel ring opening of heterobiaryl sultams with amine nucleophiles. The protocol has a wide scope of substrates warranting broad applications in the synthesis of heterobiaryls containing an *o*-sulfonal group. Furthermore, a TM-free synthetic access to a novel indole-fused dibenzosultam is in progress.

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Hydrogen Evolution Reaction catalysed by µ-Oxo Iron Complex

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Abstract:

A μ -oxo Fe complex (FeL¹), featuring pyridine carboxamide thiazoline ligand moiety has been synthesized and characterized by single crystal X-ray diffraction. Electrochemical studies reveal that FeL¹ is an efficient electrocatalyst for H₂ production when acetic acid and trifluoroacetic acid was used as source of proton. In DMF, FeL¹ displays maximum turnover frequency (TOF) of 194 s⁻¹ and 165 s⁻¹ for CH₃COOH and CF₃COOH respectively with 565 mV overpotential for acetic acid. Gas Chromatography analysis under controlled potential electrolysis confirms the formation of hydrogen gas. A thorough mechanistic study reveals that first step is the proton abstraction by μ -oxo followed by electron transfer and follows CECE mechanism for TFA. However, with CH₃COOH, it is following ECEC mechanism owing to its higher p^{Ka}.¹ Computational studies are affirmative for the above behaviour. In order to gain insights into mechanism, HER was studied using CF₃COOD, demonstrating the small Kinetic isotopic effect (KIEs) which is distinct from inverse KIEs reported for several metal hydrides^{2.3}.

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A paper-based rapid and selective detection of fluoride ions: development of Tb-based photoluminescent pro-sensitizers

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Abstract:

Fluoride ion is important for bone growth and is an essential ingredient in toothpastes and drinking water. However, higher intake leads to dental and skeletal fluorosis, nephrolithiasis, and inhibits the biosynthesis of neurotransmitters in fetuses.¹ Several dry regions in India contain higher than permissible fluoride limits (1.5 ppm) in groundwater.² Thus, it's important to design and synthesize molecular probe for the selective detection of fluoride. Lanthanides (Ln³⁺) are well known for their sharp, line-like emission, large pseudo-Stokes shift, and long excited-state lifetimes, allowing recording of the emission in the time-gated mode.³ A strategy of fluoride-triggered desilylation of *pro*-sensitizer **2** releasing sensitiser **1** was developed.^{4,5} In the optimised assaying conditions, *pro*-sensitiser **2** exhibited selective response to fluoride ions even in the presence of 6-fold higher concentrations of other interfering anions. The limit of the detection (LOD) of the system was **80 ppb**, which is lower than the permissible limit in drinking water. As the protocol is simple, rapid, and selective; so we are working on the development of paper-based detection protocols and detection in the real-life samples (toothpastes, ground water).



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A facile synthetic approach for hierarchical NiO nanoparticles from surfactant intercalated layered Ni(OH)₂ and their use as adsorbent

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Abstract:

Metal oxide nanoparticles have been explored for applications in different fields such as photocatalysis, pseudocapacitors, adsorption, battery anodes, and catalysis [1, 2]. NiO is a ptype semiconductor and it shows anomalous magnetic, electronic, and catalytic properties. High surface area and porous structure of NiO nanoparticles can make them good candidate as adsorbent [3, 4]. Surfactant intercalated layered Ni(OH)2 is one of the best precursors for the synthesis of NiO nanoparticles. The replacement of smaller anions (e.g. NO₃⁻, OCN⁻) present between the Ni(OH)₂ layers with bigger anions (e.g. dodecyl sulfate (DS⁻)) results in change in textural characteristics of NiO nanoparticles, e.g. increase in surface area, hierarchical morphology, and smaller crystallite size. In the current work, a simple synthetic route has been explored for the synthesis of NiO nanoparticles with hierarchical flower-like morphology consisting of nanosheets [5]. In this method, urea and sodium dodecyl sulfate (SDS) act as precipitating and intercalating agents, respectively. Calcination of surfactant (SDS) intercalated Ni(OH)₂ precursors at 400 °C leads to the formation of NiO nanoparticles. The effect of intercalation of SDS in Ni(OH)₂ on the morphology and size of NiO nanoparticles has been thoroughly investigated. XRD, FT-IR, FESEM, TEM, and XPS analyses were used to characterize the SDS intercalated Ni(OH)₂ precursors, and NiO nanoparticles. The NiO nanoparticles obtained from the calcination of SDS intercalated Ni(OH)₂ possess high surface area (e.g. 123 m²/g) and smaller crystallite size (~2.5 nm). Magnetic studies of NiO nanoparticles indicate superparamagnetic behaviour at RT. The NiO nanoparticles act as good adsorbent towards congo red removal from aqueous solutions with maximum adsorption capacity of 632 mg/g.

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A low cost aqueous sodium ion hybrid capacitor with Na₂NiFe(CN)₆ positive and functionalized carbon negative electrodes

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Abstract:

The low cost environmental benign aqueous sodium (Na) ion hybrid capacitor are promising candidate for large scale renewable energy (solar and wind) storage.^{1,2} Herein. We have developed Na ion hybrid capacitor with Na₂NiFe(CN)₆/Polypyrrole composite as positive electrode, functionalized carbon black (CB-F) as negative electrode and 1M Na₂SO₄ aqueous solution as electrolyte. The low-cost stainless steel (SS) and normal filter paper are used as current collector and separator, respectively. The corrosion rate of SS is minimized by a thin coating of polyaniline through *in situ* electrodeposition process. The commercially available carbon black is chemically treated in different reactions and synthesized surface functionalized carbons, namely CB-F1 and CB-F2, with improved hydrophilicity. We have developed three 1.2V full cells with pristine-carbon black (P-CB), CB-F1 and CB-F2, while the cells are designated as Cel-1, Cel-2 and Cel-3, respectively. The above-mentioned cells demonstrate respective specific capacitance of 28.65 (9.55), 48.94 (16.314) and 85.29 (28.43) F/g (mAh/g) at C/5 rate charge and discharge within 0-1.2V, whereas corresponding energy densities are 11.46, 19.57, and 34.11 Wh/kg. All the full cells depict good cyclability over 500 cycles at 1C rate. The performance study of full cells at variable temperature are also carried out and it indicates that the cells are performing well within -10 to 50°C. This results are showing prominent aspect towards solar energy storge applications.

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1,3,5-Tris[(2*H*-tetrazol-5-yl)methyl]isocyanurate and its Tricationic Salts as Thermostable and Insensitive Energetic Materials

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Abstract:

For the first time, compounds 1,3,5-tris((2H-tetrazol-5-yl)methyl)-1,3,5-triazinane-2,4,6-trione (**3**), and N,N'-(6-((1H-tetrazol-5-yl)amino)-1,3,5-triazine-2,4-diyl)bis(N-(1H-tetrazol-5-yl)nitramide) (**6**) were synthesised via simple and efficient two-step synthetic route from commercially available inexpensive starting materials. Various energetic salts (**3a-3f**) were obtained from compound **3** and confirmed by ¹H, ¹³C and IR spectroscopic studies. Single-crystal XRD studies confirmed further **3b** and **3f**. All the newly synthesised compounds show excellent density (D= 1.65-1.85 g cm⁻³), high thermal stability (T_d= 165.0-289.85 °C), detonation velocity (VOD = 7876-8832 m s⁻¹), detonation pressure (DP = 20.73-30.0 GPa), high N-content (>62 %), impact (IS= 20-40 J) and friction (FS= 360 N) sensitivity, which can be a good replacement for current benchmark explosives such as TATB (VOD = 8179 m s⁻¹) and RDX (VOD = 8748 m s⁻¹).



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Highly Stable Deep Red-to-NIR OLEDs with an External-Quantum Efficiency of 4.9% from Room Temperature Nanostructured Columnar Fluids based on Hetero Atom Bay-Annulated Perylene Bisimides

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Abstract:

A series of electron deficient perylene bisimides (PBIs) bearing 3,4,5-tridecylphenyl substituents on the imide N-atoms and bay-annulated with the hetero atoms like N, S, Se in the bay positions of the perylene core via Cadogan reaction have been synthesized. These compounds were liquid crystalline at room temperature exhibiting columnar hexagonal phase exclusively, with the exception of S-annulated PBI which exhibited columnar oblique phase. These self-organizing organic semiconductors in one-dimensional (1D) columnar structures, are unique by having better solubility, ease of purification, reproducibility and ease of handling in comparison to polymers or single crystals. Detailed photophysical studies of these compounds show that they exhibit high molar extinction coefficients with wide absorption spectra covering most of the visible spectrum and bright red fluorescence, makes them promising candidates for organic electronics. Further, they exhibited technologically important red electroluminescence. One of the solution-processed host-guest OLEDs (CBP as host at 1 wt% PBI-N10) exhibited a maximum EQE of 4.9%, a lifetime of 12.4 h with an initial brightness of 2900 cd/m2 and a deep red/NIR emission. These results indicated that these materials exhibit significant potential in the field of columnar liquid crystal-based deep red/NIR emitters.

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Ivermectin Hybrids for Multistage *Plasmodium* Targeting: Synthesis and Antiplasmodial Activity

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Abstract:

With its strong effect on vector-borne diseases, and insecticidal effect on mosquito vectors of malaria, ivermectin (IVM) inhibits sporogonic and blood-stage development of *Plasmodium falciparum*, as well as impairs *Plasmodium berghei* development inside hepatocytes *in vitro* and *in vivo*.¹ Through chemical modification of IVM, recently our group has reported the "*first-and Second-generation*" IVM hybrids (Figure 1) synthesized by appending the IVM macrolide with heterocyclic and organometallic antimalarial pharmacophores. These hybrids displayed antiplasmodial activity against the blood-stage and liver-stage infections by *Plasmodium* parasites at nM concentrations.^{2,3} In the current investigation, we present a structural modification of IVM to produce "*Third-generation*" molecular hybrids. Results of this investigation shall be presented.



Figure 1. Representative hybrids of ivermectin obtained through chemical modification.

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Pendent N-functionality mediated bimodal attribute in a microporous framework: Nanomolar detection of organo-toxins and size-selective H-bond donating catalysis

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Abstract:

As an intriguing class of novel porous materials, metal-organic frameworks (MOFs) put unique signature as luminescent scaffold for detection of assorted organo-toxins and play pivotal role as heterogeneous catalyst. In this context, acute detection of water contaminants under practical environment is an important sustainable agenda, while cooperative catalysis is crucial for several organic transformations. Among nitro-aromatics (NACs), quick and sensitive detection of 2,4,6-trinitrophenol (TNP) and 2,6-dichloro-4-nitroaniline (DCNA) are imperative as they are highly explosive and extremely toxic to human health and environment.¹ Then again, Friedel-Crafts reaction between indole and β-nitrostyrene is specifically important for the synthesis of tryptamine derivatives,² wherein Hydrogen-bond-donating (HBD) catalysis are promising and effective alternative to Lewis acid activation. Herein, we synthesized a novel Cd(II)-MOF CSMCRI-22 surmising on the incisive amalgamation of a tripodal ligand 4,4',4"tricarboxytriphenylamine (H₃TCA) and a pendent amine functionalized linker 3,5-di(pyridin-4-yl)-4H-1,2,4-triazol-4-amine (dpta). The framework shows excellent hydrolytic stability with preservation of structural integrity in wide pH ranges. The activated MOF (22a) exhibits outstanding sensing attribute towards TNP and DCNA in water with ultra-fast response, nanomolar sensitivity, high selectivity and reusability up to five consecutive cycles. Both the lumino-detection transpires through visual colorimetric change, and promises real-time potential towards naked eye monitoring. Benefitting from the pendent -NH₂ moiety, 22a further acts as heterogeneous catalyst in Friedel-Crafts alkylation reaction, where 99 % product yield was achieved at 100 °C for 12 h in toluene with high catalyst reusability. Interestingly, larger sized indole furnishes lower conversion, delineating rarest size-selectivity.

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Effect of Molecular Crowding on Ligand Binding Kinetics in G-Quadruplex DNA Probed with Fluorescence Correlation Spectroscopy

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The study of ligand binding to G-quadruplex DNA (GqDNA) structures are of paramount interest due to their role in possible anticancer therapy.¹⁻³ A large number of studies dealt with ligands/GqDNA interactions in dilute solution focusing on the thermodynamics of such interactions.⁴ However, kinetics of bi-molecular interactions provide information on ratedetermining steps; quantifying those in dilute and crowded environment can predict how crowded cellular milieu may affect the kinetics of ligand/GqDNA interactions, which is unknown. Here we tackle this problem by investigating the effect of small molecular crowders (Glucose and Sucrose) and macromolecular crowder (Ficoll 70) on the kinetic steps (association and dissociation) of a ligand's (Cresyl Violet: CV) interaction with human telometic (hybrid) GqDNA structure using fluorescence correlation spectroscopy (FCS). Results show that all crowders affect ligand's binding affinity and the kinetic steps of interaction, where Ficoll 70 decreases the binding affinity of ligand nearly by an order of magnitude and the association rate constant drastically. A detailed analysis of the FCS data unravel that there is only subtle effect on the association and dissociation rates of the ligand with GqDNA provided by the small molecular crowders (Glucose and Sucrose), but substantial effect is observed for Ficoll 70. Our data suggest that solution viscosity and excluded volume effect exerted by the larger (polysaccharide) crowder influence the ligand binding kinetics substantially which eventually decrease the binding affinity of the ligand (CV) to the human telomeric GqDNA structure drastically, compared to the monosaccharide and disaccharide.

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Ir(III)-orRh(III)-Catalyzed Allylic Amination of Alkenes

via C-H Activation

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Abstract:

For the past few years, the construction of various chemical bonds by transition metal-catalyzed allylic C-H functionalization of unactivated alkenes has gained tremendous attention in organic synthesis. In the literature, the activation of the allylic $C(sp^3)$ -H bond of terminal alkenes by palladium and other metal complexes *via* π -allyl mechanism or allylic substitution at the allylic position is well known.^[1] Recently, non-directed allylic functionalization *via* C-H activation catalyzed by Rh(III) or Ir(III) over palladium has come into the picture.^[2] In this presentation, Rh(III)- and Ir(III)-catalyzed intermolecular direct allylic C-N bond formation of internal and terminal alkenes with commercially available sulfonamides in the presence of metal and organic oxidant *via* a π -allyl intermediate will be demonstrated. These methodologies requires lower catalyst loading, shows higher selectivity, and compatible to broad range of substrates.^[3]



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Organic solvent free extraction of dye from *Butea Monosperma* (Lam.) Kuntze and its complete characterization using spectroscopic methods

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Abstract

Colorants or color additives are the substances that impart characteristic colors to food or nonfood materials. Generally, artificial colorants are used in food prospective without impacting the product's taste or stability. Notwithstanding with the coloring efficacy, several side effects, e.g., hyper-activity in children, allergenicity, toxicological, and carcinogenicity associated with such materials have been seen which led to a global ban on the use of synthetic food colorants.¹ Natural dye/pigments obtained from different parts of plants like root, bark, leaves, fruit and flowers. They have been considered non-allergic, non-toxic, noncarcinogenic, and are biodegradable in nature, therefore, pose no direct/indirect risk to the environment.²

Therefore, the present research is being carried out with explicit objective of organic solvent free dye extraction from flower petals of *Butea Monosperma* (Lam.) Kuntz followed by complete characterization of its constituents for diverse range of applications, such as colouring of food and medicines.

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Designing bioinspired supramolecular peptide hydrogels for controlling cellular behaviour

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Abstract:

Self-assembly of biomolecules to form hierarchical supramolecular ordered structures is emerging as a promising area for fabrication of highly functional smart biomaterials. Peptidebased self-assembled structures i.e. molecular hydrogels have gained tremendous interest in this field owing to their unique physicochemical properties emergent at nanoscale, which can find important biomedical applications. Owing to the inherent biocompatibility exhibited by peptides, we are exploring their potential for development of cell-instructive scaffolds. Neural tissue is a complex structure having restricted ability to regenerate after injury. In this context, cell transplantation holds a great potential in acting as a therapy for the regeneration of the injured or diseased neural tissue. However, due to lack of a proper microenvironment in a damaged tissue, maintaining a suitable number of transplanted cells along with their regenerative potential is very challenging. In this direction, we have explored the potential of Tenascin-C derived short peptide in controlling the neural cell behaviour. Tenascin C is an important component of neural ECM, which is mainly expressed during injury as well as tissue remodelling. We tried to explore the potential of this peptide sequence as a minimalistic building block for development of neural scaffold. Octapeptide sequence and its acetylated counterpart were synthesized and their self-assembling characteristics were studied. Interestingly, both peptides undergo hydrogelation in aqueous conditions at physiological pH. They self-assembled to form cross- β sheet like structures in water as confirmed by CD and FTIR spectroscopy. Furthermore, peptide nanostructures exhibited biocompatibility towards various cell lines and the hydrogel scaffolds supported neural cell growth and proliferation. Hence, tenascin C based biomaterial may hold the potential to be explored as conducive matrix for encapsulating and delivering cells for advance neural tissue engineering. Furthermore, we are also exploring the co-assembly of various plant and animal derived biopolymers with peptides as an emergent strategy to fabricate advanced bioactive nanomaterials. This approach is expected to be helpful in overcoming the shortcomings of individual component and could present the beneficial features of each to the cells for successful tissue engineering.

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Development of Functionalized Supramolecular Assemblies of Pie-Conjugated Materials: Applications in Self-assembly, Sensing and Bioimaging

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Abstract:

The development of fluorescent probes with high luminescence in aqueous medium and solid state as well have gained attention for in vitro and *in vivo* sensing of analytes having biological importance. We have designed and synthesized napthalimide and anthracene based fluorescent probes for their application in molecular recognition and bioimaging. A naphthalimide based lysosomal targeting probe has been designed, synthesized and evaluated for detecting lysosomal pH changes inside living cells. Probe is successfully applied to cells and nematodes and all the findings emphasized that it can easily detect the lysosomal pH changes in living cells. Furthermore, we developed 'metal free' supramolecular assemblies for distinct detection of organophosphate and organochlorine pesticides in aqueous medium. These supramolecular assemblies of anthracene also act as 'enzyme mimic'. The real time application of these assemblies have also been explored in different agricultural products.

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Polystyrene stabilised Pd-catalyst development for carbonylative transformations using oxalic acid as CO source

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Abstract:

The carbonylation chemistry has gained the immense interest of scientific community for incorporating the carbonyl moiety into the targeted organic substrates with the aid of various transition metal catalysts. In this context, heterogeneous nano-catalyst mediated carbonylation has emerged as a powerful tool to achieve this goal with the advantage of high/new reactivity, easy handling and appreciable recyclability. Over the past few years, our group is continuously focusing on the development of polystyrene supported transition metal nano-catalysts which are well characterized by SEM, HR-TEM, SEM-EDX, ICP-AES, P-XRD, XPS analysis and their applications in various carbonylative transformations.^[1,2] Since palladium metal is most extensively employed in carbonylation reactions, in this dimension we have explored the developed supported palladium nano-catalyst in various oxidative carbonylation reactions. However, direct utilisation of CO in chemical reactions is a challenging task due to their storage, toxicity and handling problem which require high pressure sophisticated instruments. To overcome these challenges, we have explored oxalic acid as a solid, economic and efficient in-situ as well as ex-situ CO source which exhibit remarkable synergistic effects with polystyrene stabilised nano-catalyst.³ Diaryl ketones are most important type of building block having huge applications in pharmaceuticals, agrochemicals and other industrial products.⁴ In this context, we have applied Pd@PS nano-catalyst for carbonylative Suzuki reaction for the synthesis of diversely substituted biaryl ketones using oxalic acid as an *ex-situ* C1 source. The reaction has been carried out in ppm-level catalyst loading under ligand and additive free conditions. Furthermore, we have developed a palladium catalyzed strategy for the synthesis of heteroquinazolin-4(3H)-ones framework from 2-iodophenylcarbodiimides, amines, and oxalic acid as CO source. Intriguingly, Pd@PS nano-catalyst have also displayed tremendous applications to fix two solid gaseous precursors i.e. NH₃ and CO sources respectively, for the synthesis of 2-amino-3-arylquinazolin-4(3H)-one derivatives. Furthermore, greener CO source, diverse substrate scope and high recyclability of Pd@PS catalyst were the major achievements under developed protocols.

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Design and Synthesis of Phospholipid- and PEGylated-Drug Conjugates for Engineering of Chimeric Nanomicelles to Target the Cancer Cells.

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Abstract:

Delivery of anticancer drugs to cancer cells causes sever toxicity due to availability of free drugs in the blood circulation that causes non-specific cell death in key body organs. We synthesized an esterase sensitive phosphocholine derivative of docetaxel-conjugated lithocholic acid (LCA-DTX-PC) that in combination with poly(ethylene glycol) (PEG)tethered lithocholic acid self-assemble to form supramolecular nanomicelles (DTX-NMs). DTX-NMs exhibit slow and sustain release of chemotherapeutics at tumor site, provided improved therapeutic efficacy, with better survival. DTX is a potent anti-proliferative chemotherapeutic agent, but only death of cancer cells is not sufficient to tackle complex and heterogenous tumor tissues. Therefore, we synthesized two PEGylated lipid-drug conjugates (LCA-DEX-PEG, LCA-CA4-PEG) using dexamethasone (DEX, anti-inflammatory drug) and combretastatin (CA4, anti-angiogenic drug). We then engineered chimeric NMs of sub-100 nm size using combination of LCA-DTX-PC and LCA-DEX-PEG, and of LCA-DTX-PC and LCA-CA4-PEG. Our results showed that these chimeric NMs are highly effective in tumor regression than individual drug treatments. In my poster, I will present our recent results on synthesis and engineering of different chimeric NMs that can deliver the combination of chemotherapeutic drugs to cancer cells.

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Acid Induced Nitrite Reduction On Copper centre

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Abstract:

Nitric oxide (NO) is a gaseous secondary messenger in animals, plants, fungi, and bacteria. NO plays a significant role in various physiological processes such as neurotransmission, vascular regulation, platelet disaggregation, and immune response to multiple infections in mammals. Balanced production of NO is required to maintain multiple physiological processes

(homeostasis).¹ In this regard, NO_2^- reductases (NiRs) and endothelial nitric oxide synthases (eNOSs) enzymes are available for NO biological generation.² Nitrite reductases are Fe/Cu containing enzymes that reduce nitrite to nitric oxide by utilizing two protons and one electron.^{2,3} Here we report the acid-induced reduction of $[(Me_2BPMEN)Cu^{II}(NO_2^-)]^+$ (1) in



presence of one-fold and two-fold H⁺ which leads to the formation of NO gas via the formation of H₂O₂ or H₂O depending on the amount of H⁺ utilized for the release of NO. When **1** was treated with one-fold of H⁺ that lead releases H₂O₂ as a side product via the formation of presumed Cu^{II}-nitrous acid. However, On increasing the amount of H⁺ (more than one-fold), the amount of H₂O₂ decreases and the amount of H₂O increases. For the first time, we have established the clear generation of NO(g) with (a) H₂O₂ /or (b) H₂O in the reaction of **1** with one-fold /or ~ two-fold H⁺ via a transient [Cu-ONOH]²⁺ /or [Cu-ONOH₂]³⁺ species, respectively. We have established the presence of the [Cu-ONOH]²⁺ species and N-O bond homolysis by OH• trapping experiments and detecting the significant amount of the H₂O₂ spectroscopically with the release of NO. It is important to note that H₂O formation involves a distinctive pathway of either (a) N-O bond homolytic cleavage of [Cu-ON-OH₂]³⁺ transient species, followed by the generation of the Cu^{II}-complex and NO(g) evolution as described in Cu-chemistry with NO in many different ligands frameworks or (b) by the formation of H₂O₂ intermediate species by the N-O bond homolytic cleavage of [Cu-ON-OH]²⁺ intermediate, and then protonation of H₂O₂ with the one-electron reduction to generate H₂O as reported earlier.

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Development of Porphyrin-based Nanophotosensitizers for Photodynamic Inactivation of Bacterial Biofilm

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Abstract:

Currently, microbial biofilms have been the cause of a wide variety of infections in the human body, reaching 80% of all bacterial and fungal infections. The biofilms present specific properties that increase the resistance to antimicrobial treatments. Thus, the development of new approaches is urgent, and antimicrobial photodynamic therapy (aPDT) has been shown as a promising candidate. aPDT involves a synergic association of a photosensitizer (PS), molecular oxygen and visible light, producing highly reactive oxygen species (ROS) that cause the oxidation of several cellular components. This therapy attacks many components of the biofilm, including proteins, lipids, and nucleic acids present within the biofilm matrix; causing inhibition even in the cells that are inside the extracellular polymeric substance (EPS).



The discovery of natural photosensitizers as well as the design of new synthetic ones is a key point in the successful treatment of infections, especially of those caused by biofilms. Herein, we report the synthesis of nanophotosensitizers based on *meso*-tetrapyridylporphyrin and their metal complexes which are highly stable at room temperature and evaluated for photo-inactivation of bacterial biofilm. These nanophotosensitizers found highly effective towards *S*. *Aureus* biofilm eradication *via* photodynamic treatment. The development of nanophotosensitizers described herein will find applications of photodynamic therapy for the treatment of cancer and microbial infection.

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Aqueous Supercap: Coin cell to pouch cell – with minimum facility

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Abstract:

Mostly the laboratory research in supercaps relies on fabricating and testing a coin or Swagelok cells. This is owing to the lack of availability of equipment and knowledge about large scale fabrication. Commonly, the value of energy and power densities of large devices is a multiplying scaling factor of active materials, but this does not happen always. To validate the performance of small to large cells, various factors must be considered and matched to real devices such as electrode thickness, electrolyte amount, current collector and separator properties [1]. One can estimate the performance of a large device similar way like small cells. However, this approach does not consider many of the parameters encountered during scaling up, which results in less performance than the predicted one. Even though, the difference in cell geometries (cylindrical/pouch) also highly influences the final performance of the device [2]. This work demonstrates the fabrication of a device from coin cell to pouch cell (geometric area as 3.5 x 5 cm) using 3D reduced graphene oxide as an active material and base electrolyte. Further, the effect and contribution of various parameters such as electrode thickness, number of electrodes, electrolyte mass and "parasitic" components such as packaging in the performance of supercapacitor devices were systematically studied. Finally, the performance of active materials in the coin cell and pouch cell were compared each other.

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Pd-Catalyzed Formal [3+3] Heteroannulation of Allylic *gem*-Diacetates: Synthesis of Chromene-Based Natural Products and Photophysical Studies.

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Abstract:

The novel classes of chromenes are achieved *via* the palladium-catalyzed [3+3] heteroannulation of allylic *gem*-diacetates and 2-naphthols (and *meta*-substituted phenols). This work disclosed an unusual chemical reactivity pattern of allylic *gem*-diacetates under the palladium conditions towards the complex benzo[*f*]chromene scaffolds. The described method is applicable in the synthesis of several chromene-based bioactive natural products and a new class of photochromic molecules.

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Facile Synthesis of Propargylic Cyclic Imines and Thio-/Selenopyrrolines : Chemoselectivity and Applications

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Abstract:

In the last couple of decades, the concept of donor-acceptor cyclopropanes (DACs) has evolved to its extremity and engrossed the attention of organic chemists worldwide due to its large potential and scope in synthesizing many versatile and unique molecular systems.¹ As a kind of cyclic imines, 1- pyrroline (3,4-dihydro-2H-pyrrole) is a core cyclic skeleton existing in natural products and synthetic biological molecules.² We established a chemoselective and metal-/additive free protocol for the synthesis of propargylic cyclic imine derivatives via (3+2)cycloaddtion of DACs with alkynylnitriles in the presence of $BF_3 \cdot OEt_2$ (150 mol%).³ In addition, we explored the transformation of above mentioned compounds into diasteroelective propargylic cyclic amines and stable enol derivative. On the other hand, we developed a straightforward methodology for the synthesis of thio-/selenopyrrolines via (3+2)cycloaddition of thio-/selenocyanates with donor-acceptor cyclopropanes (DACs) in the presence of SnCl₄ (30 mol%) as a Lewis acid catalyst.⁴ Furthermore, a good chemoselectivity was experienced when donor-acceptor cyclopropanes (DACs) were treated with 3-cyano phenylthiocyanate moiety. These results suggest that thiocyanate is more reactive than nitrile moiety in such (3+2)- cycloaddition reactions. Subsequently, we transformed selenopyrroline into seleno substituted 3-H pyrrole in good yield.



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Fruit Waste Derived Composite Aerogels as Greener and Efficient Adsorbents for Adsorptive Removal of Organic Pollutants

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Abstract:

Industrial effluents, agricultural runoffs, and domestic discharges contain many organic, inorganic, and microbiological contaminants. The release of non-regulated or poorly treated wastewater from these sources pollutes the surrounding environment, including water bodies, which jeopardizes the aquatic environment and leads to several health hazards. The removal of micro pollutants from wastewater *via* efficient, scalable, and sustainable approaches is gaining immense interest. Present work addresses a facile approach to synthesize porous (96.4%) and lightweight (0.018 g/cm³) aerogel via gelatinization of fruit waste (Pomelo peels)-derived cellulose with graphene oxide (GO). The macroscopic porosity established through the hydrogen bonding network between cellulose and GO generates several avenues for mass transportation of polluted water throughout the aerogel for adsorption on surface-active sites distributed in 3D scaffold of composite aerogel. The adsorption process is influenced by the size and charge of organic contaminants, morphological characteristics, and surface functionalities of composite aerogel. The FTIR, Raman, and XPS analyses revealed numerous interaction events for adsorptive separation of organic dyes, including electrostatic, hydrogen, cation- π , and π - π interactions. The composite aerogel displayed excellent recyclability, making it a practically viable material for wastewater treatment applications. The present findings revealed that fruit waste-derived composite aerogels have the prospects to be a greener and sustainable resource for wastewater treatment applications, a way forward to fight against water security.

Synthesis and Studies of Tripodal Arylazoisoxazole Based Photoswitchable Systems

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Abstract:

Azoheteroarenes are one of the recently popular photoswitches exhibiting excellent photoswitching properties, tunability and long Z-isomer stability. Through our recent work on arylazoisoxazole derivatives¹ not only we observed longer half-life of Z-isomer but also demonstrated many interesting properties such as solid-state switching, photochromism and reversible light induced phase transition. These advantages make them useful for many applications. Now the next challenge in utilizing such systems is to functionalize them and obtaining multiple azoheteroarenes connected systems.

Functionalization of small photoswitches into C_3 symmetric molecules provides many opportunities for various applications such as in actuators,² holographic gratings,³ liquid coworkers functionalized crystals⁴ etc. Thiele and the azobenzenes with benzenetricarboxamides and revealed that the H-bonding and DDDstacking limit the solubility and photoswitching.⁵ For further improvement and also gaining applications, we decided to focus on the following: (1) solubility, (2) efficient photoswitching towards single photoisomer (3) longer half-life of (ZZZ)-isomer and (4) as a multistate photochromic material (5) supramolecular self-assembly properties. In this regard, we have connected phenylazoisoxazoles with benzenetricarboxamides. The design, synthesis, photoswitching properties and their effect on supramolecular gel and liquid crystalline properties are part of this contribution.^{6,7}

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Quantum Chemical Study in Exploring the Role of Donor→Acceptor Interactions in 1,3-bis carbene stabilized Guanidinium Cations

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Abstract:

Guanidinium species are highly basic and hence mostly exist in cationic state. Because these cations carry electron deficient centres, they can be stabilized with the help of electron donating ligands like *N*-heterocyclic carbenes. A few novel guanidinium cationic species stabilized by electron donating ligands were designed and quantum chemically evaluated. It was shown that strong hydrogen bonds and tautomerism are the important characteristics of these species. Further, the possibility of donor—acceptor coordination interactions in these species have been explored between the electron donating carbenes and the central guanidinium unit. The results suggest that the title compounds can be considered as ligand-stabilized guanidinium cations similar to the ligand-stabilized N⁺ and N₃⁺ centres.

Keywords: Electronic structure analysis, Guanidinium cations, Donor-acceptor interactions, Carbene ligands.

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Coupled Substituted Perovskite Niobates for Photocatalytic Hydrogen Evolution

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Abstract:

For enhanced sunlight-driven photocatalysis, an absorption edge in the visible region and slow electron-hole pair recombination are desirable conditions. Niobate perovskite oxides (NaNbO₃) are promising materials for hydrogen production via photocatalytic water splitting; however, large bandgaps of these oxides result in their low photocatalytic activity. In this study, to enhance their photocatalytic activity coupled substituted strategy is adopted to synthesize $Na_{0.5}Ca_{0.5}M_{0.25}Nb_{0.75}O_3$ (*M* = Fe, Mn, Cr, Co) compounds by using a solid state synthesis route to introduce midgap states. The compounds are characterized by powder X-ray diffraction (P-XRD), UV-Vis diffuse reflectance (UV-Vis DRS), Field-emission scanning electron microscopy (FE-SEM), energy-dispersive X-ray spectroscopy (EDS), Transmission electron microscopy (TEM), X-ray Photoelectron Spectroscopy (XPS) and photoluminescence (PL) spectroscopy. Rietveld structure refinements of the compounds using P-XRD data suggest the formation of 3dⁿ transition metal incorporated niobates in the Pbnm(62) space group, isostructural with the parent. Since all compounds are visible light absorbers with a band gap in the range 2.1-2.8 eV, they are potentially interesting for their use in visible light-driven photocatalysis. These coupled substituted photocatalysts exhibit efficient hydrogen evolution under simulated sunlight irradiation (AM 1.5G). This heterovalent coupled substitution strategy adopted here will open up possibilities for transforming many other UV-active compounds into sunlight-active compounds.



Scheme 1: Synthesis and structure of $Na_{0.5}Ca_{0.5}M_{0.25}Nb_{0.75}O_3$ (M = Fe, Mn, Cr, Co) compounds.

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Loss of cross-correlations in β -strands adverse the force adaptation in β -rich proteins

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Abstract:

The hydrogen bond dependent correlated motions among β -strands allow the β -sheet rich proteins to adapt to external perturbations¹. The magnitude of these correlated motions also plays an important role in determining the flexibility, damping of the provided external perturbation, choice of force dissipation pathways and energy loss or accumulation during successive unfolding and folding cycles of the protein¹. Despite this motion having a lower frequency with respect to atomic breathing motion, direct visualisation isn't possible due to instrumental limitations.

Possible loss of such motions due to a mutation in Cadherin-23, which is essential for animal hearing process, causes progressive hearing-loss (PHL) in mice models. We have custom-built a low-cost Magnetic Tweezers (MT) with spatial resolution of 5 nm and temporal resolution of 1500 fps, which is being used to investigate the thermodynamic as well as kinetic stability of three variants of Cadherin-23 wild-type S47, S47P and S47V, which possess degrees of intra-domain H-bond network persistency². Here, we show that the variant with the highest persistence of the intra-domain network², is not only thermodynamically more stable but it is also more flexible as the force range where the unfolding and refolding transitions between different energetically active states happen spontaneously, is wider. We have also shown that the S47P variant, which has a less persistent intra-domain network², gets molecular fatigued quicker than the WT (S47 variant), with repetitive force pulse as external stimuli.

We hypothesise that the results could be true for all the β -sheet rich force sensor proteins that exhibit this motion, thus providing a unique insight on force adaptations by β -sheet rich proteins in the field of mechanobiology.

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Tunable redox-active pyrylium platforms: A new class of anolyte for nonaqueous organic redox flow battery

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Abstract:

Zero-carbon emitting energy sources such as solar and wind promise a clean and sustainable energy future in this current scenario of increasing environmental pollution and the global warming crisis. But the intermittency of these renewable sources requires a grid energy storage platform to store the harvested energy during off-peak hours and to deliver the same during the peak demand hours. Among the various energy storage systems (ESSs), redox flow batteries (RFBs) are one of the most suitable ESSs since they offer scalability, design flexibility, quick response, and decoupled energy and power attributes.¹ Since the redox-active organic molecules (ROMs) play an important role in the performance of RFB, the design and synthesis of ROMs (anolyte and catholyte) with good solubility, desirable voltage, and reversible cycling in the organic solvents is highly important.² Here we report, a new class of ROMs based on pyrylium salt for the first time, which can serve as a new redox motif in non-aqueous RFB. Remarkably, it is revealed that substitutions at the 2,4 and 6th positions of pyrylium salt can act as a versatile platform for tailoring the electrochemical activity and stability of the pyrylium salts. With *N*-decyl phenothiazine (DPTZ) catholyte, 2,4,6-triphenylpyryliumtetrafluoroborate (TPT) anolyte was used to construct non-aqueous RFB at a current density of 40 mA cm⁻². Fig. 1 shows the 60 cycles of charge-discharge with 97% coulombic efficiency. The results presented indicate that TPT is a promising analyte for flow battery applications.



Fig. 1 (a) Charge-discharge cycling performance of TPT/DPTZ flow battery (b) Efficiency versus cycle number

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Unveiling A Quinoidal 2,3:10,11-Dibenzoheptazethrene

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Abstract:

Open shell π -conjugated polycyclic hydrocarbons (PHs) having singlet diradicaloid ground state, which feature one or more π -electrons not tightly paired in bonding orbitals, are of great interest due to their unique electronic, optical, and magnetic properties. Recent studies have shown that aromaticity plays a major role in the stability, determining the ground state and consequently their physicochemical properties. A common way to introduce diradical character in PHs is to embed quinodimethane (QDM) subunits into the conjugation framework. However, introduction of QDM may give pro-aromatic (heptazethrene), anti-aromatic (indenofluorene), and zwitterionic scaffolds as well in the ground state.¹ Parent 2,3:10,11dibenzoheptazethrene is a singlet diradicaloid polycyclic hydrocarbon in the ground state that didn't change its diradical character with substitution (methyl/triisopropylsilylethynyl).² We reported the synthesis and characterization of a ethoxy/3,5-(CF₃)₂C₆H₃ substituted 2,3:10,11dibenzoheptazethrene that prefers to retain para-quinoidal core and shows zero diradical character, as determined by the single crystal analysis and DFT calculations. Negative solvatochromism, π - π interactions, C_{sp}^2 -H···O hydrogen bonding, intramolecular charge transfer, redox amphotericity, and narrow HOMO-LUMO energy gap make a potential candidate for optoelectronics applications.³



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Enzyme Driven Spatiotemporal Modulation of Self-assembled Structures

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Abstract:

Biological functions typically involve a series of interlinked temporal events having specific spatial coordination among the interacting components so that the temporal events occur at specific locations or among specific compartments in the organism. Thus, continued efforts towards development of programmable matter on both temporal and spatial scales would be vital to creating biomimetic, dissipative materials with controllable functionality. Until now, reports of spatiotemporal surface pattern or self-organization have been restricted by oscillatory reaction-diffusion processes. Also, the self-organization of synthetic systems under dissipative conditions or under agonistic-antagonistic relationships among multiple components has been limited in mostly solution-phase materialistic studies. Herein, we have shown how the later approach can be used to generate template-driven self-organization at a specific location of a two-dimensional (2D) space in a temporal manner. In particular, we have used two enzymes, namely alkaline phosphatase (ALP) and hexokinase (HK) to show that it is possible to dissipate or sustain an ATP-driven assembly of a surfactant having dipicolylamine (DPA)•Zn2+ as the headgroup. Furthermore, we have borrowed this approach to create spatiotemporally distinct patterns of organized assemblies when surfactant and enzymes (ALP or HK) are operating in gradients from different locations, where the template has been distributed uniformly through the entire space. We have used both theory (DFT for studying the molecular interactions, thermodynamic binding parameters etc.; Python for numerical modeling and MATLAB for diffusion-dependent spatiotemporal assembly) and experiments to complement our findings. Overall, in this work, we have shown an elegant approach for the development of the spatiotemporally flexible surface pattern of organized assemblies by using both theory and experiment, and simultaneously it also showed a new route in gaining 'spatial' adaptability in a self-organized system with interacting components for the incorporation of programmed functionality.

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Effect of Mono- or Di-cationic Ionic Liquids on Aggregation Behaviour of Bile Salt and its Application in Drug Solubilization

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Abstract:

Ionic liquids (ILs) are active research targets in the field of chemistry and biology due to its unique properties like low vapour pressure, high thermal and chemical stability and tunable nature of choosing anions and cations [1]. ILs also exhibits surface active properties based on the structure of anions or cations which explores various application in the pharmaceutical field. Most of the pharmaceutically active substance are poorly soluble in water which results in poor action in the biological system. Surfactants which exhibit aggregation property helps in the solubilisation of poorly soluble drugs by trapping them in the micellar system [2, 3]. Bile salts are well known biological surfactant and have improve the solubility and bio-availability towards poorly water-soluble drugs [4]. The binary mixture of ILs and bile salts (mixed micellar system) presents better surface properties than conventional surfactants (micellar system) [5].

The present work deals with the aggregation behaviour of sodium deoxycholate (bile salt) in water (micellar system) and in aqueous solution of imidazolium-based SAILs (mixed micellar system) comprises of mono and di-cationic ionic liquids (MIL and DIL). The critical micellar concentration (cmc) of the studied system were determined using conductivity and fluorescence experiments. Dynamic light scattering experiments were employed to understand the size of the aggregates formed. It was observed that cmc value of sodium deoxycholate (NaDC) decreased by the incorporation of ILs to the system which points out the enhancement of surface properties. The system containing hydrophobic MIL showed more affinity towards NaDC which reflects in the low cmc value of the system. As the wt% of IL increases the cmc value of the mixed micellar system decreases which confirms the easy aggregation of NaDC in IL solution rather than aqueous solution. The size of the aggregates increased as the wt% of ILs increased and after a certain wt% it decreased. Further the application of the studied micellar and mixed micellar system towards the solubilization of promethazine hydrochloride (PH) were evaluated using UV-Visible spectroscopy. The system containing 0.15 wt% of IL which has smaller aggregates was chosen for the interaction study because aggregate with smaller size should be capable of adsorbing more drug molecules. The determination of interaction parameters of micellar and mixed micellar system with drug was examined by Benesi-Hildebrand equation. It was observed that highest binding affinity towards PH was shown by mixed micellar system containing DIL.

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Polystyrene stabilised Pd-catalyst development for carbonylative transformations using oxalic acid as CO source

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Abstract:

The carbonylation chemistry has gained the immense interest of scientific community for incorporating the carbonyl moiety into the targeted organic substrates with the aid of various transition metal catalysts. In this context, heterogeneous nano-catalyst mediated carbonylation has emerged as a powerful tool to achieve this goal with the advantage of high/new reactivity, easy handling and appreciable recyclability. Over the past few years, our group is continuously focusing on the development of polystyrene supported transition metal nano-catalysts which are well characterized by SEM, HR-TEM, SEM-EDX, ICP-AES, P-XRD, XPS analysis and their applications in various carbonylative transformations.^[1,2] Since palladium metal is most extensively employed in carbonylation reactions, in this dimension we have explored the developed supported palladium nano-catalyst in various oxidative carbonylation reactions. However, direct utilisation of CO in chemical reactions is a challenging task due to their storage, toxicity and handling problem which require high pressure sophisticated instruments. To overcome these challenges, we have explored oxalic acid as a solid, economic and efficient in-situ as well as ex-situ CO source which exhibit remarkable synergistic effects with polystyrene stabilised nano-catalyst.³ Diaryl ketones are most important type of building block having huge applications in pharmaceuticals, agrochemicals and other industrial products.⁴ In this context, we have applied Pd@PS nano-catalyst for carbonylative Suzuki reaction for the synthesis of diversely substituted biaryl ketones using oxalic acid as an *ex-situ* C1 source. The reaction has been carried out in ppm-level catalyst loading under ligand and additive free conditions. Furthermore, we have developed a palladium catalyzed strategy for the synthesis of heteroquinazolin-4(3H)-ones framework from 2-iodophenylcarbodiimides, amines, and oxalic acid as CO source. Intriguingly, Pd@PS nano-catalyst have also displayed tremendous applications to fix two solid gaseous precursors i.e. NH₃ and CO sources respectively, for the synthesis of 2-amino-3-arylquinazolin-4(3H)-one derivatives. Furthermore, greener CO source, diverse substrate scope and high recyclability of Pd@PS catalyst were the major achievements under developed protocols.

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Extraction of Natural Product from plant source from cassiaGlauca

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ABSTRACT

Having D-galacto-D-mannan constitute in structure and in molar ratio of 1:2, a new polysaccharide has been isolated from ripe seeds of Cassia glauca1 Hydorlysis of methylated polysaccharide gave 2,3,4,6 tetra O methyl-D-galactose, 2,3 di-O methyl-D mannose and 2,3,6, tri-O- methyl D- mannose in the molar ratio of 1:1:1 respectively. Both periodate oxidation and methylation studies indicated 32.84% of end group. This shows similarity with the structure of polysaccharide formed on partial acid catalysed hydrolysis showed the galacto-mannan to consist of a linear chain $(1 \rightarrow 4)$ linked- β - mannopyranosyl residues some of which are substituted at 6 position by galactopyranosyl unit, glycosidically. This polysaccharide in non-ionic in nature & having presence of D-glactose in the peripheral position.

- A water soluble polysaccharide isolated from seed of cassia ovata. *.carbohydrateresearch Netherland* 1990, *Vol.*, Pages 384-386
 Notes: Peper is specific in the field of polysaccharide and also published in carbohydrateresearch Netherland which is specific for polysaccharide.
- Isolated polysaccharide will be explore from new Application**

Ionic Liquid Functionalized Zirconia-Reduced Graphene Oxide based Impedimetric Biosensor for Detection of Breast Cancer Biomarker

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Abstract:

We developed a sensitive impedimetric biosensor for the detection of a carcinoembryonic antigen (CEA), a breast cancer biomarker. The electrochemical biosensor has been fabricated by a nanocomposite of hydrothermally synthesized zirconium dioxide-reduced graphene oxide functionalized with the 1-ethyl-3-methylimidazolium tetrafluoroborate ionic liquid (ZrO₂rGO-IL) immobilized on a glassy carbon electrode (GCE). rGO consists of high current response and favors the immobilization of antibodies because of the availability of oxygen functionalities. Similarly, the O-functionality of ZrO_2 also favors the immobilization of antibodies but its low conductivity restricted its application in electrochemical biosensor Thus, 1-ethyl-3-methylimidazolium tetrafluoroborate fabrication. (EMIM.BF₄) is functionalized with the ZrO₂-rGO that facilitates electron transfer which enhances the electroconductivity of the nanomaterial to improve biosensor performance. Numerous characterization techniques such as UV-visible, Fourier-transform infrared, and Raman spectroscopy, X-ray diffraction, field emission scanning electron, and transmission electron microscopy have been employed to investigate the chemical and morphological properties of the nanocomposite. Furthermore, cyclic and differential pulse voltammetry and electrochemical impedance spectroscopy have been carried out to study their electrochemical properties. Results suggested that the ZrO₂-rGO-IL nanocomposite-based biosensor has a high sensitivity to detect the CEA. The quantitative detection of CEA has been accomplished via the EIS detection technique. It has been measured that the developed biosensor has excellent detection ability in both phosphate-buffered saline (PBS) and serum samples. Under optimum conditions, the linear detection range of the biosensor is 5.0 fg mL⁻¹ to 25.0 ng mL⁻¹, with the limit of detection of 2.20 fg mL⁻¹ in PBS for CEA. Additionally, the biosensor is highly sensitive and selective towards CEA and could be successfully applied for the detection of CEA in clinical samples.

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Lewis Acid Mediated 5/6/7-endo-dig Reductive Hydroalkoxylation of Enynyl Alcohols for the Synthesis of Tetrahydrofurans, Tetrahydropyrans, 1,4-Oxazepanes

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Abstract:

Cyclic ethers are very privileged scaffold present in many natural product and bioactive molecules.¹ The synthesis of 1,3-disubstitute cyclic ethers having aliphatic side chain is known to be difficult and challenging by hydroalkoxylation on alkynols.^{2,3} There are few reports which describe the synthesis of aliphatic substituted cyclic ether by *endo-dig* reductive hydroalkoxylation on terminal alkynols, however its limited to synthesis of only methyl substituted cyclic ether.⁴ Surprisingly, there is no report, which describe the *endo-dig* hydroalkoxylation for the synthesis of long aliphatic substitute cyclic ethers. Thus, herein we report transition metal free Lewis acid mediated 5/6/7-*endo-dig* reductive hydroalkoxylation cascade on enynyl alcohols which gave expedient access to cyclic ethers and medium sized 1,4-hextrocyles having long chain of aliphatic substituent. The brevity of devolved methodology was successfully demonstrated in the stereoselective total synthesis of (±)-isolaurepan and (±)-cis-lauthisan.⁵



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Edge-functionalization driven improved charge transfer in covalently linked C₃N₄ layers for enhanced photocatalytic hydrogen evolution

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Abstract:

Visible light-driven hydrogen (H₂) generation prospects from water (H₂O) have been triggered an extensive demand for high-abundant, low-cost semiconducting photocatalysts towards sustainable energy harvesting.¹ Even though $g-C_3N_4$ herald a great promise as a metal-free inexpensive photocatalyst, its efficiency has been limited due to low visible light absorption, stacked layers-driven restricted mass-transfer and poor charge-transfer dynamics.² Although many attempts have been made to exfoliate the layers and tune the photophysics but those finally end up with either complex synthetic steps or very low yield.³ Herein, we demonstrate a one-step synthesis of randomly curved, porous g-C₃N₄ with high surface area and counterintuitively red-shifted absorbance spectrum. The specific surface area of the synthesized sample was found to be ~ 3 times higher than the bulk g-C₃N₄, thereby offering more active sites for the catalytic reactions and eliminating the need for extra, low-yield exfoliation steps involving the high temperature or chemically hazardous exothermic conditions. In-situ generated covalent links between two adjacent C₃N₄ layers brought tremendous structural stability, arresting the mass-loss during calcination of precursors which is responsible for a high-yield of visible light active, porous thinner $g-C_3N_4$. Non-planarity arising because of sp^3 -C atoms linking two nanosheets results in loss of conductivity, reflected in increased charge transfer resistance. A facile edge-functionalization of as-synthesized doped covalently interconnected C₃N₄ troubleshoot the issue towards facile charge transfer by improved interaction with co-catalyst (Pt), boosting H₂ evolution from 6 times to 25 times compared to bare one under visible-light irradiation. Finally, the enhanced photocatalytic activities of both the photocatalysts were correlated with the charge-transfer dynamics as revealed from steadystate & time-resolved photoluminescence and transient absorption spectroscopy.

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A Base-mediated Sequential One-pot Approach to 2,3-Disubstituted Indoles from 2-(Tosylamino)aryl-substituted *para*-Quinone Methides

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Abstract:

2,3-Disubstitued indoles, which contribute as one of the important heterocyclic scaffolds, are present as an integral part of many natural and unnatural molecules that possess remarkable therapeutic properties.^{1,2} Due to their structural diversity and biological significance they are still an attractive core, thus a one-pot approach has been developed for the synthesis of 2,3-disubstituted indoles through a base-mediated N-alkylation of 2-(tosylamino)aryl-substitued *para*-quinone methides with halomethylaryl ketones followed by intramolecular cyclization and tosyl group elimination sequence. A combination of inorganic and organic base was used to effect this transformation This one-pot protocol provides direct access to a wide range of 2,3-disubstituted indoles in moderate to good yields under mild conditions.³



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Construction of Mg(II)-Organic Frameworks for Efficient Chemical Fixation of CO₂ Under Environment-Friendly Mild Conditions

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Abstract:

The immense amount of carbon dioxide (CO₂) emissions has resulted in the most serious environmental issues like ocean acidification, extreme weather, species extinction, and global warming.¹ Therefore it is highly desirable to mitigate the increasing atmospheric CO₂ concentration by its selective capture and utilization as a C1 feedstock for synthesis of value-added chemicals. However, the thermodynamic stability and kinetic inertness of CO₂ pose a great challenge for its conversion under mild conditions. In this context, intensive research efforts are being made by researchers worldwide on the design of efficient catalytic systems for fixation of CO₂ into value-added chemicals.² Towards this direction, we have developed porous metal-organic frameworks (MOFs) functionalized with polar groups suitable for the capture and conversion of CO₂ from direct air into high-value cyclic carbonates under solvent/co-catalyst-free mild conditions using a non-noble metal-based MOF as a heterogeneous catalyst. The synthesis, characterization and catalytic studies for chemical fixation of CO₂ will be presented.^{4,5}



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Synthesis, Spectral and Electrochemical Studies of Barbituric acid appended Nconfused Porphyrin and its Utilization in DNA Binding

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Abstract: *N*-Confused Porphyrin (NCP) is an analog of porphyrin in which one of the pyrrole rings is get twisted toward the outside and connected to *meso*-carbons at α and β positions.¹ This inversion of the pyrrole ring results in a change in photophysical and chemical properties. Non- π -extended NCPs have solvent-dependent spectroscopic properties since there are two stable tautomeric forms.² In polar solvents, such as dimethylsulfoxide (DMSO), an externally protonated (2H) form is favored due to hydrogen bonding and dipole-dipole interactions, while in non-polar solvents an internally protonated (2H) form is usually more stable. N-Confused porphyrin has a wide range of applications in the field of Photodynamic therapy, Non- linear Optics, Catalysis, Sensing etc.³ Barbituric acid derivatives are known to bind proteins in the cellular membrane and keeping this idea in mind we decided to synthesize barbituric acid appended N-Confused Porphyrin and their utilization in DNA binding. Herein, we report the synthesis and characterization of two different derivatives of NCP-based barbituric acid NCP(OMe)₈-DMBA and NCP(OMe)₈-H₂BA. Both of these derivatives exhibit red-shifted electronic spectral features as compared to NCP(OMe)₈ due to the extension in its π -conjugation.



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Catalytic Guanylation of carbodiimides and anilines by using zinc complex as a precatalyst supported by Imidazole-2-ylidene-N'-phenylthiourate ligand.

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Abstract:

Recently the metal-sulfur chemistry has drowned much attention because of the potential relevance of resulting complexes to active sites in metalloenzymes and their ability to adopt structural diversity. A series of zinc $[(Im^RNCS(H)Ph)_2ZnX_2; R=Mes, Dipp (X=Cl, Br, I)]$ (1a), (1b), (1c), (2a), (2b), (2c) and cadmium $[(Im^RNCS(H)Ph)_2CdX_2; R=Mes, Dipp (X=Cl, I)]$ (3a), (3b), (4a), (4b) metal complexes are prepared in excellent yield supported by imidazole-2-ylidene-N-phenylthiourate ligand $[Im^RNCS(H)Ph, R = Mes, Dipp, (L1), (L2)]$ and utilized as a catalyst for the guanylation reaction. All the zinc and cadmium complexes are air-stable and prepared from neutral ligands (L1, L2) and anhydrous metal dihalides in 2:1 and 1:1, respectively. All metal complexes were characterized by multinuclear NMR spectroscopy. Further, the solid-state structure of metal complexes such as (1c), (2a), (2c), (4a), and (4b) were established by single-crystal X-ray diffraction analysis. The zinc complex 1c showed good activity for the synthesis of guanidines with broader substrate scope.



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Spectroscopic characterization and reactivity of a putative Cu(III)-OH species supported by a proline-based pseudo peptide

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Abstract:

Inspiring by copper-based metalloenzymes, we intend to incorporate amino acids into our ligand system to enable active copper intermediates that serve as structural and functional models for the enzymes. Herein, we reported the synthesis of a C₂ symmetric proline-based pseudo peptide LH₂ (N,N'-(ethane-1,2-diyl)bis(pyrrolidine-2-carboxamide)) that can able to support an (L)Cu(III)-OH intermediate in MeOH:CH₃CN (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.The newly in situ generated (L)Cu(III)-OH can promote hydrogen atom abstraction reactions with phenolic substrates. It is noteworthy to mention that the species reported here is a protonated version of the elusive Cu(III)-oxo species proposed in catalytic cycles of the Dopamine β monooxygenase (D β M)¹ and Peptidylglycine alpha-hydroxylating monooxygenase (PHM) enzymatic.²

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Spectroscopic characterization of a Ru(III)-OCl intermediate: A structural mimic for haloperoxidase enzyme

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Abstract:

Halogenase, and haloperoxidase enzymes, found in various marine and terrestrial organisms, are accountable for halogenating aliphatic and aromatic C-H bonds to C-X (X = Cl, Br, I) in a regio, chemo, and stereoselective way.^{1,2} In the catalytic cycle of non-heme iron-dependent halogenases, particularly, CytC3 and SyrB2, a (Cl/Br)Fe^{IV}=O species generated is responsible for the halogenation of the robust aliphatic C-H bonds.³ Contrastingly, the heme irondependent and vanadium-dependent haloperoxidases employ H₂O₂ to produce Fe^{III}-OCl and V^V-OCl respectively, for similar function.⁴ The species. a reaction of $[(BnTPEN)Ru^{II}(NCCH_3)]^{2+}(BnTPEN = N^1-benzyl-N^1,N^2,N^2-tris(pyridine-2-ylmethyl)ethane-$ 1,2-diamine) with hypochlorite in the presence of acid in CH₃CN:H₂O mixtures generated a novel Ru^{III}-OCl species at room temperature. This new species has been characterized by UV/Vis absorption, EPR, resonance Raman spectroscopies, and ESI-MS. The Ru^{III}-OCl species is capable of performing oxygen atom transfer and hydrogen atom abstraction to various organic substrates.

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Metathetic Approaches to Diverse Polyquinanes: Synthetic Access to Cameroonanol Analogs, and Basic Core of Subergorgic Acid and Crinipellin

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Abstract:

Development of new strategies to highly strained complex molecules such as polyquinanes gained a great interest among synthetic chemists due to the presence of fascinating molecular architecture, contiguous stereocenters, all-carbon quaternary centers, and dense functional groups. In this context, utilization of atom-economic reactions and finding the appropriate starting materials to minimize the total number of steps are utmost important. For this purpose, utilization of a readily accessible and less explored Diels-Alder (DA) adduct, exo-dicyclopentadiene-1-one in combination with olefin-metathesis (Ring-Rearrangement Metathesis (RRM), Ring-



Opening Metathesis (ROM) and Ring-Closing Metathesis (RCM) etc.) is highly desirable. To this end, we have developed several metathetic approaches to linearly and angularly fused polyquinanes which are present as core units in many natural products such as cucumin, cameroonanol, subergorgic acid, crinepellin and presilphiperfolanol etc. Highlights include the synthesis of cameroonanol analogues and construction of complex systems such as tetraquinane derivatives, pentaquinane and fused 5/5/5/6-tetracyclic systems. The chemistry involves operationally simple reactions such as Diels-Alder reaction, alkylation, Grignard addition etc. The structure and relative stereochemistry of target compounds were established by various chemical methods and these are further supported by single-crystal X-ray diffraction studies. The present strategy is useful to design various "drug-like molecules" and expand the chemical space of cyclopentanoids that are useful in medicinal chemistry.

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Diastereoselective synthesis of carbazole-based unnatural amino acid scaffolds *via* Pd(II)-catalyzed C(sp³)-H functionalization

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Abstract

We report the synthesis of carbazole-based unnatural α -amino acid and non- α -amino acid derivatives *via* a Pd(II)-catalyzed directing group-aided β -C(sp³)-H activation/functionalization method. Several *N*-phthaloyl, racemic (DL), enantiopure (L and D) carboxamides were prepared from their corresponding α -amino acids, non- α -amino acids and aliphatic acids, respectively, which were then subjected to the Pd(II)-catalyzed β -C(sp³)-H functionalization with 3-iodocarbazoles to afford the corresponding carbazole-based unnatural amino acid derivatives with *anti* stereochemistry. We have shown the removal of directing group, deprotection of phthalimide moiety and synthesis of carbazole amino acid derivatives with free-amino and carboxylate groups.



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Pulsed Laser Ablated Co₃O₄ & WO₃ Thin Film Electrodes for Binder Free Flexible Hybrid Supercapacitor devices

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Abstract: Flexible thin-film storage devices have attracted significant devotion owing to their diminutive nature[1]. Flexible thin-film electrode fabrication, Pulsed Laser Deposition (PLD) plays a crucial role because of its tuneable nanostructures, well-regulated chemical composites, and fine thin film thickness controller[2]. The present work author tuned thin film Co₃O₄ nanostructures using PLD varying pulsed repetition rates of 2 Hz, 5 Hz, and 8 Hz, for thin energy storage device fabrications. Furthermore, we have grown WO₃ thin films nanostructures through PLD for suitable negatrode in thin-film Hybrid Supercapacitor (HSC) devices. Here we fabricated solid-state TFHSC devices such as Co₃O₄ || WO₃ consuming semi-solid gel electrolyte PVA-KOH. At foremost novel aspect of the Co₃O₄ || WO₃ TFHSC device delivered a supreme volumetric capacitance of 141.9 F cm⁻³. Also, the device reached the voltage window of 1.6 V. Further, the TFHSC device delivered a determined volumetric specific energy density of 12.62 mWh cm⁻³ at a volumetric power density of 1.27 W cm⁻³. The HSC device achieved notable stability performances in cycle life 27000 with an appropriate coulombic efficiency of above 97% along with remarkable capacitance retentions of 91%. More importantly, the TFHSC are a good approach to building portable energy systems for wearable microelectronics and bio-medical applications.

Keywords: Thin film Hybrid Supercapacitor, Pulsed Laser Deposition (PLD), Cobalt oxide nanostructure, , volumetric capacitance, specific volumetric energy density,etc.,

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Rhodamine-Sterol Bioconjugates as Stress-Responsive Probes for the Mitochondrial Live-Cell Imaging and Tracking

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Abstract:

Visualization of the cellular organelles has been a focus of great interest in understanding the functional dynamics of the cell.¹ The emergence of various fluorophores (proteins and small molecules) has played a crucial role in revealing the mystery of the cellular world.² The 'powerhouses' of the cell: mitochondria have seen an upsurge of interest in investigations pertaining to the imaging and mapping of physiological processes.³ Herein, we presented the synthesis of rhodamine-sterol conjugates and demonstrated the precise imaging of the mitochondria of healthy and stressed cells. The mitochondrial imaging was found to be independent of the mitochondrial-membrane-potential, making it unique compared with the existing set of mitochondrial probes. The sterol probes are highly biocompatible, and they can track the mitochondrial live-cell dynamics in a background-free manner with improved brightness and impressive contrast. This is the first attempt to study the stress-response using a direct fluorescence readout with bio-conjugates of rhodamine inside mitochondria.⁴ The results pave the way for developing fluorescent sterol markers for understanding cellular responses and functions.



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Large-scale, flexible 'all-organic' electrochromic devices for fast, and three states color-switching with high coloration efficiency

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Abstract:

Viologens have captivated great attraction for many electrochromic devices (ECD) due to their rapid switching, low power consumption, easy structural variability, colour tunability, long cycle stability, and high contrast ratio.^[1-3] Herein, a new viologen has been successfully synthesized and characterized by ¹H and ¹³C NMR, FTIR, and single-crystal XRD. An 'allorganic' electrochromic device has been fabricated by sandwiching viologen and poly(3hexylthiophene)(P3HT) between two ITO substrates to investigate its electrochromic properties. At different applied potentials, the ECD exhibits three states of reversible colour switching, which appear magenta at 0 V (unbiased), transparent at +1 V, and blue at +1.8 V. The colour switching from magenta to transparent is attributed oxidation of neutral P3HT to its polaronic form while from transparent to blue colour due to reduction of the dicationic form of viologen to mono cationic radical which bias-dependent Raman and UV-vis spectroscopy confirm. The device displays remarkable electrochromic properties, fast switching time (0.7 s/1.6 s), stability up to 3000 s (1000 switching cycles) at applied potential ± 1.8 . To the best of our knowledge, this is the first report on the electrochromic device based on the P3HT and viologen with coloration efficiency of as high as $\sim 464 \text{ cm}^2/\text{C}$.^[4,5] The findings could pave the way for developing high-performance energy storage devices like supercapacitors and flexible wearable electrochromic devices.

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Mitochondria specific Ratiometric Fluorescent probe for identifying active site of Esterase enzyme and discriminating live and dead cells using fluorescent imaging

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Abstract:

Esterases¹ are a class of enzymes that are widely found in various organisms. Their major function is to regulate body homeostasis by catalyzing the hydrolysis of various esters. Moreover, these are also involved in protein metabolism, detoxification, and signal transmission. These are also important targets to activate prodrugs. Most importantly, esterase plays a significant role in cell viability and cytotoxicity assays. Either abnormal activity or esterase insufficiency causes Wolman disease² accompanied by various symptoms, including abdominal swelling, diarrhoea, hepatomegaly and failure to gain weight. To develop a therapeutic prodrug, understanding the activity of esterase in the living system is of utmost necessity. Therefore, it is essential to generate an effective chemical tool for monitoring the activity of esterase in the cellular environment. Till to date, there are several biocompatible fluorescent probes³ for esterase have been developed based on their fluorescence activities. These are applied for live-cell imaging but, most do not show the active site of esterase for specific binding of probe. In addition, the probes were designed based on only fluorescent turnon property. Herein, we have developed a mitochondria-specific fluorescent probe, **PSOAc** to monitor esterase enzyme activity ratiometrically. This probe exhibited a bathochromic wavelength shift with esterase enzyme in alkaline pH due to an intramolecular charge transfer (ICT) process, which is further supported by TD-DFT calculation. Moreover, the binding of substrate *i.e.* **PSOAc** at the enzyme's active site and its mechanism of action to catalyse the cleavage of the ester bond is elucidated by QM/MM⁴ calculations. Fluorescent image-based analysis of the cellular environment reveals that our probe can successfully distinguish between live and dead cells based on esterase enzyme activity.

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Catalytic Hydroboration and Reductive Amination of Carbonyl Compounds by HBpin using a Zinc Promoter

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Abstract:

Chemoselective hydroboration of aldehydes and ketones, catalyzed by Zn(II)complexes { κ^2 -(PyCH=NR)ZnX₂}{R=CPh₃, X=Cl (1) and R=Dipp(2,6-diisopropylphenyl) and X = I (2) is presented in the presence of pinacolborane (HBpin) in ambient temperature and solvent-free conditions, which produced corresponding boronate esters in high yield, is reported. Zinc metal complexes 1 and 2 were derived in 80-90% yield from the reaction of iminopyridine [PyCH=NR] with anhydrous zinc dichloride in dichloromethane at room temperature. The solid-state structures of both zinc complexes were confirmed using X-ray crystallography. Zinc complex 1 was also used as a competent pre-catalyst in the reductive amination of carbonyl compounds with HBpin under mild and solvent-free conditions to afford a high yield (up to 97%) of the corresponding secondary amines. The wider substrate scope of both reactions was explored. Catalytic protocols using zinc as a pre-catalyst demonstrated an atom economic and green method with diverse substrates bearing excellent functional group tolerance. Computational studies established a plausible mechanism for catalytic hydroboration.



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Stereoselective synthesis of Dihydrocoumarins *via* [1, 2]-Phospha-Brook rearrangement in three-component coupling reaction of α -ketoesters, o-quinone methides, and dialkyl phosphites

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Abstract:



3,4-dihydrocoumarins are prominent heterocyclic scaffolds found ubiquitously in several natural products and pharmacological compounds.¹ Similarly, organophosphorus moieties are also found extensively in many pharmaceuticals² and often act as pro drugs³.Considering the prevalence and importance of coumarins, phosphate substituted dihydrocoumarin frameworks can be exciting molecules for accessing valuable compounds with superior biological activity. A highly regio- and diastereoselective approach for the synthesis of phosphate substituted dihydrocoumarins by utilising the [1,2]-phospha-Brook rearrangement⁴ under Brønsted base catalysis has been reported. The two-step one-pot Michael addition of *in situ* generated α -phosphonyloxy enolates formed *via* coupling of dialkyl phosphite and α -ketoesters to *o*-quinone methides and subsequent intramolecular cyclization provides novel phosphate containing 3,4-dihydrocoumarin frameworks with upto 95% yield and >20:1 *dr*.

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Electrocatlytic Hydrogen Evolution by Square-Planar Ni(II) complex and it's Mechanistic study

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Abstract:

Energy crisis and growing environmental problems motivate us to investigate sustainable energy alternatives to fossil fuels. Electrocatalytic processes are gaining interest because they offer a unique means of storing renewable energy in the form of fuel. Hydrogen evolution reaction (HER) is an important reaction in energy production & is probably the cleanest and most-efficient energy carrier, capable to substitute current fossil fuels.¹ To address this issue, it is essential to develop an efficient electrocatalyst from earthabundant transition metals that enable the reaction to proceed at high rates, together with a low driving force and increased stability. Thiosemicarbazone ligands are known to be redox-active, π -accepting, and the presence of various protonation sites are some interesting features that are relevant for electrocatalytic proton reduction.² In this context, we have analyzed the electrocatalytic behavior of neutral thiosemicarbazone ligand coordinated Ni-(II) complex; NiL (L: 2-((1Hpyrrol-2-yl)methylene)-N-methylhydrazine-1-carbothioamide)possessing a tetradentate, square planar coordination sphere for proton reduction. Due to the presence of soft donor ligands, and π -accepting moiety, ligand framework stabilizes the metal ion in it's low oxidation state and potentially enhances the catalytic properties of the metal complex. The NiL complex catalyzes HER with a maximum TOF of 2.73×10^4 s⁻¹ using CH₃COOH as an external proton source in acetonitrile. The HER mechanism is evaluated through electrochemical, spectroscopic, DFT(density functional theory) study of catalytic intermediates, and kinetic studies.

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Synthesis, Structural Characterization of Anthracene-Based Zn(II) & Cu(II) MOFs and It's Utilization in Nitro Aromatic Compound Sensing

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Abstract:

The design of sensors for nitro aromatic compounds with high selectivity and sensitivity has been subject of intensive research due to their adverse effects in environmental and health sectors.¹ A variety of instrumental techniqueshave been developed for the determination of sensors which require time-consuming procedures and sophisticated instrumentation. Now-a-days, the most attractive approach focuses on highly selective anion sensors, which allows "naked eye" detection of toxic nitro aromatic compounds by means of quenching in fluorescence intensities. Anthracene derivatives are ideally suited for chemical sensor due to their rich photoactivity and electrochemical redox properties. In general, MOFs derived from Anthracene already have luminescence properties due to that reason they are promising candidates for the detection of such hazardous compounds as they have strong emission properties, porosities and variable supramolecular interactions between frameworks as the host and target analytes as the guest^{2a}.

Herein, we report the synthesis and characterization of synthesis of Zn(II) and Cu(II) MOFs derived from anthracene based ligand 1,1'-(anthracene-9,10-diylbis(methylene))bis(4-hydroxypyridin-1-ium) H_2L and different carboxylic acid analogs. The ligand is neutral, monodentate with less hindrance and causes the coordination of more than one ligands on the metal centre. The luminescent electron rich MOFs are better sensors for the detection of explosive nitro aromatic compounds (NACs) as they are designed with pi-electron-rich ligands and typically have a good response to electron-deficient analytes^{2b,c}. These Electron rich species were tested for various nitro aromatic compounds. These exhibited very high binding constants with nitro aromatic compounds.

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Single-step insertion of M-N_x moieties in commercial carbon for sustainable bifunctional electrocatalysis: mapping insertion capacity, mass loss, and carbon reconstruction

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Abstract:

Atomically dispersed earth-abundant metals in N-doped carbon (M-N-Cs) have emerged as a new class of electroactive materials that can match not only the performance of the precious metals but can catalyze both the cathodic and the anodic reactions due to their bifunctional behaviour. This inspires the development of simpler strategies for scale-up production since the existing ones rely on precursors whose commercial viability is not yet ascertained. Herein, we demonstrate the insertion prospects of $M-N_x$ (M= Fe, Co, Ni) moieties, the electrocatalytic centers in the M-N-Cs, into commercial carbon to establish that a single-step heating of the inexpensive precursors is sufficient to generate bifunctional electrocatalysts for oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) with efficiencies that bypass the majority of the known catalysts. Further importantly, we quantify both the ORR and OER trends and the metal insertion limits for each metal while maintaining an atomic dispersion, without the formation of surface migration-induced clustering, because such clustering is inevitable in the existing processes to necessitate an extra acid-leaching step to remove them. We further quantify and explain for each metal a negative mass balance originating from anomalous mass loss of both metal and carbon content, and a massive reconstruction of the carbon backbone catalyzed by the very metal, an event documented for the first time though it ought to be associated with other M-N-C syntheses too. The study establishes an incredibly simple and inexpensive strategy for the realization of M-N-Cs, and outlines the parameters to be considered during mass-production.

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1,6-Conjugate Addition of Indoles to *para*-Quinone Methides Under Photo-redox Conditions

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Abstract:

Indole containing heterocyclic molecular entities have found interesting and important applications in pharmaceutical industry as well as materials science.¹ While working in the area of *para*-quinone methide (*p*-QM) chemistry, our group has been developed various traditional synthesize indolyl diarylmethanes using catalysed² methods to metal or bis(amino)cyclopropenium ion catalyzed³ conditions. We have also developed a direct method for the synthesis of diastereomerically pure diarylmethyl carbamates through a tropylium cation mediated 1,6-addition of (-)-menthyl carbamates to p-QMs.⁴ In this poster, we describe an efficient, mild and transition-metal free protocol to access indolyl diarylmethane derivatives via 1,6-conjugate addition of indoles to p-QMs under visible-light using an organo-photoredox catalyst.⁵



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Ruthenium Catalyzed Multiple C-H Bond Olefination and Oxidative Annulation of Phenanthro[9,10-D]Imidazoles

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Abstract:

1H-Phenanthro[9,10-d]imidazole, is a rigid π -conjugated heterocyclic skeleton fused by imidazole and phenanthrene. The phenantroimidazoles shows excellent electron transport properties, hence suitable for organic semiconductors used in organic light-emitting diodes (OLEDs) and solar cells.¹ PI chromophore were developed for dye-sensitized solar cells which exhibited good efficiencies. C– H activation is the latest technology added for efficient construction and late-stage modification of functional molecules.² As a metal catalyst, Ru(II) has the advantages of mild reaction conditions, a wide substrate scope, high reactivity, high selectivity, etc. It is widely used to achieve C–C bond construction with olefins as coupling partners, including many reports of the construction of a heterocycle. Herein, the Ru-catalyzed consecutive C–H bond olefination/annulation has been developed. In this transformation, the Ru catalyst loading at 120 °C. This method can be applied in the construction of various pharmaceutical derivatives.



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Non-Adiabaticity in Photodetachment Process of Al₆N⁻ Anion: Theoretical Investigation

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Abstract:

This work attributes to non-adiabaticity in the photodetachment spectra of Al₆N⁻ relying on its low-lying electronic states. It involves high-level electronic structure and nuclear dynamics calculations utilising time-dependent and time-independent ab initio quantum chemistry methods. A vibronic model Hamiltonian, prepared in a diabatic electronic representation corresponding to seven electronic states and fifteen vibrational modes, is used to estimate the coupling parameters. Several reduced dimensional calculations show the role of individual vibrational modes on the vibrational progression of electronic states and their coupling with them. The non-adiabatic nature and nuclear dynamics study of spectral bands are exercised in detail from the perspective of the vibronic coupling theory. Theoretically obtained photodetachment spectra reveals vibronic coupling among \tilde{A} , \tilde{B} and \tilde{C} , \tilde{D} , \tilde{E} electronic states evincing a good agreement with experimental spectra.

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Insights into switchable catalytic activity of nanoparticle surface using biomolecules

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Abstract:

To build a novel sensing and catalytic system, monolayer protected gold nanoparticles are emerging as a class of molecular systems having potential applications in molecular recognition, catalysis, signaling, and adaptation as they are derived entirely from the organic monolayer rather than the inorganic support, which is also important in origin of life study. It is the foremost criterion to incorporate adaptive and dynamic behavior in a catalytic system to gain nature-like functionality and generating physiologically relevant catalyst. Recently, we have developed a CTAB-capped cationic gold nanoparticle (GNP) based catalytic system which can be modulated for its performance by changing the number of phosphate groups (negatively charged group) in self-assembling units (AMP/ADP/ATP). As ATP has three phosphate groups, it can interact more strongly with the cationic surface as compared to AMP due to multivalent interaction. Due to stronger interactions of ATP with nanoparticles, the surface pH of the nanoparticles turns out to be acidic from basic while in the presence of AMP, the pH of the nanoparticles surface remain unchanged i.e. basic. Further, we have used these conditions to perform two different reactions, one which is favorable in acidic conditions (i.e., Hydrazone formation) and other one in basic conditions (i.e., Proton transfer, Kemp Elimination). Apart from this, we have also modulated the pH of the nanoparticles surface by using an enzyme named, Potato Apyrase in temporal manner and hence the selectivity of the nanoparticle catalytic system towards the two different reactions have been modulated.

Keywords: multivalent interaction; adaptive; dynamic; temporal manner.

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Photocatalytic Degradation of the Natural Lignin by Binuclear Cu(II) Complexes

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Abstract:

Visible-light driven photoreactions using metal complexes as catalysts are currently a research hotspot in terms of the development of environmentally friendly sustainable processes. To develop potential copper-based photo-catalysts, a Schiff base ligand viz. $2-[((3-(dimethylamino)-2,2-dimethylpropyl)imino)(phenyl)methyl]phenol (HL) has been synthesized and characterized. Two copper complexes <math>[(Cu(L)Cl)_2]$ (1) and $[(CuL(N_3))_2]$ (2) have been obtained by reacting HL with Cu(II) salts. Under the irradiation of visible light, these catalysts can cleave the C-C bonds with very good conversion in the presence of H₂O as a solvent. The photo-catalysts could be recovered almost quantitatively after completion of the catalytic cycle and recycled at least four times without much depreciation of catalytic activity. A plausible mechanistic pathway for degradation reaction has been explored through ESI-MS spectrometric, NMR spectroscopy, UV-vis and computational study.



Two together: Room Temperature Nematic Discotic Mesophase in a Luminescent Organic Dyad

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Abstract:

With the significant shift of the activities of the modern world to digital platforms, display technology is continuously evolving to meet the daily requirements of urban life. In such a scenario, mass-production of cost-effective optoelectronic devices become the need of the hour. Towards this goal, organic light-emitting and semiconducting materials score over their inorganic counterparts in terms of solution-processability and easier device-fabrication, along with reduced toxicity and synthetic costs. In this context, the present work explores a multifunctional molecular design with substantial potential to act as a pure organic emitter in organic light-emitting diodes (OLEDs). We have designed and synthesized a luminescent discotic dyad comprising of bay-annulated perylene and pentaalkynyl benzene units, linked through an alkyl chain acting as a flexible spacer between the two. From subsequent characterization through polarizing optical microscopy and X-ray diffraction, the synthesized material is found to exhibit room-temperature liquid crystalline behavior with a discotic nematic (N_D) mesophase, which persists over a broad temperature range. Thermogravimetric analysis confirms its thermal stability, assuring longevity of fabricated optoelectronic devices.

Ratiometric and colorimetric "naked eye" selective detection of CN⁻ ions by electron deficient Ni(II) porphyrins and their reversibility studies

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Abstract: In general, square planar Ni(II) porphyrins exhibited very weak axial ligation and extremely low binding constants with nitrogenous bases. We are showing an easy, rapid, reusable, selective and sensitive 'naked eye' colorimetric cyanide ion sensing by highly electron deficient planar and nonplanar β -substituted Ni(II) porphyrins with good binding constants through coordinative interactions.¹



Highly electron deficient β -substituted Ni(II) porphyrins were synthesized and utilized as novel sensors for selective rapid visual detection of CN⁻ ions. This work describes the electronic spectral and electrochemical redox properties of these sensors. The ratiometric and colorimetric responses of these porphyrins were monitored by the change in optical absorption spectra. These sensors were found to be highly selective for cyanide ions with very good binding constants through axial ligation of CN⁻ ions and are able to detect the CN⁻ ions concentration in ppm lavel. This sensors can be recovered from 2CN⁻ adducts by acid treatment and reused without loss of sensing ability. CN⁻ binding strongly perturbs the redox properties of the parent porphyrin π -system. The applicability of this porphyrin as practical visible colorimetric test kits for CN⁻ ions in aqueous and non-aqueous media has also been explored. The mode of binding was confirmed by spectroscopic studies and DFT calculations.²⁻³

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Metal-free Multicomponent Synthesis of Quinoline Fused Pyrroles

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Herein we report a metal-free one-pot multicomponent reaction for the synthesis of medicinally important quinoline fused pyrroles and pyrroloisoquinolines from the reaction of readily available starting materials. The reaction of aryl glyoxal, 4-hydroxy coumarin, or other cyclic 1,3-dicarbonyl compounds and 6-aminoquinoline/5-aminoquinoline / 5-aminoisoquinoline in HFIP (1,1,1,3,3,3-hexafluoro iso-propanol) medium under reflux conditions provided corresponding fused pyrroles in good yields. The notable features of this protocol are environmentally benign process, operational simplicity, easy purification, and presence of several bioactive moieties in the product.



Keywords: Multicomponent reaction; Quinoline Fused Pyrroles; Metal-free reaction, HFIP as solvent.

Role of Exposed Surfaces and Crystal Structure on Photocatalytic behaviour of Sr-Ti-O system

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Abstract:

Photocatalytic water splitting involves the production of oxygen and hydrogen occurring at anode and cathode respectively by using light. In this aspect, many catalysts have been explored involving the effect of size, shape, and other structural parameters. Amongst the various structural parameters, nature of exposed surfaces and crystal structure play a pivotal role. Hence, foremost, we discuss the influence of the dielectric constant of different polyols used during the synthesis of SrTiO₃[1]. We observed a significant variation in the shape of the nanostructures with an increase in the dielectric constant of the polyols, from cubes (with water as solvent) to edge truncated cubes (with PEG-300 as solvent) and hexagonal shaped particles arranged in the form of flower-like shape (with the ethylene glycol (EG) as solvent). Synergistic effect of maximum surface area, lowest crystallite/particle size, low recombination of the photogenerated electron and hole pair, a large value of Iphoto/Idark, and the presence of [001] as an exposed facet were shown to affect the photocatalytic performance of the oxide (dye degradation and Hydrogen evolution). Further, we discuss a comparative study of nanostructured SrTiO₃ and SrO–(SrTiO₃)_n viz. Sr₂TiO₄ (n = 1) and Sr₃Ti₂O₇ (n = 2) towards HER [2]. Cube-shaped morphology for nanostructured SrTiO₃ and sheet-like morphology was observed for Ruddlesden–Popper based oxides, Sr₂TiO₄ and Sr₃Ti₂O₇. Amongst the three oxides, the maximum amount of hydrogen was evolved with Sr₃Ti₂O₇ as the photocatalyst. Synergism of many factors which included the presence of SrO layer, SrTiO₃ unit, layered morphology, low crystallite size, and defects played a key role on the observed photocatalytic performance of the Ruddlesden-popper structure in comparison to cubic perovskite SrTiO₃.

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Iron-Catalyzed Reductive Cyclization to Alkenyl Vinylogous Carbonate for Stereoselective Synthesis of Highly Substituted Tetrahydrofurans, Tetrahydropyrans and Chromans

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Abstract:

Substituted tetrahydrofurans (THFs), tetrahydropyrans (THPs) and Chromans are important scaffolds present in numerous natural products and biologically active compounds.¹ Generally, HAT is involved in the process in which silanes were used as reductants and the alkyl radical intermediates were generated in situ. While vinylogous carbonates are very good radical acceptors for the synthesis of cyclic ethers, their use for synthesis of THF, THP and Chroman through HAT radical cyclization remains largely unexplored. In continuation of our interest on using vinylogous carbonates in the synthesis of cyclic ethers,^{2,3} herein we demonstrate that HAT radical cyclization on alkenyl vinylogous carbonate can give expeditious access to densely substituted cyclic ethers. An efficient protocol for the stereoselective synthesis of highly substituted tetrahydrofurans, tetrahydropyrans as well as chroman using hydrogen atom transfer (HAT) intramolecular radical cyclization to alkenyl vinylogous carbonate is described. The stereoselective synthesis of hexasubstituted THF derivative was achieved in good yield with excellent diastereoselectivity. The strategy was also used for the of oxa-spirocyclic as well as fused bicyclic scaffolds. The utility of this HAT cyclization has been demonstrated in the synthesis of tricyclic motifs bearing heteroatom substituted cyclic ring with excellent diasteroselectivity.



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Solvent- and Precursor-Dependent Fabrication of CdS Nanostructures and Their Use as a Heterogeneous Catalyst in Making Bis(indolyl)methanes

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Abstract:

Semiconductor nanomaterials have obtained huge interest because of their unique physical, chemical, and optical properties. Among all semiconductor materials, CdS possessing a band gap of 2.42 eV has a good charge carrier capacity. For the exploration of tuning band gap of CdS that connects its photocatalytic activity,¹ several parameters for its fabrication to generate different shape and morphology have been carefully optimized. Additionally, CdS possesses good Lewis acidic character due to which it is now emerging as a new and efficient contender in the field of heterogeneous catalysis for the organic transformation reactions. Until now, there is only one report for the synthesis of biological and pharmaceutical important bis(indolyl)methanes (BIMs) using CdS nanorods.² In this work, we have extended our efforts³ to fabricate and characterize diverse cadmium sulphide (CdS) nanostructures (CdS_1a to CdS 6a) using a combination of solvent and coordination polymer of Cd(II) as precursors, and to demonstrate their use in the synthesis of BIMs in a cost-effective and greener way. These nanostructures have been obtained solvothermally at 120 °C for 6 h from the reaction of $\{ [Cd_2(bpta)_2(adc)_2] \cdot 2H_2O \}_n \text{ or } \{ Cd_2(bpea)_2(adc)_2 \}_n \text{ (where bpta = N,N'-bis(pyridyl t-butyl))} \}$ amine, bpea = N,N'-bis(pyridylethyl) amine and adc = acetylene dicarboxylate), and thiourea as the Cd²⁺ and S²⁻ sources, respectively. Their varied morphologies were confirmed by fieldemission scanning electron microscopy (FESEM). Their crystallinity and bulk phase purity were confirmed by powder X-ray diffraction (PXRD), energy dispersive X-ray spectroscopy (EDX), Raman, X-ray photoelectron spectroscopy (XPS) and high-resolution transmission electron microscopy (HRTEM). Their optical properties studied by solid state UV-vis diffuse reflectance spectroscopy (DRS) and the band gaps were calculated from the Tauc plot. Their porosity and surface area have been investigated by N₂ adsorption experiments. Furthermore, the emission spectra of these nanostructures showed maximum intensity in ethanol followed by methanol and tert-butanol. Moreover, the time-dependent evolution studies of different CdS surface structures were done for the better understanding of their formation. As an example, CdS 3a was utilized as a heterogeneous catalyst to synthesize several BIMs at room temperature under solvent free conditions. The recyclability up to four cycles and stability of the catalyst was confirmed.

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Supercritical fluid assisted exfoliation of Bi₂Se₃ nanosheets for photocatalytic hydrogen production: Role of Topological Surface States

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Abstract:

Hydrogen production from photocatalytic water splitting is one of the promising avenues for direct conversion of solar energy into clean fuel. Currently, 2D layered materials are combined with many of semiconductor photocatalysts, as it provides huge active sites and also prevent photogenerated charge recombination. Specifically, Bi₂Se₃ possesses interesting properties like conducting surface states with bulk insulating behaviour, which provides unconventional electron dynamics, resulting in facile electron transport. So far, various methods are reported to produce few-layered Bi₂Se₃ nanosheets from its bulk crystals. Here, a unique and facile method is adopted to exfoliate bulk Bi₂Se₃ to few layered nanosheets with a short reaction time of 15 min via supercritical fluid processing using NMP as an exfoliating agent. Moreover, the TiO₂ photocatalyst was synthesised through sol-gel process. And different weight percentages of exfoliated Bi₂Se₃ nanosheets/TiO₂ nanoparticles were prepared and evaluated the photocatalytic activity using glycerol as a hole scavenger. The 15 wt% Bi₂Se₃/TiO₂ composite exhibit maximum of hydrogen evolution rate of 84.9 mmol/h/gcat. The enhanced rate of H2 production was also understood by DFT studies. In addition, the photostability of the nanocomposite was also verified for 4 cycles of continuous experiments and it retains 94% of activity. The detailed exfoliation of Bi2Se3, preparation of Bi2Se3/TiO2 composite, photocatalytic performance of the catalysts will be discussed in this presentation.

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Synthesis and fluorescence studies of symmetrical bis-1,2,3-triazoles

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Abstract:

A new symmetrical bis-1,2,3-triazole (1) was synthesized and incorporated to sense Fe(III) ion. Triazoles have various application in the fields of drug discovery, organic synthesis, polymer chemistry, bioconjugation, chemical biology, fluorescent imaging and materials science¹. Chemosensors are synthetic chemical compounds that can selectively bind with analytes of interest and produce detectable changes, for example, their colour, fluorescence, or redox potential². Probe **1** as excellent selectivity towards Fe(III) ion with turn-Off fluorescence and LOD is calculated as 0.45 μ M. **Probe 1** and Fe(III) ion were interacted through π to π^* transitions which were confirmed by ¹H-NMR. Due to simple synthesis and high selectivity towards Fe(III) ions, click generated 1,2,3-triazole-based chemosensors have become an important structural motif in the field of chemical sensing. The capability of click generated triazoles to interact with cations, anions and neutral analytes make them one of the most important classes of sensors in the field of sensing and biosensing³⁻⁴.

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Physiochemical Studies on Methanolic Extract of *Acorus calamus* Rhizome Loaded Nanostructured Lipid Carriers with Special Reference to Anti-allergic Activity

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Abstract:

Nanostructed lipid carriers (NLC) are considered as novel drug delivery systems because of its biocompatibility. *Acorus calamus* rhizome is known to possess anti-allergic activities. Methanolic extract of *Acorus calamus* rhizome was loaded in four different NLC formulations. NLC formulations were prepared using soy lecithin, tripalmitin, stearic acid (2:2:1; M/M/M) by cold homogenization and ultrasonic dispersion technique and where Tween-60, Poloxamer-188, polyethylene glycol, polyvinyl alcohol were separately used as stabilizers. Bare and extract loaded formulations were characterized by UV-VIS spectroscopy, FTIR spectroscopy, dynamic light scattering, X-Ray diffraction, transmission electron microscopy and atomic force microscopic studies. Comparative studies on different formulations were assessed. Further studied will be made to explore anti-allergic activities on animal model.

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- Vineet Sharma¹, Rohit Sharma^{1*}, DevNath Singh Gautam¹, Kamil Kuca^{2*}, Eugenie Nepovimova² and Natália Martins^{3,4*}, J Clin Med. 2020 Apr; 9(4): 1176

α-alkylation of Nitriles with Primary and Secondary Alcohols Catalyzed by Mn(I) Complex

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Abstract:

C-C bond formation reactions using alcohol as an alkylating agent via borrowing hydrogen methodology are the early examples of alcohol refunctionalization concept.¹ The metal-ligand cooperativity via protonation/deprotonation of an acidic -NH proton was largely explored in organometallic catalysis. In conventional methods, toxic alkyl halides are used as alkylating agent for alkylation of nitriles in the presence of stoichiometric amounts of bases which lead to the production of copious waste. Hence alkylation reaction using alcohols constitutes an atom economical and environment benign process producing water as sole byproduct.² With our continuous effort to design efficient protic bifunctional catalysts, Mn(I) complexes based on pyridyl amide/thioamide scaffold have been synthesized. The Mn-complex featuring amide functionality is found to be an excellent catalyst for α -alkylation of nitriles with primary and secondary alcohols. Isolation of active catalyst and deuterated studies have been performed to establish the mechanism of catalysis reaction.

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Effect of Nanoscopic-Confinement on the Singlet Fission Dynamics in

TIPS-pentacene

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Abstract:

In recent years, the potential of circumventing the Shockley-Queisser limit of photovoltaic efficiency through multiexciton production via singlet fission (SF) has piqued the interest of many researchers. SF is a process that involves exciton multiplication via the formation of a pair of triplet (T^1) excitons in a set of coupled organic chromophores after photoexcitation of a singlet state (S^1) [1]. The type and the strength of intermolecular interactions among the chromophores as well as the molecular packing arrangement play a crucial role in the SF dynamics and its overall efficiency. Previous studies suggest that there are two types of arrangements of chromophores in nanoparticles (NPs) of pentacene derivatives: type I (weakly coupled displaying short-range order), and type II (strongly coupled exhibiting long-range order) [2]. A substantial amount of theoretical and experimental results that underpin the singlet fission mechanism in various systems including NPs of bis (triisopropylsilylethynyl) pentacene (TIPS-Pn) are reported [3]; however, the impact of NP size on exciton dynamics within the nano-confined system remains unexplored.

Here, we present the role of confinement on the ultrafast SF dynamics of TIPS-Pn within nanosized TX-100 (neutral), CTAB (cationic), and SDS (anionic) micellar confinements using femtosecond transient absorption spectroscopy [4]. We show how the size of NPs affects the intermolecular coupling and arrangement of the TIPS-Pn molecules within the confinement and in turn affects the dynamics and efficiency of SF. Since, more chromophores may couple strongly as NP size increases (SDS > CTAB > TX-100), it results in preferential type II arrangement and a slower rate of triplet pair formation due to the generation of trapped singlet excitons that cannot undergo SF [5]. On the other hand, chromophores in smaller-sized NPs, couple weakly and favor type I arrangement resulting in the faster formation of the triplet pairs. The present study demonstrates how the fine interplay between short-range and long-range interactions among chromophores within micellar nano-cavity of different sizes influences the rate and efficiency of SF in TIPS-Pn.

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HIGH PERFORMANCE NON-AQUEOUS ORGANIC REDOX FLOW BATTERY IN AMBIENT CONDITION

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Abstract:

Redox flow battery (RFB) is a preferred energy storage option for grid stabilisation and energy arbitrage as it offers energy and power decoupling ^{1,2}. In contrast to aqueous RFBs (ARFBs), nonaqueous RFBs (NARFBs) could offer high energy densities due to the wider electrochemical window of the solvents used, which could handle high and low voltage organic redox couples without undergoing electrolysis ³. In this study, a RFB based on benzyl viologen hexafluorophosphate [BV (PF₆)₂] as anolyte and N-hexyl phenothiazine [HPT] as catholyte demonstrated. A cell operated with mixed electrolyte (1:1) containing 0.2 M [BV (PF₆)₂] and 0.2 M [HPT] delivered a coulombic efficiency (CE) of 95.3 % and energy efficiency (EE) 53%, with nearly 68.9% material utilisation at 40 mA cm⁻² current density.

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Fig-1 (a) Galvanostatic charge-discharge profile, (b) Coulombic efficiency (CE), Voltage efficiency (VE) and Energy efficiency (EE) of 0.2 M [BV (PF_6)₂] and [HPT] mixed electrolyte at 40 mA cm⁻².

Well-Defined Ni(0) and Ni(II) Complexes of Bicyclic (Alkyl)(Amino)Carbene (BICAAC): Catalytic Activity and Mechanistic Insights in Negishi Cross-Coupling Reaction

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Abstract:

Negishi cross-coupling reaction of organozinc compounds as nucleophiles with aryl halides has drawn immense focus for C-C bond formation reactions. In comparison to the wellestablished library of Pd complexes,^[1] the C-C cross-coupling of this particular approach is largely primitive with nickel-complexes.^[2,3] Herein, we describe the syntheses of Ni(II) complexes, $[(BICAAC)_2NiX_2]$ (X = Cl (1), Br (2), and I (3)) by employing the bicyclic (alkyl)(amino)carbene (BICAAC) ligand. The reduction of complexes 1-3 using KC₈ afforded the two coordinate low valent, Ni(0) complex, [(BICAAC)₂Ni(0)] (4). Complexes 1-4 have been characterized by spectroscopic techniques and their solid-state structures were also confirmed by X-ray crystallography. Furthermore, complexes 1-4 have been applied in a direct and convenient method to catalyze the Negishi cross-coupling reaction of various aryl halides with 2,6-difluorophenylzinc bromide or phenylzinc bromide as the coupling partner in the presence of 3 mol % catalyst. Comparatively, among all-pristine complexes, 1 exhibit high catalytic potential to afford value-added C-C coupled products without the use of any additive. The UV-vis studies and HRMS measurements of controlled stochiometric reactions vindicate the involvement of Ni(I)-NI(III) cycle featured with a penta-coordinated Ni(III)-aryl species as the key intermediate for 1 whereas Ni(0)/Ni(II) species are potentially involved in the catalytic cycle of 4.

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Redox-active alkylsulfones as precursors for alkyl radicals under photoredox catalysis

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Abstract:

A method for generating alkyl radicals using visible-light photoredox catalysis is described. This strategy efficiently enables a diverse collection of 1°, 2°, and 3° alkyl radicals through the single-electron transfer of sulfones under mild reaction conditions. These alkyl radicals are generated via the reductive desulfonylation of readily synthesized stable alkylsulfones^[1-2] that can be engaged in C–C bond formation in the presence of a suitable acceptor following the Giese reaction.^[3] This technique is also applicable to achieve allylation in the presence of allyl sulfone as a trapping reagent via constructing a new C–C linkage. A series of fluorescence quenching experiments were executed to shed light on the mechanism, demonstrating that SET to alkylsulfones precursor is the crucial process for generating alkyl radical species. The major success of this strategy relies on the generation of primary alkyl radicals from redox-active primary alkylsulfones under mild reaction conditions utilizing the power of visible-light photoredox catalysis.^[4]



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Effect of Ligand Modulation on Zinc Cation: Synthesis, Catalysis and Mechanistic View

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Abstract:

The environment friendly base metal zinc has gained much eminence in the past few years due to its high earth abundance, economical, biocompatibile, and mild nucleophilic characteristics. Towards the prerequisite of sustainable system, well-defined cationic zinc complexes have been found as excellent catalysts for a wide range of vital organic transformations.¹ In literature, it has been well demonstrated that the inherent Lewis acidic nature of the metal center directly correlates with its catalytic activity.²

Here, the work in the poster will demonstrate systematic study of effect of the modulation of the ligand framework on the activity of Zinc Cation. Low coordinated cationic zinc complex $[L_1Zn]$ [CH₃B(C₆F₅)₃] supported by (bis-phosphinimino) amide ligand (L₁H = [{(2,6-iPr₂C₆H₃N)P(Ph₂)}₂N]H) has been synthesized. The compound was accessed by abstraction of the methyl group from [LZn-CH₃] or [LZn-C₂H₅] using B(C₆F₅)₃ in toluene at room temperature. The molecular structure of [L₁Zn] [CH₃B(C₆F₅)₃] reveals the weak interaction of methyl protons of the anion with the zinc center which shows the importance of choice of ligand and zinc complex for the cation synthesis. The formation of exchange products [LZn-C₆F₅] and [CH₃B(C₆F₅)₂] or [HB(C₆F₅)₂] through B-C₆F₅ bond cleavage during reaction strongly affirmed the electrophilicity of [L₁Zn] [CH₃B(C₆F₅)₃]. The benefits of Lewis acidity of complex [L₁Zn] [CH₃B(C₆F₅)₃] is exploited for hydrosilylation and hydroboration of imines. The detailed mechanistic investigation shed the light on Lewis's acid activation pathway to assist the catalytic reaction.



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Electronic and optical properties of Phenanthroimidazole-Alkyl spacer-Carbazole based fluorophores for ultraviolet emissive Organic Light-Emitting Diodes

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Abstract:

Bipolar behaviour of Phenanthroimidazole has great potential to construct efficient near UV deep blue emission. The different substitution at N1 and C1 position of the imidazole moiety further enhance the optical and electrical properties. At the same time, alkyl spacer precise the π - π stacking and molecular aggregation, which leads to high photoluminescence quantum yield (PLQY) of thin film ~ 74%. All the materials showed near-UV deep blue emission and maxima of EL spectra exhibited between 395-420 nm. We fabricated the OLED doped device by using the host matrix as CBP with the same configuration as non-doped device to further enhance the device efficiency and color purity. We selectively used CBP as a host because it possesses appropriate HOMO and LUMO levels matched with the synthesized emitters which help in efficient charge trapping. Above all, the device efficiency and luminance properties. The best performing of 0.5 wt% PIPP based OLED device shows a maximum luminance of 1202 cdm⁻², a maximum power efficiency (PE) of 2.2 lm/W, a maximum current efficiency (CE) of 2.7 cd/A, and maximum external quantum efficiency (EQE) of 4.4% with Commission International de L'Eclairage (CIE) coordinates of (0.17, 0.10) emits deep blue light.

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Benzothiazoline Based Ni(II), Cd(II) and Zn(II) Complexes for Sequestration and Activation of SO₂

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Abstract:

Sequestration and activation of SO₂ is highly needed as it has harmful impact on environment and human health. Herein, [Ni(Anbt)₂], [Cd(Anbt)₂], and [Zn(Anbt)₂] complexes bearing benzothiazoline ligand were synthesized and utilized for sequestration and activation of SO₂. Tetrahedral Cd(II) and Zn(II) complexes were reacted with SO₂ and the adduct on reaction with oxygen transformed to 2-(Anthracenyl)benzothiazolium bisulfate under ambient conditions. While purging SO₂ in dichloromethane solution of [Zn(Anbt)₂] and [Cd(Anbt)₂], color of solution changed from red to yellow which indicates activation of SO₂ which is further confirmed by ESI-MS. Interestingly, interaction between two molecules of SO₂ and thiolate sulfur in Ni(II) complex was well characterized by X-ray crystallography, IR spectroscopy, and TGA.

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Why Intermolecular Nitric Oxide (NO) Transfer? Exploring the Factors and Mechanistic Aspects of NO Transfer Reaction

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Abstract:

The metal-centers and the ligand frameworks greatly influence small molecule activation & their transfer reactions in biological or catalytic reactions.^{1,2} Here, we discuss directed nitric oxide (NO) transfer chemistry in low-spin mononuclear $\{Co(NO)\}^8$, $[(12-TMC)Co^{III}(NO^-)]^{2+}$ (1-CoNO, S = 0), and $\{Cr(NO)\}^5$, $([(BPMEN)Cr(NO)(Cl)]^+)$ (4-CrNO, S =1/2), complexes. 1-CoNO transfers its bound NO moiety to a high-spin $[(BPMEN)Cr^{II}(Cl_2)]$ (2-Cr, S = 2) and generates 4-CrNO via an associative pathway; however, we did not observe the reverse reaction. Spectral titration for NO transfer reaction between 1-CoNO and 2-Cr confirmed 1:1

reaction stoichiometry. The experimental and theoretical observation supports the formation of μ -NO bridged intermediate species ($\{Cr-NO-Co\}^{4+}$). For the first time, we observed the formation of an intermediate prior NO to transfer. Mechanistic investigations using ¹⁵Nlabeled-¹⁵NO and tracking the ¹⁵N-atom established that the NO moiety in 4-CrNO is derived from 1-CoNO. Further, to investigate the factors deciding the NO transfer reactivity, we explored the NO transfer reaction between another high-spin Cr^{II} -complex, $[(12-TMC)Cr^{II}(Cl)]^+$ (5-Cr, S = 2), and 1-CoNO, showing the generation



of the low-spin $[(12-TMC)Cr(NO)(Cl)]^+$ (6-CrNO, S = 1/2); however, again there was no opposite reaction, i.e., from Cr-center to Co-center. Kinetic measurement suggests the NO transfer rate is 3.4 times faster in the latter case than the former. The above results advocate clearly that the NO transfer from Co-center generates thermally stable and low-spin & inert $\{Cr(NO)\}^5$ complexes (4-CrNO & 6-CrNO) from high-spin & labile Cr-complexes (2-Cr & 5-Cr), suggesting a metal-directed NO transfer (Cobalt to Chromium, not Chromium to Cobalt). These results explicitly highlight that the ligand can stabilize the intermediate and affect the NO transfer rate but net NO transfer is strongly influenced by the labile/inert behavior of the metal-centers and /or thermal stability rather than the ligand architecture.³

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Development of Transition-Metal-Free Lewis Acid-Initiated Double Arylation of Aldehyde: A Sustainable Approach Towards the Total Synthesis of Anti-breast Cancer Agent

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Abstract: With a wide variety of commercially available drugs having unsymmetrical di and triaryl methane pharmacophore, the synthesis of such molecules from common feedstock are considered a useful synthetic task. Though various metal-catalyzed cross-coupling methods are known to achieve the task limit the usefulness of such protocols. [1] The title work describes a sustainable and robust metal-free double hydroarylation strategy for the synthesis of symmetrical /unsymmetrical diaryl- and triarylmethanes in excellent yields using Lambert salt (0.2-1.0 mol%) as the catalyst. A highly efficient gram-scale reaction has also been reported



(TON for symmetrical product = 475 and for unsymmetrical product = 390). The synthetic utility of the methodology is demonstrated by the preparation of several unexplored diaryland triarylmethanes-based biological relevant molecules, such as arundine, vibrindole A, turbomycin B, anti-inflammatory agent.

Figure 1. Lewis-acid initiated Brønsted acid-catalyzed Friedel-Crafts hydroarylation reactions of aldehydes.

A total synthesis of phenanthrene based anti-breast cancer agent is also demonstrated in one pot. [1] Further, control experiments, Hammett analysis, HRMS and GC-MS studies reveal the reaction intermediates and reaction mechanism. [2] Hence, we envisaged a unique methodology, whether reactions could be carried out between aldehydes and electron-rich arenes to give the corresponding diaryl- and triarylmethanes *via* transition-metal-free approach under ambient conditions using *in-situ* generated Lambert salt **1a**. [3]



Figure 2. Si–H bond activation by using trityl salt (1).

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Azobenzene-based photoswitchable fluorescent sensors for selective metal ions

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Stimuli-responsive molecules are attractive in the research field because of their advantage in the modulation of functions in numerous applications. Among all external stimuli, light is the most non-invasive and tannable. Photoswitches are small organic molecules that are capable of altering their physicochemical properties in the presence of light. Among all photochromic compounds, azobenzene has been extensively used because it can undergo reversible isomerization between two isomeric states i.e. E- and Z-isomers over a number of cycles without any photodegradation.^[1] The changes in polarity, molecular size, and flexibility lead to their utility in energy storage devices, optical devices, self-healing materials, drug transportation, catalysis, etc. Rhodamine is a dye with spirolactum core, which has a large absorption coefficient, and long-wavelength emission with high fluorescence quantum yield. Rhodamine derivatives can undergo reversible ON/OFF fluorescence response on binding with certain metal ions.^[2] Hence, a colorimetric and ratiometric probe has been synthesized based on fluorescent rhodamine and photochromic azobenzene moiety. Azobenzene is nonfluorescent due to its excellent photoisomerization ability in its excited state. Rhodamine connected with azobenzene through a linker shows no effect on photoisomerization of azobenzene but the addition of metal ions inhibits the photoisomerization process of azobenzene, which makes it an excellent fluorescent chemosensor. The probe upon addition of selective metal ions also produces a visible change in color from yellow to pink. Mechanistically, metal ion addition restricts the photoisomerization of azobenzene along with spirolactum ring-opening of rhodamine dye simultaneously (Figure 1).^[3] All these selective binding and sensing applications have been investigated with the help of, UV-vis, Fluorescence, ESI-MS, ¹H-NMR spectroscopic techniques, and the results are presented through this contribution.^[4]



Fig.1 Schematic Representation of sensing mechanism and visual detection of metal ion

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Identification of Mucin 1 Biomarker from Breast Cancer Extracellular Vesicle platform using bioanalytical techniques

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Abstract:

Extracellular vesicles (EVs) are double membrane-bound nanoparticles derived from almost all types of body fluids. EVs play an important role in cell-to-cell communication and also have a high significance in cancer biology. In the tumor microenvironment, cancer cell-derived EVs are involved in enabling tumor formation and metastasis resulting in the urgent need to understand the EVs biology for the identification of biomarkers [1]. The growing interest in assessing the clinical relevance of these nanosized particles in cancers has led to the discovery of tissue- or disease-specific exosomal contents, such as nucleic acids, proteins, and lipids as a source of new biomarkers which implicate that exosome's application in the diagnostic potential for the early cancer detection.

Keeping this application in mind in this study we have targeted the Mucin 1 biomarker, which is a transmembrane glycoprotein found on the surface of nearly all epithelial cells but in the case of human malignancy, Mucin1 expression is found to be highly aberrant according to previous studies which lead to cellular change from a normal to malignant phenotype [2]. Here in this project, we tried to confirm the same finding to check the expression of Mucin1 biomarker utilizing the extracellular vesicles platform as EVs carry biomarkers associated with a specific disease with higher sensitivity and specificity. We have used various bioanalytical as well as spectroscopy techniques such as flow cytometry, ELISA and FT-IR to confirm the presence of Mucin1 biomarkers in cancer cell-derived EVs. Currently, PCA analysis is undergoing to confirm the aberrant glycosylation of Mucin1 suggesting the potential of spectroscopic techniques for the biomarker discovery. Besides this, we also tested the morphological difference in the EVs isolated from normal and cancer EVs using AFM to check the differences in the EVs. Finally, we have outlined the importance of exosomal characterization for biomarker discovery. The growing emergence of breast cancer cases has stimulated research and application of extracellular vesicles and we believe the understanding of EVs and their cargo could be a promising source of early biomarker detection.

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Ultrafast Excited State Dynamics in Fluorescent Proteins

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Abstract:

The origin of fluorescent proteins (FPs) traces its roots back to 1960s when green fluorescent protein (GFP) was first isolated from a jellyfish *Aequorea Victoria*. Since then, different colored FPs were identified from sea organisms which belongs to Anthozoa class. The fluorescence in GFP emanates from a chromophoric unit (4-(p-hydroxybenzylidene) imidazolinone) formed by the autocatalytic reaction of three consecutive amino acids. *wt*-GFP exhibits two absorption bands corresponding to neutral and anionic forms. The neutral form after excitation, undergoes excited-state proton transfer (ESPT) on ultrafast timescales to the anionic form which fluoresces and undergoes ground-state proton transfer (GSPT) to give back the neutral form [1].

Similar to *wt*-GFP, in mKeima (a variant of red fluorescent protein), ground-state equilibrium exists between the two forms over a broad range of pH and exhibits ESPT dynamics. Earlier, conformational heterogeneity of the chromophore showing "*reverse protonation*" effect in mKeima is reported in different pH environments [2]. Here, we investigated the role of the local environment of protein on the potential energy barrier of ESPT dynamics using femtosecond transient absorption spectroscopy to predict whether it follows direct-concerted mechanism or coupled with the isomerization as multiple species (i.e., *cis* and *trans* conformers of neutral and anionic form) of chromophore co-exists. Furthermore, we studied the origin of dual-fluorescence in mKeima majorly at low pH conditions.

Apart from FPs exhibiting photocycle, there are several variants which at physiological pH exist predominantly in anionic form. Of special interest is to explore the mechanism of photoconversion in the S65T/F64L mutant of *wt*-GFP, known as enhanced GFP (EGFP), which is several-fold brighter than *wt*-GFP and exists predominantly in anionic form. In spite of all the stimulating studies on EGFP, it is still not known how photoconversion proceeds in EGFP which we explore using global fluorescence lifetime analysis [3]. Using picosecond fluorescence lifetime measurements and femtosecond pump-probe spectroscopy, we discuss the excited state dynamics of a yellow fluorescent protein, Venus [4]. We compare and contrast the nature of its photophysics with those of *wt*-GFP.

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Au-Catalyzed Kornblum-type Oxidation of 2-Alkynylaryl-substituted *p*-Quinone Methides: Direct Access to Indenones

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Abstract: In recent years, the utility of stable *p*-quinone methides was explored in the synthesis of heterocycles and carbocycles.^{1a,b,c} In fact, we have also developed many methods for the synthesis of oxygen- and nitrogen- containing heterocycles.^{2a,b} Recently, we have described a Lewis acid or Brønsted acid catalyzed intramolecular cyclization of 2-alkenyl and 2-arylphenyl substituted *p*-QMs to access biologically active natural products such as (±)-Isopaucifloral F^{3a} and Selaginpulvalins,^{3b} respectively. In this poster presentation, we will discuss our recent development on the Au-catalyzed intramolecular carbocyclization of 2-alkenyl and 2-alkenyl *p*-quinone methides to access substituted indenone derivatives.⁴ This transformation allowed us to access a wide range of indenone derivatives in moderate to good yields.

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Real-time Tracking of Coherent Vibrational Motion in Ground and Excited Electronic States

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Abstract:

Light-matter interaction, driving fundamental processes in nature (for example, photosynthesis and photoisomerization in the visual pigment rhodopsin), is at the heart of sustenance of life on earth. Photoinduced charge and energy transfer processes in many natural and synthetic systems is accompanied by structural changes at ultrafast timescales which necessitates the monitoring of real-time evolution of molecular geometry. Femtosecond infrared spectroscopy and frequency-domain coherent Raman spectroscopy successfully captured full vibrational spectra but are limited by interfering lineshapes, background signals, etc. Time-domain measurement, *i.e.* impulsive stimulated Raman scattering employs a short Raman pump pulse, creating a nuclear wavepacket which evolves as a function of time and is interrogated using a time-delayed probe pulse and Fourier transform of the temporal interferogram yields the Raman spectrum whereas the scattering background can be easily removed as a zero frequency component. However, even for small chromophores in solution, identifying the origin of these vibrations, i.e., whether they arise from ground or excited electronic state of the solute, or contributed by ground electronic state of the solvent as well, has been debatable. Recently, we showed how 'spectrally dispersed' impulsive stimulated Raman spectroscopy can be employed to track the origin of coherent vibrational motions observed in femtosecond pump-probe transients and how to extricate vibrations under non-resonant/resonant impulsive excitation (in a two-pulse third-order $(\chi^{(3)})$ experiment) [1-4]. More specifically, separation of excited-state, ground-state and solvent coherences for diatomic as well as polyatomic molecules in solution is demonstrated. The origin of spectral patterns corresponding to certain vibrational modes of the solute as well as the solvent will be presented. We show how piecewise Fourier transform of the data over a select range of detection wavelengths or temporal window can aid in separating contributions from spectrally overlapping vibrational modes. In addition to this, density functional theory is employed to identify the Raman active modes, which nicely correlates with the experimental observations. Details of this method as an emerging technique and its wide-ranging applications to disentangle vibrations in complex molecular systems will be discussed.

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The Local Electric Field (LEF) as a Descriptor of Catalytic Activity

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Abstract:

current theoretical perception The of enzymatic activity is hugely reliant on the calculation of the activation energy of the chemical reactions, which is most of the time determined using computationally demanding quantum mechanical calculations. With the growing use of bioengineering techniques that produce an excessive number of variants of the same enzyme, a quick and accurate method for determining the relative efficiency of enzymes is currently in great demand. Using the example of chorismate mutase in its native form and multiple variations (R90A,



R90G, and R90K/C88S), we suggest the local electric field (LEF) of the enzyme along the reaction axis as a descriptor for enzymatic activity. For all of the complexes studied, there is a direct link between the computed enzymatic EF and the enzymatic activity. MD simulations of the Michaelis complex and the transition state analogue (TSA) reveal that the enzymatic EF exerts a stabilising force on the TSA. QM/MM and QM-only DFT calculations in the presence of an external electric field (EEF) oriented along the reaction axis disclose that the EEF interacts with the dipole moment of the TS, thereby stabilising it and thus lowers the activation energy.

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An Electron-Deficient Tris(triazole)-based Discotic Liquid Crystal that exhibit Fast Electron Transport

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Abstract:

For more than five decades, the mainstream electronics industry has been dominated by thin film transistors based on inorganic semiconductors that require high temperature and high vacuum deposition techniques, which brings about high production costs. This challenge creates a need for new organic semiconducting materials (OSCs) with innovative design and semiconducting behavior that provide opportunities to reduce the cost of production, improve display quality, and avoid the use of toxic materials.¹ The simple processing of OSCs with liquid crystalline phases can be viewed as a new generation of organic semiconductors.² It has been seen that n-type discotics with low bandgap are excellent candidates for transportation of both positive and negative charges in organic semiconductors.² Discotic liquid crystals (DLCs) based on electron-rich systems (p-type semiconductors) have been widely studied unlike electron-deficient (n-type) ones.

Motivated by this, the present work demonstrated the synthesis of a C3-symmetrical starshaped DLC material, with an electron-deficient tris(triazole) central rigid core attached to which were electron-rich alkoxy units at the periphery.³ To evaluate the potential application of synthesized compound in organic devices, charge carrier transport studies were carried out using the SCLC technique. The charge transport studies reveal fast electron transport of the order of 10^{-2} cm² V⁻¹ s⁻¹ as measured using the SCLC technique. The finding is expected to guide the development of new high-performance n-type materials for semiconducting devices.

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Redox activated amines in organophotoinduced alkylation of coumarins

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Coumarin core represents quintessential scaffold of many natural products, a diverse family, which have many medicinal properties. While C-3 alkylation is easily achievable and is well developed, effective greener C-4 alkylation strategies have been less forthcoming. Herein, we report metal-free photoinduced deaminative strategy for C-4 alkylation of coumarins from redox activated secondary and benzylic amine derived Katritzky pyridinium salts. The protocol was highlighted with its broad substrate scope, providing a powerful route for generating various new classes of highly functionalized small molecules. Additionally, the approach is also suitable for synthesis of saturated alkyl-2-oxochromane-3-carboxylate.

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Small Angle X-Ray Scattering: A tool for determining shape and size of nanostructures

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Abstract:

One of the most efficient and non destructive techniques for the analysis of the shape and size at nano-scale level is Small angle X-ray scattering (SAXS). SAXS helps in studying various organic and inorganinc materials in any forms such as solid or liquid, with the added advantage of minimum sample requirement, in-situ analysis and more statistically average information about the size and shape of the particles. In this poster, we present two studies: one is the use of SAXS for understanding the effect of surfactant on the structure of reverse micelles [1] and second, the synergistic use of model-independent and model-dependent approaches in SAXS to determine shape and size of Au nanostructures [2]. In the first study, we discuss the effect of surfactants with respect to their hydrophobic chain length, and the nature of polar head group viz. anionic, cationic, and non-ionic, on the structure, thickness of the interfacial layer, and the rigidity of the reverse micelles. In the second study, we have discuss the analysis of the SAXS data using Guinier law, PDDF (pair–distance distribution function) plots, double logarithmic plots, and electron density curves for getting primary information about the size and shape of nanostructures which was utilized for choosing an appropriate model and initial input parameters for fitting the SAXS data.

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Lignocellulosic Fiber Assembly as Sorbent for Oil Spill clean-up

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Abstract:

In the modern industrial world oil is one of the important sources of energy. Through oceans and inland transport, it is transported from the source of production to different places across the globe. Sometimes during transportation, the oil spillage occur over the water bodies accidently or deliberately and this causes water pollution. Sorbents made from the natural fibers are find to be the best to clean up the oil spillage. To overcome this problem Lignocellulosic Sheet was prepared using alkali treated bamboo fibers. The sheet was characterized by X-ray Diffraction (XRD), Fourier transform infrared (FTIR), Thermogravimetric Analysis (TGA), Scanning Electron Microscopy (SEM-EDS). Lignin -functional groups on the lignin surface, allows it to interact with the charged oil droplets and results into adsorption of 80% carbon introduced into the water by oil spills. Sorption mechanism followed includes physical adsorption, hydrogen bonding, coordination and covalent linking, and acidic-basic interaction. The sorption capacity calculated for oil, water, oil-water emulsion was 183%, 160%, 225% respectively for raw bamboo fibers whereas sorption capacity shown by Fiber sheet for oil, water, oil water emulsion was 320%, 660%, 600% respectively. So, in this framework, Sorbents made from lignocellulosic fiber assembly have great potential than synthetic sorbents. Further in context to its disposal as disposal is the major issue after use of sorbent then lignocellulosic fiber sheet can be used as fuel source due to its high calorific value. So, this lignocellulosic fiber sheet may serve as a useful sorbent to control oil-spillage.

KEYWORDS: Calorific value, Lignocellulosic fibers, Oil-Spill, SEM-EDS.

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Construction of biaryl unnatural amino acid derivatives *via* the Pd(II)catalyzed arylation of unactivated sp³ C-H bonds

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Abstract: We report the diastereoselective synthesis of racemic and enantiopure biaryl unnatural amino acid derivatives via the palladium-catalyzed directing group-aided stereoselective sp³C-H activation and arylation of amino acid derivatives with iodobiaryls. The construction of biaryl motif installed (DL-), L- and D-amino acid derivatives including norvaline, phenylalanine, leucine, norleucine and 2-aminooctanoic acid with *anti-*stereochemistry was accomplished. The synthesis of alanine derivatives with two biaryl motifs and aminoalkanoic acids with biaryl motifs was also shown. Removal of the directing group, deprotection of the phthalimide moiety and the preparation of biaryl amino acid derivatives containing free amino- and carboxylate groups were shown.

diastereoselective construction of biaryl unnatural amino acid motifs



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Isolation and Structural Characterization of Regioisomers of Terrylene Diimides

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Abstract: Terrylene diimide (TDI) is a member of a family of polycyclic aromatic hydrocarbons, collectively known as rylene diimides (RDIs). TDI gains immense attention due to its outstanding photo chemical stability and photophysical properties.¹ The optical and electrochemical signatures of TDI can be modulated by suitable functionalization at the bay positions.² Halogenation is the most preferred way to achieve such functionalization. The currently accessible tetrabrominated and mono brominated TDIs have partially served the purpose.³ However there is a need to find the missing link between these two precursors, which can tune the electronic properties of TDIs and make them useful for modern applications as well. Other bromo derivatives for this purpose are not known due to the synthetic and purification challenges. The expected formation of regioisomers further complicate the case.



Herein, we present our successful synthesis and structural characterization of three hitherto unknown brominated terrylene diimides. Interestingly, two of the regioisomers of dibromo-TDIs along with tribromo-TDI formed in a single-pot reaction have been isolated and structurally characterized. Distinctly, 1,14-dibromo TDI could be obtained in a single step, which is not possible with other shorter RDIs.⁴ The utility of these precursors have been demonstrated by anchoring ethynyl ferrocene side-arms. The two regioisomers of dibrominated TDI can serve as decent precursors and can open up new avenues for further functionalization at desired positions.

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Annulation of *ortho*-and *para*-Quinone Methides with 2-Benzylidine Dithiolanes: Synthesis of spirochroman dithiolanes

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Abstract:

Chromanes¹ an important heterocyclic scaffold is prevalent in numerous natural products and pharmaceuticals exhibiting various biological properties such as antifungal, antiviral, antioxidant, cytotoxic and anti-inflammatory². Similarly, 3, 4-dihydrocoumarin, a unique structural framework of various bioactive molecules and compounds of medicinal importance are known to displayantitumor, anti-estrogen and anti-osteoporotic properties. Considering, the importance of chromane and its derivatives, an expeditious, transition-metal-free acid approach towards the construction of spiro-chroman motif is described. *p*-Quinone methides and *insitu* generated *o*-quinone methides underwent a PTSA catalyzed annulation with 2-benzylidene dithiolanes to afford spiro-chroman dithiolanes in high yields. The synthetic versatility of the dithiolane motif³ was demonstrated by converting the adduct to coumarin, 3,4-dihydrocoumarin and chromaness derivatives.

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Spectral Studies on the Dimerisation of Methylene Blue in Water-Dioxane Mixed Solvent System

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Abstract:

Methylene blue (MB), a thiazine dye is biological relevant to treat methemoglobinemia. Spectral properties of MB depends on solvent polarity. The present work endeavours to investigate the dimerisation of MB in water (WA)-dioxane (DO) mixed solvent system, where the polarity was varied by varying the WA-DO ratio. Absorption maxima of MB pass through a maximum with increasing content of WA. Although being less polar, dimerisation constant (k_d) of MB was higher in DO than in WA. A non-systematic variation of k_d value with solvent composition was observed. Results were correlated with the excess molar volume of the binary mixed solvent system.

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Facile Synthesis of Nitroamino-1,3,4-oxadiazole with Azo Linkage: a new family of high-performance energetic materials

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Abstract:

For the first time, the compound 5,5'-dinitramino-3,3'-azo-1,3,4-oxadiazole was made from 5,5'-diamino-3,3'-azo-1,3,4-oxadiazole in a single step using commercially available inexpensive starting material and its energetic salts were synthesized in quantitative yields. All the newly synthesized compounds were fully characterized by ¹H, ¹³C, IR, HRMS, and hydroxyl ammonia and aminoguanidine salts were further characterized by ¹⁵N spectroscopy. 5,5'-dinitramino-3,3'-azo-1.3.4-Furthermore, 5,5'-diamino-3,3'-azo-1,3,4-oxadiazole, oxadiazole, and its TATOT salt were confirmed by X-Ray crystallographic studies. Nitramino substituted azo bridged compound shows the density of 1.97 g cm⁻³ at 298 K, and high positive heats of formation (405.7 kJ/mol), high detonation velocity, pressure (9358 m s⁻¹ and 39.1 GPa), good thermal stability (183 °C) and acceptable impact and friction sensitivity (6 J and 160 N). All the newly derived energetic salts show excellent density in the range of 1.73 to 2.04 g cm⁻³, detonation velocity and pressure (7389 to 9719 m s⁻¹ and 19.4 to 41.5 GPa) and good impact, friction sensitivity (10 to 20 J and 240 to 288 N), respectively. These properties are superior to those of benchmark explosives HMX ($d= 1.91 \text{ g cm}^{-3}$, VOD= 9320 m s⁻¹, DP= 39.5 GPa, IS= 7.4 J), ε -CL-20 (d= 2.04 g cm⁻³, VOD= 9455 ms⁻¹, DP= 46.7 GPa, IS= 4 J) and ICM-101 (d= 1.99 g cm^{-3} , VOD= 9481 m s^{-1} , DP= 41.9 GPa, IS= 5 J). Neutral nitramino substituted azo bridged compound was recognized as a potential less sensitive energetic material with planar structure and high symmetry in the crystal lattice. The advantages of reaction efficiency, availability of commercial reagents, and attractive energetic properties indicate the scope of synthesized compounds as secondary energetic materials in civil and military applications.

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Observation of Helical Self-assembly in Cyclic Triphosphazene-based Columnar Liquid Crystals bearing Chiral Mesogenic Units

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Abstract:

Nowadays, intensive research has focused on the design and synthesis of function-integrated smart materials resulting from the spontaneous self-assembly of the predestined functional molecules. Working in this direction, we have synthesized a new series of non-conventional, chiral columnar liquid crystals (Col LCs) where the cyclotriphosphazene core is surrounded by cholesterol-based Schiff base dimeric units. Cholesterol, which is covalently bound to the tworing Schiff base core via a flexible spacer of varying length and parity. The investigations using a number of complementary techniques clearly reveal the influence of the length of the spacer, rather than the parity, on the symmetries of 2D lattices resulting from the intrinsic columnar assemblies of the synthesized compounds. The different columnar assemblies were further confirmed through detailed electron density mapping and small-angle/wide-angle X-ray scattering (SAXS/WAXS) studies. The handedness (helicity) of the Col LCs has been confirmed by temperature-dependent chiroptical measurements where the intensity of peak in circular dichroism (CD) spectra increases with a decrease in temperature. The helicity of the mesophases was also supported by transmission electron microscopy (TEM) technique. Notably, these novel materials exhibit fluorescent "turn-on" characteristics in their solid (as synthesized) state upon exposure to hydrochloric acid (HCl) that can be visualized by naked eye instantly where the color change occurs with a low detection limit of $5.6 \,\mu$ M.

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VOLUMETRIC AND COMPRESSIBILITY STUDIES OF BINARY MIXTURES OF 2-(2-ETHOXYETHOXY)ETHANOL WITH METHYL ACRYLATE, ETHYL ACRYLATE, AND BUTYL ACRYLATE

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Volumetric and compressibility studies were investigated on the basis of measured density and speed of sound for the binary mixtures of 2-(2-Ethoxyethoxy)ethanol (carbitol) with acrylic esters (methyl acrylate (MA), ethyl acrylate (EA) and butyl acrylate (BA)) in the temperature range (288.15K- 318.15K) over the entire composition range at pressure P = 101kPa. With the help of experimentally obtained density and speed of sound data, derived parameters like molar volume (V_m^E) , isentropic compressibility(κ_s), excess excess isentropic compressibility(κ_s^E), etc. were calculated^{1,2}. On the basis of these parameters the nature and type of molecular interactions present amid the different components in the liquid mixtures were interpreted. All excess properties are negative at all temperatures for all the mixtures suggesting the compactness of binary mixture except the positive V_m^E values for some concentrations of BA mixtures. Deviation from ideality increases with rising temperature for both excess molar volume and excess isentropic compressibility

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Phosphine as a potential biosignature on Venus: An astrochemical perspective

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Abstract:

Just 3-mins after the Big Bang, chemistry came into play with the formation of the primordial nuclei, the first atoms of H and He, followed by the formation of the heavier elements (e.g. Li, Be) in the core of the stars. Given sufficient time and the frigid space conditions, the atoms formed molecules that grew complex enough to form celestial objects and complex living systems. This gave rise to a highly interdisciplinary field named 'astrochemistry' that endeavours to detect the molecules in space and study their mechanism of formation and breakdown. To date, scientists have detected more than 250 molecules in space. Understanding these molecules could help us trace the physical conditions in different regions of space and may eventually help us find an answer to the origin of life on our planet. One of the recent works done in this regard is the detection of phosphine (PH₃), on the cloud deck of Venus using astrochemical methods. There are no signs of PH₃ on the other terrestrial planet, Mars. On the other hand, PH₃ has been detected on both our gas giants, Jupiter and Saturn. Ice giants Uranus and Neptune show no indications of PH₃ whatsoever. The key difference in abundances of PH₃ in gas giants and ice giants is the enhanced shielding of the PH₃ from photolysis occurring on Jupiter and Saturn because of the existence of NH₃ and cloud particles in the upper troposphere. However, the detection of PH₃ on the Venusian cloud deck suffers from theoretical ambiguity since there are no known abiotic mechanisms in Venus producing it. Additionally, the study of the presence of PH₃ on Venus can either help us discover a novel abiotic mechanism producing it or help us get a better understanding of the chemical emergence of life. This review thus aims to demystify the debate on the presence of PH₃ (a possible biosignature) in the Venusian atmosphere using data from telescopic probes and employing spectroscopic methods.

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Spectroscopic characterization of a Mn(III)-O-Ce(IV) species: Its relevance to Photo System II

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Abstract:

High-valent manganese oxo species have been entreated as key intermediates in most enzymatic systems, particularly water oxidation by the oxygen-evolving complex (OEC) of photosystem II (PS-II). In the OEC, the Ca^{2+} ion acts as Lewis acid that plays a crucial role in the O-O bond formation step. However, the essential role of the calcium ion has yet to be clarified. A large number of artificial model compounds have been developed in the last two decades to understand the structural and mechanistic aspects of PS-II. Cerium(IV) ammonium nitrate (CAN) is a chemical oxidant that has been frequently used in artificial water oxidation reactions. In addition, several reports emerged recently where CAN acts as an oxidant and Lewis acid. In this work we reported the reaction of $[(BnTPEN)Mn(II)(OCIO_3)]^+$, (1) (BnTPEN = N1-benzyl-N1,N2,N2-tris(pyridine-2-ylmethyl)ethane-1,2-diamine) with 4 eq. aqueous ceric ammonium nitrate generates a pristine species $[(BnTPEN)Mn(III)-O-Ce(IV)(NO_3)_3]^+$ (2), which is a masked Mn(IV) species. UV-VIS absorption, EPR, resonance Raman spectroscopies, and ESI-MS have been used to characterize the newly formed intermediate. Also, species (2) can do oxygen atom transfer and hydrogen atom transfer reactions.

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The Effect of Redox Inactive Metal Ion–Nickel(III) Interaction on the Redox Properties and Proton–Coupled Electron Transfer Reactivity

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Abstract:

High-valent nickel species are frequently invoked as key intermediates in the catalytic cycle of different enzymatic systems like [NiFe]-hydrogenase, and Ni superoxide dismutase (NiSOD).¹ Also, the coordination of Lewis acid (LA) at the secondary coordination sphere of the redoxactive cofactor has an enormous effect on the reactivity.² In this regard, a mononuclear and nickel(III) complexes of a bis-amidate-bis-alkoxide nickel(II) ligand. $(NMe_4)_2[Ni^{II}(HMPAB)]$ (1) and $(NMe_4)[Ni^{III}(HMPAB)]$ (2), has been isolated and characterized respectively. The reaction of redox-inactive metal ions ($M^{n+} = Ca^{2+}, Mg^{2+}, Zn^{2+},$ Y^{3+} , and Sc^{3+}) with 2 resulted in 2-Mⁿ⁺ adducts, which was assessed by an array of spectroscopic techniques. Further, the reactivity studies of 2 and 2-Mⁿ⁺ with different 4-X-2,6di-tert-butylphenol (4-X-DTBP) and other phenol derivatives were performed and a concerted proton-electron transfer (CPET) mechanism was observed based on in-depth kinetic analysis. The k_2 values of 2-Mⁿ⁺ species with 4–OMe-2,6–DTBP increases with increasing the Lewis acidity of redox-inactive metal ions. However, the obtained k_2 values for 2-Mⁿ⁺ species are much lower compared to the k_2 value for **2**.



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Modulating reactivity of isatoic anhydrides between lysine and cysteine using chemical handles

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Controlled enzymatic functions in cells are the drivers of cells' health maintenance and survival. A shift in the concentration of enzymes or activity usually results in phenotypic changes and leads to disease phenotypes. A majority of the enzymes contain nucleophilic amino acid residues in their catalytic binding pockets and nucleophilic moieties are attractive target sites for covalent therapeutic discovery. To that end, several promising therapeutics possessing electrophilic warheads to target cysteine, serine, lysine and tyrosine amino acid residues have been successfully developed. However, the off-target effects associated with the non-selective reaction of electrophilic molecules have been a roadblock for the development of selective covalent therapeutics. The unmet need in this field is to understand the reactivity profiles of electrophilic warheads with nucleophilic amino acids and introducing selective reactivity in them. Isatoic anhydride (IA) is a potential electrophile with a capacity to react with nucleophilic amino acids with the release of thermodynamically more stable carbon dioxide during its modification. Here we show that incorporating appropriate chemical handles in the IA scaffold tips the selectivity balance between thiol (cysteine) or amine (lysine) nucleophiles in vitro and with recombinant proteins. Further, we evaluated the molecules' propensity to modify cellular proteome using activity-based protein profiling experiments with HEK cell lysate. This is a promising start for modulating electrophiles to imprint target selectivity at the stage of covalent modification

Figure 1. Profiling the reactivity of IA-derivatives with N-acetylcysteine and lysine monitored for 1 h.



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High temperature selectivity and chemical fixation of CO₂ by urea-engineered dual-functionalized metal-organic framework with mechanistic validation

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Abstract:

Post- and pre-combustion CO_2 capture and separation by porous materials are of great importance for cutting greenhouse gas emissions. Unique structural attributes of metal-organic frameworks (MOFs), including the ease to rationally functionalize and fine-tune their pore environment, paved the way for selective CO_2 capture, separation, and conversion in these class of crystalline porous solids. Based on the strategic design principle, urea grafted Cd(II)-based MOF, namely **CSMCRI-12** (**CSMCRI** = Central Salt & Marine Chemicals Research



Institute), has been derived from the self-assembly of a C_3 symmetric tripodal carboxylate ligand and a urea moiety embedded di-pyridyl linker (*L*). Activated framework (**12a**) exhibits unidirectional porous channels, with pore walls decorated by unsaturated metal sites and primary urea moieties. Gas adsorption studies revealed exceptionally high selectivity of CO₂ over N₂ and CH₄ as estimated by the ideal adsorbed solution theory (IAST theory). Interestingly, CO₂ selectivity notably increases from 237 to 387 with a temperature increase from 273 to 313 K, validating real-

time potential of this system in CO_2 capture under elevated temperature. Furthermore, **12a** acts as a bifunctional heterogeneous catalyst towards solvent-free chemical fixation of CO_2 to cyclic carbonates under relatively mild reaction condition with a wide range of substrate scope. To shade light on the mechanistic routes, configurational bias Monte Carlo molecular simulation comprehensively demonstrates that accessibility of nitrogen sites of **12a** plays crucial role in higher temperatures CO_2 selectivity, and further identifies Lewis acidic (open metal) site as potential epoxide binding sites during cycloaddition reaction.

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Metal-Free Selectfluor-Mediated C3-Alkoxylation, Sulfenylation and Amination of Quinoxalin-2(1*H*)-ones

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Abstract:

Reactions involving formation of C-O, C-N and C-S bonds are the most fundamental reactions in organic chemistry. In recent years, direct introduction of a new functionality *via* cross-dehydrogenative coupling (CDC) have become a highly attractive strategy with high atom economy for the construction of such bonds.¹ Quinoxalin-2(1*H*)-ones on the other hand represent a privileged class of *N*-heteroaromatics that have been extensively utilized in medicinal chemistry, drug discovery and material chemistry.² Considering their importance in various fields, there is continuing interest in the synthesis and functionalization of quinoxalin-2(1*H*)-ones.³ Herein, we have described a highly efficient selectfluor mediated direct oxidative coupling of quinoxalin-2(1*H*)-ones with alcohols, thiols and amines (Scheme 1). The developed method provides a wide range of C3-alkoxynated, sulfenylated and aminated quinoxalin-2(1*H*)-ones in good to excellent (73-92%) yields. Broad substrate scope including bioactive molecules, mild reaction conditions, readily available coupling partners, scalability are the highlighting features of the developed protocol. Details of the reaction conditions, mechanism and substrate scope will be presented.



Scheme 1: Regioselective C-3 alkoxylation, sulfenylation and amination of quinoxalin-2(1H)-ones

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Synthesis of Chromene and Chromenone Derivatives from *p*-Quinone Methides (*p*-QMs)

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Abstract:

Oxygen-containing heterocycles such as chromones, and chromenes are very important scafold, often found in a variety of natural products and biologically active molecules having pharmacological activities.¹ While working in the area of *para*-quinone methide chemistry,² we have developed a Brønsted-acid mediated one-pot approach for the synthesis of oxygen-containing heterocycles. This methodology provides an easy and straight-forward access to a wide range of chromenone and chromene derivatives in moderate to good yields.³



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Hyperbranched polyaminoamide based dual stimuli responsive nanogel: A nonconventional donor fluorophore for the ratiometric temperature and pH sensing

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Abstract:

Herein, a noncytotoxic ratiometric fluorescent nano-sensor (HPAMAM-Dox) was synthesized via covalently linking Doxorubicin (FRET acceptor) with a temperature and pH-responsive hyperbranched polyaminoamide (HPAMAM) nanogel (a nonconventional stimuli-responsive fluorophore acted as a FRET donor). HPAMAM-Dox displayed ultrahigh sensitivities even at a very low concentration (5 μ g/ ml, a safe concentration at which the nanogels are cytocompatible) in the physiological temperature range and at a pH below 5.2.



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Pyrazine Based Type-I Sensitizing Assemblies for Photoreduction of Cu(II) in 'One-Pot Three-Component' CuAAC reaction

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Abstract:

Copper-catalyzed azide-alkyne cycloaddition (CuAAC) reaction is one of the simple and straightforward methods to prepare synthetically important 1,2,3-triazoles with high specificity.¹ The vulnerability of catalytically active Cu(I) ion to aerial oxidation and their poor solubility in aqueous media limited the direct use of Cu(I) salts and pave the path to use Cu(II) based salts in combination with reducing agents or dyes which *in situ* reduces the Cu(II) to Cu(I). Herein, we have developed photosensitizing assemblies of pyrazine derivative (**PDA**) which forms fluorescent *J*-aggregates in mixed aqueous media [water:THF (7:3)] and exhibit high photostability, 'lighted' excited state, balanced redox potential, high transportation potential and activate oxygen *via* type-I pathway only.² These **PDA** assemblies exhibit sufficient potential to reduce Cu(II) ions to Cu(I) ions and catalyse the 'one-pot three-component' CuAAC reaction under aerial conditions *via in situ* reduction of Cu(II) ions to Cu(I) ions. This protocol offers advantages of being applicable to gram-scale and recyclability





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Domino C-C/C-X Bond Forming Transformations of gem-Dibromoalkenes: An Access to Functionalized Benzofulvenes

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Abstract:

Indenes and benzofulvenes are often found as structural motifs in several biologically important molecules and organic functional materials.¹ These fragments are considered to be effective bioisosteres of indole in drug discovery. Several transition-metal based synthetic approaches have been reported so far for the synthesis of benzofulvenes.²⁻³ We herein demonstrate an efficient one-pot Pd-catalyzed domino C–C/C-X bond forming reaction of dibromoalkenes to access various functionalized benzofulvenes. A simple intramolecular Heck coupling has been demonstrated to give substituted bromobenzofulvenes. The reaction was further extended to domino Heck/Suzuki sp²-sp³ coupling and other C-C/C-H bond formation reactions.



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Designing cellulose based smart materials for green energy related technology and biotechnological application

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Abstract:

In recent years, energy consumption by building sector is gradually increasing for maintaining the pleasant atmosphere inside the building. Due to high energy consumption in the building sector and subsequent environmental issue, environment-friendly and cost-effective thermally insulating materials are on high demand to improve the energy efficiency of the buildings. Current commercially available thermal insulating material (polystyrene) always put a challenge due to their environment unfriendly and poor insulating performance. To this end, biomass derived aerogels are receiving more interest as renewable and sustainable insulating materials. In this work, we have developed a facile strategy of synthesizing cellulose nanofibers from biomass derived wood-pulp as a cost-effective starting material by TEMPO-oxidation and incorporated iron oxide nanoparticles to synthesize nanohybrid. Interestingly, after incorporation of iron oxide nanoparticles low thermal conductivity was achieved which was coupled with enhanced mechanical strength to 4.2 MPa and the thermal stability was found to be enhanced. Hence, this nanohybrid can overcome the limitations of the commercially available thermal insulating materials in terms of their stability. Most importantly, the nanohybrid demonstrated very low thermal conductivity as low as 0.024 W/mK, indicating better insulating potential of these nanohybrids as compared to other conventional insulating materials. So, it can be used as thermal insulator to make energy efficient smart building in the future. Furthermore, the in-situ fabrication potential of these natural polymer will be highlighted towards synthesizing cellulose metal nanoparticles hybrids, which can be further explored for photocatalysis as well as photodynamic therapy for cancer treatment.

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Emergence of Long Afterglow and Room Temperature Phosphorescence Emission from Ultra Small Sulfur Dots

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Abstract:

Sulfur dots (S-dots) are one of the most recently developed non-metallic luminescent nanomaterials which possess several advantages over traditional inorganic Quantum dots (QDs). Here, we have synthesized highly luminescent ultra-small S-dots by a facile single-step mechanical grinding assisted technique without consuming additional energy and harsh chemical treatment. The morphological features are characterized by high-resolution transmission electron microscopy (HR-TEM), which is further correlated with elemental analysis by X-ray photoelectron spectroscopy (XPS) and Fourier transform infra-red (FTIR) spectroscopy. Results suggest the formation of highly homogenous ultra small S-dots with specific functional groups on the surface. The photo physical properties of as-synthesized S-dots characterized by steady-state and time-resolved the are photoluminescence (PL) spectroscopy. Furthermore, a temperature-dependent PL study has been carried out and it is correlated with the structural features of S-dots. Finally, these ultra small S-dots show efficient room-temperature phosphorescence and long-term afterglow (up to 5 sec) while embedded in the B₂O₃ and biuret matrix. The mechanistic insight behind the phosphorescence emission, kinetics of phosphorescence, and further their correlation with elemental/structural features have been investigated in depth. Finally, a reversible transformation of room temperature phosphorescence to thermally activated delayed fluorescence has been explored by a detailed temperature-dependent study. Furthermore, we have also presented the applicability of these smart materials in anti-counterfeiting applications as well as security devices.

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Cobalt anti-MXenes as Promising Anode Materials for Sodium-ion Batteries Subhadeep Banerjee,^{1,2} Sharma S. R. K. C. Yamijala^{1,2,3,4,*}

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Abstract:

The current electric vehicle market is entirely dominated by lithium-ion batteries (LIBs). However, due to the limited and unequal distribution of LIB raw materials on earth, there is a continuous effort to design alternate storage devices. Among the alternatives to LIBs, sodiumion batteries (NIBs) are at the forefront because sodium resources are ubiquitous worldwide and virtually inexhaustible.¹ However, one of the major drawbacks of the NIBs is their low specific charge capacity. Since the specific charge capacity of a cell can be improved by increasing the specific charge capacity of the anode material, there is a constant effort to find suitable anode materials. Recent studies suggested that cobalt-boride (CoB) anti-MXene material (a newly discovered two-dimensional material) can yield superior specific charge capacities for LIBs than traditional graphite-based anodes.² Inspired by these findings, in this work, we considered six cobalt-based anti-MXene materials (Co-anti-MXenes), namely, CoAs, CoB, CoP, CoS, CoSe, and CoSi, and examined their competency as anode materials for NIBs. Our findings suggest that Co-anti-MXenes possess superior specific charge capacities (~ 390-590 mAh/g) than many well-studied anode materials like MoS₂ (146 mAh/g), Cr₂C (276 mAh/g), expanded graphite (284 mAh/g), etc. Moreover, their greater affinity (-0.55 to -1.16 eV) to Na atoms, along with reasonably small diffusion energy barriers (0.32 to 0.59 eV) and low average sodiation voltages (0.2 to 0.64 V), suggest that these Co-anti-MXenes can serve as excellent anode materials for NIBs. The details of CoX's performance as anode materials and the mechanism will be explained during the presentation.

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Physicochemical Studies on Gemcitabine Loaded Nanostructured Lipid Carriers

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Abstract:

Nanostructured lipid carriers (NLC) are considered as potential drug delivery system. Gemcitabine is a potent anticancer drug towards the treatment of testicular cancer, breast cancer, ovarian cancer, non-small cell lung cancer, pancreatic cancer, and bladder cancer. Four different NLC formulations were prepared by hot homogenization and ultrasonic dispersion technique using a mixture of soy lecithin, tripalmitin and stearic acid (2:2:1; M/M/M) with four different stabilizers, *viz.*, Tween-60, Poloxamer-188, polyvinyl alcohol and polyethylene glycol. Bare and drug-loaded formulations were characterized by dynamic light scattering, FTIR spectroscopy, X-Ray diffraction, transmission electron microscopy and atomic force microscopic studies. Comparative studies on the effect of stabilizers were also investigated. Location of the drug was assessed by UV-VIS spectroscopic method. Further investigations will be made to explore activities of the formulations against breast cancer cell-line.

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Abstract:

Complete metal-free P-functionalized carbon nanomaterials are synthesized from a single molecular precursor, phytic acid, for photocatalytic solar H2 production and simultaneous organic transformation of 4-methyl benzyl alcohol to 4-methyl benzaldehyde by managing the complete redox cycle. It is observed that by increasing the carbonization time, P-functionalized amorphous carbon dots convert to the highly defined 2D sheet-like nanostructure with optimum P-functionality, resulting in efficient light absorption, charge separation, and improved active sites for photocatalysis. Finally, the highly defined sheet-like structure converts to a more defected aggregated form, resulting in the depletion of photocatalytic efficiency. The structural and elemental features are further correlated with the ongoing photophysics by means of steady-state and time-resolved fluorescence spectroscopy. Transient photocurrent responses and Mott-Schottky plots directly support the optimization of P-functionalized carbon nanostructure for efficient photocatalysis. Finally, the detailed computational studies are carried out to unveil the charge separation mechanism and the crucial role of P-functionalities as active sites for better charge accumulation as well as H2O adsorption on the surface. Overall, the in-depth structure-property correlation and critical optimization of the heteroatom functionalized carbon nonmaterials will open up new possibilities for further development of metal-free photocatalysts for solar-energy conversion devices.

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Synthesis, Structure and Heterogeneous Catalysis of Two Structurally Diverse Coordination Polymer based on 5-Nitroisophthalate

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Abstract:

The concentration of carbon dioxide (CO₂) in the atmosphere is increasing to an extraordinary level, which predominates global warming, extreme weather, and species extinction.¹⁻² Smart material for selective capture and conversion of CO₂ in view of environmental protection and energy sustainability is the need of the hour.³ Two new coordination polymers [Ni(4-ABPT)(NIPA)H₂O)], **Compound-1** and [Zn₂(ATRZ)₂(NIPA)], **Compound-2**, (4-ABPT = 3,5-di(pyridine-4-yl)-4H-1,2,4-triazol-4-amine, H₂NIPA = 5-nitroisophthalic acid, ATRZ = 3-amino-1,2,4-triazole), have been synthesized based on mixed ligand strategy. **Compound-1** possesses 4,4-net topology with Schläfli symbol 4⁴.6² whereas **Compound-2** exhibits 3,3-net (*fes*) topology with Schläfli symbol 4.8². The conversion of **Compound-1** and **Compound-2** catalyses one pot CO₂ cycloaddition are 92% and 21% respectively. This structural diversity could contribute their applications in heterogeneous catalysis.



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Highly Stretchable, Self-adhesive and Self-healing Chitosan based Double Network Hydrogel for Wearable Strain Sensor

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Abstract:

The advent of hydrogel-based strain sensors has attracted immense research interest in artificial intelligence, wearable devices, soft robotics and health-monitoring systems.¹⁻³ However, integrating the synergistic characteristics such as good mechanical properties, self-healing capability, self-adhesiveness, and high strain sensitivity during the fabrication of hydrogelbased strain sensors is still a challenge. In this work, we have fabricated double network (DN) hydrogels (CTA-X), consisting of chitosan (CS), tetraethylene glycol (TEG), and polyacrylic acid (PAA) using three different modes of cross-linking. The PAA network is covalently crosslinked and the CS network is covalently as well as ionically cross-linked. These two networks are further interlocked by physical entanglement and hydrogen bond interactions. Here, the hybrid networks are fabricated by varying the cross-linker terepthaldehyde (CTA-1), sodium hydroxide (CTA-2) and sodium chloride (CTA-3). The obtained three hydrogels show unique behaviour in mechanical strength, conductivity and self-healing capability. The rheology study shows excellent macroscopic self-healing behaviour up to 6-7 cycles between the oscillation strain of 1 and 1500%. Moreover, the hydrogels exhibit self-adhesive behaviour on various materials, including metal, plastic, polytetrafluoroethylene, wood, glass, aluminium, rubber and skin. The antibacterial property, originating from chitosan, made the hydrogels non-toxic to skin. Further, the DN hydrogel CTA-2 shows self-adhesive nature towards metal, glass and skin, in presence of water. Notably, the hydrogels can be applied as soft human-motion sensors for real-time and accurate detection of small human activities like joint motion. Simultaneously, a proper investigation was carried out to compare the mechanical properties, flexibility, self-healing, self-adhesiveness, and conductivity of the CTA-x DN hydrogels. This work provides a new prospect for the design of biocompatible chitosan-based hydrogels with stretchable, self-adhesive, self-healing, and strain-sensitive properties for potential applications in wearable electronic sensors and healthcare monitoring.

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Access to a new class of dihydro-1,3,5-triazine-2,4-dione bicyclic compounds *via* fragmentation followed by simultaneous ring expansion-contraction of bicyclic urazoles

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Abstract:

This investigation reveals a hitherto unknown class of dihydro 1,3,5-triazine-2,4-dione bicyclic compounds with diversity in ring sizes. A variety of bicyclic urazoles were prepared and treated with base to form an enlarged imine intermediate which rapidly underwent a simultaneous ring expansion-contraction, resulting in N-C-linked bicyclic compounds of different ring sizes. This atom economy approach transformed symmetrical urazole derivatives into unsymmetric heterocycle derivatives with asymmetric (racemic) centres with a bridgehead nitrogen. Furthermore, this efficient methodology allows for a range of substrates to be used in the creation of unique bicyclic heterocycles, making it appealing as a source of complex heterocycles that might be used as bioactive natural product-like scaffolds.



- ✤ Full atom economy
- ✤ A wide scope of substituents R is tolerated
- Access to diverse fused dihydro 1,3,5triazine-2,4-diones
- Useful in bioactive natural product-like scaffolds synthesis

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Folding of aromatic polyamides into a rare intrachain β-sheet type structure and further reinforcement of secondary structure through host-guest interactions

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Abstract:

Synthetic macromolecules have been successfully folded into various types of secondary structures during the last two decades by following biological principles. Since the pioneering work by Hamilton and co-workers¹, a large number of aromatic oligoamides have been designed and synthesized for folding studies. Among various folded structures, helix, planner-sheet, and zigzag structures are the most common secondary structures^{2,3,4}. Despite significant advancement, owing to their intrinsic aggregation tendency, mimicking the β -sheet structure is relatively rare⁵.

In my presentation, I will demonstrate the design and synthesis of a pair of periodically-grafted clickable aromatic polyamides and their propensity to fold into a β -sheet-like structure that have been studied experimentally and by using computational studies. Among the two polymer chains, the polymer comprises both intramolecular H-bonding as well as π -stacking motifs readily fold into a β -sheet-like secondary structure. However, the other polymer was structurally identical to the previous one except for the intramolecular H-bonding motifs, assuming random coil conformations under similar experimental conditions. In addition to demonstrating the role of H-bonding and π -stacking interactions in effecting β -sheet-like folding, the reinforcement of this secondary structure through host-guest interaction will also be demonstrated. Possible applications of these molecules as through-space electron-conducting materials and organocatalysis can be envisaged.

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Numerical simulation of absorption and emission spectra of diatomic molecules: Correlating Stokes Shift with Huang-Rhys parameter

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Abstract:

The harmonic oscillator model is usually adopted to study vibrational dynamics or obtain the optical spectra of molecular systems in the condensed/gas phase. Earlier studies show that the mirror image symmetry between the absorption and emission spectra exists for the displaced harmonic-oscillator model, which does not depend on the nuclear coordinate of the excited electronic state [1]. Here, in this theoretical study, we show for a diatomic model system, in the realm of Born-Oppenheimer (BO) approximation, the first asymmetry in the spectra occurs in the case of a dual-mode displaced harmonic oscillator model where the ground and excited electronic states are labeled with two different vibrational modes. The simulation at finite temperature is also performed, resulting in significant overlap and broadening of the spectra. We invoke the anharmonicity in the system as a Morse oscillator as the harmonic model approximation is no longer sufficient to inspect realistic molecules [2]. Using this model, more congested spectra have been observed, and as the temperature increases, the spectra become more structured as more vibrationally hot levels participate in the vibronic transitions. The spectral features have also been investigated with the relative displacement of the equilibrium ground and excited potential energy surfaces (PESs), introducing the Huang-Rhys (HR) parameter [3], which describes the microscopic details of the vibrational coupling manifested in the steady-state spectra. As the maxima of absorption and emission spectra shift while considering the finite temperature and displacement of PESs, it is very convenient to study the Stokes shift. For the case of the bound system, Stokes shift as a function of HR parameter shows parabolic feature which is very trivial. As soon as the anharmonicity is introduced, the Stokes shift significantly deviates from this regular feature, leading to a nontrivial dependency on the temperature [4].

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Koneramine-Based Highly Sensitive and Selective Fluorescent "*Turn-on*" Sensor for Cd(II) and Zn(II) and Study of Antibacterial Activities

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Abstract:

A new turn-on fluorescent probe based on a modified koneramine ligand was designed, and the photophysical properties, antibacterial activity, and cytotoxicity were studied in detail. A series of complexes of Cu^{2+} , Zn^{2+} , and Cd^{2+} were synthesized and characterized by NMR spectroscopy, ESI-MS, and SCXRD. This new chemosensor shows selective enhancement in fluorescence in the presence of Cd^{2+} and Zn^{2+} due to inhibition of photo-induced electron transfer(PET) from binding sites to the excited state of anthracene. Importantly, this probe shows high selectivity towards Cd^{2+} and Zn^{2+} in the presence of other biologically relevant metal ions. The antibacterial effects of the cadmium complex have also been examined *in vitro* against standard gram-positive bacterial strain, *Staphylococcus aureus* ATCC 29213. The results show significantly better activity for Cd(II) complex as compared to the free ligand as well as Zn(II) and Cu(II) complexes.

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Blue LED induced eco-friendly one pot synthesis of 1, 4-oxazepane and benzoxazepine from aryl acetates

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Abstract:

Heterocyclic compounds are well known because of their abundance in numerous natural products¹ and synthetic pharmaceuticals. Due to their diverse biological properties, synthesis of medium-sized rings using new protocols are always interesting.³ Seven-membered rings with two heteroatoms are known to have various biological activities. Among them, 1,4-oxazepane and 1,4-benzoxazepine continue to play a pivotal role in the development of new pharmaceuticals². Herein we have reported a blue LED induced one pot synthesis of 1, 4-oxazepanes and benzoxazepines in ethyl acetate at an ambient temperature with aryl acetates and N-methyl morpholine and benzo-morpholines in moderate to excellent yield. The strategy demonstrated an expedient, practical and metal free photolytic one pot ring expansion of oxonium ylides generated from N-methyl morpholine and benzo-morpholines by reaction with aryl ester carbenes furnished in situ from aryl esters, p-ABSA and blue LED.⁴ This strategy demonstrated an environmentally safe procedure for the synthesis of aforementioned heterocycles by eliminating the isolation and storage of unstable and to some extent unsafe diazoester compounds and by using ethyl acetate as a comparably greener organic solvent for the reaction.

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Probe The Photoluminescence and Morphological Properties of Aromatic Amino Acid Assisted Perovskite Nanocrystals

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Abstract:

The outstanding optoelectronic capabilities with high fluorescence and tunable morphology enable the lead halide perovskites to appear at the forefront of material chemistry. The functional and bidentate ligands have been proposed as a way to expand the utilization of metal halide perovskites in the modified ligand chemistry. We have implemented non-toxic aromatic amino acid as a capping ligand to produce highly fluorescent perovskite nanocrystals. The adoption of aromatic amino acids in the formation of CsPbX₃ nanocrystals allows the carboxylic and amine groups to work together with the phenyl residue, facilitating the formation of nanocrystals with high fluorescence intensity and remarkable emissive properties over the visible spectrum with long-term stability. Phenylalanine being the most hydrophobic among the implemented amino acid produces maximum PL intensity. In addition, the morphology of the nanocrystals has been tuned by controlling the halide ratio employed during the synthesis. Interestingly, a spherulite-like structure was obtained at a particular halide ratio.



Scheme 1: Synthesis and morphological tuning of lead halide perovskite nanocrystals

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All-Round Performance by a Single Molecule: Arylene-vinylene Terpyridyl Conjugates as Multifunctional Molecular Materials

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Abstract:

Design and synthesis of a single molecule that can be used for various purposes is always a demanding, appealing, and challenging. Multifunctional π -conjugated D– π –A type organic congeners emitting strong fluorescence have received much attention due to their various fascinating stimuli-responsive properties and their potential application for organic light emitting diodes, field-effect transistors, organic solid-state lasers, as well as sensing probes.^{1,2} In this direction, we have successfully designed and developed multifunctional terpyridyl based D– π –A congener offering multiple fascinating properties such as solvatochromism, vapochromism, piezofluorochromism and most importantly the ability of selective trace detection of environmentally concerned toxic metal ions, hazardous solvent vapors and explosive NACs. Various spectroscopic studies such as fluorescence titration, TCSPC, ¹H NMR titration have been carried out to understand the sensing mechanism, and the efficacy of sensing ability. In this presentation, our effort in judiciously designing the D– π –A type arylene-vinylene terpyridyl conjugates as multifunctional molecular conjugates will be discussed briefly.^{3,4}

Figure 1. Arylene-vinylene terpyridyl conjugate with multifunctional properties.



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Copper-Catalyzed hydroboration of 1,3-Diynes as a Platform for Iterative Functionalization

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Abstract:

Over the past few decades, synthetic approaches to small molecules bearing diverse functionalities have witnessed an overwhelming transformation. Targets with high structural complexity can be easily assembled using small, modular building blocks similar to a 'Lego' construction using Iterative chemistry.¹⁻³ Organoboron compounds have been in the spotlight as versatile building blocks in natural product synthesis.⁴ In this work, we present glovebox-free regioselective hydroboration of 1,3-diynes using bench stable boron source and Cu(I)/phosphine catalysis to access stable enynylboronates in a single operation. A variety of symmetrical and unsymmetrical 1,3-diynes were tolerated under these reaction conditions to produce enynylboronates in excellent yields and regioselectivities (up to >95:5). Under similar reaction conditions, one-pot dihydroboration of 1,3-diynes was also achieved to access a wide variety of bench stable dienylboronate esters in good yields and regioselectivities. Downstream transformations with enynylboronates and dienylboronates offered a range of value-added skeletons. DFT studies supported the proposed mechanism for the formation of hydroboration and dihydroboration products.



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Microwave-Assisted Vitamin C-Induced Simple Synthesis of Enamine

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Abstract:

The synthesis of enamines is an important operation in synthetic chemistry. Enamines have also served important synthetic building block to execute the 1,4-conjugate addition and annulation reaction in the synthesis of diverse heterocyclic and bioactive natural products including anti-convulsant, anti-inflammatory and antitumor agents. Enamines are synthetic equivalents of enol and enolates and are synthesized by the condensation of aldehydes or ketones with 2⁰ amines under acidic or basic condition. These are important precursors in organic synthesis because they can undergo alkylation and acylation reaction with diverse reagents with high degree of regioselectivity. Vitamin C mediated simple and high yielding protocol to synthesis of various enamines with secondary amines and ketones, is developed under microwave condition. This protocol is very convenient to accesses the enamines from cyclic amines with various carbonyl compounds in very high yield under mild reaction conditions with very short reaction time and allows the isolation of the products very easily.



SCHEME : Vitamin-C catalysed microwave induced synthesis of enamine

Key Words: Microwave, Vitamin C, Enamine.

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Highly Sensitive and Selective Sensing of Free Bilirubin Using CsPbBr₃ as a perovskite nanomaterial

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Abstract: Perovskite nanomaterial attracts researchers in this field due to its size-tunable and cost-effectiveness production of sensor and memory-based devices. Due to the quantum confinement effect, PNCs show intense fluorescence which is easily tuned by chemical composition and bandgap engineering. The electron transfer process also occurs in the natural and artificial systems which are driven by the different types of energy sources like sunlight and some other artificial system. Bright luminescence hybrid halide perovskites nanocrystals (PNCs) as a novel class of fluorophores have been broadly used in biological sensing. Herein, we synthesized highly fluorescent CsPbBr₃ PNCs through the LARP method, using oleic acid and oleyl amine as a capping ligand. Morphological and Optical properties of as-synthesized PNCs were studied using TEM, XRD, UV-Vis absorbance, and fluorescence spectroscopic analysis. Oleic acid and oleyl amine caped perovskite nanocrystal employed for sensitive and selective detection of bilirubin (BR).



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Synthesis, Spectral and Electrochemical Properties of Nonplanar N-Phenyl Fused Hexabromosubstituted Porphyrins

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Abstract:

Donor-acceptor type of dyes is widely utilized in design molecules with strong hyperpolarizabilities and depicts strong charge transfer properties between donor and acceptor moieties, leading to enhancement in the two-photon absorption and nonlinear optical (NLO) properties.¹ Highly conjugated, fused and unsymmetrical porphyrin and its analogues exhibit remarkable NLO and optical limiting properties accompanied by ultrafast dynamics.² In this work, we have synthesized N-aryl fused hexabromo-substituted metalloporphyrins; MTPP(N-Fused)Br₆ where M = Cu(II) or Ni(II) (Scheme 1). The N-aryl fused complexes were fully characterized using various spectroscopical and electrochemical techniques. Both the Soret and the Q-bands of MTPP(N-Fused)Br₆ exhibited remarkable redshifts (30-52 nm) relative to their respective precursors MTPP(NO₂)Br₆. DFT optimized geometries of CuTPP(N-Fused)Br₆ and NiTPP(N-Fused)Br₆ revealed saddled nonplanar shape conformations. The introduction of fusion on one side of the porphyrin core enhanced conjugation and planarity. These overwhelming properties helped us to get interested in exploring NLO studies. Furthermore, the NLO studies of these complexes are currently under process.



Scheme 1. Structures of Investigated Porphyrins.

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A Zr-diimide based supramolecular gel for iodine sequestration and Cr₂O₇²⁻ sensing in aqueous medium

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Abstract:

Sensing and monitoring hazardous pollutants in water and sequestering radioactive iodine are crucial due to their adverse effect on biological ecosystem. The present work describes the synthesis of a water stable zirconium-based metallogel (Zr@MG) using "heat set" method and its efficacy in environmental remediation through detection of dichromate ion in aqueous medium and sequestering iodine in both the vapour as well as in solution phases¹⁻². The assynthesized Zr@MG xerogel was found to be an excellent sensor for selective detection of $Cr_2O_7^{2-}$ (LOD = 0.12 µM). A paper strip-based detection technique was developed to detect $Cr_2O_7^{2-}$, which makes this metallogel reliable and an attractive luminescent sensor for practical use. In addition, the xerogel showed iodine adsorption capacity in vapour phase of ~ 232 wt.%. The compound showed excellent recyclability performance for $Cr_2O_7^{2-}$ sensing as well as in iodine adsorption experiments.



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Metal Free Aminoiodination/Oxyiodination of γ , δ -unsaturated N-Alkoxy Amides: Synthesis of Iminolactones and Lactams

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Abstract:

Halo amino cyclization reactions have been the subject of intensive research because of useful building blocks synthesis like lactones, lactams, pyrrolidines and piperidines in organic synthesis.^[i] The olefinic amines carry a single nitrogen nucleophile which could undergo ring closing in the presence of an electrophilic halogen source to yield N-heterocyclic products like pyrrolidines and piperidines. Whereas, the cyclization of an unactivated olefinic amide presents formidable challenges. As an amide contains both oxygen (hard) and nitrogen (soft) nucleophiles in the same system, based on the hard/soft acid-base theory (HSAB) it is difficult to selectively induce N-cyclization to give the desired lactam. Due to the higher electronegativity of oxygen compared to nitrogen in an amide system, O-cyclization favoured as the predominant pathway over N-cyclization, and consequently, there is very little or no Ncyclization. In order to overcome this problem, use of N,O-bis(trimethylsilyl) derivatives afforded N-cyclization but 2 equiv. of moisture sensitive TMSOTf are needed.^[ii] Present work focuses on direct N-cyclization of unsaturated N-alkoxy amides using the strong base and without further functionalization to obtain lactams. O-cyclization proceeded under mild conditions without use of base. We have obtained lactams up to 83% and iminolactone up to 88% isolated yield. As per our knowledge this is the first report on amino iodination and oxyiodination of N-alkoxy amides.[iii]



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Observation of "de Vries-like" properties in bent-core molecules

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Abstract:

"de Vries" liquid crystals, defined by a maximum layer shrinkage of <1% from the smectic A to C phase transition, are an integral component of ferroelectric liquid crystal (FLC) displays. Bona fide de Vries materials described in the literature are primarily perfluorinated, polysiloxane and polysilane-terminated calamitic (or rod-like) LCs [1-3]. In this work, for the first time, we report a series of newly designed achiral unsymmetrical bent-core molecules with terminal alkoxy chains exhibiting similar properties to "de Vries" LCs [4]. Detailed microscopic investigations in differently aligned (planar as well as homeotropic) cells along with small and wide-angle X-ray scattering (SAXS/WAXS) studies revealed that the materials exhibited a SmA-SmC phase sequence along with the appearance of the nematic phase at higher temperatures. Low layer shrinkage (0.19% to 0.68%) upon the SmA-SmC phase transition and temperature-dependent birefringence studies reinforce "de Vries" SmA as a probable model for this bent-core system.

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Abstract:

$$\begin{array}{c} \text{Aryl quinazolines} \\ \text{Aryl quinazol$$

Annulation reactions of ortho-substituted anilines and arylglyoxylates in the presence of K₂S₂O₈ at 80 °C under metal-free neutral conditions have been investigated, which extended a platform for the tandem synthesis of nitrogen heterocycles. While arylglyoxylic acids are known to undergo decarboxylation to form acyl radical in the presence of $K_2S_2O_8$ and used in the Minisci acylation of electron-deficient (hetero)aromatics, their reactions with electron-rich ortho-substituted anilines to form the nitrogen heterocycles have recently been studied. Depending upon the experimental conditions used in the reactions, the mechanism to the formation of heterocycles involving reactions of acyl radical or aryl iminocarboxylic acids has been postulated. Given subtle understanding of the mechanisms of annulations reactions of 2substituted anilines and arylglyoxylates in the presence of K₂S₂O₈, an extensive mechanistic investigation was undertaken. In the current study, the various mechanistic pathways including the generation of acyl, imidoyl, aminal, and N,O-hemiketal radicals have been postulated based on different possible decarboxylation modes. The protocol uses a single, inexpensive reagent K₂S₂O₈, which offers not only a transition metal- free condition, but also serves as the reagent for the key decarboxylation step. Taken together, this study complements the current development of the annulation reactions of 2-substituted anilines and arylglyoxylates in terms of synthesis and mechanistic understanding.

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Detection of 2-Naphthylamine using DNA Aptamers

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Abstract:

The increasing concentrations of numerous classes of recalcitrant, hazardous chemicals in soil and water are the by-products of industrial development. Taking awareness of the carcinogenic and erstwhile unhealthy effects of such chemicals, several environmental agencies have placed restrictions into effect on the application of such materials in manufacturing processes. One such agency is the European Chemicals Agency which implemented the REACH regulation for the control and eventual ban of highly toxic chemicals including azo dyes, PFOS, Phthalates and PAH's in textile and leather manufacturing considering the increasing proofs that these chemicals when metabolised by humans and animals led to cancers. As recently as 2022, naphthylamines have been found in sources of drinking water in industrialised nations. The absence of a point-of-source detection technique for such chemicals is of grave concern due to their bioaccumulative properties. Our work aims at developing a DNA-aptamer based sensing mechanism for the detection of 2-naphthylamine. Using SELEX (Selective Evolution of Ligands through Exponential Enrichment) we aim to identify DNA sequences which bind 2naphthylamine with high specificity and act as a detecting mechanism that can be reported using a colorimetric reporting system.



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Transcendence of Bicyclic (alkyl)(amino) Carbene (BICAAC) from a Spectator Ligand in Transition Metal-based Catalyst to an Organocatalyst: Scrutinizing Two Sides of The Same Coin

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Abstract:

BICAACs discovered by Bertrand *and co-workers* in 2017, as stable and storable singlet carbenes, have been proven to display enhanced σ -donating and π -accepting properties compared to their CAAC counterparts. Herein we have utilised Ni-BICAAC complex, $[(^{Me}BICAAC)_2NiBr_2]$ as an active catalyst for carrying out otherwise strenuous reduction *via* hydrosilylation of various functional groups such as amides, carboxylic acids and ketones to corresponding amines, primary alcohols and secondary alcohols respectively. Various control experiments evince the cleavage of a Si-H bond and *in-situ* formation of a Ni-H species which clearly demonstrates that the reaction goes through a hydride route and our catalyst acts as a hydride carrier during the course of the reaction. Owing to the favourable steric and electronic properties of the BICAAC directly as a metal-free organocatalyst for carbon-carbon coupling reaction through the direct C-H functionalisation of benzene involving *single electron transfer* pathway. Here coupling process is initiated by base-promoted HAS as K^tOBu activates BICAAC into its radical cation form thereby driving the overall reaction to the product stage.



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Photoswitchable azobenzene di- and tetracarboxylamide derivatives and their structure-property relationship

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Abstract:

Light-Responsive materials are those systems capable of altering their physicochemical properties in response to light.^[1] Light has attracted a great deal of attention due to its noninvasive nature, convenience to use, and can be directed into a specific area. Azobenzenes are one of the robust photoswitches in the photochemistry field, which upon irradiation with a suitable wavelength isomerizes from its native E(trans) state to a metastable Z(cis) state, whereas the Z-E isomerization can be achieved either thermally or photochemically. As azobenzenes can be easily functionalized, the utilization of suitable functional groups, in principle can induce supramolecular architecture through self-assembly that can be controlled by photoswitching as well as *cis*-isomeric stability.^[2] In this regard, we have designed and synthesized 18 photoresponsive molecular systems with variable connections and structural diversity in high yields through modular synthesis. We have also investigated the effect of structural modification on photoswitching characteristics and the thermal stability of the Zisomers. Apart from that, the common amide functional group in all the derivatives has been explored for their aggregation and supramolecular behavior. The changes in the morphology of supramolecular assembly/microcrystals have been studied using polarized optical microscopy (POM), and scanning electron microscopy (SEM). Apart from that, the effect of photoisomerization on their morphology has also been examined.^[3]



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TMSOTf-mediated formal [4+2] cycloaddition-retro-aza-Michael cascade of vinylogous carbamates for the synthesis of highly fluorescent pyridocarbazoles

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Abstract: Trimethylsilyl trifluoromethanesulfonate (TMSOTf) mediated dimerization reaction of vinylogous carbamates of carbazoles gave highly fluorescent pyridocarbazoles through Povarov-type formal [4+2] cycloaddition-retro-aza-Michael cascade.¹⁻³ Synthesized pyridocarbazoles possess excellent photophysical properties with high quantum yields (Φ_F). Fluorescent pyridocarbazole dicarboxylic acid showed potential as pH probe giving linear response to pH over a very wide range (7.0-3.0) reflecting high efficiency.^{4,5}



Figure 1. UV/vis absorption (solid line) and fluorescence emission (short dash line) spectra

Figure 2. Effect of pH on fluorescence emission

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Sustainable One-pot Synthesis of S-aryl Dithiocarbamates Using Diaryliodonium Salts

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Abstract:

Organic dithiocarbamates have received profound applications in the synthesis of several building blocks,¹ as protecting groups in peptide synthesis,² and serve as anticancer agents,³ monoacylglycerol lipase (MAGL) inhibitors,⁴ as well as antimethicillin-resistant Staphylococcus aureus (MRSA) agents.⁵ Accordingly, the synthesis of these compounds stands as one of the promising areas of research attracting interests of synthetic organic chemists. Traditional synthesis of aryl dithiocarbamates often requires stoichiometric and toxic organometallic reagents,⁶ harsh reaction conditions,⁷ expensive ligands and transition metal catalysts,⁸ owing to which these methods are not desirable from the sustainability point of view. Accordingly, we have developed a metal-free, mild, efficient and sustainable one-pot three-component coupling between diaryliodonium triflates, carbon disulfide, and cyclic and acyclic aliphatic amines resulting in the formation of biologically active *S*-aryl dithiocarbamates. The reaction exhibits broad scope and products are obtained in good to excellent yields. Importantly, *in silico* analysis revealed that the synthesized compounds accomplished drug-likeness and lead-like properties that are requisite for drug potency, in turn making them promising candidates for further exploration of their efficacy using biological assays.⁹



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Diindolocarbazole based Thermally Activated Delayed Fluorescent Materials for Organic Light-Emitting Diodes

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Abstract:

Thermally activated delayed fluorescence (TADF) materials have received more attention because of their potential applications in organic light-emitting diodes (OLEDs) due to the utilization of singlet (25 %) as well as triplet excitons (75 %)^{1,2}. However, for the achievement of high internal quantum efficiency (IQE), the energy gap (ΔE_{ST}) between singlet state and triplet state should be less than 0.1 eV so that efficient reverse inter system crossing (RISC) occurs. Smaller ΔE_{ST} can be achieved by decreasing HOMO and LUMO interactions of D-A molecules which further decrease the photoluminescence quantum yield (PLQY) and hence IQE decrease³. Hence, the main challenge for the synthesis of TADF material is the balance between ΔE_{ST} and PLQY. To overcome this challenge, herein, we have designed and synthesized diindolocarbazole (DI) and fluorine substituted dibenzophenazine (PF) and phenanthroimidazole (PI) TADF materials DI-PF and DI-PI whereas DI behave as electron donor and PF, PI behave as electron acceptor. Due to rigid and larger π -surface area, DI and PF, PI provide smaller ΔE_{ST} and higher PLQY. The ΔE_{ST} Values calculated through Density Functional Theory (DFT) were found to be 0.053 eV and 0.004 eV and experimentally observed to be 0.01 eV and 0.3 eV for DI-PF and DI-PI respectively. Both compounds showed positive solvatochromism and DI-PF also showed aggregate induced emission.

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Evaluation of DNA/BSA interaction and in vitro cell cytotoxicity of μ₂-oxido bridged divanadium(V) complexes containing ONO donor ligands

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Abstract:

Two new μ_2 -oxido bridged divanadium (V) complexes, $[VV_2O_3(L^{1,2})_2]$ (1 and 2) have been synthesized using bi-negative tridentate ONO-donor ligands, $H_2L^{1,2}$ (H2L1 = 4-tert-butyl-2-[[[3,5-di-tert-butyl-2-hydroxyphenyl]methylene]amino]phenol and $H_2L^2 = 5$ -bromo-2-[[[4-(diethylamino)-2-hydroxyphenyl]methylene]amino]phenol). The synthesized ligands and complexes have been characterized through FT-IR, UV-vis, NMR, and HR-ESI-MS techniques. Single crystal X-ray crystallography data confirmed distorted square pyramidal geometry for both the complexes. The aqueous phase stability of these complexes has been evaluated through HR-ESI-MS in CH₃CN:H₂O (80:20) mixture. Thereafter their interaction with calf thymus DNA (CT-DNA) have been studied using electronic absorption and fluorescence spectroscopy, revealing an intercalation mode of binding, with binding constant in the order of 10⁴ M⁻¹. Moreover, bovine serum albumin (BSA) interaction of 1 and 2 has been evaluated via fluorescence quenching experiment, which suggests that the quenching mechanism is static ($\sim 10^{13}$ M⁻¹) in nature.¹ Additionally, the in vitro cytotoxicity of the complexes has been evaluated in human cervical cancer cells (HeLa) (IC₅₀ = 13.57-16.62 µM) and normal mouse embryonic fibroblasts cells (NIH-3T3). The mechanism of cell death brought about by these complexes was studied by nuclear staining, cell cycle and Annexin V/PI double staining apoptotic assay. These studies indicate that 1 and 2 exert inhibitory effects on the S and G2M phase of cell cycle, which is an indication of apoptotic cell death.² Also, a clonogenic assay was performed, which showed that the complexes could effectively inhibit colony formation.



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Iodine catalyzed multicomponent synthesis of highly fluorescent pyrimidine-linked imidazopyridines

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Abstract:

Herein we report a metal-free one-pot three-component reaction of aryl-methyl ketones, 2aminopyridines, and barbituric acids for the synthesis of pyrimidine-linked imidazopyridines using a catalytic amount of molecular iodine in DMSO medium. This process involves one-pot C-H oxidation followed by the formation of one C-C and two C-N bonds. A wide variety of aryl methyl ketones and 2-aminopyridines were found suitable for this methodology. The UV and fluorescence properties of the synthesized products were studied in water and DMSO medium. Most of the synthesized products exhibit very good to excellent fluorescence quantum yield. Interestingly, the presence of barbituric acid moiety enhances the fluorescence property of 2-arylimidazopyridines.



Bhimal Fibre-Derived Nitrogen-Doped Activated Carbon for Adsorption of Hexavalent Chromium from Wastewater

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Abstract:

Effluents of tannery, electroplating, refractories, metallurgy, and chemical industries contain hexavalent chromium as a highly toxic micro-pollutant. Exposure of chromium-contaminated water leads to several health hazards, including teratogenesis, mutagenesis, dermatitis, chromosomal disorder, etc. Present work addresses the synthesis of high surface area activated carbon (1527 m².g⁻¹) from agro-waste Bhimal (Grewia optiva) fibers via a combinatorial approach of hydrothermal carbonization followed by thermochemical activation with ZnCl₂. The chemical, structural, textural, and morphological characteristics of Bhimal fibers-derived activated carbon (BFAC) are probed by Raman, HRTEM, XPS, and N₂ sorption analyses. The BFAC is demonstrated as an efficient adsorbent for the adsorptive separation of hexavalent chromium from simulated wastewater. The effect of the initial concentration of hexavalent chromium in wastewater and pH are probed to understand the adsorption process and mechanism. The chromium adsorption followed the pseudo-second-order kinetic and the Langmuir equilibrium isotherm with a maximum adsorption capacity of 256 mg.g⁻¹. The BFAC displayed excellent recyclability and maintained 99.7% adsorption efficiency even after seven subsequent chromium adsorption cycles. The present findings suggest the potential of lignocellulosic ago-waste-derived nitrogen-doped activated Carbon for adsorptive removal of heavy metal ions for wastewater treatment.

Design of ZIF-67 nanoflake derived NiCo-LDH/rGO hybrid nanostructures for aqueous symmetric supercapattery application under alkaline condition

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Abstract:

Transition metal layered double hydroxides (TM-LDHs) have flexible anion exchanging properties with a large specific surface area accessible to ions for surface Faradaic reactions. In particular, Zeolitic imidazolate frameworks (ZIFs), a subfamily of MOF, displays exceptional thermal stability and robust structure and is used as a sacrificial template for synthesizing various TM-LDHs with permanent porosity and unique morphologies for supercapacitor applications.^{1,2} However, their interlayer hydrogen bonding causes the agglomeration to pristine LDH, blocking the active sites and reducing electrochemical performances. Alternatively, graphene or rGO with high electrical conductivity and large surface area has proved to be unique conducting support to enhance electrochemical performances. The insertion of graphene layer into LDH prevents its agglomeration and promotes electron and ion transportation through a short diffusion path.^{3,4} Here, we have successfully prepared nickel-cobalt LDHs supported by reduced graphene oxide (rGO) by insitu etching of the ZIF-67 template under hydrothermal process at 120 °C (NiCo-LDH/rGOx). The reaction conditions were carefully optimized by taking different amounts of rGO (10, 30, 50 and 90 mg). The NiCo-LDH/rGO-30 with 30 mg of rGO was found to give the highest specific capacitance (1658 F g⁻¹), which is 2.6 times higher than pristine NiCo-LDH (630 F g⁻¹) ¹) at a current density of 1 A g⁻¹. For the practical application, the NiCo-LDH/rGO-30 is used as cathode and anode materials to fabricate a symmetric supercapattery (SSC) device that can deliver high energy density of 49.2 W h kg⁻¹ at a power density of 750.5 W kg⁻¹. The asfabricated SSC device using NiCo-LDH/rGO-30 could be a promising supercapattery electrode material for next-generation high-tech applications.

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Elucidating Liquid Crystal-Aqueous Interface for the Study of Cholesterol Mediated Action of β-Barrel Pore Forming Toxin

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Abstract:

Pore-forming toxins (PFTs) produced by the pathogenic bacteria serve as the prominent virulence factors with potent cell-killing activity. Most of the β-barrel PFTs form transmembrane oligomeric pores in the membrane lipid bilayer in the presence of cholesterol (chol).¹ Pore-formation mechanisms of the PFTs highlight well-orchestrated regulated events in the membrane environment that involve dramatic changes in the protein structure and organization. Also, concerted cross-talk between protein and membrane lipid components appear to play crucial roles in the process. Membrane-damaging lesions formed by the pore assembly of the PFTs would also be expected to impose drastic alterations in the membrane organization, details of which remain obscure in most of the cases. Prior reports have established that aqueous interfaces of liquid crystals (LC) offer promise as responsive interfaces for biomolecular events (at physiologically relevant concentrations), which can be visualized as optical signals.² Inspired by this, herein, we sought to understand the lipid membrane interactions of a β-barrel PFT i.e., Vibrio cholerae cytolysin (VCC), using LCaqueous interfaces. Our results show formation of the dendritic patterns upon the addition of VCC to the lipid embedded with cholesterol over the LC film. In contrast, we did not observe any LC reorientation upon the addition of VCC to the lipid-laden LC-aqueous interface in the absence of cholesterol. An array of techniques such as polarizing optical microscopy (POM). atomic force microscopy (AFM), and fluorescence measurements were utilized to decipher the LC response to the lipid interactions of VCC occurring at those interfaces. Altogether, results obtained from our study provide novel platform to explore the mechanistic aspects of the protein-membrane interactions, in the process of membrane pore-formation by the membranedamaging PFTs.

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Visible-light-mediated synthesis of α,β-diamino esters *via* dehydrogenative coupling of *N*,*N*-dimethylanilines and glyoxalic oxime ethers

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Abstract:

The versatility of photoredox catalysis as a method for activating the C–H bond of tertiary amines has generated contemporary interest^{1,2}. New reaction manifolds have been developed by intercepting α -amino radical by various moieties such as imines³, aldehydes, and Michael acceptors. We have developed a Ru(bpy)₃Cl₂ catalyzed visible-light-mediated protocol for the synthesis of α , β -diamino esters *via* dehydrogenative coupling of glyoxalic oxime ethers and dimethylaniline. The reaction is general, employs readily available precursors and proceeds under mild conditions.

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Blue LED mediated cycloaddition and oxidation reactions of aryldiazoacetates.

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Abstract:

Indolizines serve a niche position among heteroarenes to organic synthetic and medicinal chemists, due to their presence as natural product scaffolds and active pharmaceutical ingredients.¹ They have been reported to demonstrate anticancer, antituberculosis, antiinflammatory, and antifungal properties.² Herein we have developed a Blue light-emitting diode (blue LED)-mediated environmentally sustainable three component reactions among pyridine, aryl diazoesters, and 3-alkenyl oxindoles to provide various dihydroindolizines in excellent yield.³ The reactions were carried out under mild conditions and requires simple column purification. The principle of the strategy is photolytic generation of nitrogen ylides from N-heteroarenes and aryl diazoesters and their subsequent [3 + 2] cycloaddition reaction with dipolarophiles.

In a different project we have reported an eco-friendly synthesis of α -ketoamides under Blue LED irradiation. α -ketoamides are an interesting class of molecules. They have myriad biological properties and are also frequently used as building blocks for the synthesis of heterocyclic scaffolds.⁴ It is a one pot synthesis beginning from alkyl aryl/heteroaryl acetates with various cyclic secondary amines in molecular oxygen as the oxidant *via* diazo installation-oxidation-amidation in ethyl acetate as solvent to the target compounds. The reaction could also be performed under air with no oxidant but that facilitated major formation of the undesired NH-inserted products. Under oxygen atmosphere the formation of such by-products was minimized to 10 to 20%. Various α -ketoamides were synthesized in moderate to good yields. Control experiments provided rational for the mechanism of transformation. This protocol could be scaled up in gram scale.

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A multi responsive phosphonic acid based fluorescent sensor for sensing Fe³⁺, benzaldehyde and antibiotics.

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Abstract:

Herein, we report a multi responsive and selective fluorescent chemo sensor with anthracene as a fluorophore and phosphonic acid group as receptor (anthracene-9,10-diylbis(methylene))diphosphonic acid (ANDP) for detecting Fe³⁺, benzaldehyde and few antibiotics. The sensor was characterised by single crystal X-ray diffraction and NMR. ANDP could selectively and sensitively detect Fe³⁺ and benzaldehyde in DMSO-water with detection limits of 5.09 μ M and 39.8 μ M respectively. NMR and FT-IR proves the interaction of Fe³⁺ with the sensor. Mainly nitro group based antibiotics (furazolidone, nitrofurazone, metronidazole) and tetracycline sensitively quenched the fluorescence of the sensor with the detection limit of 2.07 μ M, 1.25 μ M, 1.19 μ M and 0.66 μ M respectively. Furthermore, the quenching mechanism was further discussed, photo induced electron transfer (PET) was responsible for the quenching of fluorescence intensity of ANDP. The HOMO and LUMO energies were estimated by DFT calculations.

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Serine Diketopiperazine (DKP) a Versatile Scaffold for Transmembrane Ion

Transport and Carboxylated Nanospheres

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Abstract:

Peptide based functionalized materials plays an important role as ion transporters and catalysts.¹⁻² Cyclic octapeptides that self-assemble to form nanotubes have been widely used as ion-transporters and their polymer conjugates have been used as functionalized materials.³⁻⁴ Diketopiperazines (DKPs) are well known self-assemble to furnish nanotubes and nanospheres⁵ and are easier to synthesize as compared to the cyclic octapeptides. However, these templates are not well-explored for developing peptide-polymer conjugates. Herein, serine derived DKPs were conjugated with norbornene units *via* an easily cleavable ester linkage. The peptide spherical self-assembly was covalently captured by polymerization of the appended norbornene units. The resulting nanospheres were hydrolyzed to remove the DKP template to furnish carboxylated nanospheres that could be used for cation-binding.⁶

The DKP units with monomer attached were also found to co-transport of cation and anion across cellular membrane. The carbonyl groups from the peptide scaffold and the dangling ester linkages helped bind cations, while the amide NH groups interacted with anions. The transport mechanism was found to be M^+/Cl^- symport and the DKP molecules behaved as ion-carriers.

The poster with highlight the versatility of these serine DKP templates as templates for carboxylated nanospheres and ion transporters.

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Computations Reveal a Crucial Role of F121 and F363 Aromatic Dyad in the Catalytic Function of CYP71D of Mint Superfamily

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Abstract:

Enzymes are highly specific for their native functions, however with advances in bioengineering tools such as directed evolution, several enzymes are being repurposed for the secondary function of contemporary significance. Due to the functional versatility, the Cytochrome P450 superfamily has become the ideal scaffold for such bioengineering. Herein, our study focuses on two plant CYPs: Limonene-6hydroxylase (L6H) and limonene-3-



hydroxylase (L3H) which belong to Spearmint and Peppermint species, respectively. Albeit L6H and L3H catalyse the hydroxylation of the same substrate (-)-4*S*-Limonene, they show significant regioselectivity. Earlier, Schalk et al. demonstrated that a single site mutation in the active site of both these enzymes at a similar position led to the emergence of promiscuous activity and catalytic efficiency in mutant L6H, whereas, mutant L3H loses its activity. In the current study, using MD simulations and hybrid QM/MM calculations, we have studied the mechanism of spontaneous emergence of a secondary function due to single site mutation in two plant CYP450 enzymes from the mint family. The MD simulations of WT CYP71D18 and CYP71D13 enzymes and their variants show a crucial gating mechanism by aromatic dyad formed by Phe120 and Phe363 which regulates the substrate recognition. The QM/MM calculations reveal that the hydroxylation reactions at C3 and C6 positions in WT CYP71D18 and CYP71D13 enzymes as well as their variants follow a hydrogen atom transfer (HAT) followed by a single electron transfer (SET) mechanism, which is different from the typical rebound mechanism shown by most of the CYP450 enzymes.

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Multifunctional Isostructural Ni(II) and Zn(II) Metal-organic Frameworks as Heterogeneous Catalysts for the Friedel-Crafts Alkylation Reaction and Size-selective CO₂ Chemical Fixation

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Abstract:

Various organic transformations for the synthesis of pharmaceutical products and biologically important molecules require a catalyst (and sometimes even a co-catalyst) that are either available from commercial sources or the newly designed materials. Generally, homogeneous catalysts are utilized for such transformations; however, their separation from the product and non-recyclability are the major issues. On the other hand, the emergence of heterogeneous catalysts with recyclability and easy separation from the product is noteworthy. In this respect, metal-organic frameworks (MOFs), made from a combination of suitable organic ligands and metal ions, have been on the leading front for their structural diversity and stability, tunable functionality, and large surface area. Similarly, MOFs play a significant role in the capture and chemical conversion of a major greenhouse gas, CO₂, to value-added cyclic carbonates for an urgent need to reduce its concentration in the atmosphere. In this work, we report the use of two isostructural amino acid-functionalized 3D metal-organic frameworks, $\{M_4(\mu_3-OH)_2(D 2,4-cbs_{2}(H_{2}O)_{4}$].5H₂O}_n (where M = Ni, Ni-CBS and M = Zn, Zn-CBS; D-2,4-cbs = 2-((4carboxybenzyl)amino)succinate), as heterogeneous catalysts for the presence of unsaturated metal centers as Lewis acidic sites and the –NH groups of the organic ligand as basic sites. The Lewis acidic behavior of Ni-CBS and Zn-CBS has been utilized for the Friedel-Crafts alkylation reaction which produces chemically and biologically important natural bis-indole products. On the other hand, both Ni-CBS and Zn-CBS behave as size-selective heterogeneous catalysts for the chemical fixation of CO₂ with diverse epoxides to form cyclic carbonates. Their recyclability up to three consecutive runs and mechanism of action have also been demonstrated.

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Synthesis and Biological Activity of Spiroindolenines and Spiroindolo-[1,2,4]-Oxadiazoles

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Abstract:

Spiroindolenine motif is widely present in numerous indole alkaloids exhibiting diverse biological activities¹, which includes antimalarial activity, antimitotic activity and insecticidal activity². They are also useful building blocks for the synthesis of veterinary products, dyes, fine chemicals and several other materials important in daily life. On the other hand, oxadiazoles³ are important class of heterocycles, which are widely occur in several bioactive molecules and natural products exhibiting useful biological activities. To the best of our knowledge, insecticidal or fungicidal activities of substituted spiroindolenines and its spiro-[1,2,4]-oxadiazoloindole derivatives have not been reported. Herein, we report the synthesis, insecticidal and fungicidal activity of several substituted spiroindolenines (4) and its [1,2,4]-oxadiazoloindoles (6). For the synthesis of [1,2,4]-oxadiazoles, imine bond (-C=N-) of spiroindolenine serves as a good dienophile for cycloaddition reactions with nitrile oxide, generated *in-situ* from chloroaldoxime (5) under slow addition condition.



Some of the synthesized spiroindolenines have shown moderate to good fungicidal and insecticidal activities. Two of the synthesized Spiro-[1,2,4]-oxadiazoloindoles have shown mild fungicidal activity, but good insecticidal activity on *Tetranychus urticae* (TETRUR), which causes infection and damage to vegetables and food crops.

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Engineering of a Highly Specific, Selective, and Sensitive Fluorescent Probe for Detection of Mycobacteria in Human Tissues.

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Abstract:

Tuberculosis (TB), caused by Mycobacterium tuberculosis (Mtb), is one of the most prevalent and serious infectious diseases worldwide with an estimated annual global mortality of 1.4 million. Diagnosis of TB is very challenging due to limited available techniques as existing methods of detection of mycobacteria have poor sensitivity, selectivity, and specificity. As mycobacterial membrane can be potential diagnostic and therapeutic targets, we designed and synthesized different facial amphiphilic Cholic Acid (CA)-derived probes mimicking the naturally occurring antimicrobial peptides. We incorporated a fluorophore at C24 position of CA via click chemistry, and different headgroups were tethered at C3, C7, and C12-hydroxyl positions of CA. Among these probes, we observed that Dimethyl aminopyridine (DMAP) conjugated probe (P4 probe) was highly specific for mycobacteria. P4 probe can identify mycobacteria in a polymicrobial planktonic cultures and biofilms with high specificity, selectivity, and sensitivity. Biochemical studies demonstrated that P4 probe specifically binds with mycobacterial lipids, trehalose monomycolate, and phosphatidylinositol mannoside 6. Moreover, it can detect a single mycobacterium in the presence of 10,000 other bacilli. Unlike other probes that depend on activity of mycobacterial enzymes, the membrane specific P4 probe can detect mycobacteria even in formalin-fixed paraffin-embedded mice and human tissue sections. In my poster, I will present our recent results on ability of the P4 probe to detect mycobacteria in different biological milieu that makes it a potential candidate for diagnostic and prognostic applications in clinical settings.

Reference:

Gupta, Siddhi, Deepakkumar Mishra, Mehak Zahoor Khan, Varsha Saini, Devashish Mehta, Sandeep Kumar, Aditya Yadav et al. "Development of a Highly Specific, Selective, and Sensitive Fluorescent Probe for Detection of Mycobacteria in Human Tissues." *Advanced Healthcare Materials* (2022): 2102640.

Synthesis, Spectral and Electrochemical Studies of β-Cyanoporphyrins with Mixed Substituent Pattern

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Abstract:

Porphyrins are known to possess a wide variety of interdisciplinary applications which can easily be controlled by the alteration around the periphery of the ring. Different types of functionalization on the *meso/β*-position of the macrocycle facilitate the utilization of the molecule.¹⁻⁵ In the trend, cyano moiety is less sensitive towards steric factors and has the potential to create pronounced effect. In general, β -Cyano containing mixed substituted porphyrins are not explored much in the literature, hence they possess a wide scope of subsequent developments and applications.

Herein, a synthetic aspect for the monocyano appended β -functionalized porphyrins are reported. The pathway to prepare phenylethynyl appended β -cyanoporphyrin traverses through bromination at β -position followed by Stille coupling. Further, treating the phenylethynyl group with tetracyanoethylene gives an unsymmetrical tetracyanobutadiene appended cyanoporphyrin. The series of metalloporphyrins thus obtained is characterized by various spectroscopic techniques such as UV-vis, fluorescence and NMR, MALDI mass spectrometry, cyclic voltammetry and density functional theory (DFT) studies.

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Antibacterial Peptide Gel Incorporating Y₂O₃ Nanoparticles: A Multi-Target Approach to Wound Healing

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Abstract:

Wound healing is a complex, multistep but well-coordinated process, which encompasses a series of overlapping phases- Hemostasis, inflammation, granulation and remodelling to restore the structural and functional integrity of the tissue. These phases are characterized by a cascade of events and coordinated interactions of blood cells, proteases, growth factors, proteins, and extracellular matrix components. When these sequences are dysregulated, the healing process gets compromised. Persistent inflammation, bacterial infections, vascular impairment, and inadequate re-epithelialization interfere with the healing and cause chronic wounds. Bacterial infection can prolong the inflammatory phase of wound healing and prevent re-epithelization and tissue regeneration. Antibiotics have been used to treat bacterial infections. However, bacteria have developed an innate capability and pathway to tolerate the toxic effects of antibiotics, making them ineffective against that particular strain.¹ In the last two decades, short and cationic peptides have drawn plenty of attraction by showing great potential as antibacterial agents. The half-life of AMPs in the biological milieu, however, limits their therapeutic use. Our current research focuses on developing a multi-targeted biomaterial that entails the fabrication of a peptide-alkyl conjugate-based nanofibrous gel loaded with mesoporous Y₂O₃ nanoparticles for chronic wound healing. Y₂O₃ nanoparticles will promote the upregulation of VEGF and FGF genes, promoting vascularization.² A lauric acid-peptide conjugate (LA-L-Lys-D-Phe-L-Lys-NH₂) was synthesized and self-assembled into a nanofibrous gel at room temperature under alkaline conditions. FT-IR studies showed that the gel possesses the betasheet secondary structure and the surface morphology of the gel was characterized by SEM. Mesoporous Y₂O₃ NPs were prepared using the sol-gel technique and characterized by PXRD, FT-IR, and UV-Visible spectroscopy. Scanning electron microscopy (SEM) was used to detect the morphology and porosity of NPs, while DLS was used to measure its average size (139.7 nm). NPs were incorporated into the gel and the gel was investigated for its viscoelastic and self-healing characteristics using rheology. The gel demonstrated excellent stability in the presence of a cocktail of proteolytic enzymes and showed only around 8% degradation in 36 hours. The gel exhibited over 93% antioxidant activity when analyzed using the ABTS assay, and a potent bactericidal effect, with more than 90% activity against both Gram-positive (S. aureus) and Gram-negative (E. coli) bacteria. The cell viability of the gel (MTT assay) on the L929 fibroblast cell line was measured and found to be 155%, indicating its cell proliferative nature. Live-dead assay further confirmed its cytocompatibility. When analyzed with scratch assay ,the gel was found to have healing and wound closure abilities. Thus, Y₂O₃ NP-loaded peptide-conjugate gel shows strong potential as a matrix for chronic wound healing.

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Vanadyl Tetrabromo And Vanadyl Tetracyano Porphyrins As Catalysts For oxidative

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Bromination Of Phenol Derivatives And Epoxidation Of Olefins

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Abstract:

In this section, two highly electron deficient catalysts have been synthesized, characterized and used as catalysts for the oxidative bromination of phenol and its derivatives in an aqueous medium at room temperature (25 °C). Selective bromination of phenols have been done by electron-deficient vanadyl-porphyrins *ca*. vanadyl 2,3,12,13-tetrabromo-5,10,15,20tetraphenylporphyrin (1) and vanadyl-2,3,12,13-tetracyano-5,10,15,20-tetraphenylporphyrin (2). The TOF value for (2) is found to be 127 874-155 944 h⁻¹. The product selectivity of a few phenols viz. phenol, p-cresol and 4-methoxyphenol have been studied with time. As catalyst 1 has been already reported as an efficient catalyst for the epoxidation of olefins,^[3] catalyst 2 can also be used as a good catalyst for the epoxidation of various olefins. Also, catalysts 1 and 2 recyclability properties above-mentioned show for the catalytic reaction.



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Cholesterol-based bent-shaped liquid crystals exhibiting blue liquid crystalline phase and mechanochromic behavior

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Abstract:

Chirality is significant in liquid crystalline systems because it induces a range of exotic mesophases such as blue phase (BP), twist grain boundary (TGB) phase, smectic blue phase (SmBPs), and others. BP liquid crystal (LC) has gained a great deal of attention in the past couple of years because of its sub-millisecond response time and its potential applications in the field of tunable photonic bandgap materials, sensing, lasers, etc. Despite their many enticing characteristics, BPs have a major drawback that hinders them from being commercialized in devices i.e. their limited temperature range. Therefore, we focussed on stabilizing BPLCs in bent-shaped LCs over a wide temperature range.

Here, we synthesized two series (1/n and 2/n) of unsymmetrical cholesterol-based bent-shaped liquid crystalline materials in which the cholesterol moiety is directly connected to a 1,3disubstituted phenyl unit. The series (1/n) containing an electron-donating moiety (-CH₃, +I effect) at the transverse of the central core stabilized a number of exotic mesophases, including BPI/II, N*, N_{cyb}*, SmX₁ and SmX₂, with BPI/II stabilized in the short temperature range. However, in one of the homologues of series 2/n, the addition of an electronegative moiety (-Cl, chloro group) at the transverse position resulted in the stabilization of BPI/II over a temperature range of 19.0 °C, which is unusual for a single component bent-shaped LCs. The design of this series of compounds is inspired by the previous report where BPI/II stabilization of 16.4 °C was attained. [1,2] The inclusion of an electron-withdrawing moiety resulted in a considerable change in the mesomorphic characteristics, highlighting the relevance of structure-property correlation. BPI/II monodomain film was also achieved, which is required for a variety of device applications. Furthermore, these salicylideneanline and cholesterolcontaining compounds exhibited mechanochromic activity. On dropwise addition of solvent, the series 1/n showed reversible mechanochromic behavior, whereas the series 2/ndemonstrated the reversibility of the ground sample on annealing.

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Conversion of Bio-derived crude glycerol into renewable high-octane gasolinestock

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Abstract:

Crude glycerol is an attractive bio-based platform chemical that can be converted into a variety of chemicals. Here we report an efficient catalytic process that operates on a bi-metallic ZSM-5 supported catalyst (0.1Ga-1Zn/ZSM-5) for 100% carbon conversion of glycerol to produce 71.4C% liquid fuel stocks possessing a high concentration of alkyl-aromatics and octane potential (>97 RON) for fuel applications achieved and reported for the first time to the best of our knowledge. In addition, the H₂-rich (36 mol%) gas stream produced as a by-product attracts the green fuel applications. The process adds up to the ~80% increase in the value addition of bio-glycerol that improves the overall fuel yield of the biodiesel production process towards improved atom efficiency and process economy. Thus the enhanced carbon conversion and aromatics yield in the glycerol aromatization process observed on metal-functionalized ZSM-5 might be understood by main factors, namely; (i) decreased strong Bronsted acid sites to suppress undesirable cracking reactions (ii) increased Lewis acid sites to promote dehydrogenation reactions (iii) high anti-coking and hydrogen spill over capacity resulting in the minimized coke formation. Thus the production of high octane gasoline hydrocarbons and valuable gases from the bio-derived glycerol can be considered an important process toward a sustainable energy future.

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Redox noninnocence of the formazanate ligand applied to catalytic formation of α -ketoamides

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Abstract:

The formazan ligands have been investigated as redox-noninnocent backbones for a long time. Despite their well-established behaviour as redox reservoirs, the demonstration of catalytic efficiency governed by redox noninnocence remains elusive. We report an iron–formazanate molecule for efficiently preparing α -keto amides, where a crucial reductive cleavage of the substrate molecule is tightly regulated by the electron donation from the formazanate, in a reversible manner.

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Amphiphilic cyanine-based nano vesicular NIR probe for the selective detection of H₂S in water and food products

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Abstract:

 H_2S has been recognized as one of the three gasotransmitters along with nitric oxide (NO) and carbon monoxide (CO). The physiological levels of H_2S appear to be involved in various biological functions and essential for maintaining the human health. Considering their biological importance several chemical sensors are developed for the detection of H_2S in pure aqueous solution. Most of the probes possess short emission and absorbance wavelength (<600 nm), which often suffer from photo damage and limit their application in biological field. The near-infrared (NIR) probe can offset these drawbacks due to its advantages including minimal interfering absorption and fluorescence from biological samples and enhanced tissue penetration ability.



Here we report an amphiphilic cyanine based NIR probe (**Cy-Amp**) and **Cy-Amp** embedded nanoscale vesicles for the selection detection H₂S. nano scale vesicle displayed a very good selectivity towards H₂S at neutral pH. A typical UV visible change at 810 nm was observed with the addition of H₂S. The LOD was calculated as low as 18.7 μ M exhibiting a colour change from green to lightest yellow. The other anions and thiols do not show any interference in the sensing system. The detection of H₂S was established through replacement of Cl⁻ by SH⁻ group in the cyanine moiety. The UV-visible spectroscopy and the naked eye as the signal readout studies confirm the high selectivity, sensitivity and lower detection limit of the vesicular NIR receptor. The compound **Cy-Amp** was also applied for sensing of H₂S in real food samples such as cabbage and cauliflower.

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In situ lactonization facilitates anti-staphylococcal activity of membrane

targeting 2-bromomethyl-3-nitrobenzoate esters

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Staphylococcus aureus, a gram-positive human pathogenic bacterium, has been linked to several serious infections with high fatality rates. Increased bacterial resistance to commonly used antibiotics, as well as a shortage of new antibiotics to address antimicrobial resistance (AMR), is a global challenge that necessitates alternative therapeutic techniques. Small molecules have the potential to be translated into new treatments. Our findings show a lactonization mechanism pathway to generate IITK2020 in situ S. aureus using whole-cell viability screening of small compounds followed by structure-function-relationship analysis (SAR). At a minimal inhibitory dosage of 2-4 mg/L, both IITK2020 and its predecessor IITK2001 inhibit S. aureus and its multidrug-resistant strains. The interaction of the lead compounds with the cell wall biosynthesis enzymes MurA and MurZ was demonstrated in a molecular docking experiment, which was corroborated by chemoproteomics and membrane depolarisation experiments. Atomic force microscopy studies have revealed a cracked morphology and increased volume of the bacterial cell wall after treatment with IITK2020, which validates our idea. Overall, our research led to the discovery of a small molecule that potentially targets S. aureus cell wall enzymes via in situ lactonization while retaining its potency against multiple drug-resistant S. aureus strains.



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Chiral LC-MS/MS method development for the estimation of Viloxazine enantiomers in rat plasma and application to pharmacokinetic study

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Abstract:

Despite having similar thermodynamic properties in achiral contexts, enantiomers generally behave differently in chiral environments, such as biological systems. Because of the chirality of biological compounds (receptors, enzymes, etc.), the pharmacokinetics might be different for two enantiomers. In recent years, there has been an increase in interest in enantiomerically pure compounds in pharmacology and medical science, because, in addition to the benefits of administering drugs as single isomer, side effects can be linked to the other enantiomer. As a result, the pharmacokinetics and toxicity of a racemate vs an enantiomerically pure medication differ and must be investigated. As a consequence of the chiral switch technique, which included the production of single enantiomers as a result of re-examining the racemates, a superior isomer with better pharmacological and therapeutical effects can be achieved. One of the benefits of chiral switch technology is that it improves the therapeutic index by enhancing potency and selectivity while reducing negative consequences. Viloxazine is a chiral molecule with a single stereo centre (results in two enantiomers) which is marketed as racemic (equal ratio of R- and S-enantiomer). A Chiral-LC-MS/MS technique was developed to separate and quantify the enantiomers in rat plasma and applied for the pharmacokinetics study of the viloxazine enantiomers in male SD rats. The separation of the enantiomers was attained on cellulose tris (3,5-dichlorophenylcarbamate) immobilized on silica-gel column in the presence of methanol and ammonia buffer. The LLOQ was found to be 1ng/mL for both the enantiomers. A good correlation was found between concentration and the response at a concentration range of 1-2000 ng/mL. The T_{max} was found to be at 0.5Hr and C_{max} of R-Viloxazine was 946 ng/mL and for S-Viloxaxzine was 1241 ng/mL.

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Pd-(II)-catalyzed, γ -C(sp²)-H alkoxylation in enantiopure α -methyl benzylamine, phenylglycinol, 3-amino-3-phenylpropanol toward enantiopure aryl alkyl ethers

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Abstract:

We report the synthesis of aryl alkyl ethers via the Pd(II)-catalysed, directing group-aided γ -C(sp²)-H alkoxylation of enantiopure α -methyl benzylamine, phenylglycinol, 3-amino-3-phenylpropanol using alcohols. The details including the C-H functionalization, etherification by C-O bond forming process giving access to racemic and enantiopure *ortho*- alkoxylated α -methyl benzylamines, phenylglycinols and 3-amino-3-phenylpropanol derivatives possessing aryl alkyl ether functionality will be presented.



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A Dual-Function Highly Crystalline Covalent Organic Framework for HCl Sensing and Visible-Light Heterogeneous Photocatalysis

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Abstract:

Covalent organic frameworks (COFs) offer great potential for various advanced applications such as photocatalysis, sensing, and so on because of their fully conjugated, porous, and chemically stable unique structural architecture.^{1,2} In this work, we have designed and developed a truxene-based ultrastable COF (**Tx-COF-2**) by Schiff-base condensation between 1,3,5-tris(4-aminophenyl)benzene (TAPB) and 5,5,10,10,15,15-hexamethyl-10,15-dihydro-5*H*-diindeno(1,2-*a*:1',2'-*c*)fluorene-2,7,12-tricarbaldehyde (Tx-CHO) for the first time. The resulting COF possesses excellent crystallinity, permanent porosity, and high Brunauer–Emmett–Teller (BET) surface areas (up to 1137 m² g⁻¹). The COF was found to be a heterogeneous, recyclable photocatalyst for efficient conversion of arylboronic acids to phenols under visible-light irradiation, an environmentally friendly alternative approach to conventional metal-based photocatalysis. Besides, **Tx-COF-2** provides an immediate naked-eye color change (<1 s) and fluorescence "turn-on" phenomena upon exposure to HCl. The response is highly sensitive, with an ultralow detection limit of up to 4.5 nmol L⁻¹.³

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An Efficient protocol for the Thioamidation of the Aldehyde in Aqueous Medium

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Abstract:

Thioamide play important role in the field of biochemistry and medicinal chemistry due to their highly pharmaceutical and biological activity. Recently, we reported the synthesis of Thioamides by direct installation of elemental sulphur and amine in aldehyde at room temperature in aqueous medium. The present protocol demonstrate the broad substrate scope with different type of aliphatic, aromatic, heteroaromatic aldehyde with the use of different array amines in gram scale. The use of no catalyst, oxidants or additives makes this method unique. Biologically active molecules such as thionicotinamide, thioisonicotinamide which exhibit anticancer activity can be synthesized by our protocol.



Keywords: Thioamide, Elemental Sulfur, water based organic reaction and Amine

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