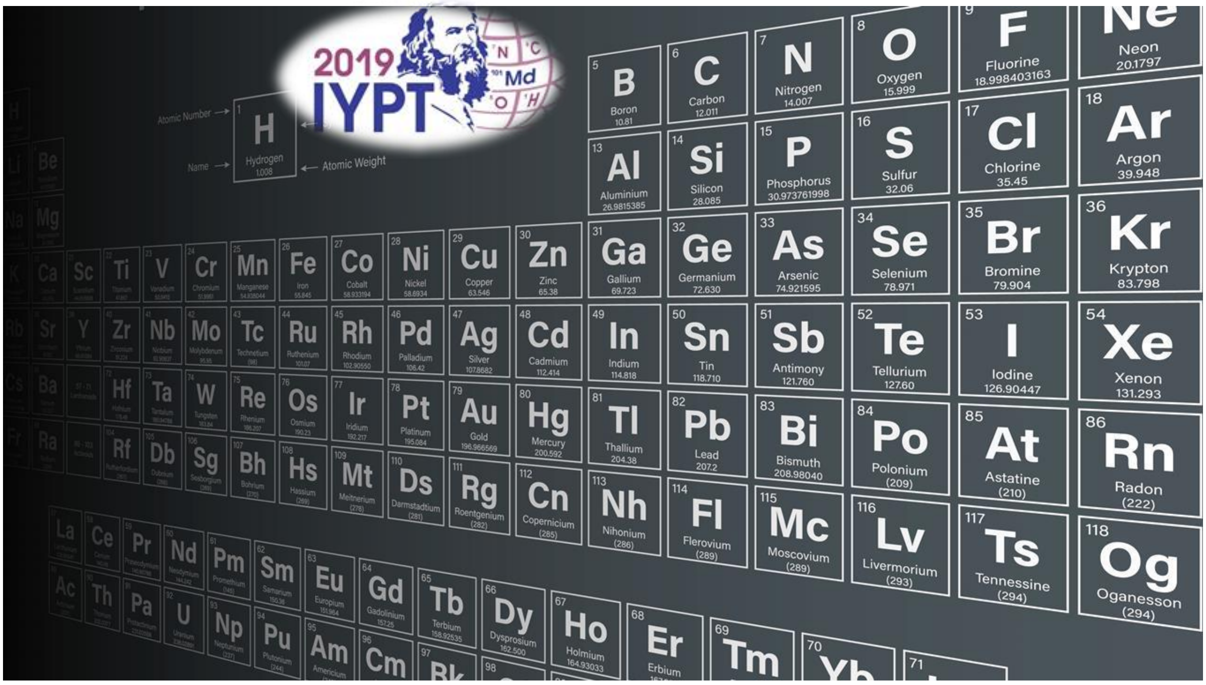
Abstract Book

Department Day 2019

Department of Chemical Sciences



Meghnad Saha Lecture Theatre

8 March

IISER KOLKATA

Indian Institute of Science Education and Research Kolkata

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Plenary Lectures

Excitons and plasmons: A tale of two elementary excitations and their interaction

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Coupling of elementary excitations in the presence of light results in several newer optical phenomena.[1] The coupling can be categorized as strong, weak and very weak, depending on the magnitude of the interaction. We have demonstrated examples of these interactions and its consequence on their optical properties.[1-5]Our group has earlier demonstrated examples of exciton-exciton coupling in molecules,and plasmon-plasmon coupling in plasmonic systems by organizing them in symmetric as well as asymmetric fashion.[1,2] As a consequence of such interactions, several fascinating chiroptical properties emerge.[2] These aspects, along with our recent results on the generation of plexcitonic states[5] will be presented in the first part of the talk. Precise assembly of plasmonic materials of desired size and shape allows further modulation of their optical and field effects, opening up several plasmonically powered processes such as surface enhanced spectroscopy.[6-9] We have translated the principles of surface-enhanced spectroscopy for the design of plasmonic platforms, which can identify molecules of importance in health, environment and safety.[9]Another aspect of discussion will be on the degree of covalency in quantum dots (QDs) which influences the depth of surface trap states and in turn affects the exciton recombination process. We have investigated these aspects by taking relatively ionic cadmium selenide QDs with shallow trap states and covalent indium phosphide QDs having deep trap states as examples, using time-resolved spectroscopic studies.[10]

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PL-02

An Unexpected de tour into the Synthesis of Simple Alkaloids from Polyols and Macrolactones

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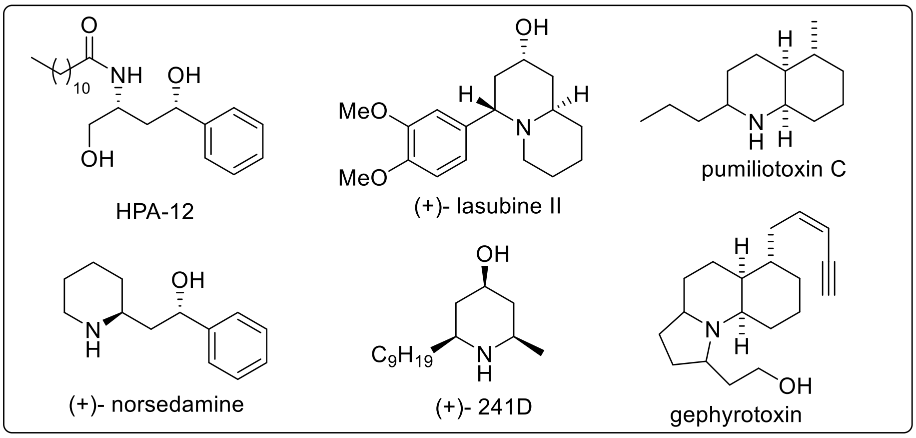
Abstract:

Our research group has been involved in the total synthesis of polyketide macrolactone natural products using chiral pool tartaric acid and chiral furyl carbinols as a four carbon four hydroxy synthon. During the course of our synthesis of the natural product schulzienes, we had an unexpected entry to the realm of sulfinimine chemistry. This led to us to develop procedures for the direct addition of ketones, substituted methyl enones and other nucleophiles to non-racemic sulfinimines. In this talk, these addition reactions and their application to the total synthesis of alkaloids will be discussed.[1-4]



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PL-03

Materials of Low Valent Silicon and Low Valent Metals

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Invited Lectures

IL-01

Nanomedical consequences expressed through spectroscopy

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Detection, prevention and treatment of diseases are performed through a branch of research called "Nanomedicine" that applies the knowledge of nanotechnology. Biocompatible nanomaterials are involved in such cases for sensing, detecting, diagnosing and delivering drugs in living cells. The present talk describes some interesting phenomena formulating some ideas in nanomedical research applying under biological conditions. It has been shown that thiosemicarbazide and semicarbazide functionalized pyrene labelled Schiff base compounds result in formation of π-π coupled complexes in aqueous medium in the excited state. Involvement of γ-cyclodextrin (γ-CD) allows incorporation of the pyrene heads inside its less polar core promoting hydrogen bonding of the thio and oxo groups of the Schiff bases with its rim hydroxyl groups to ‘‘stabilise’’ the monomers.[1] γ-CD can also be involved in detecting the microenvironment of a developing tumour. A unique pH sensitive non-cytotoxic gold nanocluster (Au NC) based probe can precisely detect sharp change in biological pH. Dihydrolipoic acid protecting the Au NCs are incorporated in γ-CDs which eject out during change in the environment pH showing red emission.[2] Medically potent indoloquinoline derivatives interact with DNA in the ground state which can be studied using steady state fluorescence spectroscopy and circular dichroism (CD) spectroscopy. Fluorescence quenching and CD signals indicate that the drugs intercalate into the DNA depending upon the position/s of the chloro group/s in the compounds.[3] Sequenced DNA oligos can be used to determine the selectivity of drug molecules to DNA. Selectivity of Thioflavin T (ThT) to sequence exchanged single strand DNA (ssDNA) oligomers in absence and presence of surface charged lipid vesicles is noteworthy. The dye shows special affinity for TCTTA sequence and π-interaction with adenine in 5'-CCCTCTTAACCC-3' (TC4). Fluorescence spectroscopy and molecular docking suggest that the dye is perfectly aligned to the TAA sequence in 5'-CCCTTAATCCCC-3' (TT4). Fluorescence intensity of ThT increases significantly due to interaction with charged liposomes (biological cell mimics) along with a considerable hypsochromic shift.[4] Distribution of dopamine, an essential neurotransmitter in mammalian central and peripheral nervous systems, inside and on the surface of lipid bilayer can be studied using fluorescence lifetime imaging (FLIM) technique.[5] Thiazole orange (TO) exists mainly as a monomer in aqueous medium, where its fluorescence is negligibly small. However, in giant unilamellar vesicles, TO prefers to form H-dimer and H-aggregates at low lipid concentrations. The non-fluorescent form of TO (monomer) starts fluorescing in the aggregated or dimeric forms.[6]

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IL-02

COMPUTATIONAL STUDY IN UNDERSTANDING THE UNIQUE ISOMERIZATION ACTIVITY OF DINUCLEAR PALLADIUM(I) CATALYST

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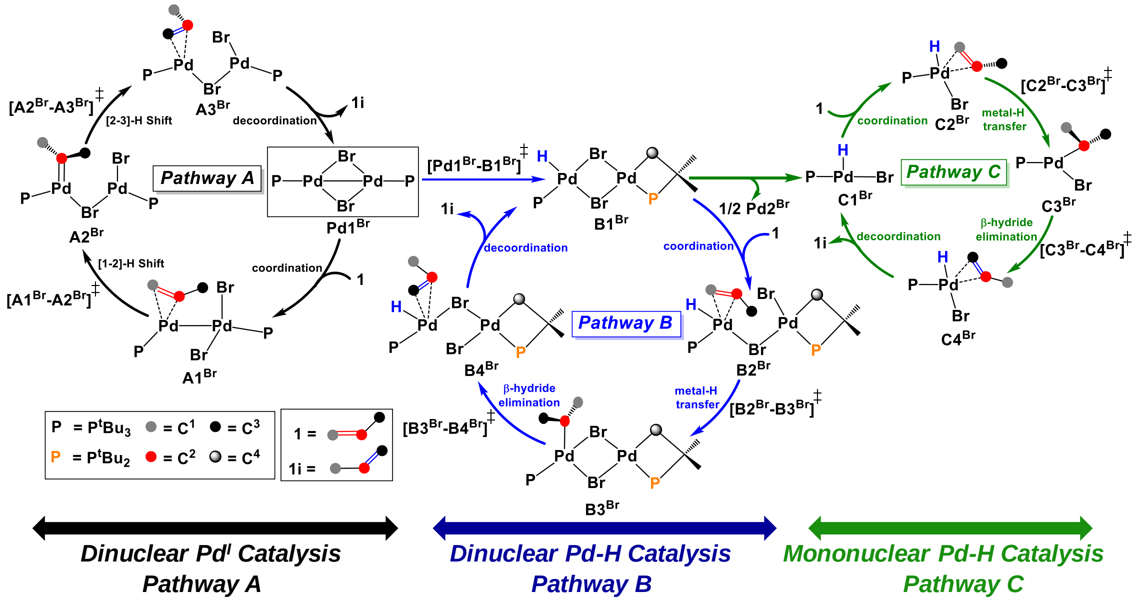
Enol esters are considered as one of the most valuable precursors in a variety of organic transformations.[1] Due to their importance in organic transformations, several studies have been performed towards the development of enol ester synthesis.[2] Recently, Gooβen and coworkers have developed an olefin isomerization reaction strategy for the formation of enol esters with the help of highly active dimeric $[Pd(\mu\text{-}Br)(P^tBu_3)]_2$ catalyst $\mathbf{Pd1^{Br}}$.[3] Our calculations reveal that the dimeric pre-catalyst undergoes ligand-based C-H activation to provide dimeric, cyclometalated species $\mathbf{B1^{Br}}$, which then dissociates to the monomeric Pd-H species $\mathbf{C1^{Br}}$ (Scheme 1). The isomerization of propene follows the most favorable "pathway C" with an overall energy span of 22.0 kcal/mol. The study also includes the possible deactivation routes for the active catalyst giving rise to the double-cyclometalated Pd intermediate $\mathbf{Pd2^{Br}}$. Furthermore, our investigation also considers a systemic development of catalyst showing higher isomerization activity and lower deactivation route. This development along with the calculated results gains strong correspondence with the experimental observations.[4]



Scheme 1. Overview over isomerization pathways accessible from the pre-catalyst $[Pd(\mu\text{-}Br)(P^tBu_3)]_2$

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IL-03

Catalytic Chemical Networks with Dynamic Minimal Systems

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There remain critical gaps in our understanding of the emergence of functional biopolymers in the origins of Earth's biosphere. These knowledge gaps include a more detailed understanding of the roles of polymer synthesis, morphological assembly and feedback function, all functioning within mutualistic biopolymer networks that achieve progressive open-ended evolution. For instance, extant proteins, evolved over millions of years, carry out an impressive array of responsibilities, from catalysis and molecular recognition to motility and compartmentalization. One of the prime objectives of our lab is to investigate the possible origins of these advanced proteins from folds of short peptide based nanomaterials.[1-3] Furthermore, as recent phylogenetic analyses have hinted towards independent protein evolution, we propose to find out a synergistic functional nano-assembly between peptide and nucleic acid fragments which can template phosphodiester bond formations, hence setting the stage for functional biopolymer collaboration. Looking beyond, simplicity of preparation of these hybrid nanostructures coupled with the design flexibility has already started to unearth materials adaptable for industrial applications.[2-4] Through this talk, I will encompass the above concepts through the prism of the results from my group[2-4] where we are currently witnessing a remarkable overlap of self-assembled soft materials, nanomaterials and 2D materials with the worlds of biology.[2-4] Also, I will share our recent results on dissipative self-assemblies.[5] In living systems, dissipative processes are driven by the endergonic hydrolysis of chemical fuels such as nucleotide triphosphates. Recently we have demonstrated through a simple model system, the realization of a transient self-assembled state by utilizing the catalytic effect of histidine on the formation and breaking of ester bonds.[4]

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IL-04

Lanthanide-doped Colloidal Luminescent Nanocrystals Phosphor and Detection Applications

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The scientific quest towards lanthanide (Ln^{3+})-doped nanomaterials is continuously increasing due to their unique optical properties resulting from their inner 4*f* electrons.[1] They undergo intra 4*f* transitions covering a wide range, say from ultraviolet (UV) to near infrared (NIR) region. In addition to the generally observed Stokes emission, they show interesting upconverting property, where one or more low energy photons are combined to produce high energy light.[2] These materials find various applications such as phosphors, sensors, biological probes, anti-counterfeiting agents, etc. This talk will discuss some of the works from our group on Ln^{3+}-doped colloidal materials for light emitting and detection applications.[3] The first part of the talk will cover the synthesis and characterization of colloidal $Ce^{3+}/Mn^{2+}/Tm^{3+}$-doped $NaYF_4$ with strong white light emission[4] This colloidal phosphor was easily incorporated into a polymer to develop transparent films. The resulting Ce^{3+}/Tm^{3+}-doped $NaYF_4$ displays strong white light whose spectral patterns matches closely with commercially used Ce^{3+}-doped YAG phosphor.[5]

In the second part of the talk I will discuss how the ability of the resonance energy transfer of Ln^{3+}-doped materials can be explored for the detection applications. Representative examples where the Ln^{3+}-doped colloidal nanoparticles used in the detection of Cu^{2+} ions, [6] H_2O_2,[7] melamine,[8]etc. will be discussed. Finally, design of multifucntional ligands which are able to sensitize Ln^{3+} emissions as well as assist in the detection of nitroaromatics and carbonates will be discussed.

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IL-05

Base Metal Catalyzed Borylation of Aryl Halides and Alkenes

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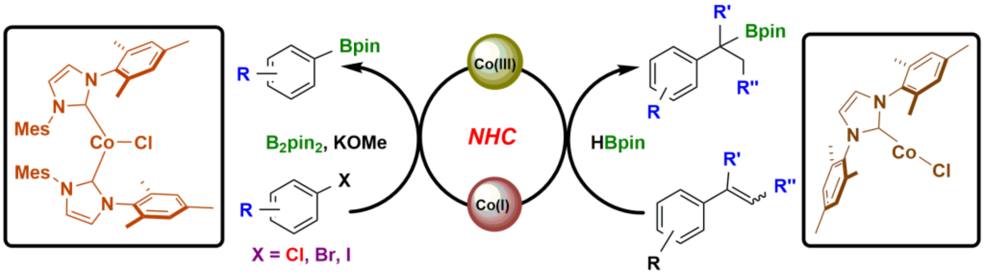
Organoboronates have been well recognized as indispensable building blocks in organic synthesis. Their importance in current scenario of chemical, medicinal and material science is manifested by its ubiquity in these fields, mainly because these stable esters can be selectively transformed into wide number of functionalities by vast number of available protocols.[1] However, most of their efficient synthetic routes rely on heavy metal based catalysts such as Pd, Rh, Ir etc. which suffers from inherent toxicity, cost and sustainability concerns.[2] This obviously put forth the needful for the development of catalytic systems based on earth abundant metals like Mn, Fe, Co etc. We have developed *N*-heterocyclic carbene supported cobalt catalyst for the synthesis of aryl and alkyl boronic esters using cheap as well as challenging precursors, such as aryl chlorides[3] and substituted alkenes.[4] The cobalt-complex Co(IMes)$_2$Cl$_2$ in presence of base and *bis*(pinacolato)diboron (B$_2$pin$_2$) affords aryl halide borylation with good to excellent yieldsunder mild reaction conditions. Mechanistic investigation verifies the involvement of *in situ* generated reduced complex Co(IMes)$_2$Cl as an active catalyst which undergoes Co(I)-Co(III) catalytic cycle. The potential of Co(I) complex,Co(IMes)$_2$Cl to undergo oxidative addition was further utilized in hydroboration of substituted vinyl arenes with HBpin in an unusual Markovnikov fashion. The key results will be discussed.



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Student lectures

SL-01

pH-Responsive Autofluorescent Amphiphilic Brush Copolymer for Efficient Delivery of Nonfluorescent Chemotherapeutic Agents

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Nowadays, delivery of clinically approved nonfluorescent drugs is facing lot of challenges because it is difficult to monitor the intracellular drug delivery without having any integrated fluorescent moiety into the drug delivery vehicle. Nonfluorescent drug such as, chlorambucil (CBL), an aromatic nitrogen mustard has been emerged as a suitable candidate for cancer therapy owing to their ability to alkylate deoxyribonucleic acid (DNA) *via* the construction of aziridinium ring as an intermediate. Herein, we have strategically developed an autofluorescent acid-disintegrable polymeric nanocarrier based on poly(maleimide-*alt*-styrene) skeleton by virtue of the sequence-specific copolymerization of two rationally designed monomers, PEG bearing styrene and CBL conjugated *N*-substituted maleimide *via* reversible addition-fragmentation chain transfer (RAFT) polymerization. The as-synthesized amphiphilic brush copolymers could self-assemble into 100-150 nm diameter nanoparticles depending on the copolymer compositions in water. *In vitro* release studies revealed that about 70% drug was retained under physiological conditions at pH 7.4. Notably, at endolysosomal pH 5.0, 90% of the CBL was released by the pH-induced cleavage of the aliphatic ester linkages connecting CBL to the maleimide unit. Cytotoxic analysis implies the superior cell killing property of the nanocarrier towards cervical cancer (HeLa) cell lines compared to the normal cell lines. The copolymers can exhibit photoluminescence under UV light irradiation although it doesn't contain any conventional fluorophore unit into it. This facet assists us to track the CBL conjugated autofluorescent nanocarriers intracellularly through fluorescence microscope imaging technique. Ultimately, 4-(4-nitrobenzyl)pyridine (NBP) colorimetric assay was executed to evaluate the ability of CBL-based polymeric nanocarriers towards DNA alkylation.

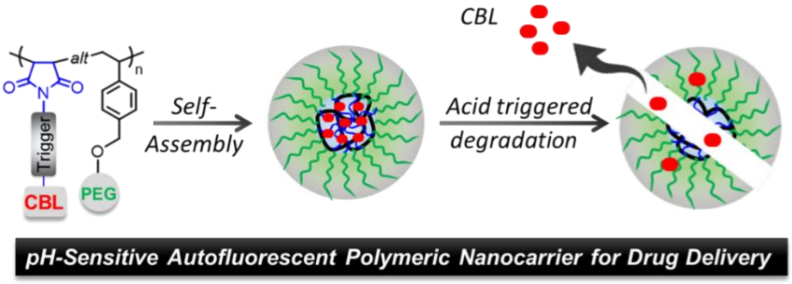

Figure 1. Graphical abstract.

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SL-02

pH-induced phase transition and crystallization ofsoft-oxometalates (SOMs) into polyoxometalates(POMs): a study on crystallization from colloids

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Crystallization has long been an important tool for studyingand exploring oxometalate chemistry in theform of polyoxometalates (POMs). Oxometalates often existin the colloidal length scale regime and exploration of theirstructural diversities can only be accomplished by fine tuningthe reaction conditions towards crystallization.[1]This technique often neglects the existence of a rich diversityof entities that are possible in the colloidal regime.[2] In order tocontrol the structure and to achieve desired properties ofPOMs, a proper understanding of crystallization is required.Thus in this presentation, we demonstrate that POMs nucleate fromcolloidal soft-oxometalates (SOMs)[1] and a better understandingof the SOM phase can be beneficial in understandingthe crystallization process of POMs.In this work, we demonstrate a simple approach for growing 1D (one-dimensional) inorganic chains of $K(C_6H_{16}N)_3Mo_8O_{26}.H_2O$ POM from its corresponding colloidal SOM phase through the variation of pH. Crystal structure andHirshfeld surface studies reveal the role of triethylammonium cations inrestricting the growth of the 1D chain into 2D/3D (two-/three-dimensional)structures.[3] During the nucleation process from the heterogeneous SOM phase,some of the intermolecular interactions in the dispersion phase are retained inthe crystal structure, which was evident from residual O···O interactions. Thecrystallization of the species from its colloidal form as a function of pH wasstudied by the use of Raman spectroscopy, time-dependent DLS (dynamic light scattering) measurement and zeta-potentialstudies, revealing the co-existence of both the crystal and the colloidal forms atpH 3–2. This brings us to the conclusion that in the crystallization of POMs, thecolloidal SOM phase precedes the crystalline POM phase which occurs via aphase transition. This work could open up avenues for the study of POMformation from the stand-point of colloidal chemistry and SOMs.

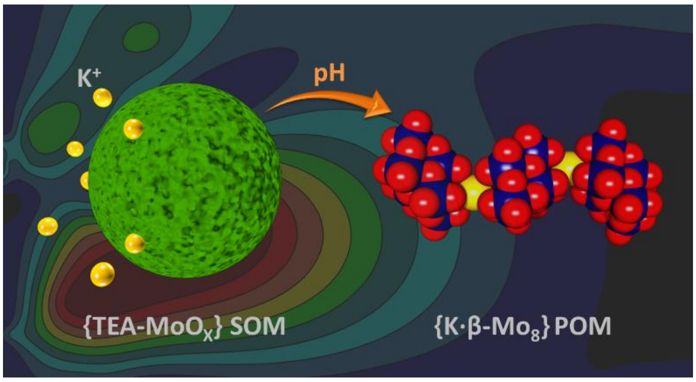

Figure 1. Phase transition of colloidal {TEA-MoO_X} SOM to crystalline {K·β-Mo_8} POM depicting pre-existence of SOM phase in crystallization of POMs.

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SL-03

Probing the Effect of Glucose on the Activity and Stability of aβ-Glucosidase: An All Atom Molecular Dynamic Simulation Investigation

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β-Glucosidase (EC 3.2.1.21) plays an essential role in the removal of glycosyl residues from the disaccharide cellobiose to produce glucose during the hydrolysis of lignocellulosic biomass. While there exist a few β-glucosidase that are tolerant to large concentrations of glucose, these enzymes are typically prone to glucose inhibition. Understanding the basis of this inhibition is important for the production of cheaper biofuels from lignocellulose.[1–3] In this study, the molecular basis of glucose inhibition of the GH1 β-Glucosidase (B8CYA8) from *Halothermothrixorenii* was probed through all-atom molecular dynamic simulation at different temperatures and glucose concentrations with various substrate (p-NPGlc) concentration. Our results show that glucose induces a broadening of the active site tunnel through residues lining the tunnel and facilitates the accumulation of glucose. In particular, we observed that glucose accumulates at the tunnel entrance and near the catalytic sites to block substrate accessibility and inhibit enzyme activity. Though at very low substrate concentrations, enzyme activity decreases with glucose concentrations, at moderate to high substrate concentrations B8CYA8 activity is maximum for 0.5 M glucose concentration. Our studies explain the enhancement of enzyme activity for an intermediate glucose concentration. Overall, the results emphasize understanding the role of residues along the active site tunnel for the engineering of glucose tolerant β-glucosidase

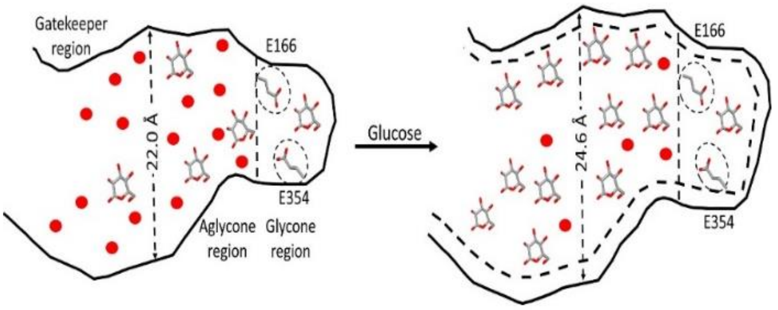

Figure 1. Tunnel view of the protein β-Glucosidase (B8CYA8). Red dot represents water molecules present in the tunnel of the protein.

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SL-04

Synergistic Tricolor Emission-Based White light from Organic-Inorganic Hybrid Gel

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The development of engineered hybrid systems by encapsulating nanoparticles in gel scaffolds and their synergistic effects are highly important for fabrication of advance functional materials. Herein, a series of dipeptides containing aromatic amino acids at the N-terminal and aliphatic amino acid at the C- terminal were synthesized and studied. Among them, only the dipeptide L-Phe-L-Val forms both hydrogelator and organogelaor, depending on the N and C terminal protecting groups. The organogel shows bright blue emission under 366 nm UV irradiation, however the hydrogel does not show such blue emission. The blue emitting organogel efficiently encapsulate green emission source CdSe quantum dots and red emission source LD 700 perchlorate dye. The resulting organic-inorganic hybrid gel exhibits pure white light emission due to the synergistic effect under 366 nm UV irradiation.

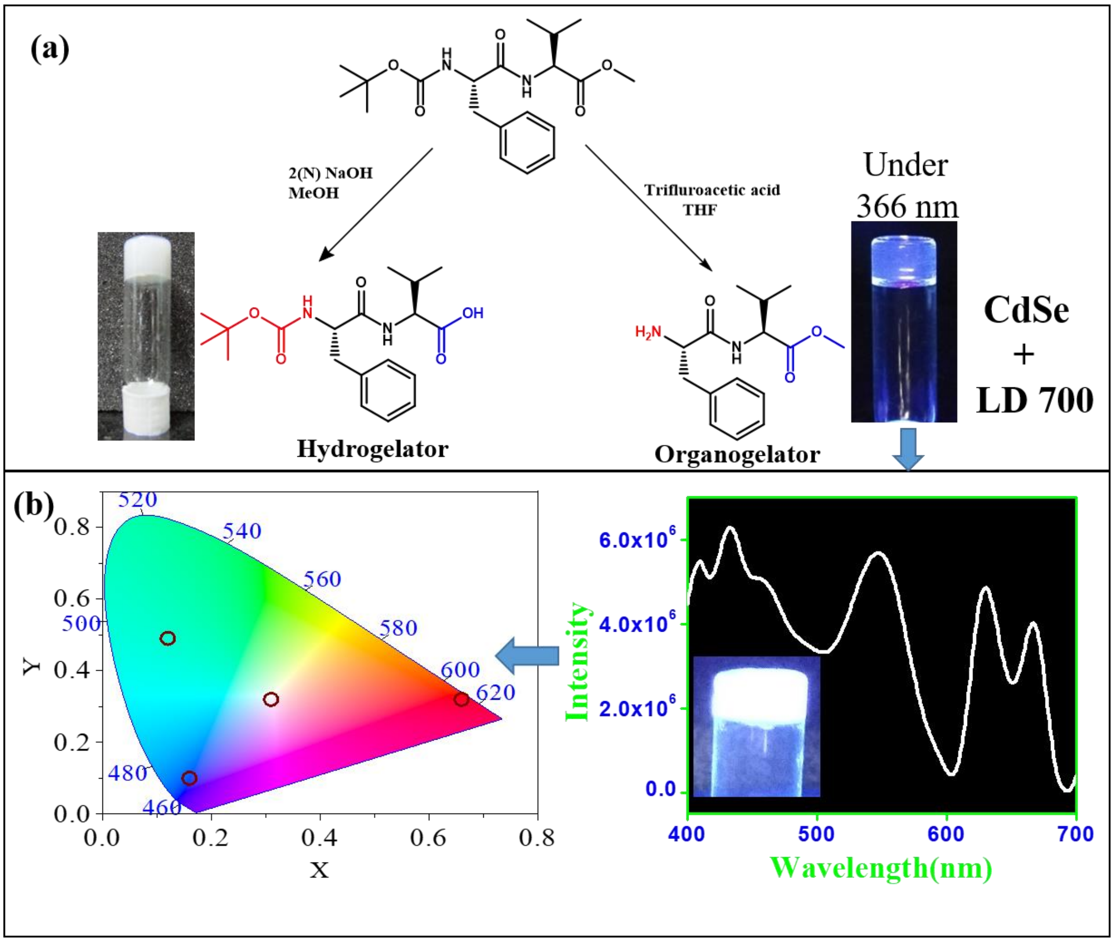

Figure 1: (a) Formation of hydrogelator and organogelator from a common scaffolds. (b) Fluorescence spectra and CIE color coordinate of white light emitting organic-inorganic hybrid gel under excitation at 366 nm.

SL-05

Selective Photocatalytic Oxygenation by a Molecular Iron complex using Water as O-atom Source

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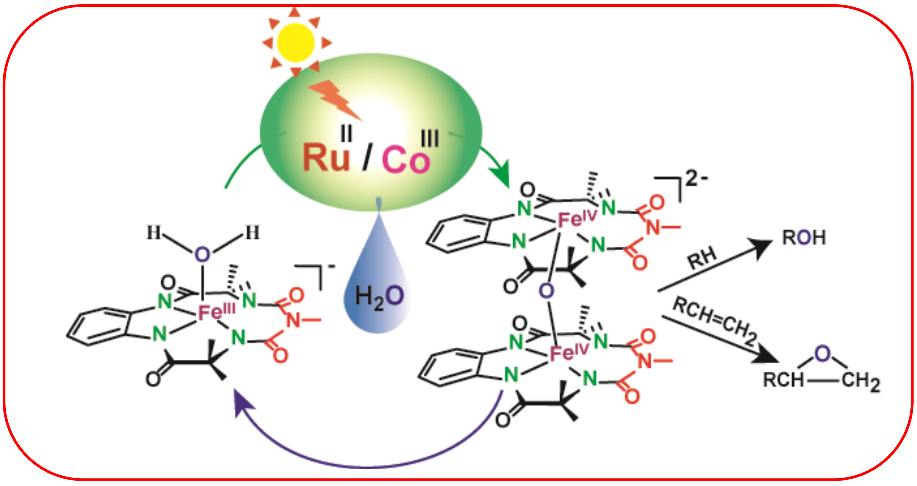
The conversion of sunlight to chemical energy has been one of the great challenges for chemists in the quest for a sustainable world. The inspiration for such a process comes from photosynthesis, wherein sunlight is used to accomplish the energetically uphill water oxidation reaction. During photosynthesis, a high-valent manganese-oxo cluster has been proposed to be the active intermediate for water oxidation. Similarly, high valent iron-oxo complexes have been shown to be the active intermediates for heme/non-heme enzymes and their model complexes which catalyse hydrocarbon oxidation using O_2 as the oxidant. Combining these two concepts, we have demonstrated that visible light can be utilized for the oxidation of organic substrates using water as the oxygen atom source.

My talk will be mainly focusing on a molecular iron complex [(bTAML)Fe^{III}–OH_2] which selectively catalyzes the photocatalytic hydroxylation and epoxidation reactions of alkanes and alkenes, respectively, using water as the oxygen-atom source. Upon the oxidation of unactivated alkanes, which included several substrates including natural products, hydroxylation was observed mostly at the 3^o C–H bonds with 3^o : 2^o selectivity up to 100 : 1. When alkenes were used as the substrates, epoxides were predominantly formed with high yields. In the presence of $H_2{}^{18}O$, more than 90% of the ^{18}O-labelled oxygen atoms were incorporated into the hydroxylated and epoxide product indicating that water was the primary oxygen source. Mechanistic studies indicate the formation of an active [{(bTAML)Fe^{IV}}$_2$-m-oxo]$_2$ dimer from the starting complex via PCET. The subsequent disproportionation of dimer upon addition of substrate, leading to the formation of Fe^V(O), renders the high selectivity observed in these reactions.



Posters

P-01

Synthesis of the Isomerically Pure Thienoacene and Ladder Polymer and Their Electronic, Mechanical and Optical Properties

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Small molecule semiconductors are gaining significant attention as active materials in the organic electronic devices as these molecules are easy to purify and form crystalline films for the fabrication of the desired high-performance devices. With their electron rich skeletons, thienoacenes have traditionally been used as the hole transporting small molecule semiconductors. A small change in the molecular structure of thienoacenes results in a significant change in their properties and OFET device performance. The crystals of syn- and anti-isomers of thienopentacene (Fig. 2, the smallest members of the synthesized thienoacene series) showed different mechanical properties. The crystal of anti-isomer displays excellent elasticity. Here, we develop the new, simple yet amazing synthon, (3,4-di(hex-1-yn-1-yl)thiophene-2,5-diyl)bis(trimethylstannane), for the synthesis of a wide variety of thienoacenes. One of the advantages of this synthon is its ability to give isomerically pure thienoacenes in excellent yields. Using this synthon, we have synthesized a "nonathienocene" having all syn-oriented thiophenes. It can be further exploited to obtain thienoacene-based ladder polymers.

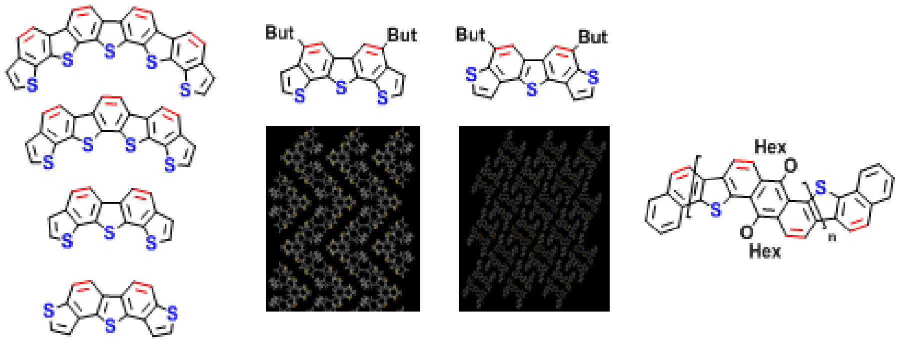

Fig : 1 Fig : 2 Fig : 3

Figure 1.Isomerically pure ThienoaceneAnd Ladder Polymer

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P-02

Resistive switching in organic semiconductor devices: a mechanistic approach

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In the past decades, organic resistive memory devices (RMD) have drawn a lot of attention in the field of data storage devices.[1-2] Unlike traditional silicon-based memory devices with binary memory states, organic resistive memory devices possess multiple resistive states which enhance their data storage capacity.[3-5] There are many switching mechanism have been proposed and clarified in organic devices, mainly categorized into thermochemical reaction, ion migration, interfacial reaction, charge trapping/de-trapping, charge transfer, electrochemical redox reaction, and conformational change. Among them charge trapping/de-trapping is one of the most important. In our study, we are showing this mechanism for RRAM device application. In order to explore the molecular assembly in solution and on different substrates as films, photophysical properties and self assembling properties on film states of these compounds were studied. This poster will demonstrate the systematic investigation of the mechanism of selective flaunt of resistive switching in one of the derivative over other, by the supporting evidence from various electrical and microscopic techniques.

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P-03

Redox-active Phenalenyl Ligand in Catalysis

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Bhagat Singh, Soumi Chakraborty, Pavan K Vardhanapu, Arup Mukherjee, Anand Pariyar,
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Phenalenyl (PLY) ligand is a well-known odd alternate hydrocarbon molecule; owing to availability of its non-bonding molecular orbital can serve as excellent building block for construction of organic radical based materials, quantum simulator, molecular switch and spintronics devices etc. More than a half-century ago, Hückel calculations have revealed[1] that the phenalenyl moiety can switch its electronic state between electronically active open shell neutral radical and closed shell cation and anion. But the PLY chemistry did not observe any utilization in catalysisto do organic transformations before last decade.

Taking the advantage of switching property of PLY,first time we explored in homogeneous as well as heterogeneous catalysis using transition metal or transition metal free catalysts. Transition metals such as Fe, Co, Ni, Mn based complexes have been utilized in single compartment H_2O_2 fuel cell[2], C-H arylation, reduction of various functional groups. Interestingly, PLY based transition metal mimicking catalysts were also developed and utilized in C-H arylation of activated and unactivatedarenes with diazo[3] as well as challenging halo partners. The concept was successfully improvised for heterogeneous catalysis in C-H arylation reaction.

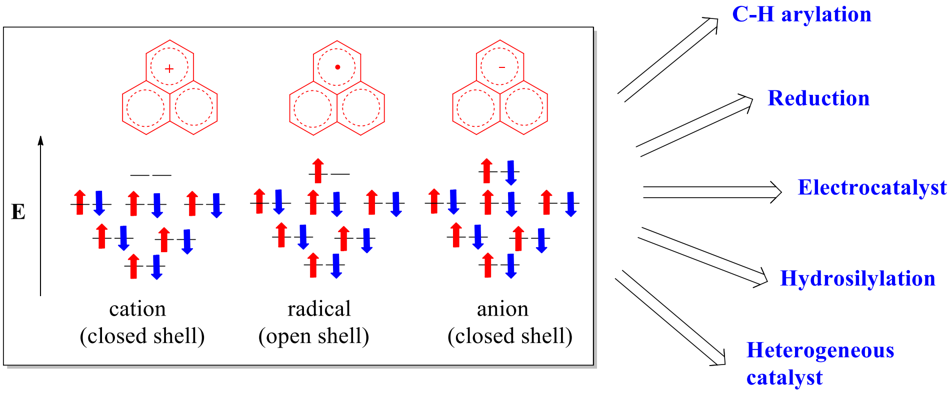

Figure 1.Phenalenyl ligand in catalysis

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P-04

A Water-Soluble Tryptophan Based Dual-Action Polymeric Probe for Turn-On Sensing, Bioimaging and Removal of Mercury(II) Ions; Chemosensor for Hydrogen Sulphate Ions

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At present, selective recognition and sensing of both cations and anions by a single fluorescent receptors have attracted a considerable research interest in terms of their potential environmental and biological applications. In this context, a new tryptophan-dithiocarbamate based fluorescence polymeric probe was synthesized and has been targeted with a view for sensing both cation and anion in aqueous media. Upon addition of various metal ions, the probe afforded an irreversible change only with Hg^{2+} ions in aqueous media with a five-fold enhancement of the fluorescence ($\Phi = 0.055 \rightarrow 0.250$) attributed to photo-induced electron transfer (PET) process. Intracellular detection of Hg^{2+} ions was achieved in human breast cancer cell line, MDA-MB-468 using the synthesized macromolecular probe. Moreover, this unique design has an unprecedented detection sensitivity of 300 parts per trillion (ppt) for Hg^{2+} ions, the most effective water-soluble amino acid-based polymeric sensor reported till so far. Hg^{2+} ions gets trapped when it passed through a column containing polymeric probe with 94% removal capacity as verified using ICP-OES instrument. In addition, the probe can also be able detect parts per million (ppm) level of hydrogen sulphate anion (HSO_4^-) among various anions with high selectivity in aqueous medium, induced by the hydrogen bonding interactions of polymeric probe with the anion. Even though our synthesized polymeric probe possesses two separate binding site for HSO_4^- and Hg^{2+} ions, it has been shown that the presence of the cation influences the binding of the anion.

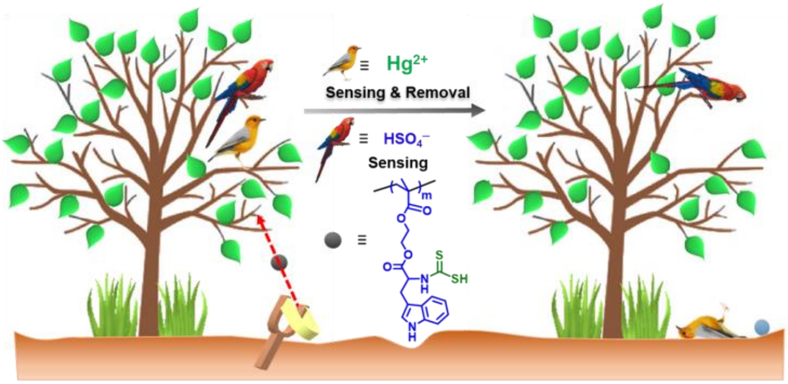

Figure 1. Graphical abstract

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Kinetic and thermodynamic control over crystallization to yield H and J type dimmers in single crystal: Excitonic coupling and resulting optical outputs in the solid state

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Optical properties of molecular semiconductors are exceedingly dependent on intermolecular electronic coupling and are very much illustrious in their solid state and thin film devices.[1] The photophysical behaviour in such films and devices are known to be governed by the mode of aggregate which is dominated by columbic intermolecular interaction and is classified in two most authoritative forms of *J* and *H* aggregates, described by Devydov and Kasha in their molecular exciton theory.[2] In molecular aggregates, the columbic coupling between two neighbour chromophores results in the band energy change of excitons in *J* and *H* aggregates states leading to the change of their optical properties.[3]

Here we present a donor-acceptor small molecular semiconductor (**25TR**) in which the thiophene and rhodanine groups were defined as donor and acceptor units respectively. Interestingly, **25TR** crystallizes in two different forms which were distinctly different in their colour and shape of the crystals. One was yellow in colour which crystallize in monoclinic form whereas the other form appeared to be crimson red in colour which crystallizes in triclinic phase. The most fascinating observations about these two polymorphs is as follows: their single crystal molecular packing revealed that the yellow form subsist as perfect co-facially arranged molecular stack whereas the crimson form in a slipped stack configuration. It was a unique example of a single molecular semiconductor crystallized in two forms of their molecular aggregates *viz*, *H* (Yellow) and *J* (Crimson) states with the characteristic optical outputs of the respective aggregated state. Interestingly the yellow form was non fluorescent, while the crimson form of the same compound afforded bright orange fluorescence upon exposure to UV light. Upon mechanical grinding or shearing of the yellow crystalline form of the **25TR**, we observed the transformation of the non-fluorescent form to the fluorescent form. A detailed spectroscopic and X-ray diffraction data analysis and computational analysis will be presented in the poster to divulge the mechanism of these phenomenon.

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P-06

Selective Hydroboration of Carboxylic Acids with a Homogeneous Manganese Catalyst

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Catalytic reduction of carboxylic acid to its corresponding alcohol in is a challenging task of great importance for the production of a variety of value-added chemicals. Herein, earth abundant metal manganese-catalyzed chemoselective hydroboration of acids has been developed with a high turnover number (>99000) and turnover frequency (>2000 h^{-1}) at 25 ^{O}C. This method displayed tolerance of electronically and sterically differentiated substrates with high chemoselectivity. Importantly, aliphatic long chain fatty acids, including biomass-derived compounds, can be efficiently reduced. Mechanistic studies revealed that the reaction is going through the formation of active Manganese-hydride species via an insertion and bond metathesis type mechanism. Boronated compounds could be hydrolysed to their corresponding alcohols with high yields.

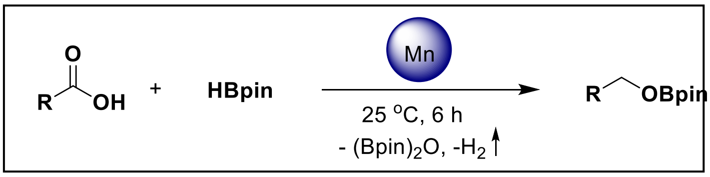

Figure 1. Manganese catalysed Hydroboration of Carboxylic Acid

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Engineering peptide-based sealants to facilitate faster blood-clotting.

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Self-assembled peptide based functional biomaterials are promising tools for biomedical applications. We aim to engineer fibrin inspired peptide-based sealant to faciliate efficient blood clotting to handle bleeding disorder of accident victims, injured soldiers and hemophilia patients. Our designed sealants are stabilized by lysine-aspartate ionic interactions and also by *N*-ε-(γ-glutamyl) lysine isopeptide bond mediated covalent interactions which actually mimics natural fibrinogen γ chain. Designed sealant exhibited strong mechanical properties like indigenous fibrin and biocompatibility as well as biodegradability evidenced from AFM, FE-SEM and cell-based studies. Such nature-inspired peptide-based sealants might be potentially translated into clinics to promote efficient blood clotting while handling traumatic coagulopathy and impaired bleeding disorder.

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A reversible photoresponsive activity of a carbonic anhydrase mimic

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Abstract: Carbonic anhydrase (CA) is an enzyme that reversibly transforms carbondioxide and water to a carbonate ion and a proton. Considering the importance of the enzyme, a number of CA-mimics have been reported previously. However, photoresponsive enzyme mimics, where the CA-activity can be turned on and off with light, has not been reported so far. Considering the active site of the enzyme, we have designed an active site mimic that can offer reversible control on the catalytic activity using light. Moreover, in the presence of a polymeric system, we demonstrate that the carbonic anhydrase activity can show a better rate enhancement in the active *cis*-form of the photoisomer**.** A photochromic azobenzene based Zn^{2+}-complex shows efficient carbonic anhydrase activity in the *cis*-form. In the presence of a cationic polymer that can stabilize the transition state, the activity further improves. Reversible control of the activity was achieved by the photoswitching of the complex with light.

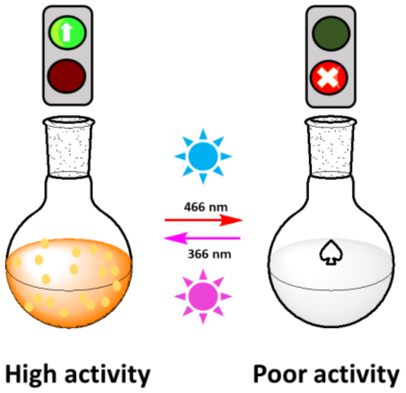

Figure1.Reversible catalytic-activity of photoswitching complex with light

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Templated assembly formed by ATP and GTP and their morphological study

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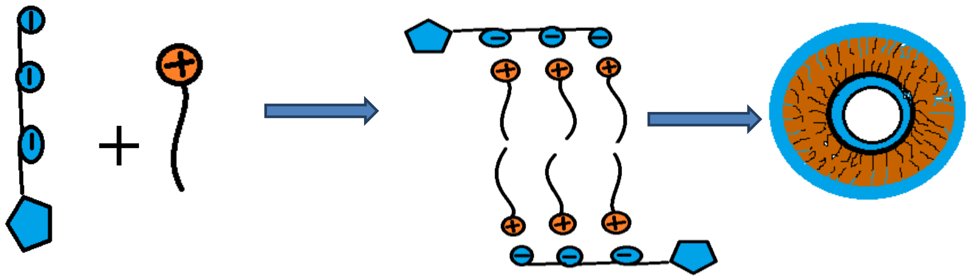
In nature there are many examples where one molecule can act as a template for other molecules to form assembly. For example in nature, ATP binds with G-actin and polymerises to form F-actin. ATP and GTP are very important molecules for biological system. They serve as energy source for living systems. In our project we show how they act as template to form assembly with positively charged lipid and the difference in their morphology. We also studied the stability of these assemblies under different conditions. We also studied the causes and effects on templated assembly by varying the parameters a little bit.



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P-10

Base Promoted Acceptorless Dehydrogenation/Homolytic Aromatic Substitution Cascade toward the Synthesis of Phenanthridines

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Phenanthridines represent a highly important class of *N*-heteroaryl framework, possessing wide occurrence in natural products and biologically active alkaloids, bearing antitumor, antibacterial properties. Moreover, broad application of these framework and its derivatives impose improvement of physical properties in functional materials. Mainly transition metals were applied for the generation of phenanthridines by cross coupling or radical pathways.[1]
Herein, we report a transition metal free dehydrogenative oxidation of alcohol and direct condensation reaction with amine to drive C-N bond construction followed by C-C coupling in a cascade sequence to achieve the targeted phenanthridine moiety. The used base KO^tBu played a dual role in acceptorless dehydrogenation [2] and homolytic aromatic substitution reaction.[3,4] Several mechanistic studies were performed to have a clear picture on the reaction pathway. This protocol demonstrates synthetic advantages in terms of cheap starting materials like alcohols over corresponding carbonyl compounds or alkyl halides and also shows the challenging reactivity control by tuning the electronic nature of different reaction intermediates.

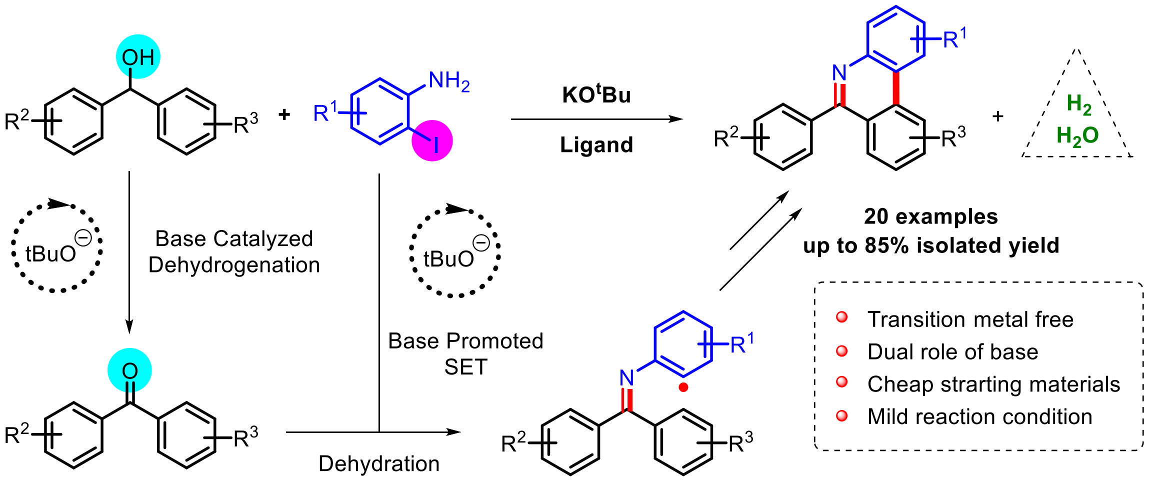

Figure 1. Base Promoted Cascade Synthesis of Phenanthridines

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P-11

Nickel(II) Tetraphenylporphyrin as an Efficient Photocatalyst Featuring Visible Light Promoted Dual Redox Activities

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Light is the most abundant, inexpensive, everlasting and unpolluted energy source in nature and has been utilized in copious synthetic applications. Apart from less discriminating and high energetic UV sources, visible light mediated photoredox catalysis has become a trustable and influential synthetic tool for organic synthesis over the last few years. Herein we present a macrocyclic *meso*-tetraphenylporphyrin ligand coordinated Ni(II) complex (NiTPP) as a robust, cost-effective and efficient visible light induced photoredox catalyst with great synthetic efficiency. The ground state electrochemical data (CV) and electronic absorption (UV-Vis) spectra reveals the excited state redox potentials for $[\text{NiTPP}]^*/[\text{NiTPP}]^{\cdot-}$ and $\text{NiTPP}]^{\cdot+}/[\text{NiTPP}]^*$ couples as +1.17 V and -1.57 V vs SCE respectively. The potential values represent NiTPP as a more potent photocatalyst compare to the well explored $[\text{Ru(bpy)}_3]^{2+}$.

The non-precious photocatalyst exhibits excited state redox reactions in dual fashions, i.e., it is capable of undergoing both oxidative quenching as well as reductive quenching pathways, which is efficacious even in gram scale synthesis too. Such versatility of a photocatalyst based on first row transition metals is very scarce.[1] This unique phenomenon allows one to perform diverse types of redox reactions by employing a single catalyst. Two different sets of chemical reactions have been performed to represent the synthetic utility. The catalyst showed superior efficiency in both C-C (annulation)[2] and C-heteroatom (chalcogention)[3] bond forming reactions. Thus, considering the earth-abundant, less-toxic core metal and readily accessible ligand framework, mild reaction conditions and high catalytic efficiency, we believe that NiTPP is a valuable addition to the photocatalyst library and this study will lead to more practical green and economical synthetic applications using earth-abundant photoredox catalysts.

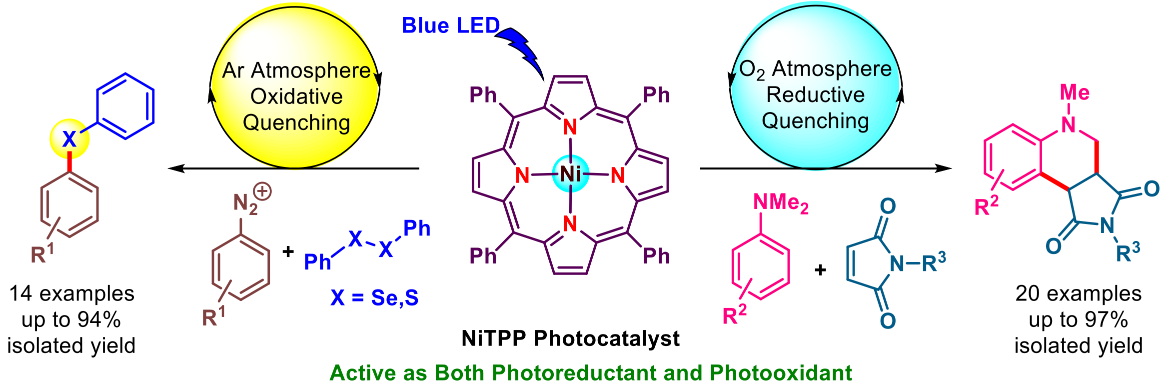

Figure 1. Application of NiTPP as Both Photoreductant and Photooxidant.

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(3+*d*)–dimensional superspace formalism applied to molecular crystals

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Investigation of high Z' structures (where Z' is the number of molecules in the asymmetric unit) have now spanned over two decades[1, 2, 3]. It is found that "In 50% of the structures n molecules are related by a pseudo-translation that would be a crystallographic translation but for small molecular displacements and rotations."Are high-Z' structuresvariants of an incommensurately modulated crystal (an infinite-Z' structure).We have employed (3+1)*D*superspace to describe high Z' superstructures as commensurately modulated structures[4].

Here, we intend to demonstrate Superspace description of diffraction patterns of few molecular crystals which consists of superlattice reflections.

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A flavonol that acts as a potential DNA minor groove binder as also an efficient G-quadruplex loop binder

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A fisetin derivative, belonging to the flavonol family, has been synthesized. Fisetin is obtained from natural resources and is a very important small compound in treating neurological disorders. The synthesized compound, 2-(3,4-diethoxyphenyl)-3-hydroxy-4H-benzo[h]chromen-4-one (abbreviated as DEPHBC) has been found to bind to the minor groove of ctDNA in contrast to fisetin, which is a DNA intercalator. However, DEPHBC can further stabilize the DNA helix. Like fisetin, DEPHBC also serves as a loop binder to G-quadruplex, but the binding is much stronger compared to many loop binders. This provides appreciable stability to G-quadruplex DNA. DEPHBC can undergo excited state intramolecular proton transfer (ESIPT) and hence exists in its normal and tautomeric (proton transferred) forms in the excited state. DNA minor groove and G-quadruplex loop binding facilitates the tautomer emission over the normal form and hence can act as a reporter for the binding processes.[1]

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Mechanical landscape of organic crystals

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Single crystals are typically brittle, inelastic materials. Such mechanical responses limit their use in practical applications, particularly in flexible electronics and optical devices.Now, the elastic organic single crystals[1]are a research area in its infancy stage and attract the attention of the researcher. Here we describe single crystals of polyhalogenated imine, which exhibit remarkable elastic and plastic flexibility along with twisting behavior. There are few reports on plastic organic crystals that also undergo twisting,[2] but the organic crystal which is elastically bendable as well as shifting of the twisting position along the crystallength is rarest. To the best of our knowledge this is the first example in organic crystal.The presence of these two distinct propertiesin the same crystal is unusual and unprecedented because in general theyfollow respectively from isotropy and anisotropy in the crystalpacking. Besides we are presenting isostructurality and polymorphism in the context of crystal structure and mechanical property.

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P-15

Room Temperature, Open Air Atmosphere, and Instantaneous Synthesis of Perovskite Quantum Dots Through Halide Exchange Employing Non-Metal Based Inexpensive Halide Sources HCl/HI

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Abstract: Instantaneous synthesis of blue to green to yellow to red emitting all inorganic perovskite quantum dots ($CsPbBr_3$ and mixed halide PQDs) have been achieved at room temperature, in open air atmosphere (no glove box) and through halide exchange employing easily available, inexpensive and non-metal based halide sources like HCl and HI. Direct use of the halide sources (HCl, HI) to the PQD solution in ambient condition is capable of performing the successful halide exchange instantaneously alleviating the complicated pre-treatment of the halide sources as reported in literature.[1] Halide exchange has been observed to be reversible in nature. All PQDs are highly crystalline and cubic in shape with a size uniformity of ca. 11.3 ± 0.1 nm. These PQDs are stable in solution phase for a few weeks in open air atmosphere. PL emission spectra are quite narrow (FWHM varying from 17 – 39 nm) and PLQY are quite high (80% for even Br/I mixed PQDs). A very regular increase of PL lifetime has been observed as we move from Cl rich to Br rich to I rich PQDs[2]. Ultrafast dynamics revealed excited state time constants from femtosecond to nanosecond timescales, similar to PQDs synthesized through hot injection, inert atmosphere procedure.[3] These blue-green-yellow-red emitting PQDs are quite bright and mostly ON (average ON fraction from 75 to 85 %) even at the single particle level. This kind of room temperature (no use of heat energy/electrical energy), open air atmosphere (no use of cumbersome inert atmosphere), instantaneous (less time consuming) near quantitative synthesis of PQDs using inexpensive (thrifty) and easily available non-metal based halides (HCl/HI) are extremely important for large scale synthesis of PQDs for various applications.[4]

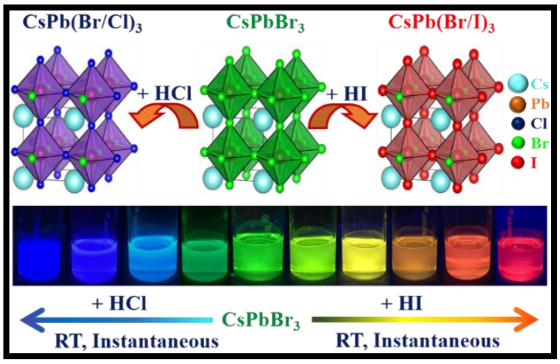

Figure 1. Formation of mixed halide PQDs after addition of HCl and HI to $CsPbBr_3$

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P-16

Computational Investigation of $B(C_6F_5)_3$-Catalyzed Heterocyclization of *N*-tosylhydrazones with Aniline

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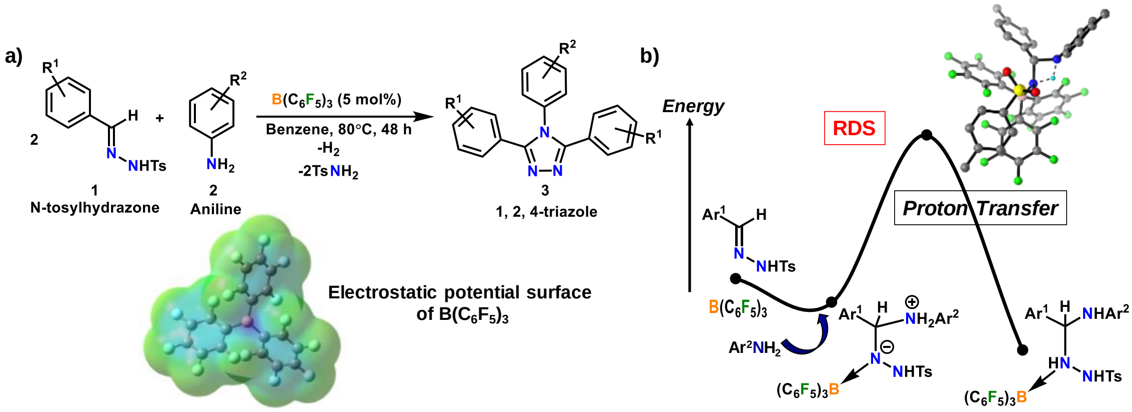
Heterocyclization of *N*-Tosylhydrazones with anilines affords a powerful strategy for the development of biologically and chemically active 1,2,4-triazole complexes.[1] In addition to the biological activity, 1,2,4-triazoles show remarkable potential towards metal binding due to presence of multiple heteroatoms that can easily coordinate to the metal center. Various 1,2,4-triazole derivatives have been described as having a wide variety of uses in materials science and in transition-metal complexes or metal-organic frameworks (MOFs). However, metal-free 1,2,4-triazole derivatives have also exhibited interesting and useful properties as advanced materials.[2] Recently, Maji and co-workers have developed metal free Tris(pentafluorophenyl)borane (BCF) catalysed heterocyclization of *N*-tosylhydrazones with anilines.[3] (Scheme 1a) Based on the experimental findings, we have reported a thorough state-of-the-art theoretical analysis of the mechanism employing DFT calculations at the B3LYP-D3/TZVP/CPCM(Benzene)//B3LYP/SVP level of theory. Our calculations suggest that the overall mechanistic pathway has four consecutive steps viz., Step I: formation of aniline assisted BCF coordinated intermediate; Step II: coordination of another *N*-tosylhydrazone and elimination of $TsNH_2$; Step III: cyclization and another $TsNH_2$ elimination step; and finally Step IV: H_2 elimination step. In addition, step I remains the rate-determining step for the overall reaction leading to the triazole formation. (Scheme 1b)



Scheme 1. (a) $B(C_6F_5)_3$catalyzedheterocyclization reaction. (b) Rate-determining step involving intramolecular proton transfer mechanism.

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P-17

Low-lying excited states of Diphenylpolyene and its derivatives towards singlet fission.

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The low-lying excited states of α,ω-Diphenylpolyenes namely 1,6-diphenyl-1,3,5-hexatriene (DPH), 1,8-diphenyl-1,3,5,7-octatetraene (DPO) and 1,10-diphenyl-1,3,5,7-decapentaene (DPD) have been studied using the Density Matrix Renormalization Group technique[1] within the Pariser-Parr-Pople model Hamiltonian[2]. We calculated the low-lying excited states of DPH, DPO and DPD molecules and their halogenated conformers in the singlet and triplet manifold which are crucial in understanding their photophysical properties. From the energy ordering of the singlet and triplet excited states we can infer the possibility of singlet fission[3](SF) mechanism in these systems. SF is a process where a singlet exciton gives rise to a pair of triplet excitons. Therefore, the efficiency of the solar cells can be enhanced through doping of SF materials. The DMRG calculation reveals that the above-mentioned systems satisfy the condition for SF[3] $[E(S_1) \leq 2*E(T_1)]$ and can act as potential materials for solar cell applications. The calculated lowest dipole allowed singlet excited state (S_1) of DPH was found to be 3.58eV which is in very good agreement with the experimental value of 3.31eV[4]. Theoretically calculated lowest triplet state T_1 lies at 1.35eV which is a good agreement with the experimental value of 1.53eV[4].

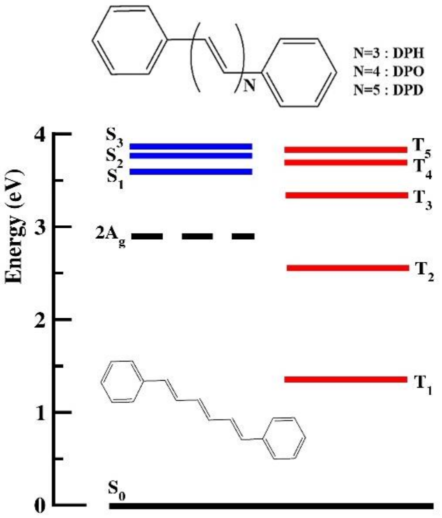

Figure 1. Low-lying singlet (S_n) and triplet (T_n) excited states of 1,6-diphenyl-1,3,5-hexatriene (DPH) molecule.

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Development of Nickel Cobalt Sulfide within an Organic Nanorod Array: An Efficient Catalyst for Oxygen Evolution Reaction

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Electrochemical splitting of water into hydrogen and oxygen is being considered as one of the most promising technologies for energy storage. Recently, transition metal (TM) based materials have demonstrated high catalytic efficiency toward oxygen evolution reaction and their integration with other conductive materials have resulted in further enhancement of activity. However, high-temperature annealing is an integral part of their synthesis. This motivated us to develop a room-temperature fabrication of conductive nanoarray with encapsulated TM-based nanocatalysts for highly efficient and durable water oxidation. Our group have experimentally figured out the advantages of transition metal sulfides over their oxide counterparts for promoting oxygen evolution reaction as an electrocatalyst in the recent past [1]. Taking a cue from the previous work, we prepared nickel cobalt sulfide nanoparticles embedded in TCNQ nanowire array ($NiCo_2S_x$-TCNQ nanoarray) on a copper mesh substrate as the pre-catalyst in this work. Via the anodization process, the TM-sulfide was then converted into corresponding hydroxides/oxyhydroxides that in turn acts as the active sites for electrocatalysis. The ratio of Ni and Co was varied to figure out the optimum ratio and after the sulfurization $NiCo_2S_x$ was found to show best electrocatalytic performance in terms of both overpotential requirement (248 mV for 10mA/cm^2) and stability under alkaline conditions. Interestingly, the activity of this $NiCo_2S_x$-TCNQ nanoarray was found to be much superior compared to only TCNQ (420 mV for 10mA/cm^2) or $NiCo_2S_x$ (414 mV for 10mA/cm^2) thereby suggesting the presence of synergistic effect between the two behind the promotion of oxygen evolution. Systematic studies using electrochemistry, microscopy and elemental analysis were performed to further validate the effect of this synergistic effect.

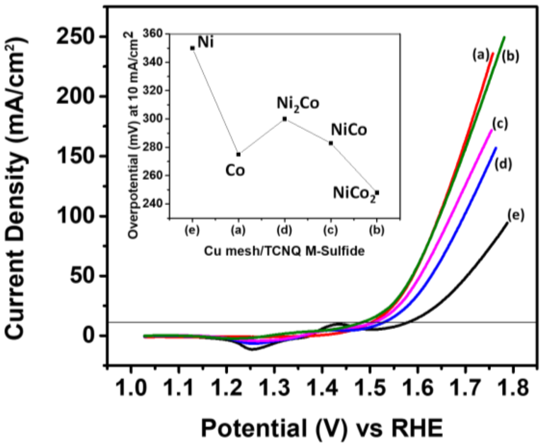

Figure 1. CV curves (iR and Capacitance corrected) of OER for (a) Co, (b) $NiCo_2$, (c) NiCo, (d) Ni_2Co and (e) Ni. Inset shows corresponding overpotential values for 10mA/cm^2 current density.

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Total Synthesis of the Pentasaccharide Repeating Unit of O-antigen from *E. coli* O132

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E. coli is a gram negative bacterium. O-antigens associated with the LPS of *E. coli* are strongly implicated in bacterial pathogenesis. *E. coli* O132 is recognized as a notorious gastrointestinal pathogen affecting humans and also reported to cause diarrhoea in children under the age of three.[9]

Recently in 2016, Knirel *et al.* reported the O-polysaccharide of serotype *E. coli* O132 that consists of a pentasaccharide repeating unit (**Figure 1**).[10] The present poster demonstrates the total synthesis of the pentasaccharide as its aminoethyl glycoside. The presence of α-linked glucopyranose and α-linked galactofuranose[11] residue make the total synthesis of this pentasaccharide challenging. Retrosynthetic analysis suggested that the synthesis of the target structure could best be achieved through a block (3+2) synthesis. Judicious protecting group manipulations and remote participation mediated stereo-selective glycosylation is the key for this oligosaccharide synthesis. Finally this structure has the potential to be immobilized on carrier protein and be evaluated for its immunogenic character for potential carbohydrate based vaccine design.[12]

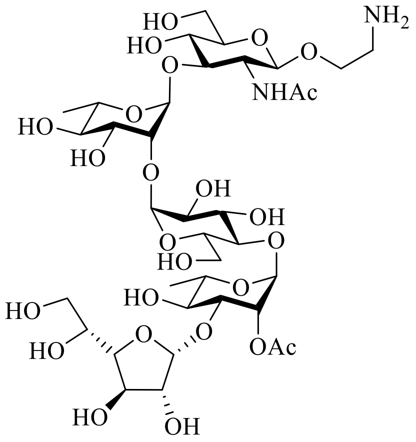

Figure 1: Repeating Unit Cell Wall Structure of *E. coli* O132

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P-20

Role of the lability of the metal-halide bond in providing selective toxicity to a tyramine based Ru^{II}-*p*-cymene complex against the pancreatic cancer cell line MIA PaCa-2

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Tyramine is a naturally occurring monoamine which acts as a catecholamine precursor and a part of our physiological system.[1]Organometallic half-sandwich ruthenium (II) complexes of the type $[(YZ)Ru^{II}(\eta^6\text{-arene})(X)]^+$, (YZ= chelating ligand, X= halide) have exhibited significant therapeutic potential against resistant cancers.[2] Herein, we designed four Ru(II) *p*-cymene complexes (**1-4**), using two tyramine based ligand frameworks (Figure 1). The complexes are highly stable in solution when the halide is iodide and does not exchange with chloride even in presence of 4 mM NaCl upto 24 h. One of the complexes shows selective cytotoxic activity *in vitro* against the pancreatic cancer cell line, MIA PaCa-2 (IC_{50} = 32± 1 µM). In normal fibroblast cells, less than 30% killing was observed even at 200 µM.

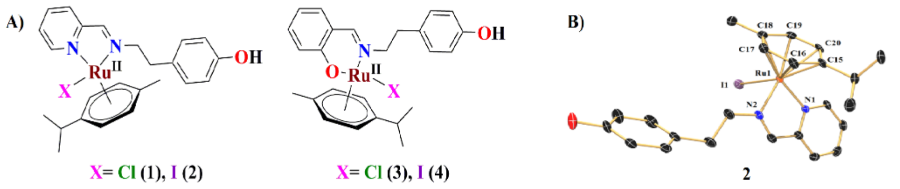

Figure 1: A) A representative diagram showing Ru^{II} complexes of two tyramine based ligand systems with different coordinated halides. **B)** ORTEP diagram of complex **2**. Thermal ellipsoids are drawn at 50% probability level.

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P-21

Trinuclear Ru-Ir-Ru complex: Stepwise synthesis and photophysics

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Cyclometalated iridium (III) complexes with rich photophysical and electrochemical properties have variety of applications in the field of sensors, organic light-emitting diodes, light-emitting electrochemical cells, biological imaging agents, catalysts for water splitting, dye-sensitized solar cells (DSSCs) and organic transformations. The large spin-orbit coupling constant of iridium can lead to efficient phosphorescence from triplet states, even at room temperature, a process rarely possible in all-organic systems. Ruthenium(II) polypyridyls are well known for their electron transfer reaction. The $Ru(bpy)_3^{2+}$/TPrA (tripropylamine) system is well known for electrochemiluminesence(ECL) with outstanding efficiency. The combination of cyclometalatediridium(III) complex with $Ru(bpy)_2^{2+}$ system has been targeted to explore extensive redox and photophysical properties of such polynuclear heterometallic system.

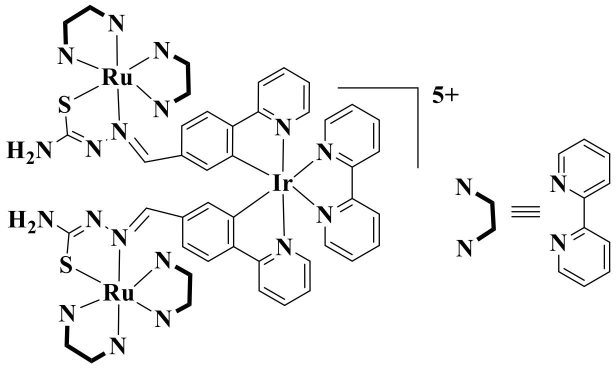

Figure 1: A representative trinuclear complex

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P-22

Natural Selection of Lysine over Other Analogues "Biological Phenomenon from Chemist's Perception"

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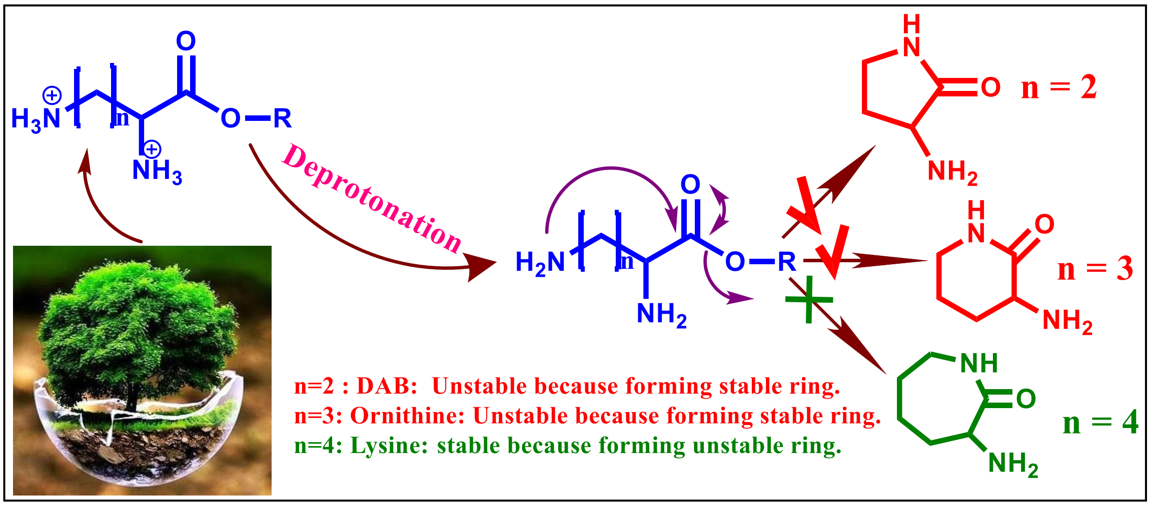
Mother nature is the master behind almost every biological mysteries. So, understanding the mysteries of mother nature from chemist's perception is very important since in past such revealations of some mysteries were transferred to huge applications including catalytic antibodies, ribozymes, polymerases etc. This indicates that close collaboration between Biology and Chemistry can provide solutions to the global questions of biological mysteries and those mysteries may be transferred into potential applications for mankind. In an issue of Journal of Molecular Evolution, Weber et al. proposed some reasons behind the occurrence of twenty coded protein amino acids[1]. So, in our project we thoroughly chemically tried to investigate the reasons behind natural selection of lysine as one of the basic amino acids over other analogous. Also currently we are trying to extract some application out of it.



n=2 : DAB: Unstable because forming stable ring.
n=3: Ornithine: Unstable because forming stable ring.
n=4: Lysine: stable because forming unstable ring.

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Applications of Manganese Catalyzed Dehydrogenative Coupling Reactions

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The replacement of precious metals by earth abundant base metals as a catalyst is the need of the hour for developing sustainable chemistry. Recent years have witnessed the development of various 3d-metals like iron, cobalt, nickel and copper as non-noble transition metal catalyst. In this regard, manganese whose global reserve is high, has risen as an excellent candidate for being a noble metal replacer. In recent years, a huge development using low-valent manganese complexes in hydrogenation, dehydrogenation and their cascade reactions have been made.[1-2] Our research focus is on the development of robust manganese catalysts based on cheap and readily available starting materials. Applications of such recently developed manganese catalyzed dehydrogenative coupling reactions will be discussed in this short presentation.[3-7] These reactions are highly environmentally benign producing only water (and hydrogen gas) as by-product.

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The Role of Aliphatic chains on Crystalline Property of Fatty Acid Based Styrenic Degradable Polyperoxides

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Vinyl polyperoxides belong to an important class of degradable polymers, which is alternating copolymers of vinyl monomers and molecular oxygen. Polyperoxide contains flexible peroxy (-O-O-) bonds in the back bone due to that they are commonly viscous amorphous material. In the present study, crystalline polyperoxides have been synthesized by radical oxidative polymerization from styrenic monomers having fatty acid moieties attached to the phenyl ring at 100 psi of molecular oxygen pressure.The peroxide content as active oxygen was determined form I_2 calibration curve where I_2 is produced from the reaction between KI and polyperoxide. The ^{13}CNMR spectroscopy and electron impact mass spectroscopy (EI-MS) have been employed to confirm the alternating placement of -O-O- bonds in the copolymer main chain. From differential scanning calorimetry (DSC), it was observed that polyperoxide degrades highly exothermically and degradations products have been recognized from EI-MS study. The crystalline behaviour of the polymer was investigated from DSC and powder X-ray diffraction (PXRD) studies. The crystallinity of the polymer was further studied by polarized optical microscopy (POM), where a birefringence texture which is characteristic of semicrystalline polymer was formed for polyperoxides with fatty acid side chain having C $\geq$12. The thickness, and crystal structure of the polymers were defined using transmission electron microscope (TEM). Theoretical studies have been performed by density functional theory (DFT) to support the experimental interlamellar distance from X-ray diffraction studies.

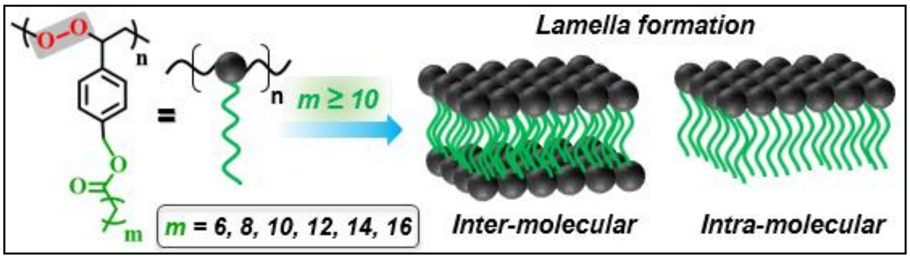

Figure 1. Crystalline domain formation in the polyperoxides.

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P-25

Attuning electronic properties of two-dimensional materials for accelerating electrochemical water dissociation reactions

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Exploration of renewable and alternative energy sources for conversion to fossil-fuel has attracted increased attention for the increasing energy demand.[1] Therefore, designing efficient and durable electrocatalysts is an urgent need to attain hydrogen economy.[2] In this regard, two-dimensional (2D) nanomaterials impart great opportunity as electrocatalysts due to their unique physiochemical properties. Layered double hydroxides (LDH) belong to the well-known 2D materials for water splitting reactions with a large abundance of active sites and decent surface area. Herein, we will demonstrate the transformation of bimetallic LDH structure to semi crystalline 2D oxide nanoplates that can maneuver their electronic properties and hence accelerate the electrocatalytic water dissociation process. The bimetallic oxide requires only 280 and 177 mV overpotentials for oxygen/hydrogen evolution reactions (OER and HER) to achieve current densities of ±10 mAcm^{-2} in 1M KOH, respectively. Moreover, in a two-electrode water splitting cell, this bifunctional catalyst needs only 1.69 V to deliver 10 mAcm^{-2}, while the LDH precursor demands a cell voltage of 1.93 V with incessant durability for more than 200h for both the catalysts. The main contributing factor for the better activity of the oxide nanoplates is the abundance of low coordinated Co^{2+} and Fe^{2+}centers along with unsaturated oxygen sites. Upon integrating the perovskite solar cells in series, solar to hydrogen (STH) efficiency of 9.3% can be achieved for the bimetallic oxide electrolyzer. This is the first instance of better electrocatalytic performance of LDH-derived oxide nanoplates as compared to the widely celebrated LDH precursor.

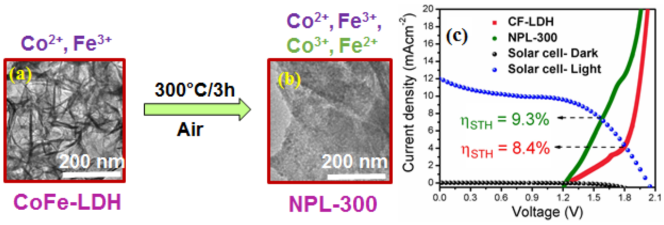

Figure 1. (a, b) Transmission electron microscopy images of CoFe-LDH and NPL-300, respectively; (c) J–V curve of the two perovskite solar cells integrated into series separately with the NPL-300 and CF-LDH electrolyzers in dark and under 1.5G 100 mWcm^{-2} illumination.

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Structural tailoring of two-dimensional all inorganic halide perovskites for photovoltaic devices

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In present scenario, hybrid organic-inorganic based perovskite solar cells (PSCs) with common formula ABX_3 have become a prominent candidate as cost effective photovoltaic devices by acquiring ~23.3% efficiency in a very short time domain. Though these devices have shown efficiency comparable to commercially available Si based solar cells on laboratory scale but ambient stability of these devices is one of the major issues. Therefore a meteoric rise in the development of all-inorganic perovskite materials has been observed as a promising alternative due to their excellent optoelectronic and ambient stability. Moreover materials with two-dimensional (2D) confinement offer unique advantages over their 3D counter part in terms of narrow photoluminescence (PL) bands, strong excitonic absorption, high PL quantum yield and increased surface area. Here we report colloidal synthesis of 2D all-inorganic cesium lead halide ($CsPbX_3$; X=Br, I) perovskite nanosheets of lateral size few hundreds of nanometer and thickness of few nanometers, by altering the ratio of ligands. The electrical conductivity of the nanosheets depends on their thickness. The as-synthesized $CsPbX_3$ nanosheets exhibit bright PL emission with broad wavelength tunability by composition modulation. To demonstrate their applications in photovoltaic devices, solar cells were fabricated using these nanosheets as photoactive materials. Our findings suggest that modulation of dimensionality of 2D nanosheets highly influence the device performance, especially in terms of ambient stability.

DFT based engineering of N-heterocyclic carbene to exacerbate its catalytic activity for SO_2 fixation and storage

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Abstract:

Carbene compounds are very reactive to SO_2 which asserts their candidature to seize this greenhouse gas. Unfortunately, most of the carbenes which produce S,S-dioxide with SO_2 , undergo dissociation to yield ketone derivative and SO through an intermediate formation of oxathiirane S-oxide derivative. Thus, these carbenes are excluded from the list of catalyst for SO_2 fixation and storage technology. To eradicate this retardation, the stability of different oxathiirane S-oxide derivatives obtained from SO_2 and 56 carbenes of various structures are studied using Density Functional Theory (DFT). Through our study, we are able to find out three oxathiirane S-oxide derivatives which have positive ΔG value for their decomposition to the respective ketone derivatives. This study corroborates that proper engineering of carbene leads to produce a stable oxathiirane S-oxide derivative as a stable product. We observed that carbenes are highly efficient to nab SO_2 at room temperature as well as lower than room temperature and susceptible to detain it up to a temperature range of 25°C to 800° C. This finding should necessitate the recommencement of the use of carbene for SO_2 fixation and storage technology. These carbenes are found useful as the catalyst for sulfur transfer reaction within a wide range of temperature and for pressure and temperature tunable SO_2 storage. We also found three carbenes which are able to produce sulfene derivative ($C-S$ bond length is less than 1.7 Å) on reaction with SO_2 .

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P-28

Urea-modified amino acids to promote fermentation of carbohydrates into biodiesel

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Abstract:

The enormous growth of world population, increased technical development and standard of living in industrial nations, has led to the requirement of energy supply and demand. But underground-natural source of energy decreases gradually. Also, the problems of waste generation and management in most cities has become one of the intractable environmental problems facing urban centres. In this regard, we are trying to generate biodiesel using urea modified amino acid in the fermentation reaction. Urea serves an important role in the metabolism of nitrogen-containing compounds.[1] Yeast species converts carbohydrates to carbon dioxide (CO_2) and alcohols through fermentation.[2] Keeping both in mind we have designed and synthesized urea-modified amino acid and use them to promote fermentation of Carbohydrate to carbon dioxide and biodiesel. The urea-modified charged amino acid promotes the growth of the yeast in a neutral aqueous medium in around 20 hr. and produced ethanol from glucose. They also promote the growth of other carbohydrates such as mannose, galactose, lactose and sucrose to generate ethanol.

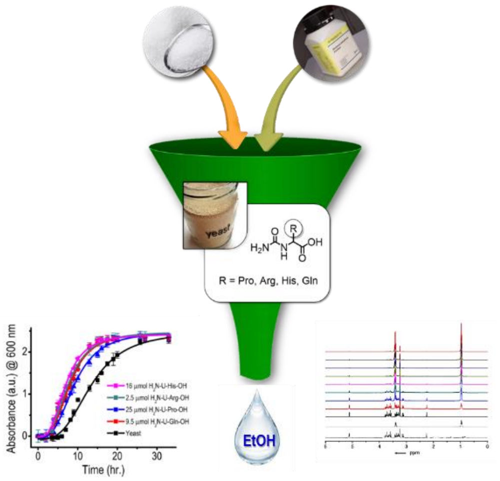

Figure 1. The formation of biodiesel by fermentation reaction in presence of urea-modified amino acid.

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INFORMATION THEORETICAL STUDY OF FREE AND CONFINED QUANTUM SYSTEMS

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Fisher information (I), Renyi entropy (R), Shannon entropy (S), Onicescu energy (E) and several statistical measures similar to LMC and Fisher-Shannon complexity have been studied for free model and spherically confined atomic systems, in conjugate spaces. For model (ro-vibrational state of diatomic molecules with generalized Kratzer potential) and H-atom, representative calculations are done by employing exact analytical wave functions in r space. For many electron systems, a method to solve Kohn−Sham (KS) equation numerically to study the electronic structure of atoms, confined under impenetrable spherical boundary is presented. Generalized pseudospectral method is used to construct the optimized non−uniformly discretized spatial grid for solving the KS differential equation within non−relativistic approach. KS model employed here uses non-variational work function exchange potential in combination with (i) parameterized local Wigner and (ii) non-local Lee−Yang−Parr correlation potentials. Confinement has been imposed by emphasizing the constraint that the electron density vanishes at the confinement radius. The exchange only results are as accurate as the one obtained from Hartree-Fock method. The present method provides a computationally efficient and accurate scheme to study confined atomic systems within density functional theory. Accurate p-space wave functions are generated numerically by performing Fourier transform on respective r-space counterpart. In many aspects, inferences in confined systems are significantly different from free counterpart.

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P-30

Ammonium chloride mediated trifluoromethylthiolation of *p*-quinone methides *via* 1,6-conjugate addition

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An ammonium chloride mediated nucleophilic trifluoromethylthiolation of *p*-quinone methides (*p*-QMs) has been developed using inexpensive, bench stable $AgSCF_3$ as $-SCF_3$ nucleophile source. This method could be an excellent example for benzylic $C(sp^3)–SCF_3$ bond formation enabled by 1,6-conjugate addition/aromatisation of $-SCF_3$ nucleophile under mild reaction condition in the absence of any oxidising agents. In recent years, fluorinated functionalities (like $–SCF_3$, $–CF_3$, $–CF_2CO_2Et$ etc.) are of interest in pharmaceutical, agrochemical and material research fields[1] as fluorinated moieties improve transmembrane permeability and metabolic stability of bioactive metabolites.[2]The 1,4/1,6-conjugate addition of various nucleophiles to an electron deficient unsaturated acceptor is a versatile and well-studied reaction for C–C/C–heteroatom bond construction in organic chemistry. *p*-QMs have been known as reactive intermediate for more than a century and are also present in various natural products and drug molecules.[3]*p*-QMs are constructed with zwitterionic resonance structure of cyclohexadiene moiety in para conjugation with a carbonyl group, which enhances the electrophilic character at δ-position and makes it more prone for 1,6-conjugate addition.[4] Here, we report a new strategy for direct trifluoromethyl thiolation of *p*-quinone methides. In this protocol, the readily prepared and stable $AgSCF_3$ is used as the trifluoromethyl thiolating agent in presence of mild and cheap NH_4Cl as reaction mediator under ambient conditions.

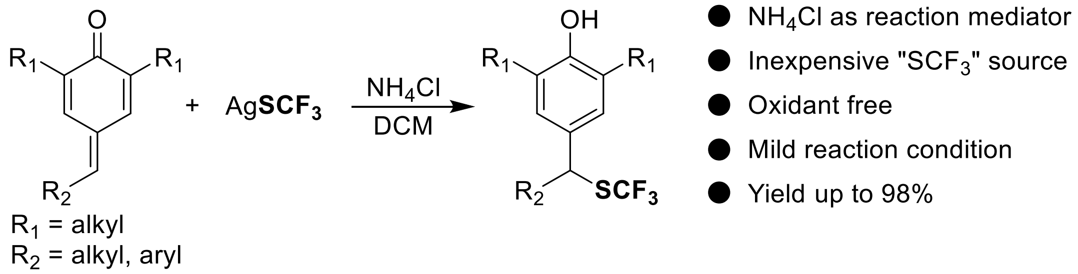

Figure 1.Trifluoromethylthiolation of *p*-quinone methides (*p*-QMs) *via* 1,6-conjugate addition[5]

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P-31

Meta-Fluorophores: Inception of a New Generation of Single Benzenic Ultra Small Fluorophores Exhibiting Red-NIR Fluorescence

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Designing small fluorophores to achieve red-NIR emission has been an ominous challenge towards vast applications such as OLEDs, bioimaging, chemical sensor etc.[1] To achieve red emission, extended π-conjugation is intended and/ or several benzene rings are fused together in which donor-acceptor groups are para-oriented.[1] Herein, a general methodology for designing red-NIR emitting ultra-small fluorophores in which donor-acceptor groups are meta-oriented (henceforth termed as meta-fluorophores) have been presented. Based on this approach, several meta-oriented single benzenic fluorophores, 1-8 (Fig. 1) are synthesized. These ultra-small fluorophores exhibit fascinating emission properties such as tunable emission (blue-green-red-NIR) in solution as well as in solid state, large Stokes shift and large solvatochromic shift. Smallest fluorophores which have been reported in literature to exhibit red emission has a lowest MW of 252.5.[2, 3] Moreover that particular reported fluorophore does not exhibit any significant Stokes shift or solvatochromic shift.[2, 3] Employing current approach red emission have been achieved with ultra-small meta fluorophores having lowest molecular weight of only 177.1 in water. Interestingly, the magnitude of the Stokes shift (260 nm) and solvatochromic shift (160 nm) (Fig. 1) are much higher than the same for the corresponding para derivatives reported in literature. These simply synthesizable, small sized single benzenic meta fluorophores, could be utilized in making cost-effective, bright white light emission as white ink and white LED (Fig. 1).

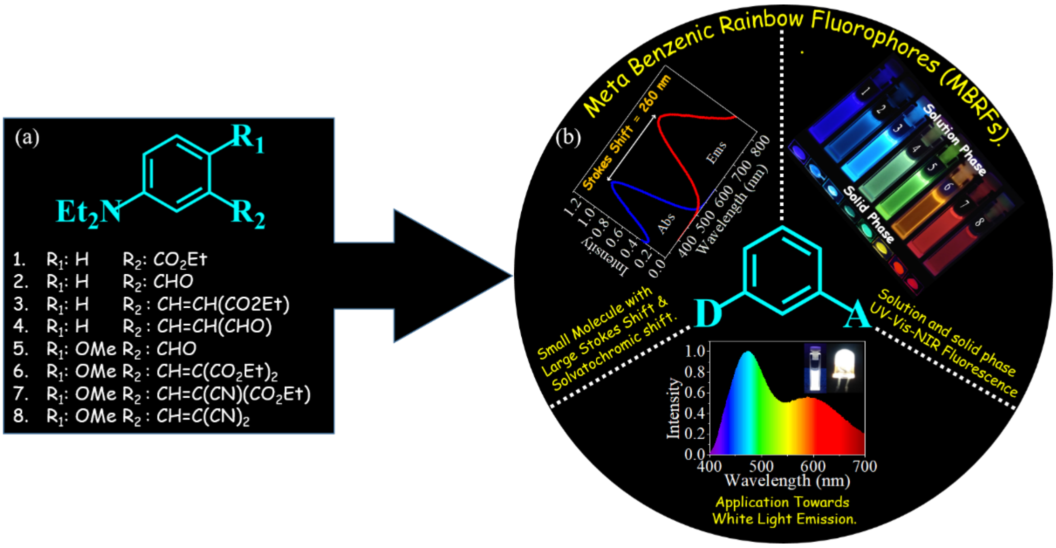

Figure 1. Meta benzenic rainbow fluorophores (MBRFs) (a) and different properties of MBRFs (b).

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Static polarizability and hyperpolarizability in atoms and molecules through a Cartesian-grid DFT

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Static electric response properties of atoms and molecules are presented within the real-space Cartesian grid implementation of pseudopotential Kohn-Sham density functional theory. A detailed systematic investigation is made for a representative set of 15 atoms and 25 molecules, through a number of properties like total ground-state electronic energies, permanent dipole moment, static average dipole polarizability. This is further extended to first-hyperpolarizability in molecules. It employs a recently developed non-uniform grid optimization technique, with a suitably chosen fixed initial applied field. A simple variant of the finite-field method, using a rational function fit to the dipole moment with respect to electric field, is adopted. We make use of Labello-Ferreira-Kurtz (LFK) basis set, which has performed quite well in these scenarios. To assess the efficacy and feasibility, four XC functionals such as LDA, BLYP, PBE and LBVWN are chosen. Present results are compared with available literature (both theoretical and experimental) values, whenever possible. In all instances, they show excellent agreement with the respective atom-centered-grid results, very widely used in many quantum chemistry programs. This demonstrates a viable alternative towards accurate prediction of response properties of many-electron systems in Cartesian coordinate grid within DFT.

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Effects of Alloying on Mode-Selectivity in H_2O dissociation on Cu/Ni bimetallic surfaces

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The influence of alloying on mode-selectivity in H_2O dissociation on Cu/Ni bimetallic surfaces has been studied using a fully quantum approach based on Reaction Path Hamiltonian (RPH). Both the metal alloy catalyst surface and the normal modes of H_2O impact the chemical reactivity of H_2O dissociation. A combination of these two different factors will enhance their influence reasonably. Among all the bimetallic surfaces one monolayer (Ni4_Cu(111)) and ½ monolayer of Ni on Cu surface (Ni2_Cu(111)) shows lowest barrier to the dissociation. Excitation of bending mode and symmetric stretching mode enhances the reactivity remarkably due to a significant decrease in their frequencies near transition state (TS) in the vibrational adiabatic approximation. In the presence of non-adiabatic coupling between the modes, asymmetric stretching also show similar enhancement in reactivity as that of symmetric stretching for all the systems. Inclusion of lattice motion using sudden model enhances the dissociation probability at surface temperature 300K and at lower incident energy, compared to that of static surface approximation. The mode selective behaviour of H_2O molecule is almost similar on all the Cu and Ni-based surfaces. The excitation of symmetric stretching vibration by one quanta is shown to have largest efficacy for promoting reaction for all the systems. Overall the dissociation probabilities for all the systems are enhanced by vibrational excitation of normal modes and become more significant with non-adiabatic coupling effect.

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P-34

Development of Biomimetic Hydrolase

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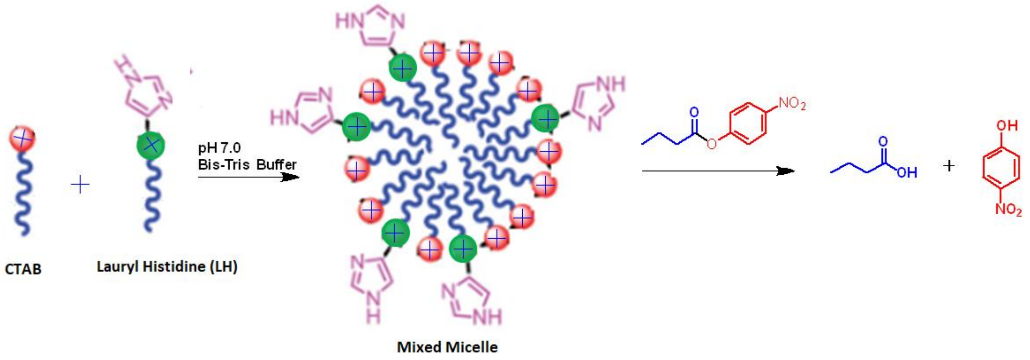
Mixed micelle consisting of Cetyl Trimethyl Ammonium Bromide (CTAB) & lipidated Histidine (Lauryl-Histidine) with imidazole group on the surface produce esterase activity. The imidazole containing mixed micelle catalyse the hydrolysis of active ester because in presence of positive imidazole on the surface, pK_a value of imidazole decreases and protonation-deprotonation equilibrium shifts towards more deprotonated form of imidazole, which is the active catalyst responsible for esterase activity. Moreover, when we are attaching positive charge containing group i.e. NH_3^+, $NHMe_2^+$ on lipidated histidine, then the resulting mixed micelle can enhance the esterase activity by almost two fold via synergistic repulsive effect.



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Engineered pH-responsive peptide based siRNA transporters for enabling enhanced siRNA delivery

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Abstract: Cell-penetrating peptide based molecular transporters have gained significant importance for intracellular delivery of functional siRNA. The cellular internalization pathway of CPP-cargo complex is determined by the size, charge and concentration of CPP-cargo complexes and cell types used for the study and mainly occur by endocytic pathways and suffer from endosomal entrapment. The endosomal entrapment and inefficient release of cargo from endosome prevents high yield cytosolic delivery of functional siRNA. Designing clinically safe and effective transporter for cytosolic delivery of siRNA in biologically active form remains as key hurdle. To overcome these challenges, we have designed protease-resistant peptide based molecular transporters having Arg-(D)His-Arg moiety in the sequence and evaluated their physicochemical properties and gene silencing efficacies. Computational studies show that at physiological condition, Arg-His hydrogen bonding interaction stabilizes Arg-^{D}His-Arg template, whereas such interaction disappears at lower pH. pH-sensitive residue, histidine exhibits proton sponge effect in endosomal acidic environment and facilitates the release of entrapped CPP-cargo complexes to the cytosol. Interestingly, our designed histidine-rich molecular transporters demonstrated functional siRNA delivery in breast cancer cell lines like commercial transfection agent HiPerfect and exhibited significant gene silencing in MAPK/ERK signaling pathway as evidenced by RT-PCR and immunofluorescence studies. MAPK pathway promotes cell proliferation, metastasis and drug resistance in triple negative breast cancer cells, MDA-MB-231. We anticipate such molecular transporters might be translated to clinics for developing next-generation siRNA based nanotherapeutics against triple negative breast cancer.

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P-36

Abnormal Nucleophilic Substitution on Regioisomers of Allyl Substituted 2-Methoxytropone: steric-guided synthesis of 5-substituted azulenes

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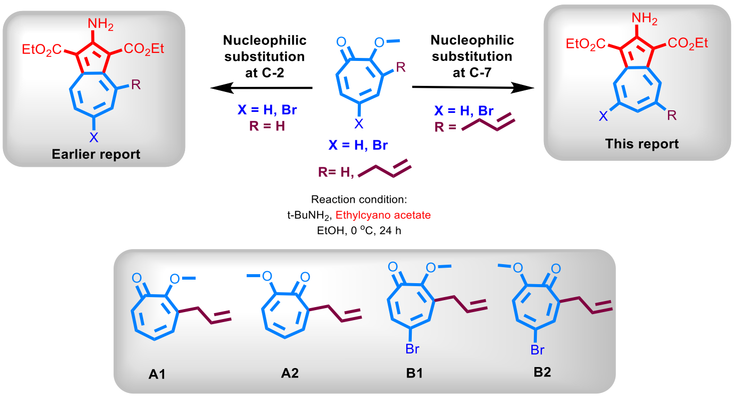
Being a non-alternant non-benzenoid aromatic system, azulene possesses unusual photophysical properties. Azulene-based conjugated systems are receiving increasing interest in recent years as optoelectronic materials. However, there are very few methods to create substituted azulene derivatives. One of the synthetic methods to create the azulene core is the reaction of 2-methoxy- or 2-halotropone with diethylmalonate in presence of base. This report explores the reactivity of substituted tropolones and also provides the new guidelines to create 5-substituted and 5,7-disubstituted azulenes. The reactivity differences of allyl substituted 2-methoxytropone (**A1**and **A2**) and allyl substituted 5-bromo-2-methoxytropone (**B1**and **B2**) towards azulene synthesis have been explored. The mechanistic pathway depends on the substituent and its position on the tropolone derivative. Unsubstituted tropolone undergoes azulene formation via the attack of the nucleophile on C-2 center whereas allyl substituted derivatives (**A1**and **B1**) undergo nucleophilic addition at C-7 guided by the steric hindrance for the attack of nucleophile at C-2. The isomers of **A1** and **B1** i.e. **A2** and **B2**, do not undergo azulene ring formation due to hyperconjugation/tautomerism in presence of the allyl chain which hinders the first step of the reaction i.e. the attack of a nucleophile. The allyl and bromo-substituents play a synergistic effect on **B2** that leads to nucleophilic substitution at the carbon bearing bromine in **B2** which finally rearranges to ethyl cinnamate derivative whereas **A2** remains inert to the similar reaction conditions. Density functional theory calculations were in agreement with experimental observationsand it pave the way to the new synthetic strategy of synthesizing 5-substituted and 5,7-disubstituted azulenes.



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P-37

Theoretical (Bio/In)-organics? Do the semantics matter?

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Theoretical Methods of popular use in modern chemical sciences range in a wide array of regimes and implementations. From small home-grown methods to large scale implementations of Molecular Dynamics, Density Functional Theory and QM/MM protocols. However, as an age old question arises, which seeks to find out which method better suits Inorganics and which one suits Organics, or Biochemical systems, computational chemists often seek to side with arguments that support the class of systems that they seek to test. However, this work aims to show how one can transcend techniques used in Chemical Biophysics to Inorganic materials and organic materials, and also aims to show how one can transcend techniques of theoretical simulation and computation from Organics and Inorganics into each other, by very simple and logical parametric changes. In all essentiality, the aim is towards bringing an end-all be-all answer to closing the gap between these sciences and establishing a rigorous theoretical framework to test processes in these systems and decipher mechanisms without worrying about the model or technique being used.

In this direction I will also present some salient results from my own research encompassing the usage of these simple cross-disciplinary theoretical protocols to enormously challenging problems in the fields of DeNovo Drug Design, Materials Design and Mechanism Elucidation of processes in materials and in reactions!

This presentation will additionally provide both theoreticians with new perspectives towards tackling problems and experimentalists with some simple ideas on how to perform basic computational calculations and what they mean in practice.

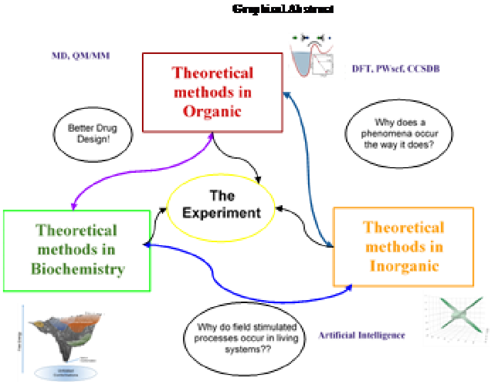

Figure: The hypothetical interface of theoretical and experimental chemistry with snippets of different methods

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P-38

Stable Abnormal N-Heterocyclic Carbene in Homogeneous Catalysis

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Carbenes were traditionally considered as the highly reactive transient intermediates in organic transformations. The first stable abnormal N-heterocyclic carbene (*a*NHC) was isolated by Bertrand in 2009.[1] This isolated *a*NHC was introduced as a metal-free catalyst for the first time in polymerisation reaction. Later on, the strong sigma donor ability of *a*NHC was utilised to prepare a series of transition-metal based complexes to design homogeneous catalysts. Moreover, the main group metal catalysts were prepared to address the reduction of primary amides. Activation of greenhouse gases like CO_2 and N_2O was also achieved using *a*NHC-boron compound.

Catalytic reduction of thermodynamically stable CO_2 was successfully carried out by *a*NHC resulting among the highest TON value of 6000 through the isolation of reactive intermediates.[2]Additionally, CO_2 was captured from air (400 ppm) by *a*NHC-borane adduct in solid state as well as in solution state[3], which can be converted to either formic acid or methanol equivalents. Recently, reductive functionalization of CO_2 with amides was also accomplished using *a*NHC for the first time under ambient conditions.[4]

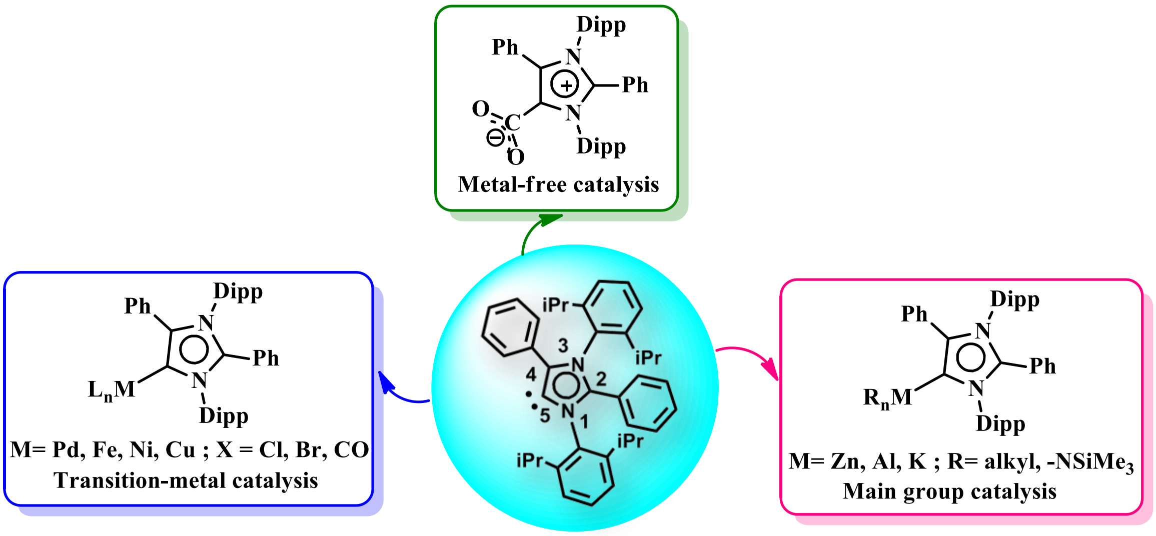

Figure 1. Abnomal N-heterocyclic carbene in homogeneous catalysis.

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Supramolecular Gel to Reduce Tool Wear and Protect Metal Surface in Metal working

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Metalworking includes creating tiny designer parts, fitting of the parts and assemblies to large scale structures by forming, cutting, and joining.[1] The processes produce lots of dust, pollutants, noise and heat.[2] A metalworking supramolecular gel has been developed to improve workpiece quality, to reduce tool wear and protect newly cut metal surface.[3]An efficient NDI-based gelator for silicon oil has been synthesized and investigated. From X-ray single crystal studies, the dodecyl groups adopt all anti conformation on both side of the diimide and the compound self-assembled to form supramolecular sheet-like structure. The compound successfully imbololized silicon oil and formed a soft gel at 4 wt% (w/v). From mechanical response, storage modulus (G') was greater than loss modulus (G") and did not cross each other over the entire range of angular frequency, which indicates that the gel is elastic in nature. The FE-SEM images showed that the gel is made of entangled fibers. Further the gel was used during metal cutting and grinding to reduce tool wear, and was found to prevent the sparking, absorb the dust and finally release the silicon oil to protect newly cut metal surface.

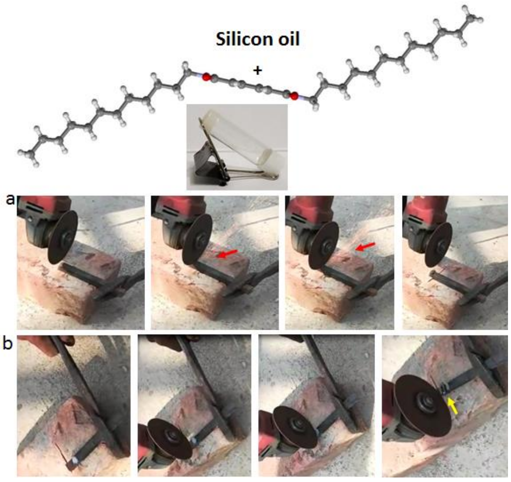

Figure 1: Schematic representation of metalworking supramolecular gel.

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Chemically Fueled Dissipative Self-Assembly that Exploits Cooperative Catalysis

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In living systems, dissipative processes are driven by the endergonic hydrolysis of chemical fuels such as nucleoside triphosphates. Now, through a simple model system, a transient self-assembled state is realized by utilizing the catalytic effect of histidine on the formation and breaking of ester bonds. First, histidine facilitates the ester bond formation, which then rapidly co assembles to form a self-supporting gel. An out of equilibrium state is realized owing to the cooperative catalysis by the proximal histidines in the assembled state, driving the second pathway and resulting in disassembly to sol. Cooperative effects that use the dual role of imidazoles as nucleophile and as proton donor is utilized to achieve transient assemblies. This simple system mimics the structural journey seen in microtubule formation where the substrate GTP facilitates the non-covalent assembly and triggers a cooperative catalytic process, leading to substrate hydrolysis and subsequent disassembly.

P-41

Donor−Acceptor Interactions in Early Transition Metal Halides and Group-14 Compounds: A Theoretical Insight

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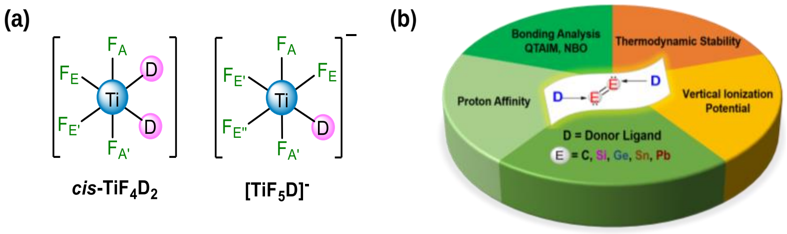
During the past two decades, Lewis acid-base chemistry has undergone a profound revolution.[1] Though, till date, Lewis acid-base adducts of electron-deficient group 13 halides (ECl_3, E = B−In) are widely explored,[2] very few similar benchmark studies exploiting Lewis acidic early transition metal compounds e.g. titanium tetrahalides (TiF_4, $TiCl_4$) have been reported.[3,4] In this context, we have investigated the electronic structure and bonding scenarios in different *cis*-TiF_4D_2 and $[TiF_5D]^-$ complexes (D = neutral donor ligand), employing DFT calculations (Scheme 1a).[5] Additionally, we have computed the formation energies of these complexes for various reaction routes both in the gas phase and solution medium. Significant effort has been paid to obtain intrinsic Lewis base strengths of the ligands with respect to TiF_4 as reference Lewis acid. Furthermore, the isomerism of mixed chloro and fluoro titanium complexes supported by neutral ligands is studied. The unique electronic feature of the neutral ligands specially carbene results the ongoing "renaissance" in the stabilization of various unstable chemical species, radicals and elements in their different unusual oxidation states.[6] Since the isolation of the diatomic silicon(0) compound[7] employing *N*-heterocyclic carbene (NHC), the unprecedented chemistry of the diatomic group 14 elements has been explored both theoretically and experimentally.[8]Similarly, we have made an attempt to explore theoretically the electronic structure and bonding perspectives in different bis-donor stabilized E_2 (E=C−Pb) compounds (D−E_2−D; Scheme 1b).[9] The thermodynamic stabilities of these compounds are computed to identify the viable targets for synthesis.



Scheme 1. (a) Schematic representation of the *cis*-TiF_4D_2 and $[TiF_5D]^-$ complexes. (b) Schematic representation of the D−E_2−D compounds.

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P-42

Synthesis of tetrasaccharide repeating unit related to the O-antigen of *Escherichia coli* O131 containing *N*-acetylneuraminic acid

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Escherichia coli is considered one of the most notorious strains of pathogenic bacteria, particularly *Escherichia coli* O131 known to cause post-weaning diarrhea in pigs.[1] Recently in 2016, Knirel *et.al* isolated repeating unit of the O-antigen of *E. coli* O131 stain as a tetrasaccharide (**Figure 1**).[2]

The present poster presents the total synthesis of the O-antigen of *Escherichia coli* O131. Critical analysis of the structure shows the tetrasaccharide consisting of a reducing end Galactosamine unit, two Galactose unit and one highly biologically relevant *N*-acetyl neuraminic acid unit. The total synthesis of this tetrasaccharide as its aminopropyl form has been achieved through rational protecting group manipulation as well as solvent induced stereoselective glycosylation with *N*-acetylneuraminic acid. The validation of such synthetic enterprise lies in the fact that O-antigens are deeply involved in bacterial pathogenesis and in turn provide potential candidates for vaccine development.[3]

→8)-α-Neup5Ac-(2→6)-β-D-Galp-(1→6)-β-D-Galp-(1→3)-β-D-GalpNAc-(1→

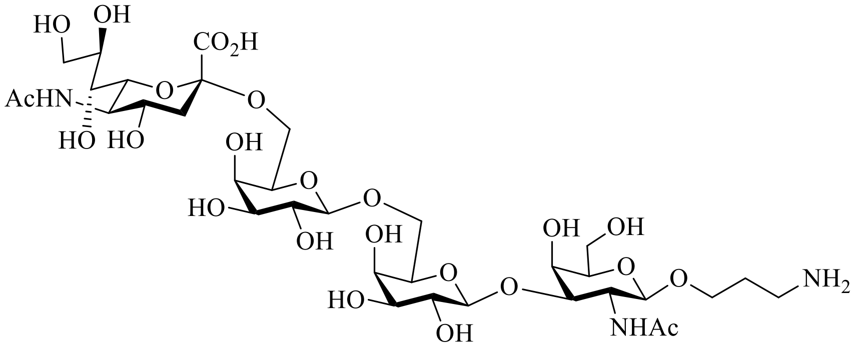

Figure 1.

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