Abstract Book

CHEM CONVENE '17

A platform for the young minds to showcase their concepts and innovations

In-House Symposium,
Department of Chemistry, IITG,
July 25, 2017

Detailed Programme Schedule: CHEMCONVENE 2017

25-07-2017	
9:00-9:30 AM	Inaugural Session and Opening Remarks
SESSION I: FACULTY PRESENTATIONS (CHAIR : Prof. A. N. PANDA)	
9.30-11:00 AM	Prof. A. Chattopadhyay, Prof. B.K. Patel, Prof. M. Ray
11:00-11:30 AM	Tea Break
SESSION II: STUDENT PRESENTATIONS (CHAIR: Dr. Bh. Mandal)	
11:30 AM-1:00 PM	Mr. Radhakrishna Gattu, Mr. Uday Pan, Mr. Soumen Saha, Ms. Jyoti Chandra, Mr. Subhankar Panda, Mr. Rana Dalapati
1:00-2:30 PM	Lunch and Poster Session
SESSION III: FACULTY PRESENTATIONS (CHAIR: Prof. A. PAUL)	
2:30-4:50 PM	Prof. T. Punniyamurthy , Prof. G. Das, Dr. M. Sarma, Dr. L.M Kundu, Dr. C. Mukherjee, Dr. K. Raidongia
4:50-5:10 PM	Tea Break
SESSION IV: STUDENT PRESENTATIONS (CHAIR: Dr. A. S. ACHALKUMAR)	
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FP1

Organizing Nanoscale Particles in three dimensions

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An imagination that is persistent amongst the scientists practicing nanoscale science and technology is to be able to organize the particles in one, two and three dimensions. This is akin to organization of atoms into molecules. Nature's greatest gifts to living beings may arguably be the molecules. The chemical bond defines the nature of the molecule in three dimensions. Such a system does not exist in nature as far as assembly of nanoscale particles are concerned.

We have been trying to work on the principles to develop systematic organizations of particles at the nanoscale. We are currently focusing on organizing metal nanoparticles, quantum dots and atomic clusters. For example, complexation on the surface of quantum dots leads to important new properties[1-3] and may also hold the clues to their organization. On the other hand, organization of noble metal nanoparticles are a bit more challenging as functional groups on the surface are typically zero valent metal atoms.[4]

Howbeit, our latest works suggest the ease of organization of atomic clusters into three-dimensional crystals using complexation reaction. For example, zinc ion mediated assembly of Au clusters in the liquid medium has been observed to be facile. The so produced nanoscale particles could be used for the reversible storage of hydrogen with the ability to sense the storage using the luminescence of the Au clusters.[5] Similar principles was used to develop three-dimensionally organized Au nanoclusters for chiral recognition and separation of molecules.[6] We have also pursued biomimetic crystallization of zinc phosphate in presence of protein fragments stabilized Au nanoclusters. Crystallized zinc phosphate decorated with Au nanoclusters served as an effective bio imaging agent.[7]

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FP2

Catalytic Cascade Strategies for the Construction of Novel Heterocyclic Scaffold

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Our group has developed several cascade and annulations strategies for the simultaneous construction of C–C, C–N, C–O leading to the construction of various novel scaffolds. Many of these strategies often involve functionalization of sp, sp^2, sp^3 carbons either under a metal or a metal free condition. Some of these strategies shall be discussed.

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FP3

The Curious Case of Chiral Molecules

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Separation of chiral isomers, which is mirror image of one another, is a strange problem. Individually, the molecules look the same, behaves the same in most chemical reaction unless the reaction involves other chiral agents. Yet they function quite differently in biochemical environment. Of course that has to do with the fact that biological agents such as proteins, amino acids, sugars or ribonucleic acids are also chiral. But the differences in function of the chiral isomers does not necessarily always be same. In some cases, it is just a difference of reaction efficiency but quite a bit dramatic. For example, (S, S)- (+) ethambutol cures tuberculosis white it's isomer (R, R)- (-) ethambutol causes visual impairment. Thus we see a necessity in separation of chiral isomers which necessitates understanding of the interaction between chiral isomers with another pure chiral isomer. Understanding of chemical reaction alone cannot solve it as the isomers differ in their orientation of chemical groups in three dimensional space. Thus the solution of the problem involves geometry and symmetry other than chemistry. If we take the specific case of an organic molecule with one chiral center, then the problem boils down to recognizing three out four group around chiral carbon. It sounds easy and it is easy if you have a molecule which has binding/interacting part for three different group. How do we do it? That will be told in this presentation.

FP4

Regioselective C-H Functionalization and Carbon-Heteroatom Bonds Formation

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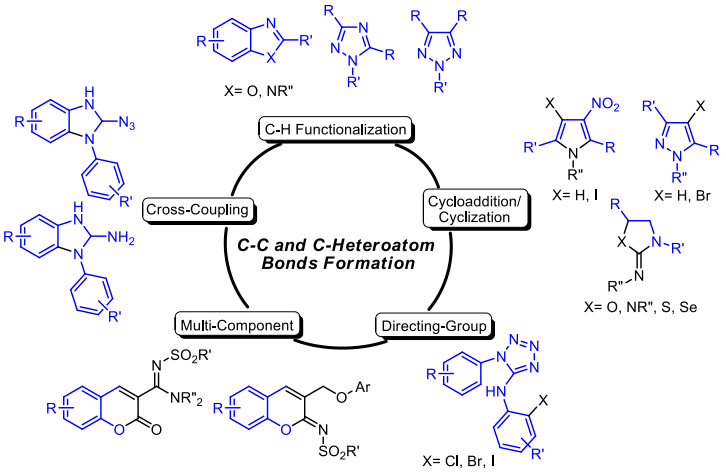
C-H functionalization is a fundamental and important process both in academia and chemical industries. It provides high atom economy and broad substrates. However, the selectivity is the major issue when the substrate has more than one C-H bond with similar reactivity. One of the solutions to this problem is try to have functional group five and six bonds away from the C-H bond and use the functional group as a directing group with catalyst to activate the C-H bond through cyclometalation. This concept has attracted considerable attention during the past decade and significant progress has been made for the selective C-H functionalization and carbon-heteroatom bonds formation. In this talk I would like present our contribution that has been made during the past few years on the regioselective C-H functionalization reaction. The synthetic and mechanistic aspects will be presented.



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FP5

Positional Isomeric Effect of Substituents on Supramolecular Anion-Assemblies of Diamine Based Urea Receptors

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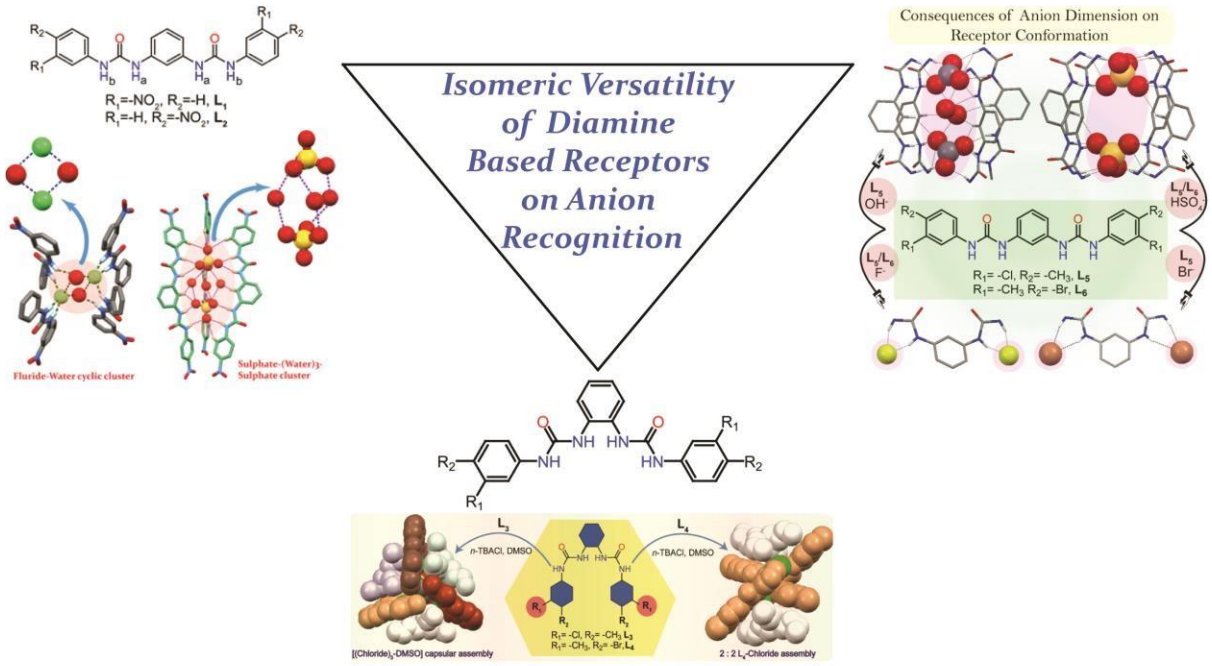
Anions exist in their hydrated form in natural and biological environments such as marine water and various ecosystems,[1] thus the significance of hydrated-anion recognition within the self-assembled architecture of neutral host molecules are essential and contemporary aspects of supramolecular chemistry.[2] SC-XRD is extensively used in solid state structural determination of naturally and biologically occurring anion glued self-assembly of synthetic organic ligand, which becomes one of the essential and contemporary aspects in modern research followed by solution state studies. Herein, we have been carried out structural elucidation of some anion/hydrated anion templated host-guest assembly of easy-to-make aromatic diamine-based receptors from SC-XRD analysis and determination of binding stoichiometry from solution state. The crystal structures of complexes reveal the proficient encapsulation/entrapment of nonhydrated/solvated F^-, Cl^-, Br^-, $OCOCH_3^-$, CO_3^{2-}, SO_4^{2-}, SiF_6^{2-} anions, besides significant $[(F^-)_2(H_2O)_2]$ cyclic tetramer, rugby-ball shaped $[(SO_4^{2-})(H_2O)_3(SO_4^{2})]$ cluster, $[(Cl)_3$-DMSO] triangular co-crystal, carbonate-water $[(CO_3^{2-})(H_2O)_2(CO_3^{2-})]$ cluster within suitable receptor architecture. Depending upon either the dimension of anions (spherical, planar, tetrahedral, and octahedral) or positional/electronic effect of terminal aromatic substituents (one or more) of receptor moieties, the overall architecture of host-guest assembly becomes systematically and consistently varied. Basically, for effective anion recognition, the high solvation energies of guest must be compensated for by the host molecules.



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FP6

Interplay between Structure and Dynamics

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Quantum Chemistry can be categorized into two main branches, viz., time independent and time dependent. In time independent quantum chemistry, we get the energy and structure of a system. Many important observables can be obtained using time independent quantum chemistry. On the other hand, in time dependent quantum chemistry, we get the information about the future state at any time. In other words, time dependent quantum chemistry offers the dynamics of any system. Therefore, it is my purpose in this talk to give a brief outline of how structure and dynamics are related with application to some specific examples those have been studied in our research group.

FP7

Modified Nucleic Acids and Peptides: From Base-Pairing to Drug Delivery

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Nucleic acids and peptides are two most important biomolecules that control and conduct most of the biological reactions and functions. These are also the most targeted biomolecules which could be chemically modified, owing to the functional groups present in nucleosides and the amino acids, respectively. Many of the synthesized nucleobases and nucleosides are active pharmaceutical drugs. Artificial nucleic acids, such as, peptide nucleic acids (PNA), locked nucleic acids (LNA) and other modifications are widely explored for improved base-pairing and therefore, as biomolecular probes for gene sequencing, disease diagnosis and gene targeting. Synthetic peptides, on the other hand, are immensely important to understand proteins' structure-functions, bio-mimicking and as drug-carriers.

In this report, we present synthesis, physical properties and scope of applications of substituted pyrimidine nucleobases and its analogs. We also demonstrate development of nucleic acid-drug, peptide-drug as well as chitosan-drug conjugates, containing a cleavable linker, for targeted delivery and controlled release of antitumor drugs, such as, 5-fluorouracil.

FP8

Transition Metal Complexes: Biomimetic Applications and Therapeutic Potentials

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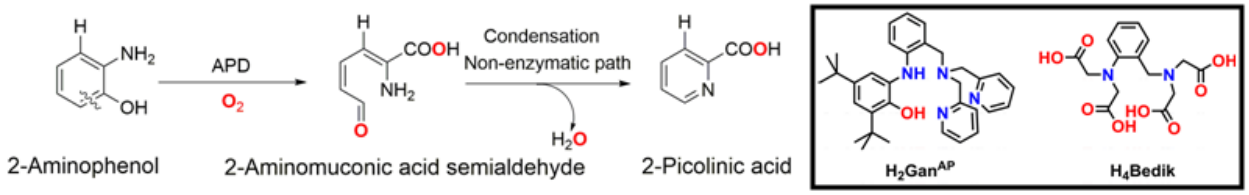
Transition metal complexes have achieved immense importance: I) in understanding enzymatic reactivity via model complex study, and II) in therapeutic applications. Employing transition metal complexes for biomimetic study of 2-Aminophenol-1,6-dioxygenase (APD)1 and therapeutic application as MRI contrast agent,2 the following results have been achieved and will be presented.

2-Aminophenol-1,6-dioxygenase (APD) belongs to dioxygenases family and catalyses the biodegradation of 2-aminophenol derivatives via oxidative extradiol-type aromatic C-C bond cleavage at the meta-position (C1-C6) under aerial atmosphere (Scheme 1).



Scheme 1.

To mimic the function of APD and to identify crystallographically the final oxidative aromatic C-C cleavage product, ligand H_2GanAP (Scheme 1), which contains both 2-aminophenol and tripodal N_3 iron coordination site, has been synthesized and reacted with $Fe(ClO_4)_2 \cdot 2H_2O$. This reaction will be discussed in details.

Magnetic resonance imaging (MRI) is a noninvasive modern clinical technique that is widely used for high resolution imaging of soft tissues. MRI measurements are often carried out in the presence of paramagnetic metal complexes, called contrast agents (CAs), to enhance image contrast. The contrast-ability decreases with increase in applied-magnetic field, while, the MR image acquisition-time decreases at high magnetic fields. Thus, in finding of new contrast agent that will provide high relaxivity at a high-field, ligand H_4Bedik (Scheme 1) was synthesized and employed to prepare the corresponding Mn(II) complex. The complex behaves as a promising positive contrast agent at high-field, 14.1 T ($r1 = 6.2\ mM^{-1}s^{-1}$).

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FP9

Reconstruction of Soil Components as Freestanding Membranes for Futuristic Applications

Dr. Kalyan Raidongia

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We recently demonstrated the possibility of creating multifunctional advanced materials by tuning the structure of natural soil components. For example, multifunctional freestanding membranes are prepared by tuning ubiquitous chemical interactions between natural soil components, *viz* humic acids and clay. Crosslinking of exfoliated clay layers with purified humic acids conferred mechanical and chemical strength on the membranes. The percolated network of molecularly sized channels of the soil membranes exhibit characteristic nanofluidic phenomena and shown to harvest green energy up to 2.63 Wm^{-2}, from electrolytes with threefold concentration difference. Electrical conductivity is fetched to otherwise insulating soil membranes by heating at 550 °C, without affecting their nanofluidic ionic conductivity. This system could provide a new platform to prepare and study mixed conducting materials. Stripes of heated membranes shown to exhibit excellent sensitivity towards NH_3 gas under atmospheric conditions.

Soil components are also assembled as self-morphing bilayer membrane that responds to change in environmental conditions. To proof the concept layers of naturally occurring clay minerals are rearranged to prepare highly sensitive multi responsive clay–clay bilayer membrane (CCBM). The CCBM introduced here responds to the minuscule changes in the surrounding environments including temperature, humidity, and presence of solvent vapors by morphing in specific

manners. Strips cut from CCBM exhibit up to 588 N kg^{-1} force output when exposed to temperature fluctuations. Inheriting the natural stability of clay minerals, CCBM demonstrates extreme robustness, heating up to 500 °C, cooling with liquid N_2 and exposure to corrosive chemical vapors did not deteriorate its bending performance. Mechanistic studies suggest that shape transformations of CCBM are driven by the unequal response of its components to external stimuli.

SP1

Regioselective Synthesis of 3-Aryl Substituted Indoles through Cyclization of Aryl Amines to Nitroalkenes

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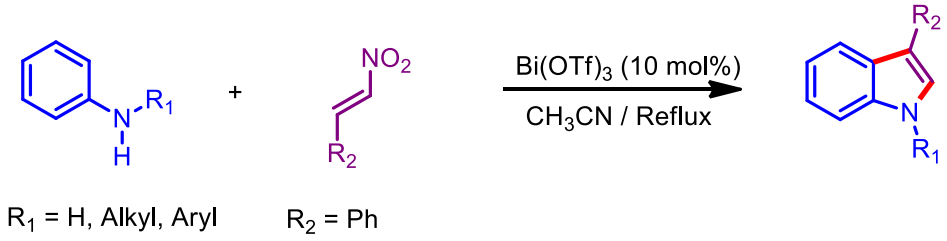

Scheme 12. Synthesis of Indoles from *N*-Alkyl Amines and Nitroalkene

A simple, novel and an efficient protocol for the synthesis of indoles has been demonstrated using Arylamine and *β*-Nitrostyrene in presence of 10 mol% of $Bi(OTf)_3$ as a catalyst in CH_3CN solvent under reflux condition. The advantages of present protocol are formation of new *C-C* and *C-N* bond shorter reaction time, mild reaction conditions and broad substrate scope with good yields.

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SP2

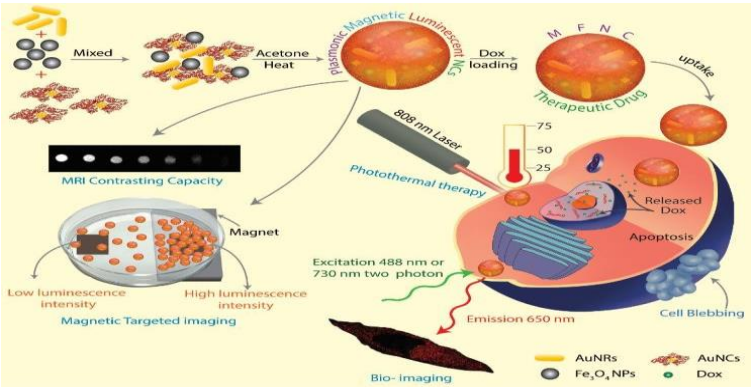
BSA Based Plasmonic and Magneto-Luminescent Multifunctional Nanocarriers for Imaging, Photothermal Therapy and Anti-Cancer Drug Delivery

Uday Narayan Pan[a], Rumi Khandelia[a], Pallab Sanpui[b], Subhojit Das[a], Anumita Paul[a]* and Arun Chattopadhyaya[b]* aDepartment of Chemistry, [b]Centre for Nanotechnology, Indian Institute of Technology Guwahati, Guwahati-781039, Assam, India, (uday.pan@iitg.ernet.in)

Construction of multifunctional nano-platform, able to instantaneously identify disease, target delivery of drugs and control release of drugs, all in one dais, remains a challenge in modern day theranostics. This can be achieved by integrating different functional nanomaterials mainly luminescencent, plasmonic and magnetic in a single platform. [1,2,3] Combining all three key functionalities of inorganic nanomaterials herein we report construction of plasmonic and magneto-luminescent multifunctional nanocarriers (MFNCs). Gold nanorods, iron oxide nanoparticles and gold nanoclusters were embedded in BSA nanoparticles to prepare MFNCs.

MFNCs showed strong luminescence emission at 663 nm providing self-tracking ability in both single photon and two photon mode. Moreover, the observed superparamagnetic with reasonably high magnetization make them excellent candidate for in vitro magnetic targeting therapy as good MRI contrast agent. In addition, in vitro plasmonic photothermal therapy (PPTT) was carried out on MFNCs treated HeLa cells, whereby considerable increase in temperature and killing efficiency upon irradiation with 808 nm laser light was observed. Furthermore, the MFNCs were capable of carrying the chemotherapeutic drug, doxorubicin, with high loading efficiency, and with excellent releasing capacity on HeLa cells. Multimodal image based diagnostic ability, PPTT and chemotherapeutic drug based therapeutic ability make these MFNCs strong contender for cancer theranostics. [1]

Schematic Representation:



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SP3

Formation and Decomposition Pathways of Metal Peroxynitrite Intermediates

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Nitric oxide (NO) is a ubiquitous intercellular messenger in all vertebrates, modulating blood flow, thrombosis, and many more neural activities. Although NO is often described as highly toxic and reactive, inhaling low concentrations of gaseous NO is approved by the Food and Drug Administration for the treatment of persistent pulmonary hypertension of the newborn. In addition, the excess production of the same molecule can become highly damaging to the neurons within a few seconds during pathological challenges as occur after cerebral ischemia due to the reaction of NO with superoxide ($O_2^{\bullet\,-}$) to form the much more powerful oxidant peroxynitrite (ONOO−), which is a key element in resolving the contrasting roles of NO in physiology and pathology. On the other way PN can be generated by the reaction of H_2O_2 and nitrite (NO_2^-) in presence of peroxidase enzymes. This reactive species directs oxidation and nitrosation of biomolecules. The primary effect of peroxynitrite on proteins is nitration of tyrosine residues which leads to the cardiovascular disease. Several heme and non-heme system with manganese, iron, and copper have been identified as potential formation of metal-peroxynitrites as transient intermediate in the reaction of metal-oxygen species with NO or metal-nitrosyls with oxidants like O_2, O_2^- or H_2O_2.

In this contrast, Two Co(II) complexes, [Co$\mathbf{L_1}$] and [Co($\mathbf{L_2}$)$_2$]Cl_2 of ligands $\mathbf{L_1}$ and $\mathbf{L_2}$ {$\mathbf{L_1}$ = 5,10,15,20-*tetrakis*(4'-chlorophenyl) porphyrinate dianion; $\mathbf{L_2}$ = *bis*(2-ethyl-4-methylimidazol-5-yl)methane)} respectively, have been synthesized and characterized via spectroscopic analyses as well as structurally. Complex [Co$\mathbf{L_1}$], in dichloromethane solution was subjected to react with NO and resulted in the formation of the corresponding nitrosyl complex, [($\mathbf{L_1}$)Co(NO)] having {CoNO}^{8} description. It was characterized by spectroscopic studies and single crystal X-ray structure determination. It did not react with dioxygen. However, in CH_2Cl_2/CH_3CN solution, it

reacted with H_2O_2 to result in the Co-nitrito complex, [(**L**$_1$)Co(NO_2)] with the simultaneous release of O_2. This reaction proceeds via the putative formation Co(III)-peroxynitrite intermediate. Whereas Complex [Co(**L**$_2$)$_2$]Cl_2 upon reaction with H_2O_2 in presence of triethyl amine in methanol solution at -40 °C resulted in the formation of the corresponding Co(III)-peroxo complex, [Co(**L**$_2$)$_2$(O_2)]$^+$. The addition of NO to the freshly generated solution of this peroxo complex led to the formation of the Co(II)-nitrato complex through the putative formation of a Co(II)-peroxynitrite intermediate. In both the cases the peroxynitrite intermediate was found to mediate the nitration of the externally added 2, 4-di-*tert*-butylphenol resembling the nitration of tyrosine in biological systems.

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SP4

o-NosylOXY: The Best Coupling Reagent for Peptide Synthesis

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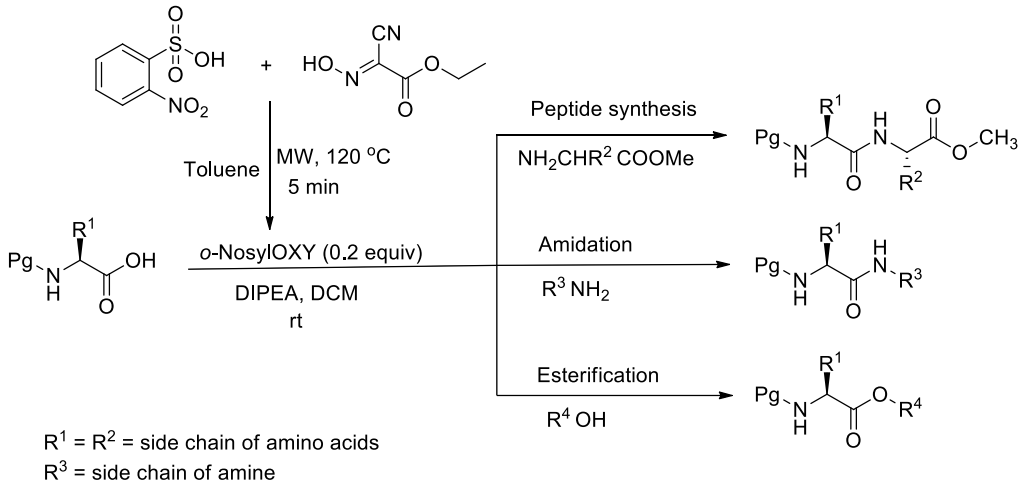
Amidation and esterification are important reactions in organic synthesis and used in the synthesis of many important molecules of biological interest.1 Till date, numerous coupling reagents have been developed but they are neither environment friendly nor cost effective. We found o-NosylOXY (Ethyl-2-cyano-2-(2-nitrobenzenesulfonyloxyimino) acetate) can generate best quality products in a greener fashion.2 We developed the catalytic behavior of o-NosylOXY (coupling reagent) for esterification, amidation, peptide synthesis and also for synthesis of 1,2,4-oxadiazoles. To reduce the chemical waste generation, we developed a new protocol for the synthesis of o-NosylOXY, sulphonates of alcohols, and Oxime-O-sulphonates. This condensation does not generate any byproduct other than water and we could also recover the starting materials very easily and reused for the next batch. Therefore, our method is environment friendly.



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SP5

Inhibition of Indoleamine 2,3-dioxygenase-1 Enzyme: A Promising Strategy for Cancer Treatment

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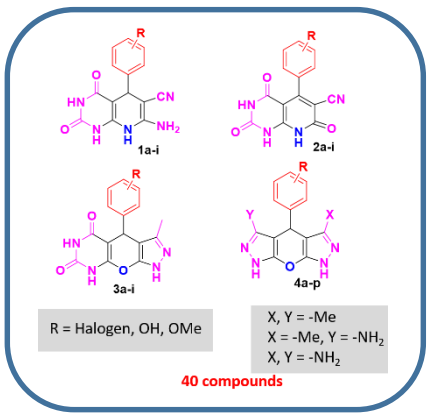
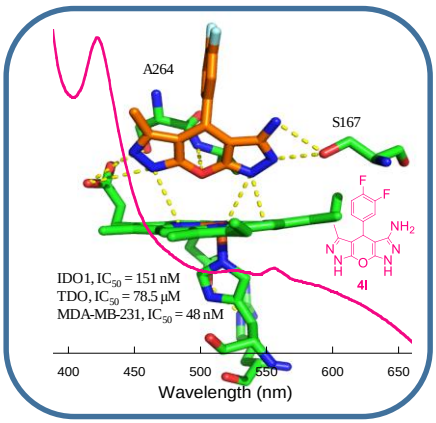
The principle of cancer immunotherapy is that the immune system can be induced to identify and obliterate malignant cells within the human body.[1] Recent accomplishment with the immune checkpoint inhibitors against a wide range of cancers has made cancer immunotherapy as one of the most encouraging developments. Induced metabolism of L-tryptophan (L-Trp) through kynurenine pathway and consequential production of kynurenine, 3-hydroxy kynurenine, kynurenic acid, excitotoxin quinolinic acid and other metabolites are primarily responsible for local immunosuppression. Indoleamine 2,3-dioxygenase 1 is catalyses the rate limiting step of tryptophan catabolism in kynurenine pathways within the immune system. Hence, IDO1 has emerged as a therapeutic target for the treatment of diseases that are associated with immune suppression like chronic infections, cancer and others. Few potent inhibitors like Epacadostat, Indoximod, NLG-919 with monoclonal antibody (like ipilimumab, pembrolizumab, atezolizumab etc) is under clinical trial for the diseases like glioblastoma, advanced solid tumor, metastatic melanoma, urothelial carcinoma, breast cancer and etc.[2] In this study, we synthesized a series of pyridopyrimidine, pyrazolopyranopyrimidine and dipyrazolopyran derivatives. Further lead optimizations directed to the identification of dipyrazolopyran derivatives as the potent compounds (**4j** and **4l**; IC_{50} = 260 and 151 nM, respectively).[3] These compounds also exhibited IDO1 inhibitory activities in the low nano-molar range in MDA-MB-231 cells with very low cytotoxicity. Stronger selectivity for IDO1 enzyme (> 300-fold) over tryptophan 2,3-dioxygenase (TDO) enzyme was also observed for these compounds. Hence, these fused heterocyclic compounds are very attractive target for the advance study of IDO1-dependent cellular function and immunotherapeutic applications.





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SP6

A thienothiophene based cerium metal-organic framework with redox enzyme-mimicking activity for colorimetric biosensing and aerobic oxidation of thiols

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Metal-organic frameworks (MOFs),[1] are a new class of porous materials that have received great attention in the last two decades for their potential applications in gas storage, separation, chemical sensing, heterogeneous catalysis and drug delivery. Cerium oxide nanoparticles (nanoceria) occur as mixed valence state oxides of Ce^{3+} and Ce^{4+}, and are able to reversibly switch between the two oxidation states. Due to this phenomenon, nanoceria has been found to possess oxidase-like activity for colorimetric biosensing.[2] MOFs with intrinsic oxidase-like activity and their applications in biosensing are still infrequent. Zhao et al. recently employed a mixed valence state (Ce^{3+}/Ce^{4+}) Ce-MOF (MVCM) for colorimetric sensing of biothiols.[3] On the other hand, few Ce(IV) complexes have been reported to act as homogeneous oxidation catalysts for the aerobic oxidation of thiols to disulfides.[4] Therefore, the development of Ce(IV)-based MOFs could be ideal choice for colorimetric biosensing and heterogeneous catalysis.

Encouraged by the advantage of cerium chemistry in colorimetric sensing and oxidation catalysis, we have synthesized a Ce(IV)-based MOF (**1**) incorporating 3,4-dimethylthieno[2,3-b] thiophene-2,5-dicarboxylic acid (H_2DMTDC) as ligand under solvothermal reaction conditions. The MOF material was entirely characterized by X-ray powder diffraction analyses, infrared spectroscopy and thermogravimetric analyses.

The activated MOF (**1'**) features an intrinsic oxidase-like activity in NaAc buffer at acidic pH, since it can quickly oxidize the chromogenic peroxidase substrates 3,3′,5,5′-tetramethylbenzidine (TMB) or 2,2′-azinobis (3-ethylbenzothizoline-6-sulfonic acid) (AzBTS) without the need of any external oxidizing agent (e.g. H_2O_2). On the basis of these results, we have established a colorimetric sensing platform for biothiols in NaAc buffer (pH = 4.0). Additionally, the heterogeneous catalytic activity of **1'** is investigated using thiophenol as a model substrate under oxygen atmosphere. Hot filtration test was performed in order to confirm the heterogeneity of the reaction.

SP7

Short Tryptophan containing Antimicrobial Peptides

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Antimicrobial peptides are part of the innate immune response found among all classes of life[1]. The rise and spread of antibiotic-resistant bacteria and fungi[2], is becoming menacing to public health[3]. The novel drug discovery and development rates are slowing, particularly in the field of antibiotics. Therefore, it is essential to identify and design alternative novel antimicrobial agents that can abolish resistant bacteria and fungus infection[4] effectively. AMP's have attracted great attention because they not only possess direct activity against bacteria, fungi, viruses, protozoa, but also have indirect immune modulating activity in the host. Unlike conventional antibiotics, which functions primarily by interacting with specific intracellular targets, AMP's have a very diverse mode[5] of action thereby reducing the possibility of developing bacterial resistance. This has led to active research in the field of antimicrobial peptides over the last few decades as potential drugs[6] of the future. We designed two seven residue peptides (Peptide 1 and 2) by modifying the inactive LK peptide LKLLKKL-COOH, and found them to be highly active against bacterial (E. coli DH5 and Pseudomonas Aeruginosa) and fungal (*Candida albicans* and *Cryptococcus grubii* strains. Peptides 1 and 2 were non cytotoxic and NMR and MD simulations showed that they do not adopt any particular secondary structure. Peptide 1 was shown to however have a very specific interaction with the membrane, thereby deforming it. Whether such deformation leads to membrane permeability is still being probed.

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SP8

Bio-inspired Robust Under-Water Extreme Oil-wettability; For Both Prevention and Clean-up of the Oil- contamination

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Bioinspired underwater super-oil-wettability (superoleophilic/superoleophobic) properties are always considered as most important findings being a potential avenue in different aspects related to healthcare, environment, energy etc. 1-2 However, the inherent poor durability of these materials that are mostly developed using polymeric hydrogel3-4, metal oxide coating5-6 and electrostatic multilayers often in concern at practical scenarios. Here, 'amine-reactive' polymeric multilayers of nano-complex7 were developed to fabricate 'internal underwater superoleophobic/ superoleophilic coatings with impeccable physical/chemical durability. This allows the super-wetting properties to exist beyond the surface of the material and remain intact even after severe physical damage, including erosion of the material and continuous exposure to an artificial-marine environment for more than 80 days. Besides, the wettability is highly useful for any kind of oil-aqueous contamination either by protection/prevention or separation process. Moreover, this current design8 allowed us to attempt for a surface-independent modification having unprecedented durability with direct experimental demonstrations, and provided a basis to develop highly durable super-oil-wettability properties under water. It is believed that this contemporary will make a worthwhile contribution on developing multifunctional materials for widespread practical applications by exploiting this super-oil-wetting properties.

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SP9

Synthesis and study of an acridine-diimide system, a polycyclic aromatic hydrocarbon

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Both planar and nonplanar polycyclic aromatic hydrocarbons (PAHs) have attracted a great deal of interest owing to their versatility for application in organic light emitting diods (OLEDs), organic field affect transistor(OFETs), organic photovoltaic cells(OPVCs). The beauty of such molecules lies in its broad absorption range with high fluorescence quantum yield and chemical stability. The vast range of structural possibilities along with presence of different heteroatom like N, O, S, Se and covering a wide wavelength and self-assembly behaviours fascinated the idea of an acridine-based system. Our goal is to design a practically scalable synthetic route, and then study the photophysical and self-assembly behaviour of the prepared compound.

P1

Azidophosphonate chemistry as route to a novel class of vesicle forming phosphonolipids

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Keywords: liposome, vesicle leakage and doxorubicin delivery.

Membrane forming synthetic lipids show impressive applications in the field of biological and pharmaceutical applications. we have utilized β-azidophosphonate chemistry to gain access to a unique class of triazolephosphonate (TP) amphiphiles with fascinating physicochemical properties of lipids. These TP-lipids show stable vesicles and giant unilamellar vesicles formation aptitudes in aqueous solution. The vesicles of TP-lipids are anionic across a broad pH range and have high phase-transition temperature. These TP-lipids also show low vesicle leakage, phospholipase resistance, and moderate doxorubicin delivery efficacy. We hypothesize that these readily synthesizable phosphonolipids could find several applications as phospholipid substituents.

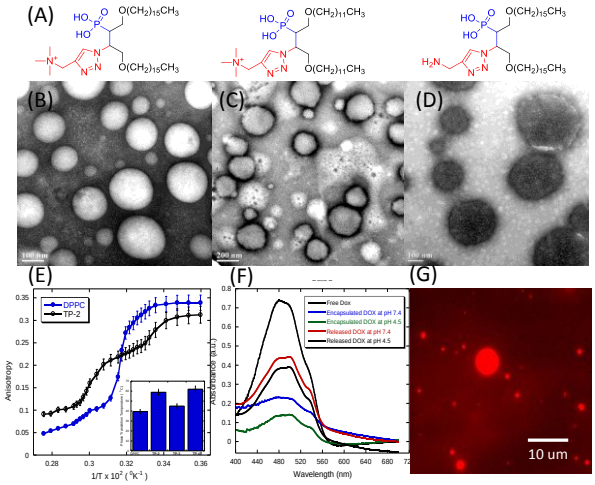

Fig.1. (A) Chemical structure of the TP-lipids. **(B-D)** Morphology of the corresponding lipids by hydration. **Fig.2. (E)** T_m values of the TP-lipids. **(F)** UV-VIS absorption spectra of doxorubicin in free and encapsulated state **(G)** Fluorescence microscopic images of the doxorubicin encapsulated GUVs of TP-lipid, red channel.

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P2

Stretchable and Durable Superhydrophobicity That Acts both in Air and Under Oil

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The stretchable and durable superhydrophobic materials are of potential interest for developing flexible microfluidics, functional textiles, gas sensors, ultra-flexible electronics, wearable devices etc.1-6 However the physical deformation of the material due to streching is likely to damage the embedded anti-fouling property through perturbation of essential topography and appeared as potential 'Achilles heel' of the application of anti-fouling property at practical settings. Here we report a highly stretchable and durable superhydrophobic membrane that extremely repel aqueous phase both in air and under oil, by exploiting a facile 1,4 conjugated addition reaction, where direct immobilization of 'reactive' nanocomplex on polyurethane fibrous substrate provided appropriate topography, and further covalent modification of these immobilized 'reactive' nanocomplex with strategically selected small molecules (i.e.; octadecylamine) adopted essential surface chemistry.7 This, scalable and covalent dip coating approach provided a highly durable superhydrophobicity property—which remained unaltered even after 150% deformation of the material, moreover, the synthesized material can survive the exposure to various other physical and chemical harsh conditions. The synthesized material is appropriate for energy efficient and rapid separation of both heavy and light oil from oil/water mixture, where oil can be separated with the rate of 115 mL/min and with efficiency above 99 % for multiple times.

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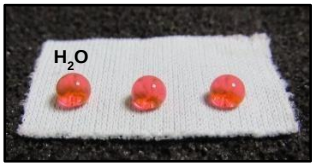

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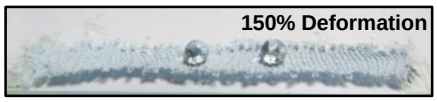

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P3

Selective Synthesis of Aryl Substituted Alkynes from Solid Calcium Carbide

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Acetylene undergoes a variety of chemical reactions, including electrophilic addition to its triple bond, and nucleophilic reactions after abstraction of the acidic terminal hydrogens. However, acetylene as a flammable and explosive gas is not easily handled in a standard laboratory setup for corresponding reactions. The risk of explosion and technical difficulties drastically complicate the equipment and greatly increase the cost. CaC2 is a sustainable source of acetylene whose global production is more than 15 million metric tons per year. Therefore, the exploration of the reactions directly using calcium carbide is very necessary. The direct usage of calcium carbide can avoid many protection and de-protection steps that greatly reduce the number of synthetic steps, resulting in more efficient and greener organic synthesis. The new synthetic methods will be presented here to demonstrate that calcium carbide could play a major role as a sustainable and cost efficient carbon source in modern organic synthesis and also to achieve an industrial safety improvement without additional cost, a less hazardous and more economical starting material is highly desirable. We are working to develop the method for synthesizing both internal alkyne as well as terminal alkyne selectively by using calcium carbide and iodonium salts through copper-catalyzed cross-coupling reaction and also explore to develop a new method in one pot for synthesis of substituted triazole derivatives from solid calcium carbide as a source of acetylene.

P4

Metal Free Sequential C(sp2)-H and C(sp3)-H Functionalization: A Facile Access of Fused Benzimidazole

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Fused and substituted benzimidazole derivatives are very important specially in medicinal chemistry as these molecules possess important biological activity including anti-bacterial, antivirus, anticancer, antiulcer, antihypertensive activities.1 A very few methods have been developed for synthesis of fused benzimidazole. Most of the methods involve metallic reagents, toxic oxidants producing unwanted chemical waste. A novel method for synthesis these important pharmacophores from nitrosoarenes under metal and oxidant free condition will be presented sequential functionalization of nitrosoarenes followed by C(sp3)-H-functionalization of saturated N-heterocycles like pyrrolidines, piperidine, 4- methylpiperidine, azepane occurred to provide the desired compounds.2 This method was found to be applicable in gram scale synthesis. The synthesised molecules can also be further derivatized easily.

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P5

Studies on supramolecular assemblies, metal complexes of oxime related compounds for detection of fluoride ions and molecular recognition

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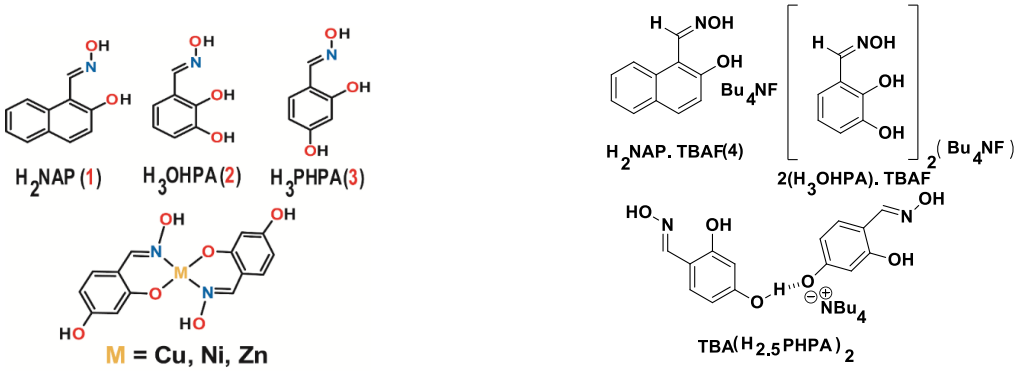
Supramolecular assemblies of oximes are well studied, but their utility in multicomponent complexes remains less explored. Due to possibilities of various chemical transformations of oximes at ambient conditions they are attractive to make new assemblies which may be modified to new assemblies. Furthermore, metal complexation ability of oximes makes scopes for new supramolecular architecture to make a secondary environment of guests in a metal complex.



(a) (b)

Figure 1: (a) Oxime molecules and metal complexes of 2,4-dihydroxybenzaldoxime and (b) Supramolecular assemblies of oxime molecules with tetrabutylammonium fluoride (TBAF).

Besides these oxime together with another functional group provides large scope to make new assemblies. In this presentation utility of oxime molecules (Fig. 1a) for preparation of different architectures (Fig. 1b) with fluoride ion via recognition study will be presented. Self-assemblies and stability of a series of copper and nickel oxime complexes (Fig. 1a) will be discussed. A through comparison on ability to detect fluoride ions by these complexes with respect to free ligand will be presented. Further to this, how one can take advantage of basicity of fluoride ions to make multi-component self-assemblies will be presented. Extension of the work to build guest-included self-assemblies with expansion of synthons will be presented.

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P6

Nitrobenzofurazan Derivatives of N'-hydroxyamidines as potent Indoleamine 2,3-dioxygenase 1 Inhibitors

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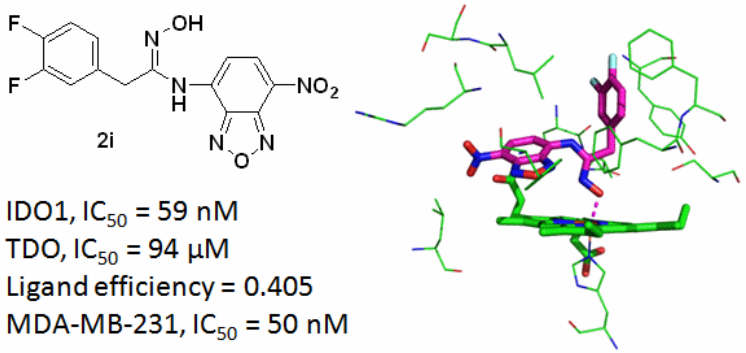
Tryptophan metabolism through the kynurenine pathway is considered as a crucial mechanism in immune tolerance. Indoleamine 2,3-dioxygenase 1 (IDO1) plays a key role in tryptophan catabolism in the immune system and it is also considered as an important therapeutic target for the treatment of cancer and other diseases that are linked with kynurenine pathway. In this study, a series of nitrobenzofurazan derivatives of *N*'-hydroxybenzimidamides (1) and *N*'-hydroxy-2-phenylacetimidamides (2) were synthesized and their inhibitory activities against human IDO1 enzyme were tested using in-vitro and cellular enzyme activity assay. The optimization leads to the identification of potent compounds, 1d, 2i and 2k (IC_{50} = 39-80 nM), which are either competitive or uncompetitive inhibitors of IDO1 enzyme. These compounds also showed IDO1 inhibition potencies in the nanomolar range (IC_{50} = 50-71 nM) in MDA-MB-231 cells with no/negligible amount of cytotoxicity. The stronger selectivity of the potent compounds for IDO1 enzyme over tryptophan 2,3-dioxygenase (TDO) enzyme (312-1593-fold) also makes them very attractive for further immunotherapeutic applications.



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P7

Self-Healable Superhydrophobic Print of Water Soluble Agents

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Recovery of the compromised anti-fouling property because of the perturbation in the essential chemistry on top of the hierarchical topography of superhydrophobic coating, is commonly achieved through some stimuli (temperature, humidity, pH etc.) driven re-association of the low surface energy molecules on top of the macro/nano features. However, the attempts for self-healing of superhydrophobicity in the physically-damaged material having inappropriate topography, which is extremely important and challenging aspect for practical utility of the bio-inspired property are rare in the literature. Recently, very few materials are introduced that are appropriate for recovering the hierarchical features—but after application of appropriate external stimuli. Further, the optimization of appropriate stimuli is likely to be a challenging problem at practical scenarios. Here, we have strategically exploited a simple and robust 1,4 conjugate addition reaction between aliphatic amine and aliphatic acrylate groups for appropriate and covalent integration of modified-graphene oxide nano sheets—which are well recognized for expectational mechanical property, in the polymeric coatings. The synthesized material was embedded with remarkable property that protected the antifouling property from various harsh physical and chemical insults including the physical abrasions that are even involved in the removal of the top surface of the polymeric coating, and after incurring the physical deformation on the polymeric coating, 2) the lost-anti-fouling was self-healed—without demanding any external interventions. On application of pressure, bio-inspired, non-adhesive (contact angle hysteresis <5°) superhydrophobicity in the current polymeric coating was compromised, and the physically damaged material became highly adhesive (contact angle hysteresis ~ 50°) superhydrophobic, however, after releasing the pressure, the non-adhesive (contact angle hysteresis <5°) property in the material was restored back with time through recovering the essential hierarchical topography, without application of any external stimulus. Thus, the synthesized material is appropriate for diverse and prospective applications of the bio-inspired interfaces at complex and harsh practical settings. This unique material having impeccable durability and absolute self-healing capability was further explored in i) developing rewritable aqueous pattern on the extremely water repellent surface and b) selective impregnation of water soluble agents—without permanent change in the native anti-fouling property in the polymeric coating and eventually provided superhydrophobic print that made out of hydrophilic small molecule, and that even directly from aqueous medium, which are extremely hard to achieve using conventional superhydrophobic material, and such multifunctional interfaces could be

provide important avenue for various smart applications including delivery systems, catalysis, self-assembly of colloids, reusable chemical sensing etc.

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P8

Efficient "Turn-on" Detection of Histone by a Naphthalenediimide Derivative via Threading Intercalation of DNA

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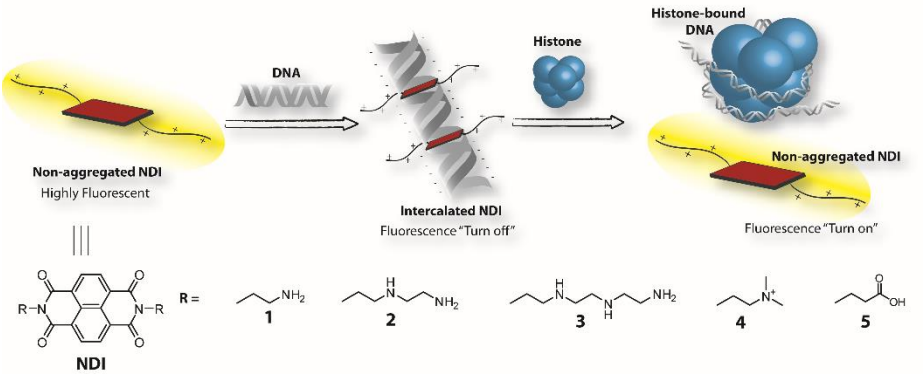
Amine and acid functionalized naphthalenediiimde (NDI) derivatives were designed and synthesized. The binding affinity of these derivatives were analyzed in presence of DNA to identify the most suitable NDI derivative that can be utilized for the detection of histone, a DNA-binding protein. In the monomeric state, the NDI derivatives show high fluorescence but in presence of DNA, the emission quenched. The "turn-of" of emission can be attributed to the formation of NDI-DNA nano-hybrid. Histone, having a stronger binding affinity toward DNA, displaces NDI from DNA. The displacement of NDI leads to fluorescence back to the original monomeric state. So, the quenching of the fluorescence of NDI upon binding with DNA is used to quantitative "turn on" detection of histone with extremely high efficiency and selectivity.



P9

Iron(III) Catalyzed Peroxide Mediated C-3 Functionalizations of Flavones

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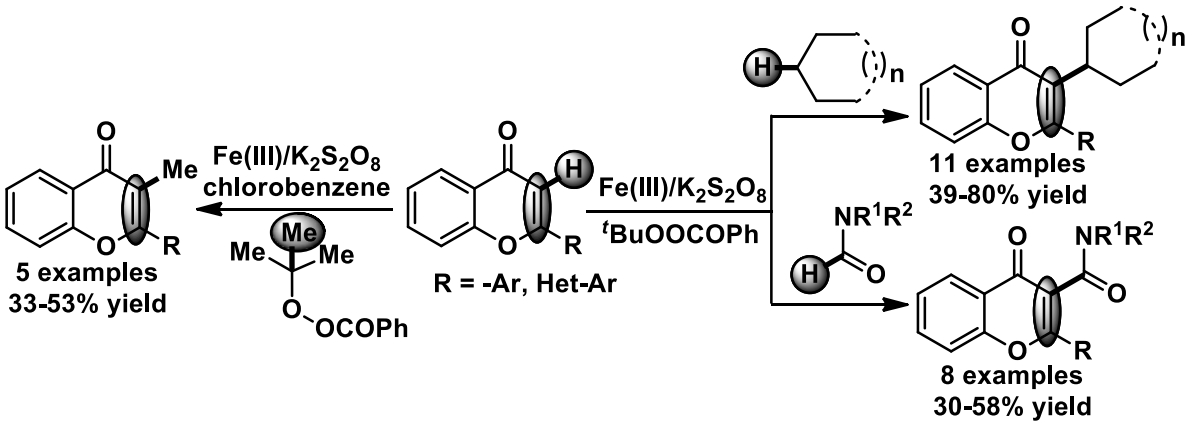
Transition metal catalyzed C-H functionalization via cross-dehydrogenative coupling (CDC) protocols has emerged as a promising and powerful tool towards the formation of Csp-Csp, Csp-Csp^2 Csp^2-Csp^2 and Csp^3-C bonds. In this context cycloalkanes have been employed for CDC reactions (Csp^3-H functionalization) in the absence or presence of transition metal catalysts albeit with limited examples. Aliphatic Csp^3-H bonds are the most available natural resource. Thus, methodologies for the direct functionalization of aliphatic Csp^3-H bonds will expand the synthetic toolbox, allowing access to value-added products with various important applications. Herein, an iron(III) catalyzed C-3 functionalizations of flavones have been achieved using tert-butyl peroxybenzoate (TBPB)/potassium persulfate ($K_2S_2O_8$) oxidant combinations with a suitable solvent. In the presence of iron(III)/tert-butyl peroxybenzoate/$K_2S_2O_8$, reaction of flavones in cycloalkanes afforded exclusive C-3 cycloalkylation via Csp^2-Csp^3 coupling, whereas solvent N, N-dialkylformamide provided C-3 amidation via Csp^2-Csp^2 coupling. Under an identical reaction condition just by switching the solvent to chlorobenzene, C-3 methylated flavones were obtained where tert-butyl peroxybenzoate (TBPB) served as the source of the methyl group.



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P10

Highly Selective and Sensitive Detection of 2,4,6-Trinitrophenol by an Amino-Decorated Zr(IV)-Based Luminescent Metal-Organic Framework

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The development of metal-organic frameworks (MOFs) has provided an excellent platform for national design and synthesis of functional materials with desired properties [1]. They have become one of the most promising materials for a wide range of uses and applications [2]. Among them, the implementation of MOFs as fluorescent chemical sensors has aroused great interest in the scientific community. Currently, the sensitive and selective detection of nitroaromatic explosives is attracting immense attention due to their broad range of applications in security operation, environmental protection, forensic investigations and mine-field analysis [3]. Among different MOFs, Zr(IV)-based MOFs are very attractive systems due to their high chemical and hydrolytical stability.

Herein, we present a new luminescent Zr(IV)-based MOF, which was synthesized by the solvothermal method using a mixture of $ZrOCl_2 \cdot 8H_2O$ and 1-aminonaphthalene-3,7-dicarboxylic acid ($H_2NDC\text{-}NH_2$) ligand in DMF in the presence of trifluoroacetic acid as modulator. The high luminescence [4] of naphthalene moiety offers opportunities to enhance the luminescent behaviour of the MOF. The phase-purity of the compound was confirmed by X-ray powder diffraction (XRPD) analysis, infrared spectroscopy and thermogravimetric analysis.

From the steady-state fluorescence titration experiments, it is reveal that the fluorescence intensity of the MOF can be quenched efficiently by trace amount of 2,4,6-trinitrophenol (TNP) or picric acid (Fig.1a), even in the presence of other competing analogues with a detection limit of 0.45 ppb (Fig.1b). Recyclability experiments reveal that this MOF retains its initial fluorescence intensity even after several cycles, suggesting high photostability and reusability useful for long-term sensing application. Since TNP or picric acid is an extremely hazardous and strong explosive, this new MOF can be used for the construction of a selective, rapid and highly sensitive detection device for the in-field sensing of TNP.

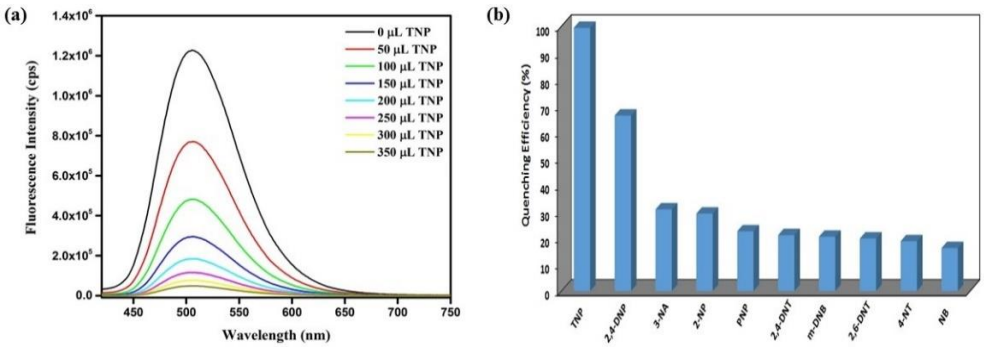

Fig. 1. (a) Quenching of the fluorescence intensity by gradual addition of 3 mM TNP solution to a 3 mL of well-dispersed DMSO suspension of the MOF. (b) Fluorescence quenching efficiencies of various nitroaromatic explosives (at 3 mM concentration) towards the MOF suspension.

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P11

Thermally Activated Delayed Fluorescence Organic Noble Metal-free Molecules and Towards the Breakthrough of Organic-Electronics

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In fluorescence materials an exciton formation under electrical excitation typically results in 25% singlet excitons and 75% triplet excitons. However, 75% of the electrically generated energy is dissipated as heat by triplet excitons, leading to the theoretically highest external quantum efficiency (EQE) of 5%. To harvests light from both triplet and singlet excitons, allowing the internal quantum efficiency of the device to reach nearly 100%. Many efforts to utilize the non-emissive triplet excitons have been devoted to breaking through the 5% limitation. The most successful one is by incorporating heavy metals into the organic aromatic frameworks to increase spin–orbit interactions. However, used heavy metals for phosphorescence are confined to Iridium (Ir) and Platinum (Pt), which are very expensive. In order to avoid the use of expensive metals in practical applications, several other strategies such as triplet–triplet annihilation (TTA), hybridized local and charge transfer (HLCT) and thermally activated delayed fluorescence (TADF) have also been proposed to harvest the 75% triplet excitons.

Among them, TADF materials have drawn tremendous attention in the field of OLEDs, with their state-of-the-art performance in terms of EQEs, turn-on voltages, and color coordinates. Noble metal-free TADF molecules having small singlet–triplet energy gap offers to harvest triplet excitons for fluorescence through facilitated reverse intersystem crossing "RISC" (T1→S1). Moreover, these materials are purely organic and thus not costly. Therefore, the TADF approach provides the best alternative to conventional fluorescent and phosphorescent OLEDs, regarding device efficiency and cost. The success in the breakthrough of the theoretical and technical challenges that arise in developing high-performance TADF materials may pave the way to shape the future of organoelectronics.

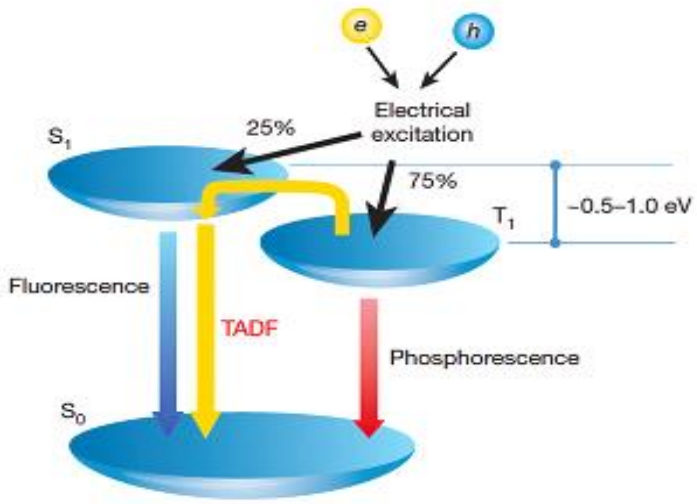

Fig. 1. Summary of TADF processes in harvesting the triplet excitons for luminescence in OLED devices.

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P12

Atom Based 3D-QSAR Studies on 2,4-Dioxopyrimidine-1-carboxamide Analogues: Validation of Experimental Inhibitory Potencies towards Acid Ceramidase

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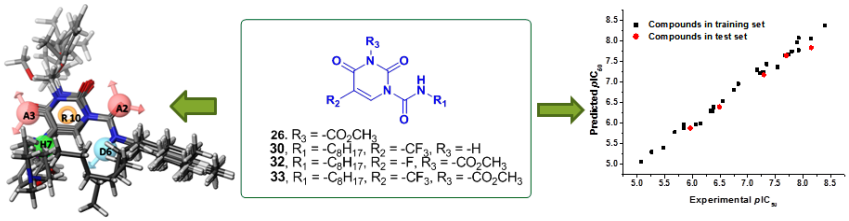
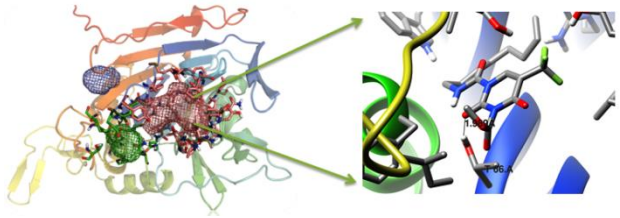
Sphingolipids, the major membrane constituents of eukaryotic cells, play important roles as signaling molecules. They actively function for cell growth, cell differentiation and cell death (apoptosis), thus being indispensable for cell homeostasis and normal cell development [1]. Ceramide, the central lipid molecule of sphingolipid family undergoes enzymatic hydrolysis by Ceramidases (CDases) to produce Sphingosine. Interestingly, while the accumulation of Ceramide induces apoptosis, the overproduction of the hydrolyzed product Sphingosine promotes cell proliferation [2]. Therefore, a proper balance of Ceramide and Sphingosine is extremely important for normal cell development. Interestingly, an overproduction of acid ceramidase (aCDase) has been observed in cancerous cells and therefore, pharmacological inhibition of aCDase could be a chemotherapeutic approach as it increases the cellular concentration of ceramide inducing apoptosis. As the crystallographic information of aCDase is not known, we have performed quantitative structure activity relationship (QSAR) studies for the inhibition of aCDase with a series of literature reported 2,4-dioxopyrimidine-1-carboxamide derivatives (carmofur derivatives) as shown in Figure 1a [3]. In this study the experimental dataset was divided into training (83%) and test (17%) sets and the best model was chosen based on randomized trial distributions consisting of five compounds in a test set with a wide range of activity profile and superior values of statistical parameters such as Q2 and R2 values. The inhibitory potencies of lead compounds were further justified by their efficient molecular interactions at the active site of homology modeled protein human N-acylethanolamine hydrolyzing acid amidase (hNAAA) as evidenced by molecular docking study [4].



(a)



(b)

Figure 1. (a) Chemical structures of some lead carmofur derivatives along with their predicted and experimental pIC50 values; (b) Molecular interaction of compound 33 with the homology modeled protein hNAAA.

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P13

Dynamics of 2D and 3D waves in Chemical Excitable Media

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2-Dimenisonal spirals and 3-dimensional scrolls are nonlinear wave forms found in systems ranging from the sub-micronic neuronal tissues to the super-massive galaxies. It is also found in the heart tissues and has deep connections to fatal heart diseases. Study and control of these waves poses an interesting problem. The Belousov-Zhabotinsky (BZ) reaction forms a table-top laboratory model for the study of the dynamics of spiral and scroll waves.

We use gel-stabilized Ferroin-catalyzed BZ reaction to carry out our experimental studies. Here we present some of our findings. In one of our studies, we show how substrate concentrations affect wave properties and dynamics. We have also explored how scrolls and spirals interact with one another and with unexcitable heterogeneities. These waves can also be externally controlled by employing thermal gradients and electrical fields.

In order to gain a better understanding of the experimental results, we carry out numerical simulations of a model two-variable reaction-diffusion system.

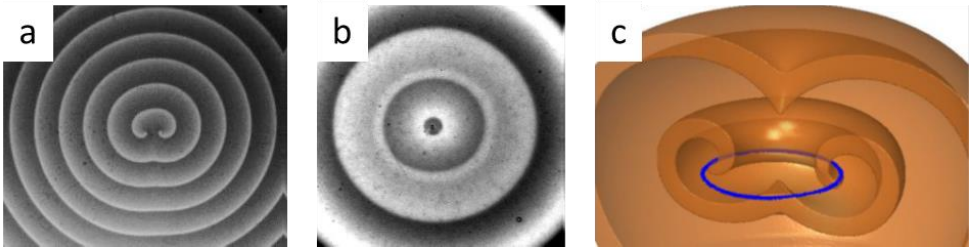

Fig. Snapshot of (a) a spiral wave and (b) a scroll wave in the Ferroin catalysed Belousov-Zhabotinsky system. (c) is the three dimensional view of a scroll wave obtained from numerical simulation.

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P14

A General and Facile Chemical Approach for Controlled and Extreme Regulation of Liquids (Oil/Water) Wettability

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The controlled regulation of both oil (under water) and water (in air) wettability is an emerging approach to address several functional materials for various prospective applications like oil/water separation, anti-corrosive coating, underwater robotics, protein crystallization, drug delivery, open microfluidics, water harvesting etc1-3. Herein, we report a 'reactive' and covalently cross-linked polymeric coating through a facile and robust 1,4-conjugate addition reaction, which is appropriate for controlled and extreme regulation of both water and oil wettability in air and under water respectively. Though, the extreme-wettability (super-philicity and super-phobicity) of water (in air) and oil (under water) are the main concern of our study, but along with this the special liquid wettability of the multilayer can also be tuned (i.e.; extremely liquid repellent—but with controlled adhesive property) both in air and under water, after strategic post chemical modifications through again Michael addition reaction. The super-wetting properties of the materials were able to withstand various physical and chemical abrasions including adhesive tape test, sand drop test, and several harsh chemical exposures like extremes of pH, salt, surfactant contaminated aqueous media whereas in generally the property is compromised under such abrasions4-5. Besides, this current findings were also proved to be a substrate-independent approach that can eventually allowed to decorate various flexible and rigid substrates (i.e.; wood, Al-foil, synthetic fabric etc.) irrespective of their material composition as well as regular nature of wettability with various bio-inspired wettability properties including 1) non-adhesive superhydrophobicity (lotus leaf)6, 2) adhesive superhydrophobicity (rose petal), and 3) underwater superoleophobicity (fish scale)6-7 etc. This single polymeric coating—which is capable of displaying several bio-inspired interfaces both in air and under water, even after harsh physical/chemical insults8, would be useful in various prospective and relevant applications at practical scenarios.

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P15

Characterizing optical properties, composition of stabilizer-free copper nanoclusters and its interaction with bovine serum albumin

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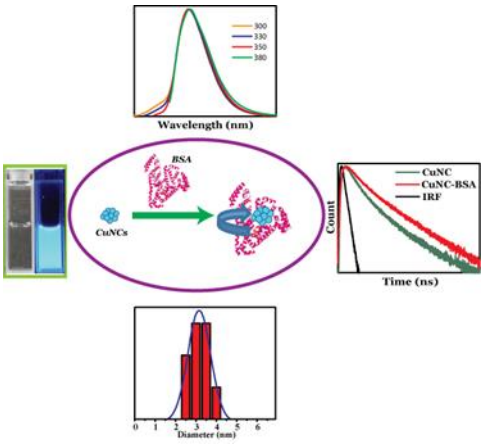
Very recently, synthesis of a stabilizer-free copper nanocluster (CuNC) with enhanced catalytical activity was proposed by simply refluxing copper salt in dimethylformamide (DMF) at elevated temperature. Herein, we characterize the optical properties of CuNCs with steady-state and time-resolved spectroscopy; determine the composition and surface ligation of the CuNC with matrix assisted laser desorption ionization (MALDI) mass and Fourier transformed infrared (FTIR) Spectroscopy measurements. We also investigated the interaction of CuNC with a representative protein, bovine serum albumin (BSA). The CuNC exhibits bright fluorescence in aqueous medium, remains stable over a broad pH range (2-12) and can be easily conjugated to the protein. The interaction of BSA with the CuNC leads to a very minor loss of the secondary structure of the protein. The fluorescence of CuNC-BSA nanocomposite fluorescence is modulated dramatically due to Förster resonance energy transfer (FRET) from tryptophan to CuNC.



P16

Monoradical-Containing Four-Coordinate Co(III) Complexes: Homolytic S-S, Se-Se Bond Cleavage and Catalytic Isocyanate to Urea Conversion Under Sunlight

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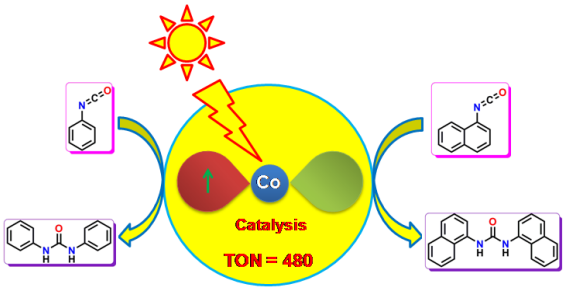
Redox–active aminophenol ligand containing square planar cobalt(III) complexes are very much susceptible for C–C bond formation reaction.[1,2] Due to the strong nucleophilic nature of the complexes it can easily react with alkyl halides, CH_2Cl_2 or $CHCl_3$ to generate stable square pyramidal cobalt(III) complexes. Here we describe the synthesis of aminophenol based non–innocent ligands $\mathbf{H_2L^{AP(R)}}$ (R = –Me and –Ph). Both ligands $\mathbf{H_2L^{AP(R)}}$ (R = –Me and –Ph) reacted with $Co(ClO_4)_2 \bullet 6H_2O$ in the presence of Et_3N under air provided monoradical–containing, four–coordinate square planar cobalt (III) complexes (**1** and **2**,$[Co^{III}(L^{AP(R)})(L^{ISQ(R)}]^0$). The formed complexes reduced diphenyl disulfide and diphenyl diselenide by one electron and provided the corresponding five–coordinate, diradical–containing suquare pyramidal complexes, where axial position was occupied by an –XPh group (X = S(**1a**/**2a**) and Se(**2b**), $[Co^{III}(L^{ISQ(R)})_2XPh]^0$. Crystallographic and spectroscopic studies revealed geometric and electronic structures of all these cobalt (III) radical complexes. In the presence of catalytic amount of four–coordinate cobalt (III) complexes (**1** and **2,** $[Co^{III}(L^{AP(R)})(L^{ISQ(R)}]^0$) (R = –Me and –Ph), and five–coordinate, diradical–containing cobalt (III) complex (**2a**, $[Co^{III}(L^{ISQ(Ph)})_2SPh]^0$), conversion of RNCO (R = phenyl and naphthyl) to the corresponding C–N coupled urea derivatives (TON 480) in dry CH_2Cl_2 has been take place under sunlight stimulus.[3]



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P17

Tryptophan Containing Peptide Nanovescicles as Potential Drug Delivery Vehicle

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The naturally occurring bio macromolecules like peptides, or proteins have drawn attention in the domain of nano (bio) technology owing to their tremendous applications such as chemo sensors, drug delivery system, artificial ion channels etc.[1] There are literature reports where peptide nanovesicles have been shown to entrap drug molecules and release them reversibly in response to various stimuli like pH, temperature, ionic strength which induce distinguishable change in the morphology of the self-assembly[2]. Diphenylalanine and its derivatives are one of the most studied peptide motifs which self- assemble into various morphologies wherein aromatic and hydrophobic interactions are thought to play crucial roles[3]. However, Ditryptophan peptide, which is also composed of aromatic amino acid residues fails to show such behavior[4]. We decided to study the self-assembly of Tryptophan containing peptides where Tryptophan residues are spaced away from each other. Boc-Trp-Leu-Trp-Leu-OMe tetra peptide with one Leucine in between two aromatic Tryptophan residues, self-assembled into nano vesicles in Acetonitrile Methanol and physiologically compatible Ethanol. This prompted us to probe if it could be used as a potential drug delivery vehicle. Here we demonstrate that it can encapsulate carboxy fluorescein dye and curcumin drug for about 24 hours, which can be released in the presence physiologically relevant salts like KCl and NaCl. This self-assembled Tryptophan peptide shows promise as a potential drug delivery vehicle.

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P18

Spectroscopic study of dual fluorescence and aggregation in 2-((phenyl)amino)-5-(2 hydroxybenzono)-1,3,4-thiadiazole

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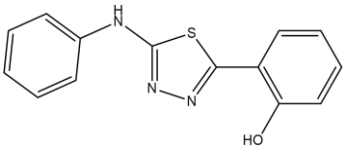
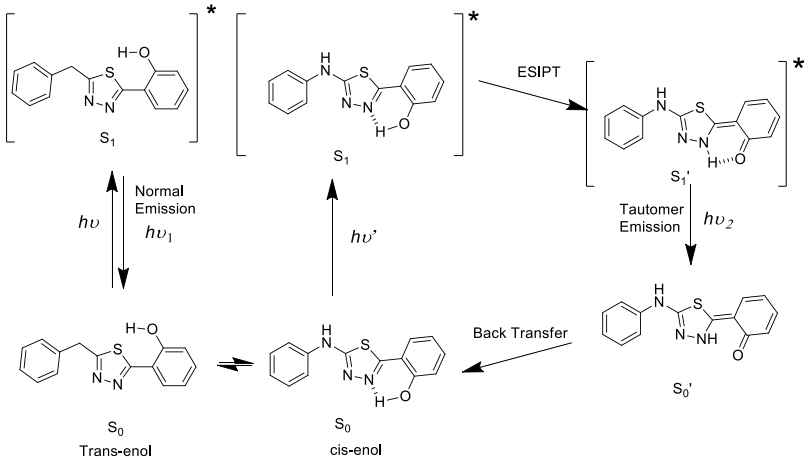
A 1,3,4-thiadiazole derivative, 2-((phenyl)amino)-5-(2 hydroxybenzono)-1,3,4-thiadiazole (PHBT) belonging to the class of biologically active compounds was synthesized and its emission properties were investigated in various solvents and solvent mixtures. PHBT shows Excited State Intramolecular Proton Transfer (ESIPT) and gives two emissions, the normal band at ~ 410 nm (Stokes' shift = 5020 cm-1) and the tautomer band at 520 nm (Stokes' shift = 10,180 cm-1). The tautomer band predominates over the normal band in non-polar solvents like hexane and chloroform and vice-versa is the case in polar solvents. The presence of two species in the excited state was also confirmed by the lifetime measurements at the two emission wavelengths. Studies were also conducted in some binary solvent mixtures. The molecule also showed a 2.5 times Aggregation Induced Enhancement of Emission (AIEE) when dissolved in a solution of 90:10 (v/v) THF:Water.



2-((phenyl)amino)-5-(2 hydroxybenzono)-1,3,4-thiadiazole (PHBT)



The four step process of ESIPT in PHBT

P19

An Interactive Quantum Dot and Carbon Dot Conjugate for pH-Sensitive and Ratiometric Cu^{2+} Sensing

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Herein we report the photoinduced electron transfer from Mn^{2+}-doped ZnS quantum dots (Qdots) to carbon dots (Cdots) in an aqueous dispersion. We also report that the electron transfer was observed for low pH values, at which the oppositely charged nanoparticles (NPs) interacted with each other. Conversely, at higher pH values the NPs were both negatively charged and thus not in contact with each other, so the electron transfer was absent. Steady-state and time-resolved photoluminescence studies revealed that interacting particle conjugates were responsible for the electron transfer. The phenomenon could be used to detect the presence of Cu^{2+} ions, which preferentially, ratiometrically, and efficiently quenched the luminescence of the Qdots.

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P20

Development of Peptide and Nucleobase Derived Drug Delivery System for Efficient and Controlled Delivery of Antitumor Drug

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5 –Fluorouracil (5-Fu) is very commonly used as anticancer drug. Despite of being used, it suffers from some disadvantages, like non–selective cytotoxicity that contributes to its lower therapeutic index1. Therefore, the controlled release of the drug to the specific site of the tumor cell is very important so that it acts only on the targeted area, leaving the normal cells unaffected. Most of the release mechanisms involve chemical and enzymatic reactions, which showed poor selectivity and produce various side effects. In our lab, we are trying to develop drug delivery systems for controlled and dose-dependent release of 5-Fu as well as 5-FC, based on deoxyribose sugar and peptides3 conjugated through a photolabile linker that can be cleaved at λ_{ex}365 nm, releasing the active drug at the targeted site efficiently and in a controlled manner.

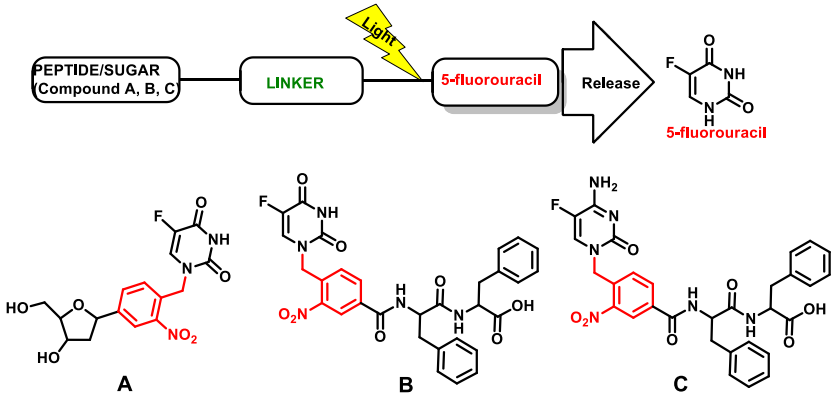

Figure 1: Schematic diagram of photocleavage of 5-fluorouracil from the conjugate

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P21

K_2CO_3 Catalyzed Regioselective Synthesis of Thieno[2,3-b]thiochromen-4-one Oximes as a Valuable Synthon: Access to the Corresponding Amine and Nitroso Derivatives

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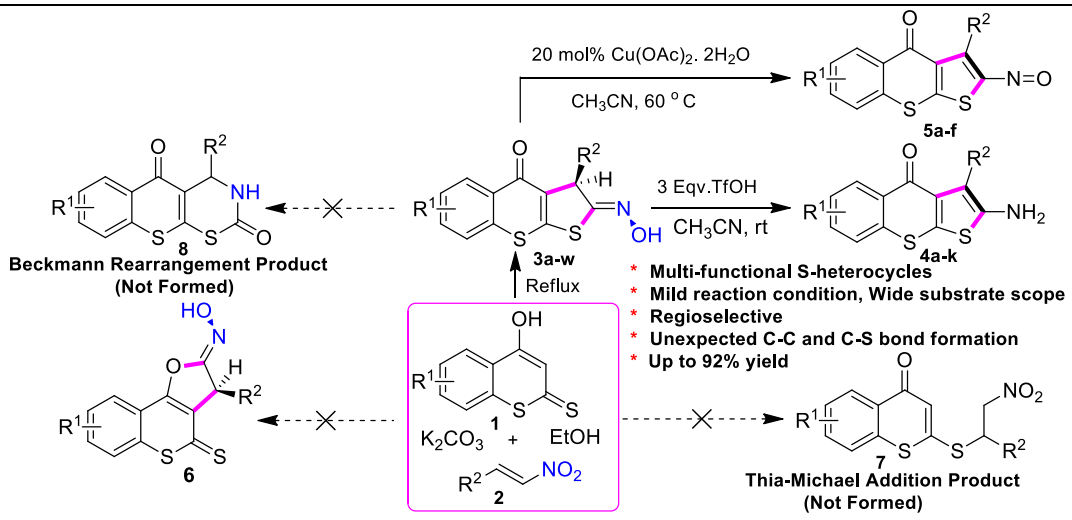
A facile method for the synthesis of useful thieno[2,3-*b*]thiochromen-4-one oximes is accomplished via a thio[3+2]cyclization reaction of 4-hydroxydithicoumarins and *trans*-β-nitrostyrenes in the presence of 10 mol% K_2CO_3 in ethanol under reflux conditions. Further, these precursors were converted into the corresponding hitherto 2-amino thieno[2,3-*b*]thiochromen-4-one and 2-nitroso thieno[2,3-*b*]thiochromen-4-one derivatives respectively. The salient features of the present protocol are mild reaction conditions, shorter reaction time, good yields and unexpected formation of C–C and C–S bonds in a regioselective manner.



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P22

Synthesis of 2,5-Disubstituted Furans From $Sc(OTf)_3$Catalyzed Reaction of Aryl Oxiranediesters with γ-Hydroxyenones

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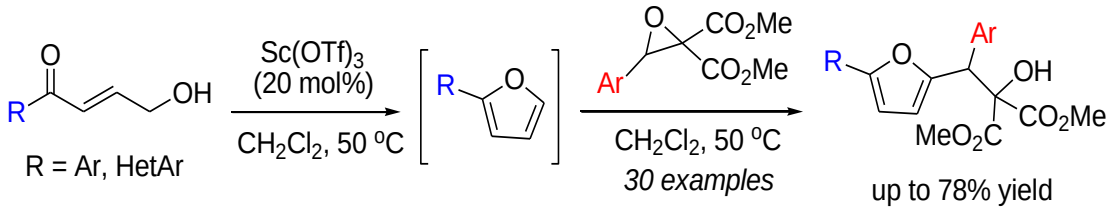
A convenient synthesis of 2,5-disubstituted furan[1] has been developed by employing donor-acceptor oxiranes in a new reaction with γ-hydroxyenones[2]. $Sc(OTf)_3$ was found to be the best catalyst and 2,5-disubstituted furans are obtained in moderate to good yields under mild reaction conditions. The scope of the reaction is quite broad allowing for the synthesis of disubstituted furans having aryl and heteroaromatic groups.



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P23

Dioxygenation reaction of a Cobalt-nitrosyl: Putative formation of a Cobalt–peroxynitrite *via* a {$Co^{III}(NO)(O_2^-)$} intermediate

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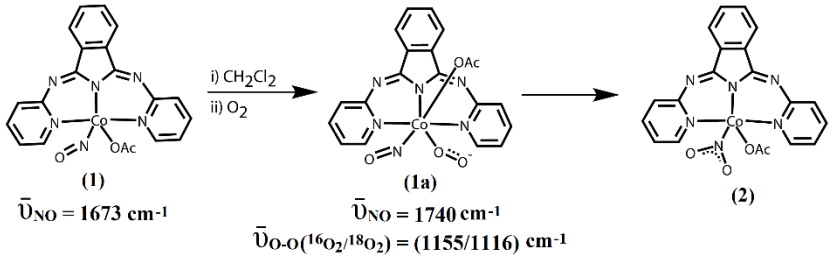
A cobalt-nitrosyl complex, [(BPI)Co(NO)(OAc)], **1** {BPI = bis(pyridylimino)isoindol} was prepared and characterized. Structural characterization revealed that the cobalt center is having a distorted square pyramidal geometry with the NO group coordinated from the apical position in a bent fashion. The addition of dioxygen (O_2) to the dichloromethane solution of complex **1** resulted in the formation of N-nitrito complex, [(BPI)Co(NO_2)(OAc)], **2**. It was characterized structurally. Kinetic studies suggested the involvement of an associative mechanism. FT-IR spectroscopic studies suggested the formation of the intermediate **1a** [(BPI)$Co^{III}(NO)(O_2^-)$(OAc)] in the reaction. The intermediate **1a** decomposed to complex **2** *via* a presumed peroxynitrite intermediate which was implicated by its characteristic phenol ring nitration reaction.



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P24

Application of Enigmatic Enantioselectivity of Natural Clay Minerals for Chiral Resolution.

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One of the greatest unsolved mysteries in chemistry is the origin of chirality, the row is commonly extended up to the starting point of highly specific and complex molecules of life. Here, we have demonstrated that natural clay minerals without any known chiral components possess enantioselectivity, which could provide a clue about the origin of the first chiral molecule on earth at the backdrop of the messy reaction vessel of the prebiotic condition. The enigmatic enantioselectivity of clay layers has been exploited here to prepare freestanding membranes capable of separating enantiomeric mixtures. Raw vermiculite crystals are heated to various temperatures (500, 600, 700 and 800°C), and exfoliated into 2D sheets by using concentrated HCl solution. Racemic mixtures of natural amino acids were vacuum filtered through freestanding membranes fabricated by layer by layer deposition of exfoliated vermiculite layers. The filtrates were analyzed by various analytical techniques such as HPLC, UV-Vis spectroscopy, circular dichroism, and polarimetry. The vermiculite sample heated to 800 °C yields a highest enantiomeric excess of 20 % for racemic tryptophan. Membrane fabricated with highest weight (350 mg) of exfoliated vermiculite gives the maximum enantiomeric excess of 9.9 % for racemic tryptophan. Under stirring condition, clay samples heated at 600°C demonstrated a chiral selectivity of 41%.

P25

Synthesis of Azatricyclic Derivatives via Aza-Prins Cyclization Reaction

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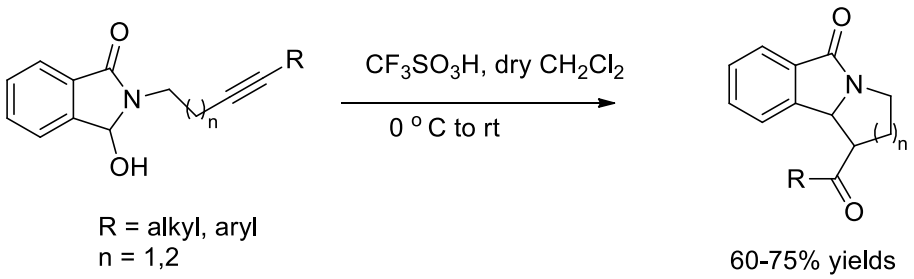
Azatricyclic compounds are present as core units several highly significant natural products,[1] which have been shown to exhibit broad biological activity and diverse pharmacological profile. More recently, tetrahydropyrido [1,2-a] isoindolone derivatives (valmerins) have been reported as potent cyclin-dependent kinase/ gyclon synthase kinase-3 inhibitors and also show antitumor properties.[2] Similarly a marine alkaloid, lepadiformine shows moderate cytotoxic activity.[3] Cyclic N-acyliminium ions are versatile reaction intermediates for construction of various azabicyclic scaffolds. N-acyliminium ions are used for the synthesis of azatricyclic compunds via intramolecular Friedel-Crafts, aza-cope rearrangement, intramolecular ene, aza-Nazarov cyclization cascade, and endo-trig cyclization reactions (aza-Prins type) on alkene, alkyne, allene and with various nucleophiles such as formate, hydroxyl, and halo groups. In continuation of our research in aza-Prins cyclization reaction, herein we report a methodology for the synthesis of aza-tricyclic compounds via aza-Prins cyclization reaction using *N*-acyl-iminium-ion as intermediate .[4]



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P26

Regiodivergent Remote Arylation of Cycloalkanols: Expeditious Access to anti-Cancer Dysideanone's Fused- and Bridged-Carbotetracycles.

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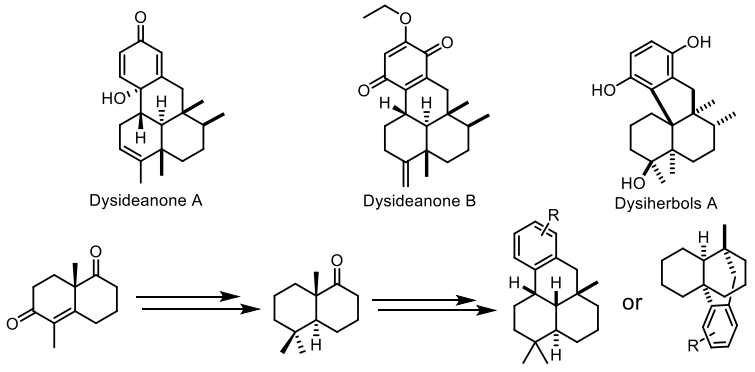
Natural products and their mimics have historically been the significant source of medicinal drug[1]. They continuously inspire the synthetic chemist to synthesize the biologically significant compound for drug discovery. Terpenoids are one of the largest class of secondary metabolites. Therefore, continued efforts have been devoted to the isolation, synthesis and structure-activity studies of new molecules for identifying the most potent one.[2] However, the chemical synthesis of terpenoids often encounters significant difficulty due to their inherent structural and stereochemical complexities.[2] Dysideanones natural products have attracted our attention for their interesting fused tetracyclic framework and highly functionalized aromatic system. We have developed a first example of diastereoselective regiodivergent γ and γ' arylations across an all-carbon quaternary center of cycloalkanols to access a series of enantioenriched fused and bridged-carbotetracycles of Dysideanones natural products. Remarkably, carbotetracycles that are non-toxic to normal cells, suppressed survival and proliferation of colon cancer cells through down regulation of COX-2 and survivin.



Wieland-Miescher ketone and its derivative was transfered to ketone. Then chiral ketone was extended to carbotetracycles via Barbier reaction and followed by intra-molecular cyclization.

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P27

Cyanomethylation of Aldehydes Catalyzed by Pincer-Based Nickel Complexes: An Experimental and Computational Study

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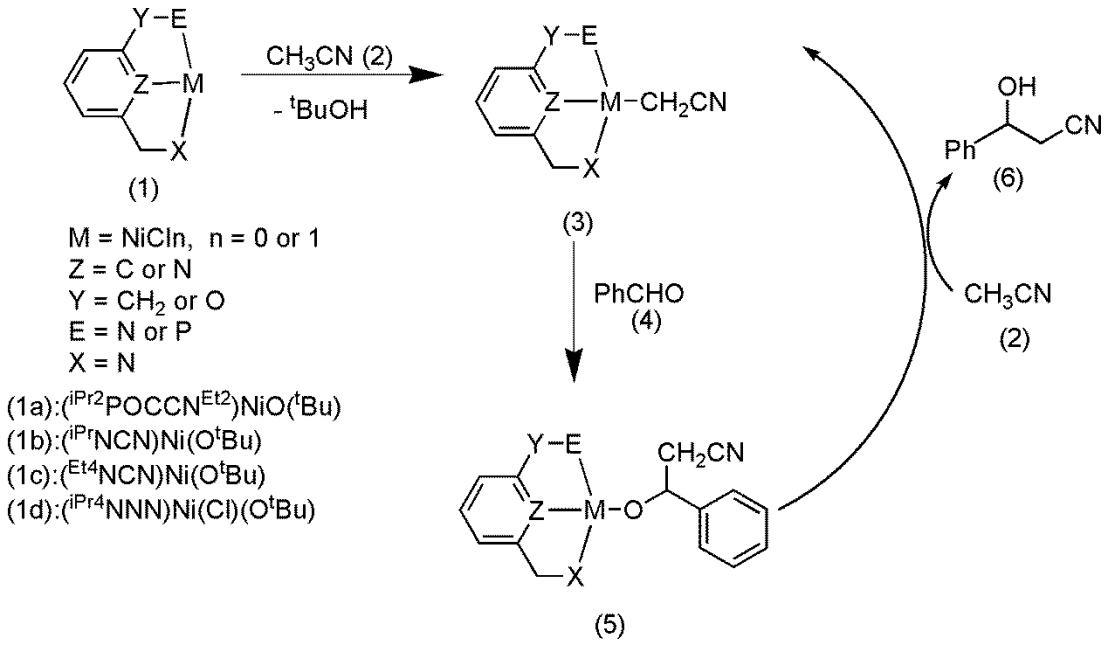
Ever since the first report by Moulton and Shaw in 1976[1], the chemistry of pincer metal complexes has witnessed an explosive growth and have found wide spread utility. Pincer complexes have been used either in stoichiometric or in catalytic fashion to bring about the synthesis of fuels, commodity and fine chemicals[2-4]. The rigidity of the pincer framework[5-6] along with the high thermal stability that it imparts allows pincer-metal systems to operate at temperatures not normally accessible to other homogeneous systems. In addition, the modularity of the pincer complex allows for a plethora of possible modifications to the three coordinating groups thereby facilitating excellent ligand tuning. In the current work, an attempt has been made to rationally design efficient systems based on pincer-nickel complexes for the activation of acetonitrile and its catalytic addition to aldehydes[7] (Scheme 1). Experimental and computational studies have been used to probe this reactivity from a synthetic and mechanistic point of view.



Scheme 1: Mechanistic pathway involved in the cyanomethylation of benzaldehyde

Reference

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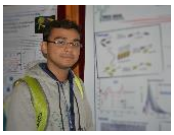

P28

Stepwise Hydrogelation of a Naphthalene Diimide Appended Peptide Amphiphile and its Application in Drug Delivery, Cell-Imaging and Intracellular pH Sensing

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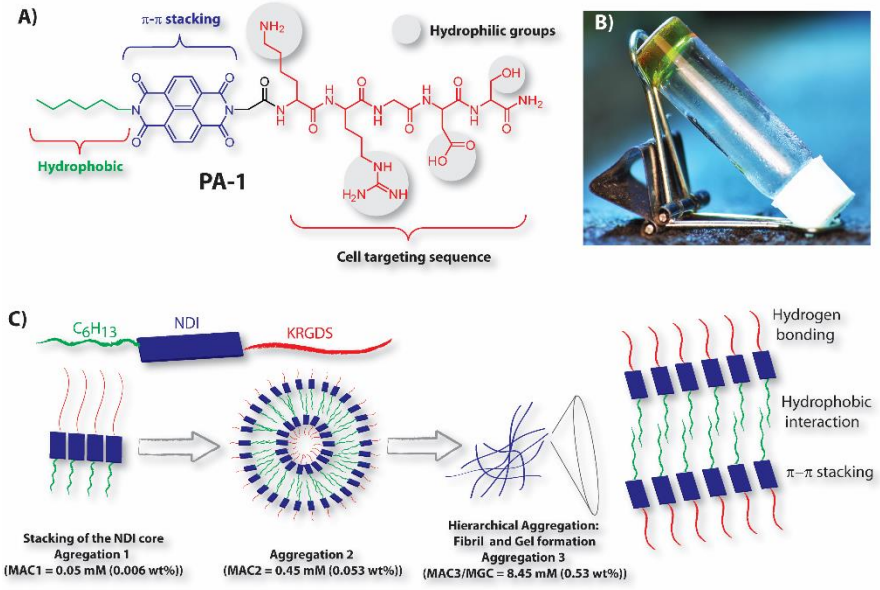
This study reports the self-assembly and application of a naphthalene diimide (NDI)-appended peptide amphiphile (PA). H-bonding among the peptide moiety in conjunction with π-stacking between NDI and hydrophobic interactions are the major driving forces behind the stepwise aggregation to form hydrogel. The PA produced efficient self-assemblies in water at physiological conditions, forming nanofibrous network which further formed self-supportive hydrogel. Importantly, this water soluble conjugate was found to be non-toxic, cell permeable and was used for cell imaging at very low concentrations and has an extended biological application to assess intracellular pH. Additionally, was found to entrap and slowly release an anticancer drug, doxorubicin from the gel matrix. The relatively good biocompatibility, intracellular pH determining and drug delivery capability suggests it as a promising candidate for use as a supramolecular material in biomedical applications.



P29

Copper-catalyzed ring opening of aziridines/aerobic oxidative C-H amination: a facile route to imidazobenzimidazoles

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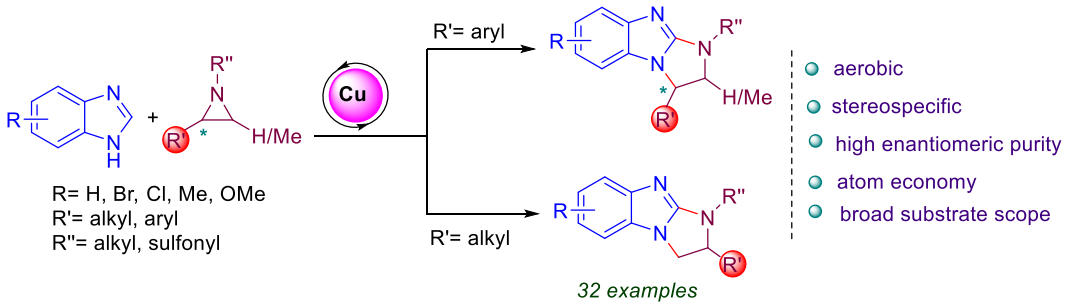
Transition-metal-catalyzed oxidative C-H functionalization has become a powerful synthetic tool for the construction of pharmaceutical scaffolds *via* regioselective C-C and C-N bond formation using air as the oxidant.[1] In addition, imidazo-fused heterocyclic fragments are privileged structural scaffolds found in natural products and pharmaceuticles.[2] In particular, tricyclic benzimidazole derivatives exhibit antimycobacterial, anticancer, antiarrhythmic, neuropsychiatric disorders and selective enzyme inhibitory activities.[3] Herein, we report an elegant and facile route for the preparation of benzo[*d*]imidazo[1,2-*a*]imidazole from aziridines and benzimidazoles *via* copper-catalyzed regioselective ring opening of aziridines with benzimidazole followed by the intramolecular oxidative C-H amination.[4] This newly discovered reaction is simple and uses inexpensive copper catalyst, and converts readily available substrates into important benzo[*d*]imidazo[1,2-*a*]imidazole core structures that tolerate an array of various functional groups.



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P30

Influence of Ligand Architecture in Tuning Reaction Bifurcation Pathways for Chlorite Oxidation by Non-Heme Iron Complexes

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Reaction bifurcation processes are often encountered in the oxidation of substrates by enzymes and generally lead to a mixture of products. One particular bifurcation process that is common in biology relates to electron transfer versus oxygen atom transfer by high-valent iron(IV)–oxo complexes, which nature uses for the oxidation of metabolites and drugs. In biomimicry and bioremediation, an important reaction relates to the detoxification of ClO_x^- in water, which can lead to a mixture of products through bifurcated reactions. Herein we report the first three water-soluble non-heme iron(II) complexes that can generate chlorine dioxide from chlorite at ambient temperature and physiological pH. These complexes are highly active oxygenation oxidants and convert ClO_2– into either ClO_2 or ClO_3^- via high-valent iron(IV)–oxo intermediates. We characterize the short-lived iron(IV)–oxo species and establish rate constants for the bifurcation mechanism leading to ClO_2 and ClO_3^- products. We show that the ligand architecture of the metal center plays a dominant role by lowering the reduction potential of the metal center. Our experiments are supported by computational modeling, and a predictive valence bond model highlights the various factors relating to the substrate and oxidant that determine the bifurcation pathway and explains the origins of the product distributions. Our combined kinetic, spectroscopic, and computational studies reveal the key components necessary for the future development of efficient chlorite oxidation catalysts.

P31

Tert-Butyl Nitrite Mediated Domino Synthesis of Isoxazolines and Isoxazoles from Terminal Aryl Alkenes and Alkynes

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A Sequential construction of C-C, C-O, C=N and C=O bonds from alkenes leading to the direct synthesis of isoxazolines in the presence of tert-butyl nitrite, quinoline and $Sc(OTf)_3$ catalyst in DCE at 80 ^oC has been accomplished. An unprecedented consecutive three C-H functionalisations of two styrenes are involved during this isoxazoline synthesis. In this radical mediated reaction one half of the aryl alkene is converted into intermediate 2-nitro ketone which serve as a 1,3-dipolarophile and undergo cycloaddition with the other half of unreacted aromatic terminal alkene. The use of alkyne in lieu of alkene leads to the formation of isoxazole under aidentical reaction condition.

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Sau, P.; Santra, S. K.; Rakshit, A.; Patel, B. K. J. Org. Chem. 2017, 82, 6358

P32

Organocatalytic Asymmetric Michael/Aromatization/ Hemiketalization/Retro-aldol Reaction of α-Nitroketones with Unsaturated Pyrazolones: Synthesis of 3-Acyloxy Pyrazoles

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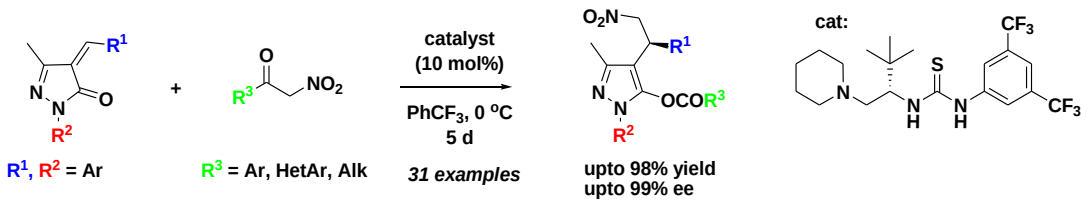
An organocatalytic asymmetric cascade/Michael/aromatization/hemiketalization/retro-aldol reaction between unsaturated pyrazolones and α-nitroketones is described. Bifunctional thiourea catalyst was found to be efficient for this reaction.[1] With 10 mol% of catalyst, high yields as well as excellent enantioselectivities are attained for a variety of 3-acyloxy pyrazoles under mild reaction condition.



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P33

A Concise Route Synthesis of Benzo[1,4]oxazepine Fused Tetrahydroisoquinoline and Tetrahydro-β-carboline Analogous

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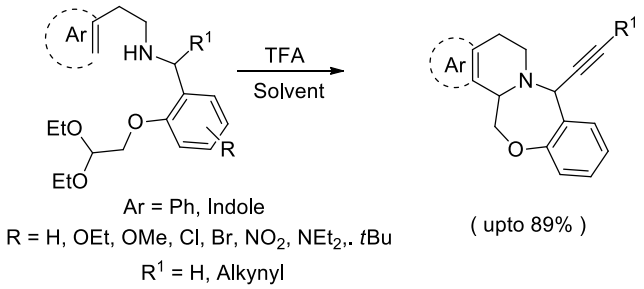
Synthesis of fused tetrahydroisoquinoline and tetrahydro-*β*-carboline scaffolds has a special interest to synthetic community. The Pictet-Spengler reaction is one of the leading techniques for construction of such valuable nitrogen heterocyclic compounds with wide range of biological activity and a diverse pharmacological profile.[1] Recently, Ugi multicomponent reaction and subsequent acid promoted intramolecular *N*-acyliminium Pictet-Spengler sequence has been used for the synthesis of such privileged architectures.[2] Majority of these methods restricted to synthesis of fused five and six membered ring systems. However, there are very few reports have been developed for the construction of fused seven-membered nitrogen heterocyclic ring system *via* Pictet-Spengler reaction due their great importance in alkaloids and natural products chemistry.[3] Here in, we have developed a concise protocol for the synthesis of substituted benzo[1,4]oxazepine fused tetrahydroisoquinoline andtetrahydro-β-carboline analogous using secondary amine intermediates via iminium ion mediated Pictet-Spengler reaction. Such ring systems are of potential interest for studying their biological activities. The corresponding secondary amines were prepared by A^3-coupling as well as imine reduction process. Both reactions can be performed to generate in good yields.



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P34

Luminescent stilbene based star-shaped molecules stabilizing wide range columnar phase

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Stilbene based molecules are gaining importance in material science due to their unique photophysical and photochemical properties. The energy levels of vinylene chromophore in the molecular structure can be easily tuned by the appropriate molecular design aimed towards specific applications like organic light emitting diodes (OLEDs), solar cells, photoconductors, nonlinear optically (NLO) active materials, photoswitchable materials.[1-4] The ease of synthesis, structural tunability and planar molecular structure made them compatible in the design of self-assembled supramolecular structures like gels and liquid crystals.

Here, we have prepared two novel Tris(N-salicylideneanilines) [TSANs] through a multistep synthesis to incorporate a cyanovinylene chromophore between the two benzene rings. The position of the cyano group was altered and the target molecules were compared with the stilbene derivative for their thermal and photophysical behavior. The presence of the cyano group enhanced the mesophase range in comparison to the non-cyano stilbene derivative. Further enhanced intermolecular interactions led to the stabilization of columnar rectangular phase in comparison to the columnar hexagonal phase of simple stilbene derivative. These compounds exhibited a red shifted absorption maximum in comparison to the stilbene based TSANs reported earlier.[5] The solution state emission of ***α*-CNST** was similar to stilbene based TSANs **(ST)**, while the ***β*-CNST** exhibited a blue shifted emission with good luminescence quantum yields. These compounds were emissive in the thin film state also, which means that they are emissive in columnar phase. Thus the stabilization of room temperature columnar phase along with the emissive nature is promising from the viewpoint of emissive displays.

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P35

Advanced White Light Emitting Nanocomposites

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Herein we report that the chemical combination of luminescent inorganic complexes either with the pre-synthesized doped quantum dots (Qdots) or with Qdots present in a protein matrix along with nanoclusters or with the core/shell Qdots leading to fabrication of a single component nanocomposite, that emits bright natural white light, with near to perfect white light chromaticity color coordinates (0.33, 0.33), high color rendering indices (CRI) (≥80) and high correlated color temperatures (CCT) closer to day light (6000 K).[1-3]For example, a single component photostable white light emitting (WLE) nanocomposite, can be fabricated followed by the formation of a greenish blue emitting zinc quinolate complex (using 8-hydroxyquinoline (HQ) as a complexation agent) on the surface of the ZnS shell of $CuInS_2$/ZnS core/shell quantum dots, which exhibited bright natural cool white light emission with chromaticity color coordinates of (0.32, 0.35) and (0.32, 0.33), CRI of 91 and 83 and CCT of 6087 K and 5930 K in the solution and solid phase, respectively.[1] Similarly, we have also demonstrated by forming two different luminescent inorganic complexes (metal acetylsalicylate and zinc quinolates) on the surface of Mn^{2+}-doped ZnS Qdots or by incorporating gold nanoclusters and zinc quinolate complex attached ZnS Qdots in a BSA protein matrix, to make Qdot glow white.[2-3]This is expected to open up a new dimension towards the development of cost-effective biofriendlyWLE materials.

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P36

Ethyl Viologen Conjugated Perylenediimide to Drive Insulin Hexamer Assembly: pH-responsive Features for its Uptake and Release

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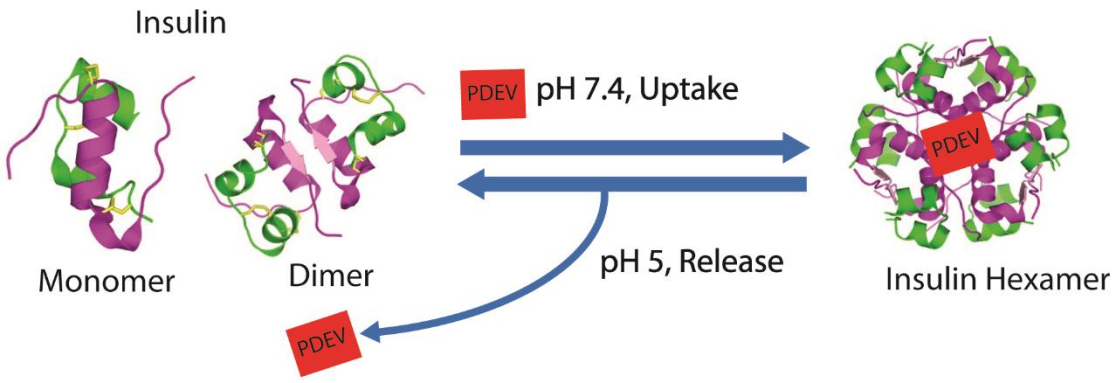
Insulin, a small helical protein hormone, is responsible for regulating blood glucose levels. Thus its biochemical synthesis and pharmacological properties are very much crucial in the treatment of diabetes and its recombinant pharmaceutical preparations. Insulin can exist in dimer, tetramers, and hexamers depending on the environment. Insulin is stored in the pancreatic vesicles in a hexameric form, complexed with zinc ions, and is released in response to the blood glucose level. This hexameric moiety is relatively resistant to degradation/fibrillation. In the present study, the hexamerization of insulin by introducing a water soluble ethyl viologen-conjugated perylenediimide (PDEV) dye, in the absence of Zn^{2+} at pH ~7.4, has been demonstrated. Furthermore, the insulin hexameric assembly is very sensitive to the pH of the solution and dissociates in to monomeric form at lower pH ~5. Such assembly-disassembly processes have been confirmed using different spectroscopic and microscopic techniques and can be exploited beneficially toward developing slow release insulin formulations, drug delivery vehicles and as phototherapeutics.



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P37

Computer Simulation Studies of the Mechanism of Hydrotrope Assisted Solubilization of Sparingly Soluble Drug Molecule

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The effect of hydrotrope sodium cumene sulfonate (SCS) on the solubility of a sparingly watersoluble drug griseofulvin is studied by employing classical molecular dynamics simulation technique. We mainly focus on the underlying mechanism by which SCS enhances the solubility of a sparingly soluble or insoluble solute in water. The main observations are: (a) The self-aggregation of SCS molecules (through its hydrophobic tail) above minimum hydrotrope concentration (MHC) causes the formation of micellar like frameworks. Interestingly, though the drug griseofulvin possesses both polar and non-polar group, it prefers to get encapsulated inside the hydrophobic core of SCS aggregates. The decomposition of total SCS-drug interaction energy into van der Waals and electrostatic components suggests that the former plays a major role in this interaction; (b) The calculated Flory-Huggins interaction parameter values give a strong indication of the mixing ability of hydrotrope SCS and griseofulvin drug molecules; and (c) As expected, we do not observe any strong effect of SCS aggregates on SCS-water and water-water average hydrogen bond number but, it affects water-drug griseofulvin average hydrogen bond number. With the help of these observations we try to elucidate the hydrotropic action of hydrotrope SCS on the solubility of drug griseofulvin.

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P38

Effect of Substituents on Single Strand Breaks in a Selected DNA Fragment Induced by Low Energy Electrons

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We have computationally investigated the effect of electron withdrawing (Flouride) and electron donating (methyl) substituents in the low energy electron (LEE) attachment to the 5th position of the 2′-deoxy-Cytidine-3′-monophosphate (3'-dCMPH) DNA fragment to propound the mechanism for the single strand break (SSB)s [3' C-O bond cleavage] at the backbone. The effect of electron withdrawing and electron donating substituents on 3'-dCMPH has not been investigated theoretically so far hence we are keen to study the same to draw out a plausible route using our method for SSB in e-DNA scattering and their role in gene mutation. It is predicted that electron donating groups like -CH_3 to our modeled fragment shortens their detachment lifetime while electron withdrawing groups like -F enhance the lifetime on detachment with the modeled fragment. Here, it is our intent to explore theoretically the comprehensive path to SSB, induced by LEEs (0-3 eV) using electronic structure theory and local complex potential based time dependent wave packet (LCP-TDWP) approach. We have used G09 program suite to generate the potential energy (PE) curves of our modeled neutral systems and its corresponding anions. Subsequently we have also generated the SOMOs to pinpoint the movement of electron densities throughout the dissociation process. Finally, we compare our results with the available experimental data and those obtained in other investigations.

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P39

Chiral recognition of 1-amino-2-propanol by a binuclear Ni-complex through non covalent host-guest interaction

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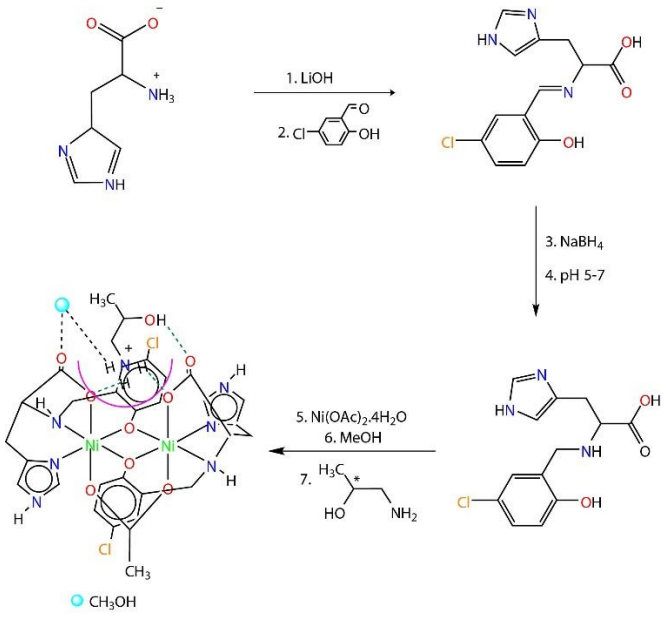
Chiral recognition through non bonded interaction occurs in biological systems [1]. Recognition using inorganic complex or assembly has gained considerable attention in recent years [2]. The importance of structural characterization of the host-guest adduct, showing the interactions responsible for recognition, has been pointed out in the literature [3]. There are examples wherein chiral recognition of small molecules has been obtained by organic hosts, but examples using structurally characterized metal complex are few [2,4]. Here we have studied the interaction of 1-amino-2-propanol within a chiral Nickel complex. The complex, a binuclear Ni-complex of L-histidine derived ligand, has been structurally characterized. The enantiomeric enhancement measured by chiral HPLC analysis showed >95% ee.



Scheme 1. Synthesis of the ligand and the complex.

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P40

A novel strategy for drug design against diabetes type II (T2D) by disaggregation of amylin aggregation by conformationally restricted hybrid peptidomimetics

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Type II diabetes mellitus (T2DM), that occurs due to protein aggregation and amyloid deposition, is one of the most common disease in the world.[1] Amylin or hIAPP is a peptide hormone, which is secreted with insulin from the pancreatic β-cells. At physiological conditions, it aggregate extensively and inhibits the activities of insulin, which control the glucose level in the blood stream and finally leads to T2DM. Lots of strategies have been carried out against T2D, but still no complete cure has been found towards it. Existing strategies suffers from lots of drawback including solubility, oral bioavailability, cost of preparation etc. Herein, we have introduced a novel strategy for efficient inhibition and disruption of amyloid formation of Amylin by a class of conformationally restricted β-sheet breaker hybrid peptidomimetcs (BSBHPs). We have synthesized α/β, α/γ and α/δ hybrid peptidomimetics respectively by inserting β, γ and δ aminobenzoic acid separately into an amyloidogenic peptide sequence. We observed the aggregation inhibitory efficacy of α/β and α/γ BSBHPs but not of α/δ analogue. They also disrupted the aggregated amyloids into non-toxic forms.[2] These results can be a stepping stone for newer discovery of drug design against T2DM and other amyloid related disease.

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P41

Exploiting Directing Group Assisted Proximal C-H Activation: A Case Study for Regioselective N-Arylation of Azoles

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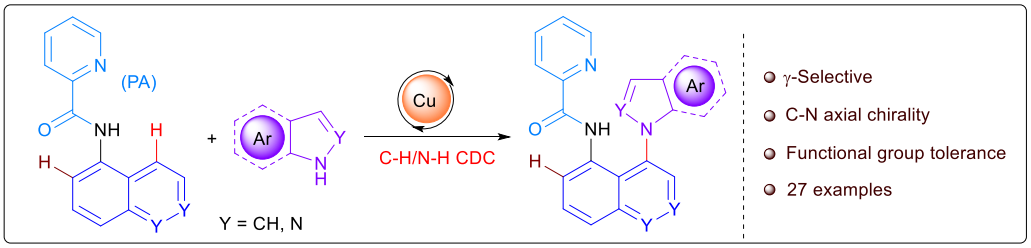
Directing group controlled C-H activation provides a blueprints for newer disconnection to molecular complexity sacrificing simple chemical feedstocks. Herein, the γ-amination of *α*-naphthylamine derivatives with azoles has been developed by a copper(II)-catalyzed auxiliary assisted C-H activation. The reaction shows generality with different azoles such as indoles, pyrazoles and pyrrole, and the products of indole exhibit a C-N*tert* axial chirality. Bio-relevant azoles installed into aromatic systems via a cross-dehydrogenative strategy to assemble *N*-arylated azoles. The methodology was highlighted in the implementation of inexpensive first row transition metal catalyst, functional group competence and removable auxiliay.



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P42

An Azide-Functionalized Al(III)-Based Metal-Organic Framework for the Fast, Selective and Highly Sensitive Detection of Exogenous and Endogenous H_2S

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MOFs, which are a new class of crystalline porous compounds, possess versatile application potentials ranging from gas storage/separation, chemical sensing and heterogeneous catalysis to biomedical imaging and drug delivery [1]. They have been employed as fluorescent probes for the detection of various analytes [2] due to their extraordinary chemical stability, adjustable pore sizes and pore surface functionalities as well as highly π-conjugated backbones [3]. For these advantages, several luminescent MOFs have been designed and applied so far for the sensing of anions, cations, small molecules, biological signaling molecules and volatile organic species [4].

Inspired by the above-mentioned facts, we report a new, azide-functionalized Al(III)-based metal-organic framework (MOF) (Fig. 1a) denoted as CAU-10-N_3 (CAU = Christian-Albrechts-University) incorporating 5-azido-isophthalic acid (H_2IPA-N_3) as ligand. The MOF was synthesized under solvothermal conditions using a mixture of H_2IPA-N_3 ligand and 2(M) $AlCl_3 \cdot 6H_2O$ solution in DMF/H_2O mixture. The phase purity of the material was confirmed by a combination of X-ray powder diffraction analysis, infrared spectroscopy, thermogravimetric and elemental analysis.

As confirmed by the steady-state fluorescence titration experiments, the MOF compound features significant capabilities for the highly selective and sensitive (detection limit: 2.65 µM) detection of H_2S by reducing the azide functional group to the corresponding amine (Fig. 1b). Remarkably, the compound exhibits short response time (420 s) and significant increase (20-fold and 26-fold after 1 and 7 min of addition of Na_2S, respectively) in the fluorescence intensity towards H_2S. In addition, this material can be successfully utilized for the detection of H_2S in living cells (Fig. 1c). The selectivity for detection of H_2S retained even in the existence of other potentially competing biomolecules and anions found in biological system, which makes the presented material a potential candidate for the real-time detection of H_2S in biological systems.

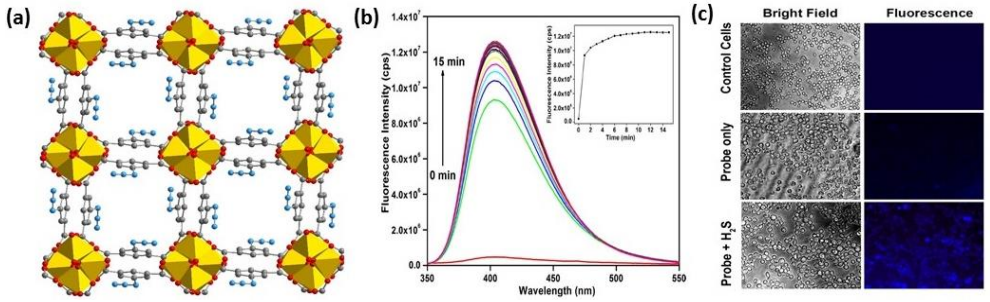

Fig. 1. (a) Structure of the CAU-10-N_3 MOF. (b) Fluorescence turn-on response of the MOF suspension in HEPES buffer (10 mM, pH = 7.4) towards addition of Na_2S. (c) Ability of the MOF to detect H_2S in macrophage J774A.1 cells.

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P43

One Pot Reduction of Amino Acids to Corresponding Amino Alcohols

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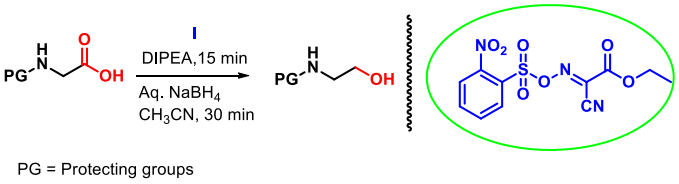
β-Amino alcohol moieties are present in many biologically active peptaibols and have broad range of applications in synthetic organic chemistry.[1] They also have been used as key synthetic starting materials for the synthesis of β-amino acids, optically active *α*-amino aldehydes, diamines, triamines and *α*-halo-*β*-amines. Because of manifold interest of peptide alcohols versatile methods have been developed. Usually carboxylic acids are reduced via *in situ* formation of active species such as acyl halides, mixed anhydrides, or active esters prior to borohydride reduction. Several reagents used as acid activators such as BOP, $BF_3.Et_2O$, cyanuric fluoride, 1,1-carbonyldiimidazole, sulfonylbenzotriazole derivatives, 1-propanephosphonic acid cyclic anhydride and 3,4,5-trifluorophenylboronic acids have been used. These approaches till have some limitations including the use of expensive reagents, difficulty to prepare reagents, and in work-up. Here we described a mild and efficient method to obtain the *N*-protected amino alcohols directly from *N*-protected amino acids by using ethyl 2-cyano-2-(2-nitrobenzenesulfonyloxyimino) acetate (*o*-NosylOXY)[2a,b] as an acid group activator and sodium borohydride as a reductant.



PG = Protecting groups

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P44

Metal And Oxidant Free Sequential C(sp^2)–OH and C(sp^3)–H Aminations of Nitrosoarenes and *N*-Heterocycles: A Simple and Efficient Route To Fused Naphtho-Imidazoles

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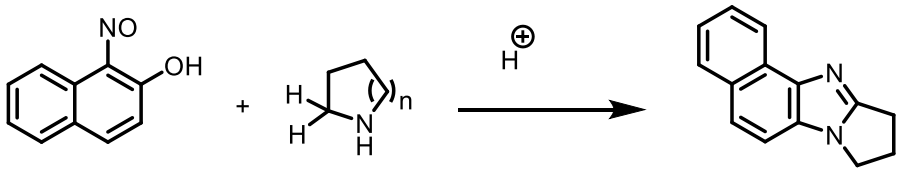
The imidazole core is one of the most common moiety present in a large number of natural products, particularly in bioactive molecules targeted as pharmaceuticals.[i] Various strategies have been developed so far by various research groups to produce this moiety synthetically.[ii,iii,iv] Thus, the development of new methodologies for imidazole derivatives remains an active area of research. However, the existing methods using metals and oxidants have their own limitations due to their sensitive reaction conditions and production of toxic by-products. We have developed an efficient and simple method for direct C–H functionalization of saturated *N*-heterocycles for the synthesis of imidazole derivatives without using metal or external oxidant.[v] Nucleophilic substitution reaction of a wide range of various substituted nitroso-naphthols on reaction with secondary amines in presence of acid afforded fused imidazole derivatives in good yields. Moreover, the same reaction conditions were observed to be effective for the primary amines also. Apart from the nitroso-naphthols, the reaction also proceeded well with other nitroso-derivatives of Phenanthrene, Dimedone and Coumarin.



Metal-free double C-H amination

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P45

Contrasting effects of heterocycle substitution and branched tails in the arms of star-shaped molecules

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Herein, star-shaped tris(N-salicylideneaniline)s (TSANs) containing 1,3,4-oxadiazole based and 1,3,4-thiadiazole based arms are synthesized and characterized. The introduction of branched tails at their peripheries has different effects on these tris(N-salicylideneaniline)s, which are dependent on the type of heterocycle. The TSANs bearing 1,3,4-oxadiazole arms with branched tails exhibit a room temperature columnar rectangular phase in comparison to the high temperature columnar hexagonal phase exhibited by their hexadecyloxy chain analogues. In the case of the thiadiazole based TSANs, the compound with hexadecyloxy chains exhibits a columnar rectangular phase over a wide temperature range including room temperature, whereas its branched chain analogue is a liquid. Thus, in the case of star-shaped molecules, the type of peripheral tails not only affects the transition temperature, but also affects the type of self-assembly, which is in contrast to conventional discotic liquid crystals. The introduction of substituted 1,3,4-thiadiazole rings helps in the reduction of their melting points and enhances their mesophase width. The presence of bulky branched tails at their peripheries enhances the intermolecular interactions between the cores of the 1,3,4-oxadiazole based TSANs, which leads to the stabilization of the columnar rectangular phase. The 1,3,4-thiadiazole based TSANs exhibit a columnar rectangular phase even with straight peripheral chains because of the attractive intermolecular interactions of the thiadiazole ring.

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P46

Direct *β*-C(sp^3)-H Functionalization of Aliphatic Amines to *α,β*-Unsaturated Imines, Aldehydes and Chromenes

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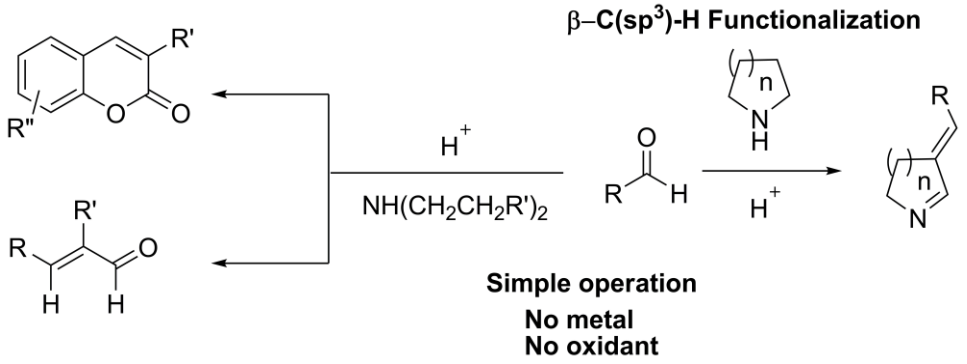
Keywords: *α*, *β* unsaturated imine, 2-alkyl cinnamaldehyde, chromene

β-Functionalized aliphatic amines are known as one of the important structural moiety that appears in various set of natural products and biologically active molecules [1]. A large number of examples on *α*-C−H functionalization of amines has been developed during recent years, but examples of more challenging *β*-C(sp3)−H functionalization are very few[2]. We have developed a simple, metal and oxidant free novel method for direct *β* (–sp^3) C-H bond functionalization of secondary amines. The method is based on a reaction that yields enamine directly from corresponding aliphatic amine without metallic reagent or external oxidant [3]. In this method *α,β*-unsaturated imines were obtained in a reaction of aldehyde with pyrrolidine in the presence of 3,5-dinitrobenzoic acid (DNBA) in refluxing xylene. Acyclic amines provided 2-alkyl cinnamaldehyde with excellent *E/Z*-selectivity while salicyldehyde gave chromene derivative [4].



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P47

Regio- and Diastereoselective and EnantiospecificMetal –Free C(sp^3)-H Arylation : Faciel Acess to optically active 5-aryl 2,5- Disubstituted Pyrrolidines

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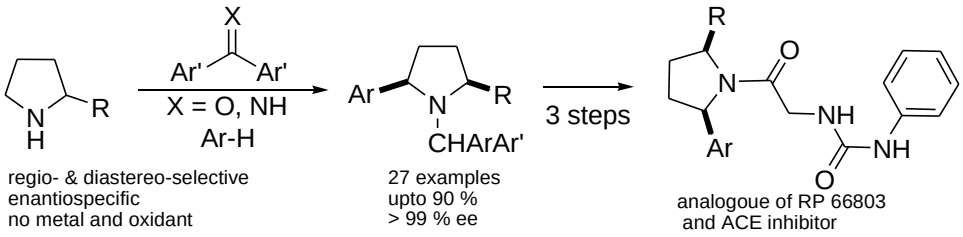
Abstract

Arylated aliphatic *N*-heterocycles, particularly, optically active 5-aryl 2,5- disubstituted pyrrolidines are the principal structural moiety of many bioactive compounds including natural products and catalyst for asymmetric synthesis.[1] Chemical synthesis of these functional compounds mainly relied on metal and oxidant mediated reaction producing unwanted toxic waste.[2] We have developed the first example of Regio- and Diastereoselective and Enantiospecific metal and oxidant free method for direct sp^3 C-H-arylation of pyrrolidine to get optically active 5-aryl 2,5- disubstituted pyrrolidines via a highly atom economic three component reaction.[3]



Furthermore, the complex analogue structures of CCK antagonist RP 66803 and angiotension-converting enzyme inhibitors were formed using the synthesized optically active pyrrrolidine derivatives. DFT calculations were also performed to show the mechanishm and high level of stereocontrol in this reaction.

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P48

MODELING ANTI-TB COMPOUNDS WITH THE HELP OF ADVANCED COMPUTATIONAL TECHNIQUE

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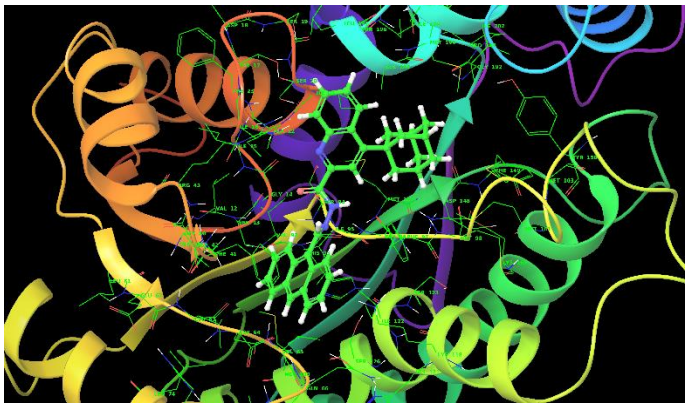

Tuberculosis (TB), an infectious disease caused by *Mycobacterium tuberculosis*, is one of the leading killer that has plagued humanity for centuries. According to global tuberculosis report 2016, TB was one of the top ten causes of death worldwide and was responsible for more deaths than HIV and malaria [1,2]. The importance of modeling in drug discovery efforts has been revealed by numerous QSAR, pharmacophore based, and/or docking based studies [3,4]. Most of the available QSAR and docking studies on anti-TB compounds either are local models (focused on specific class of anti-TB compounds) or based on a small dataset [5]. DFT based modeling on a large dataset is not available in the literature. Considering this, we collected around 1000 anti-TB molecules with their experimental activity values. All the collected molecules are optimized at B3LYP/6-31G(d) level of theory to get the reliable input geometry for analogue and structure based modeling and to calculate DFT based descriptors. Molecular docking calculations are performed on these ligands with 12 different anti-TB receptors collected from the protein data bank (1DF7, 1G3U, 1MDB, 2CIB, 2DFT, 2FUM, 3ORM, 3S9I, 4U0J, 1UZN, 2AQK and 2WTZ) using Autodock and GOLD docking programs. Docking results show the type of interactions between ligands and their receptors. DFT based QSAR models are generated for various cell lines and activity types (pMIC, pKi, pIC_{50}, pIC_{50} Human, pIC_{50} Ribosome, pIC_{50} Vero Cell, $pMIC_{50}$ 7H12, $pMIC_{50}$ H37rv, $pMIC_{50}$ ICB59, $pMCI_{50}$ Iron Deficiency, $pMIC_{50}$ Iron Rec., $pMIC_{50}$ LM13, $pMIC_{50}$ LORA, $pMIC_{50}$ MABA, $pMIC_{50}$ MABA Gas, $pMIC_{50}$ Newman, $pMIC_{50}$ RV129C and pMIC $\log_p$). The generated QSAR models are statistically relevant with correlation coefficient values vary from 0.75-0.99 for most of the cell lines and activity types. Training and test set division is performed to validate the generated models. Higher active anti-TB candidates are designed based on our models. Molecular dynamics simulations and further modeling studies is ongoing to validate the findings.

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P49

Secondary Amine Salts as Weak Cationic Bronsted Acid Catalysts for the Controlled Activation of Anomeric hemiacetals towards Stereoselective Dehydrative Glycosylation of 2-deoxy Sugars

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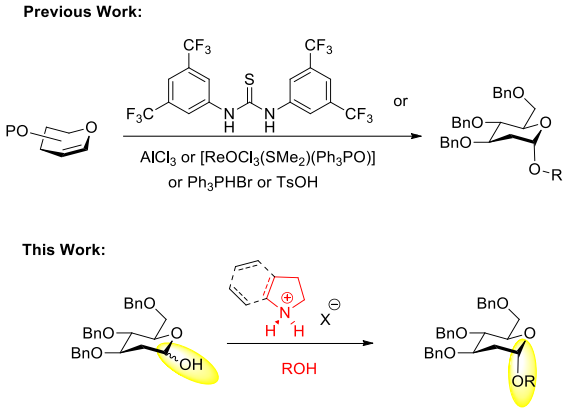

An organocatalytic α-selective direct dehydrative glycosylation of 2-deoxysugar hemi-acetals has been described for the first time using the cooperative pyrrolidinium/pyrrolidine catalysis. Generation of glycosyl oxacarbenium ions by the weak Bronsted-acid catalysis of pyrrolidinium hydrochloride in combination with the simultaneous deprotonation of the acceptors by the concomitant activity of pyrrolidine, affects the diastereoselective glycosylation. The high diastereoselectivity has been explained based on the controversial reverse anomeric effect. This novel organocatalytic activation of hemi-acetals that is neutral to the activation of thioglycosides has also been successfully shown to be an effective orthogonal glycosylation technique.

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P50

Breaking or strengthening of excited state hydrogen bond? New prediction of proton coupled electron transfer in the excited coumarin-phenol complex

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Two contradictory ideas, whether intermolecular H-bond of coumarin 102-phenol complex cleaves or strengthens in the electronically excited state, have been successfully linked together, for the first time, using time dependent density functional theory (TD-DFT). Evaluating the excited state potential energy surface along the full H atom transfer coordinate, we surprisingly found two distinct minima which unambiguously account for the two contrasting interpretations. One of the minima corresponds to the H-bond shortened complex consistent with the TDDFT calculations of Zhao and Han. On the other hand, frequency calculation at the other minimum matches very well with the excited state frequencies reported by Nibbering and coworkers. Finally, charge calculations strongly recommend that the excited state dynamics should be interpreted as H-bond mediated proton-coupled electron transfer rather than H-bond breaking or strengthening.

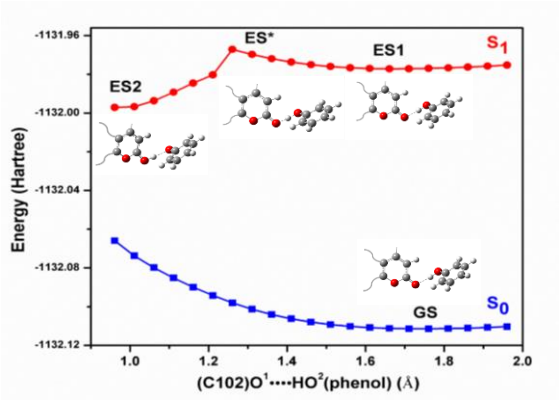

Fig 1: Computed relaxed PES of the C102-phenol complex in cyclohexane solution as a function of the proton transfer scan coordinate (C=O•••H–O, in Å)

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P51

Efficient and Rapid Removal of Environmental Malignant Arsenic(III) and Industrial Dyes Using Reusable, Recoverable Ternary Iron Oxide - ORMOSIL - Reduced Graphene Oxide Composite

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The reliable accessibility and safety of drinking water are basic human needs. Less than 3% of the total water is freshwater on the surface of the Earth, and only one-third of this freshwater is available for drinking. Contamination of these natural water sources due to industrial effluents and human activities makes it unhealthy for consumption. In this work, we have demonstrated an efficient and simple reusable catalyst, which can be operated on site for water remediation. In the present report, we have proposed a near 100% dye adsorption and the effective removal of arsenic(III) using a ternary composite consisting of ORMOSIL-Fe_3O_4-RGO. A simple and low-temperature synthesis to prepare an ORMOSIL-Fe_3O_4-RGO composite has been developed as a one stop solution for water remediation. Particularly, this composite was employed for the elimination of arsenite (III) ions and Rhodamine B dye from water, which has a huge impact in developing/underdeveloped countries in South Asian and some of the American regions. The structural, physical, and chemical properties of this composite were investigated through various characterization techniques like powder Xray diffraction (PXRD), fourier transform infrared spectroscopy (FT-IR), field emission scanning electron microscopy (FESEM), energy dispersion X-ray (EDS), transmission electron microscopy (TEM), and vibrating sample magnetometer (VSM). Using Langmuir isotherms, we calculated the adsorption capacity of the ORMOSIL-Fe_3O_4-RGO composite for Rhodamine B to be ~1339 mg/g, which is much higher as compared to that of the Fe_3O_4-RGO composite (~342 mg/g). Furthermore, the capacity of arsenic adsorption of this novel composite material is ~25% higher than that of Fe_3O_4-RGO according to the Langmuir adsorption isotherm.

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P52

Application of Natural Humic Acids as a Spacer for Simultaneous Enhancement of Selectivity and Permeability of Graphene Oxide Membrane

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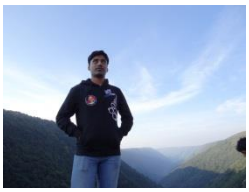
The synergic analogy between graphene oxide (GO) and a biogenic polymer *viz.* humic acid is exploited to develop nanocomposite membranes which is demonstrated to be an enhancer of ionic conductivity, molecular selectivity and water permeability. GO sheets are synthesized by modified Hummers' method and are imbibed by humic acid extracted from innate soil. Humic acid used herein act as an embryonic spacer between the stacked GO nanosheets and tunneled a facile pathway for vehiculating specific ions and molecules. The confined 2D nanochannels of the composite membranes exhibit distinctive nanofludic phenomena- for instance surface-charge-govern ionic transport concomitant with many fold increment in ionic conductivity. Humic acid enriched nano crevice membranes allow fast water permeation but impede the methanol flux. Intrigued by its high water permeability, the composite membranes are employed to trigger a time efficient productive dye separation. Assimilating its tremendous chemical stability, composite membranes are implemented to harvest energy through concentration gradient available from KCl solution with three-fold concentration differences. Conjointly a homogeneous mixture subsuming 20 weight % of humic acid is fabricated in order to make a responsive material that can response to change in chemical stimuli by changing its shape in a control manner.



P53

An unusual Carbonate-(Water)$_2$-Carbonate Cluster Trapping *via* Atmospheric CO_2 Fixation Within Linear Tetrameric Barrel: Consequences of anion size on receptor architecture

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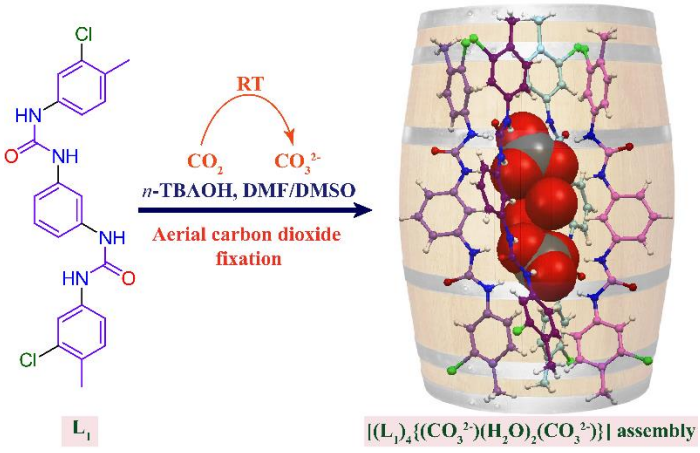
Abstract

Anions exist in their hydrated form in natural and biological environments such as marine water and various ecosystems,[1] thus the significance of hydrated-anion recognition within the self-assembled architecture of neutral host molecules are essential and contemporary aspects of supramolecular chemistry.[2] A *meta*-phenylenediamine based disubstituted bis-urea receptor **L$_1$** with electron withdrawing 3-chloro and electron donating 4-methylphenyl terminals has been established as a potential system to fix and efficient capture of atmospheric CO_2 as air stable entrapment of an unprecedented $\{CO_3^{2-}\text{-}(H_2O)_2\text{-}CO_3^{2-}\}$ cluster (complex **1a**) within its tetrameric long straight pillar like barrel assembly. Whereas, **L$_1$** and its isomeric 4-bromo-3-methyl disubstituted bis-urea receptor **L$_2$** have been found to entrap similar kind of nonhydrated sulfate-sulfate double-anion (complex **1b** and **2a**). In contrast, halides conform regular semicircular non-cooperative receptor assembly to both **L$_1$** and **L$_2$** in solid state (complex **1c**, **1d**, **2b**). X-ray crystallographic study reveals that halide and oxyanion recognition is consistently affected by the size and dimension of the anions rather than terminal aromatic substituent effect.[3]



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P54

Synthesis of Functionalized Imidazolidines *via* Intramolecular C_{sp3}–H Alkylamination

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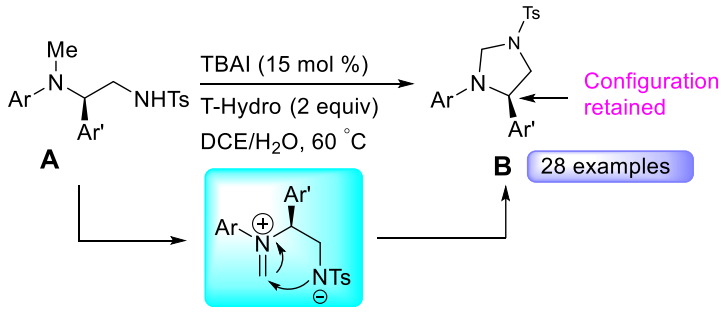
Functionalized imidazolidines are privileged structural scaffolds of many bioactive natural products.[1] Apart from that its find abroad utilities as auxiliaries and ligands for metal catalysts.[2] In recent decades, intermolecular C-O, C-N bond formation reactions to functionalize the *N*-methyl C(sp^3)-H bond is well documented.[3] Besides heavy metal salts,[4] simple catalytic system containing catalytic amounts of an iodide salt can be very effective to perform such functionalization. Herein, we report the employment of T-Hydro and TBAI-catalyzed intra-molecular cyclization of *N*-methyl 1,2-diamine (**A**) by cross dehydroginative coupling (CDC) to synthesis corresponding substituted Imidazolidines (**B**).



Specific *N*-Me group Oxidation

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