Chemical Society, Department of Chemistry, IIT Kanpur presents

Research Scholar’s Day

Poster Presentations

Oral Presentations

Join us on 14th August, 2021 11:00 AM
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Oral Presentations
Vaccine design to alleviate the activity of hormones, peptides, and synthetic psychostimulants

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In the last decade, abuse of synthetic psychostimulant drugs (SPD) has become an epidemic. Drugs consisting of a phenylalkylamine scaffold, and their derivatives are among the earliest and most widely abused illegal substances in the United States. One such psychostimulant is fenethylline, which is marketed under the trade name of “Captagon” and is a Schedule I drug. Captagon has an estimated 40% users in the age range of 12-22 in the Middle East. Moreover, the continued abuse of fenethylline leads to severe adverse events like myocardial infarction, neurotoxicity, and psychosis, yet there is no FDA-approved medication to treat fenethylline’s abuse or its toxicity. In an effort to develop such therapeutics we utilized immunopharmacotherapy as a means to limit abuse and potential overdose. Hereby, I detail the development of first and second generation haptems and identification of a vaccine that elicits a robust “anti-FEN” immune response in rodents, which in turn dampened fenethylline’s psychostimulant effect. Importantly, we will also detail a binary mixture study, which established that the psychostimulant activity of fenethylline originates from the synergistic interaction between two of its metabolites, amphetamine, and theophylline. An unanticipated finding from this study was that a binary mixture can have an impact on both the reinforcing potency, and an effectiveness of the drug.

Figure 1. Simplified representation of drug conjugate immunological pathway and mechanism of action

References

Multi-functional Porus Organic Polymers (POPs): Design, Synthesis and Applications

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Development of porous materials that are purely inorganic (zeolites and mesoporous silica), inorganic-organic hybrid (MOFs) and purely organic (POPs, porous organic polymers) continues to be an exciting enterprise in view of their myriad of applications such as gas adsorption/storage, separations, catalysis, sensing, etc. In particular, infinitely extended and hydrothermally stable porous organic polymers (POPs) formed by covalent polymerization have engendered surge of interest owing to their high surface areas and exotic properties.\(^1\) POPs permit tunability of pore size, high porosity, surface area, thermal and physiochemical stability, etc. based on a ‘bottom-up’ synthetic approach, and can be constructed in tailored fashion for various applications as stated above by a judicious selection of organic building blocks and diligent choice of reaction for covalent polymerization.

We have been concerned with de novo development of POPs based on organic building blocks with certain attributes that necessarily lead, upon covalent polymerization, to porosity. POPs thus obtained can be engineered by simple manipulations for application in gas sorption, catalysis, and dye separations. I will present the design principles that my research has relied on to access POPs with predefined properties for application in catalysis.\(^2\)

References

When reactions involve breaking and forming of multiple bonds, a key issue is to ascertain whether the reaction proceeds through a concerted or a sequential mechanism. The ongoing debate over concerted and sequential mechanism is not straightforward to resolve and requires a dynamical perspective.\[^{1,2}\] In this talk, I will take a model Hamiltonian for double proton transfer in order to illustrate the role of dynamics in understanding reaction mechanism.\[^{3}\]

References

MauG is a terminal enzyme involved in the biosynthesis of the catalytic tryptophan tryptophenylquinone (TTQ) cofactor of methylamine dehydrogenase (MADH). Although two heme units are physically separated in the enzyme, they share electron efficiently behaving as a single diheme unit. A tryptophan residue, positioned midway between the heme centers, has been postulated to act as a bridge for electronic communications. MauG-catalyzed TTQ biosynthesis is accomplished through radical chemistry and initiated using H$_2$O$_2$ as the oxidant which produces bis-Fe(IV) redox state (Figure 1). As the two hemes are physically separated by 14.5 Å, a hole-hopping mechanism has been proposed in which the tryptophan residue reversibly oxidized and reduced during electronic communication. These attractive features have prompted us to investigate on such diheme enzyme and the results will be highlighted in the talk.\[^{1-4}\]

**Figure 1.** Relative orientation of hemes and the intervening tryptophan residue in MauG (PDB ID code 3L4M), top, and formation of bis-Fe(IV) state of MauG, bottom.

**References**

Synthesis of Green High Energy Density Materials

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The history of high energy density materials is demonstrating the development of green high-performance explosive material is always a challenging problem for energetic material chemists worldwide. In recent days, the new family of green energetic materials and their salts were synthesized using five, six-membered strained and fused rings, which are derived from commercially available starting materials. Taking this into the consideration, herein, I intent to present the synthesis and uses of some known explosives, those of ammonium nitrate (AN), pentaerythritol tetranitrate (PETN), trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), etc. This presentation also includes the newly synthesized green high energy density molecules, energetic properties, and where these molecules will stand with the comparison of high-performance energetic materials those of TNT, RDX, HMX, and CL-20.

References

Molecules have been the fascinating candidates for constructing tunable electrically conducting devices by assembling either a single or ensemble of molecules between two electrical contacts followed by their current-voltage (I-V) analysis are often termed ‘molecular electronics’.\cite{1,2} Among the available techniques for surface engineering, electrodeposition (ED) of diazonium salt on a substrate is prominent as it provides strong, stable, reliable substrate-molecule interfaces.\cite{3–5} Using this ED technique, we investigated the thickness, surface roughness, surface coverage, and charge transport properties of oligo-naphthalene thin film on the different substrates such as indium tin oxide (ITO), gold (Au), doped silicon (Si), and nickel (Ni). The thickness of the film is varied by varying the number of electrochemical cycles, scan rates, potential window, and the concentration of respective diazonium salt. The blocking behaviour of aryl-modified electrodes in the presence of ferrocene and ferric ferrocyanide redox probe was studied using cyclic voltammetry. The results evidently demonstrated that the blocking behaviour depended highly on diazonium salt and the modification procedure used. Since Ni being ferromagnetic, we further examined its magnetic study using a Superconducting quantum interference device (SQUID) before and after modifications.

**Figure 1.** Schematic illustration of the fabrication of naphthalene thin film on various substrate by electrochemical reduction method. Upon applying a reduction potential (between working and reference electrode), aryl diazonium salts are reduced forming reactive radical, which creates stable substrate-molecule interfaces.

**References**

When a thin Ge film is deposited on the Si(001) surface, it undergoes a series of morphological changes with increasing deposition. The initially flat film spontaneously forms three-dimensional islands called quantum dots. These islands undergo shape changes and increase in size with increasing film thickness. Additionally, it is noticed that a significant amount of silicon from the substrate enters into the film in the region under the 3D islands. It is widely believed that intermixing relieves the strain in the film. In this work, we have incorporated intermixing in the existing lattice-based kinetic Monte Carlo simulations of Ge/Si(001) heteroepitaxial growth. Intermixing is simulated by swaps between Si and Ge, controlled by an effective barrier, that has both a surface energy term and an elastic energy term. Our results show how the small intermixing observed at 2ML coverage rapidly increases as we go beyond 3ML. Though intermixing is mainly favored by elastic energy, we see that surface energy can also favor intermixing. Intermixed islands are rectangular in shape, contrary to non-intermixed surface where islands are mostly square in shape. Islands are larger in size in the intermixed surface than non-intermixed surface. As expected, intermixing increases with increasing coverage and temperature and slows down the 3D island formation.

**Figure 1.** Schematic diagram showing intermixing in Ge/Si system

**References**

Synthetic routes to nonracemic spiropiperidino indolenines, piperazines, and imidazoquinolines via S\textsubscript{N}2-type ring opening of aziridines

Navya Chauhan and Manas K. Ghorai*

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Highly substituted 3-Spiropiperidino indolenines have been synthesized via Lewis acid-catalyzed S\textsubscript{N}2-type ring opening of activated aziridines with 1H-indoles followed by Pd-catalyzed dearomative spirocyclization with propargyl carbonates in excellent yields (up to 90%).\textsuperscript{1} The transformation comprises sequential C–C, C–N, and C–C bond forming steps generating two stereogenic centers including an all-carbon quaternary stereocenter to furnish the products in diastereomerically pure (dr >99:1) forms with excellent enantiomeric excess (ee up to >99%). The S\textsubscript{N}2-type ring-opening of N-activated aziridines by anilines followed by Pd-catalyzed annulation with propargyl carbonates gives rise to highly substituted piperazine products.\textsuperscript{2} The simple and efficient one-pot three component synthetic route delivers piperazines with an exocyclic double bond in high yields (up to 91%) with excellent stereoselectivity (de, ee >99%).

An efficient single-pot synthetic approach to construct 1,2,3,3a,4,5-hexahydroimidazo[1,2-a]quinolines is described via Lewis acid-catalyzed S\textsubscript{N}2-type ring opening of activated aziridines with N-propargylanilines followed by intramolecular cascade cyclization. The methodology expeditiously delivers the products in high yields (up to 75% yield) with excellent diastereoselectivity (up to 94:6 dr) and enantiospecificity (up to >99% ee).\textsuperscript{3}

![Figure 1. Synthesis of 3-spiropiperidino indolenines, piperazines, and hexahydroimidazo[1,2-a]quinolines.](image)

References

The curious case of Density Functional Theory

Mainak Sadhukhan*

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In this short pedagogical talk, we will try to discuss some of the myths, facts, and challenges in modern density functional theory for electronic structure calculations. We will discuss some of the unusual roads that this interesting subject traversed so far. Simultaneously, some of the myths that encapsulates the subject will be addressed. The talk will conclude with some of the challenges that we are pursuing in our laboratory at present.
Trimethylamine biodegradation by paracoccus sp. strain DMF

Shiwangi Maurya, Chetan Arya and Gurunath Ramanathan*

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Paracoccus sp. strain DMF (P. DMF) is a gram-negative heterotroph that degrades dimethylformamide. This strain was isolated from Kanpur by our group[1] and found to survive high concentrations of the toxic anthropogenic organic solvent N, N-dimethylformamide (DMF). Previously, the strain was characterized for growth on DMF as a sole carbon and nitrogen source. The draft of the complete genome for P. DMF on analysis showed that a trimethylamine monooxygenase (Tmm) gene was also present in the genome.[2] Hence, the bacteria were grown on trimethylamine as a sole carbon and nitrogen source. The current study further elaborates the understating of metabolic and regulatory capabilities related to the utilization of unconventional C1 compounds such as aliphatic amides and prevalent methylated amines. We also determined the biokinetic parameters of microbial growth. Bacterial growth in trimethylamine resulted in a maximum specific growth rate (μmax), saturation constant (K_s) and inhibition constant (K_i) as 0.9132 h⁻¹, 229.04 mg/L and 467.29 mg/L, respectively. The results have shown good agreement, which indicates that Paracoccus sp. strain DMF can degrade trimethylamine up to a very high concentration. The results presented here suggest that the strain can effectively treat waste containing trimethylamine, a factor responsible for air and water pollution.

Figure 1. TMA dependent bacterial growth and biokinetic growth parameters of P. DMF. (A) Growth of P. DMF on different initial concentrations of TMA, (~-) 200 mg/L, (~-) 400 mg/L, (~-) 600 mg/L, 10,000 mg/L, (~-)20,000 mg/L; Growth (B) Plot of specific growth rate (h⁻¹) v/s initial substrate concentration (mg/L). (C) of P. DMF on TMA (400 mg/L) and TOC (ppm) determination; (D) Degradation of TMA along with the accumulation of DMA and ammonia, increase in the biomass and decrease in TOC with respect to time for 400 mg/L of initial DMF concentration. (~•-) TMA; (~o-) ammonia; (~-) DMA; (~-) control ;(~-) OD₅₅₅nm.

References
Simultaneous utilization of hot holes and hot electrons in plasmon mediated amine photooxidation

Swathi Swaminathan, Vishal Govind Rao, Jitendra K. Bera and Manabendra Chandra*

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Plasmon resonances represent a strong form of light-matter interaction, which enables the transfer of energy from photons to hot charge carriers. These charge carriers are agents that aid the photochemical transformation of molecules chemisorbed on nanoparticles. The majority of the generated charge carriers rapidly decay within the nanostructure before they can get transferred to the adsorbed molecule or semiconductor support and thus reduce the efficiency of charge transfer. In this work, we explore and utilize the charge separation phenomenon within the excited gold nanoparticles for selective and high throughput catalytic conversion of amine into imine. Under ambient laboratory conditions, these reactions were solely driven by visible light source without any additional reagents or support. SERS and NMR techniques were employed to monitor the reaction and product formation. Detailed mechanistic studies unequivocally show the involvement of both hot electrons and holes in the photoactivation of adsorbates, which is quite underutilized in plasmonic photocatalysis unlike semiconductors. The simultaneous involvement of hot electrons and hot holes in gold nanoparticle significantly increases the reaction yield in comparison to the conventional models. Low temperatures favor highly selective amine oxidation, thus enhancing conversion by 30-40 times relative to controls. The experimental framework outlined in this work improves the understanding of the fundamental characteristics of LSPR-mediated photocatalysis.

References

Shedding light on transient species involved in Ru-based water oxidation catalysis

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The efficient production of environmentally friendly fuels is one of the biggest challenges ever faced by modern scientists.[1] Photosystem II, which contains the Mn$_4$CaO$_5$ cluster, can oxidize water (2H$_2$O $\rightarrow$ O$_2$ + 4H$^+$ + 4e$^-$). The process produces H$_2$ and O$_2$ that are considered ideal fuels with water generation upon combustion as a by-product.[2] Ru-based complexes are among the most explored water oxidation catalysts (WOCs) due to their versatile redox properties and stability in water at various pH values.[3] It is proposed that high valent intermediates are involved during the catalytic cycle (Scheme 1).[4],[5] However, direct spectroscopic evidences for those intermediates are scarce. Therefore, our study focuses on developing new ruthenium-based WOCs, and spectroscopic characterization of such transient species (i.e., (L)Ru$^{IV/III}$=O, (L)Ru$^{IV}$OOH, (L)Ru$^{IV}$-OO, and (L)Ru$^{IV}$-OO-Ru$^{IV}$) in water oxidation catalysis.[6] In the present work, four new Ru(II) complexes with neutral amino pyridine/benzimidazole based ligand frameworks were synthesized and crystallographically characterized. Their reactivities were examined with various oxidants like ammonium ceric nitrate (CAN), NaOCl, mCPBA, etc. The preliminary results from UV-Vis absorption, resonance Raman, EPR spectroscopies and mass spectrometry clued towards the formation of high valent intermediates. This discussion will unveil the mechanistic aspects involved in Ruthenium-based WOCs that undoubtedly will lead the scientific community to our present degree of understanding.

References

Poster Presentations
Tandem Synthesis of Pyrroles from Nitroarenes and Diols Utilizing Caffeine Carbon Supported Cobalt Catalyst

Sabuj Kundu*, Dibyajyoti Panja, Anirban Sau, Bhuvaneshwari Balasubramaniam, Partha Dhara, and Raju K. Gupta

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Separation and recyclability of the catalyst is one of the important issues in the sustainable catalysis. Nowadays, the non-precious, bio-compatible, and abundant transition metal catalysts received increasing interest in both academia and industry as a replacement of expensive noble metal-based systems. In these greener prospective, a methodology was developed for the synthesis of pyrrole scaffolds directly from nitroarenes, employing bio-waste caffeine carbon-supported heterogeneous cobalt catalyst. A series of caffeine carbon-supported cobalt catalysts (CoX$_2$-CC-T) were prepared; among them, Co(OAc)$_2$-CC-800 displayed the highest catalytic activity for this transformation. Preparative scale synthesis of pyrroles and synthesis of anti-tubercular agent 5-(4-(1H-pyrrol-1-yl)phenyl)-1,3,4-oxadiazole-2-thiol revealed the practical applicability of this protocol. The retention of the catalytic efficiency even after 6 times reuses showed good stability of the catalyst, and the plausible mechanism and electronics effect were understood on the basis of several kinetic experiments and Hammett studies.

Scheme 1. Synthesis of pyrrole from alkenyl diol.

References

Enhanced Two-Photon Activity with Extended Molecular Conjugation

Habib Ali and Debabrata Goswami*

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The absorption of two photons of identical or different frequencies in order to excite a molecule from its ground to its excited state is two-photon absorption. The measured laser intensity through a sample during two-photon absorption process follows the relation: \( I(z, \lambda) = \frac{I_0(\lambda)}{1 + \beta(\lambda)I_0(\lambda)z} \) \[^{[1,2]}\]

Here, \( I_0(\lambda) \) is the incident Gaussian laser beam profile, \( z \) is the propagation length in medium, \( \beta(\lambda) \) is the two-photon coefficient, which is related to the two-photon cross-section \( (\sigma_2) \) as, 

\[ \sigma_2(\lambda) = \beta h\nu \times 10^3 / N_A c \]

and is reported in GM units that correspond to \( 10^5 \) cm\(^4\) s. We use 120 fs laser pulses at 800nm with 600mW average power from a commercial Ti:Sapphire oscillator (Mira-900F) to excite various azepine samples dissolved in dichloromethane. The samples were made to flow through a 1 mm closed circulating cuvette to ensure that there were no cumulative pulse-to-pulse effects. It has been conjectured that extended molecular conjugation is more favored towards two-photon absorption. \[^{[3]}\]

In this work we specifically show that two azepine like molecules having cis-trans conjugated structures (Fig. 1) show a drastic change in their two-photon absorption (TPA) characteristics. Conformer (a) in Fig. 1 has more extended conjugation as compared to conformer (b) and find a strong correlation between the TPA signal and the molecular conjugation.

![Figure 1](image.png)

**Figure 1.** Cis-Trans isomers of the important segments of the azepine based moieties that show drastic difference in TPA.

References

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

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The use of water as a formal oxidant has become an emerging trend in recent era. Several challenges have to be encountered for participating water in chemical reaction such as strong O-H bonds (enthalpy 436 kJ/mol) that not easily breaks, high heat capacity, strong pressure dependency of the viscosity and high cohesive energy density. Oxidation by water with the liberation of H₂ helps to achieve a high atom economy and high E factor. [1]

During past few years, few catalytic system have been designed to employ water for oxidative transformations such as conversion of alcohol to acid, [2] aldehyde–water shift reaction, [3] oxidation of olefins to carbonyl, [4] cyclic amine to lactam, [5] homobenzylic oxygenation [6] etc. We synthesized pyridyl functionalized water soluble Ni(II)-NHC complex with appended hydrophilic SO₃⁻ group. It offers a green and efficient protocol for catalytic oxidative deamination of primary amines to afford aldehyde which couples with parent amine that ultimately gives rise to homocoupled imine in aqueous medium. In presence of 2-aminothiophenol, benzothiazole predominates over imine. Notably, this reaction strategy avoids the use of any sacrificial oxidant, in which water plays pivotal role as an oxidant with the liberation of H₂.

Scheme 1. Oxidative deamination of primary amines

References

1. R. A. Sheldon, Green Chem. 2007, 9, 1273.
Synthesis Of Cyclic Palladium-formamidinate Complex and its Reactivity Towards Small Molecules Activation

Sadhana and Ganapathi Anantharaman*

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The synthesis of chelated palladium formamidinate complex by deprotonation of acyclic formamidine palladium complex in presence of base. The chelated palladium complex was found to electron rich and act as a important precursor for preparation of various organic compounds containing hetroatomic ligands. This complex act as a nucleophile for substrates containing electrophillic carbon atom. This nucleophillicity is due the presence of lone pair electrons on NCN framework of amidinate unit. So, via chelated palladium complex the activation of small molecules such as CS$_2$, nitriles and isothiocynates were done, where these molecules were found to inserted between Pd-N bond of complex resulted in the formation of four- membered and six-membered palladium complexes through C-N coupling.

References

Anthrax Bacillus is a rod shaped, gram positive and spore forming bacterium that can cause Anthrax, further resulting in a deadly infection against living organism. Accordingly, the bacillus anthracis spore act as potential biological warfare agent has attracted great attention recently.\(^1\) A rapid and sensitive detection of Bacillus anthracis is therefore crucial to minimize the probability of anthrax infection and prevent bioterrorism. The Luminescence from Ln(III) shows intrinsic narrow f-f emission bands, long lifetime and large Stokes’ shift, which keep off the interference from auto fluorescence from biological medium.\(^2\) Dipicolinic acid (DPA) present in anthrax spores (10% wt) act as unique biomarker via strong binding affinity to Tb(III) and act as efficient antenna to populate Tb(III) excited states. This set off intense green luminescence from Tb(III) due to intraconfigurational f→f emissions from \(^{5}\text{D}_4\rightarrow^{7}\text{F}_2\) transitions. Herein, we have designed a coordinately unsaturated \([\text{Tb}(\text{Br}-\text{TPY- (COOH)}_2(3\text{H}_2\text{O}))\text{(Cl)}]\) as a luminescent probe for efficient binding and detection of DPA\(^2\), showing remarkable enhancement of time-resolved luminescence and present its binding interactions, photo physical aspects and sensor parameters.\(^3\)

**Scheme 1.** Schematic design principle and proposed mechanism of the Tb-probe ‘Turn-On’ sensing for the dipicolinate biomarker via blocking the non-radiative vibrational energy transfer (VET).

**References**

Theoretical Studies of Hydrogen bond Dynamics and Two-Dimensional Infrared Spectroscopy of Binary Water-tert-Butyl Alcohol Mixtures

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Binary aqueous mixtures of tert-butyl alcohol (TBA) exhibit a large number of structural and thermodynamic anomalies at low TBA concentration with \( x_{\text{TBA}} = 0.03-0.07 \).[1] Further, there is a long-standing debate on whether water molecules around hydrophilic or hydrophobic groups of an amphiphile show slow dynamics as compared to bulk water.[2,3] In the present study, concentration induced binary aqueous mixtures of TBA are investigated by means of molecular dynamics simulations. Two-dimensional infrared (2D IR) spectroscopic techniques are employed to probe the hydrogen bond network fluctuations and their connection to H-bond dynamics. Non-monotonic decrease in the number of first solvation shell water molecules is observed which is an indication of TBA self-aggregation. We have separately probed water O-H vibrational frequency fluctuation around hydrophilic and hydrophobic groups to study the water dynamics. There was no evidence of any unusual dynamics in the concentration range where structural anomalies exist. On increasing TBA concentration, water dynamics slows down monotonically. Our spectral calculations show that both the hydrophilic and hydrophobic groups equally retard the water dynamics.

![Figure 1. 2D IR metrics derived at cumulant level. (a) Central line slope for water near hydrophilic group (b) Central line slope for water near hydrophobic groups.](image)

**References**

High-Valent Cobalt Catalyzed Hydrogen Borrowing Reactions and its Mechanistic Investigations

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Transition-metal catalyst mediated dehydrogenative reactions have evolved as an atom-economical and selective methodology for upgrading small molecules into higher order products. In general, the initial dehydrogenation reaction reveals a more reactive organic synthon that can undergo tandem functionalization reactivity to construct new C-C and C-N bonds.\(^1\) Alcohols is one of the key feed stocks for the manufacture of basic chemicals in industries and its reactivity expands enormously on activation. Traditional methods of alcohol oxidation often require hazardous organic or organometallic coupling partners to drive the reaction forward which decreases the atom economy by contributing to unwanted waste products.\(^2\) Although significant advances using noble transition metals have been made in the past few decades, use of cost effective and environmentally benign base metals guides this methodology towards a new dimension.\(^3\) In this regard, we have described the use of high valent Cp*Co(III) system in the alkylation of several carbonucleophiles with secondary alcohols.\(^4\)\(^5\)\(^6\) DFT calculations and experimental investigations to explore the mechanistic pathway of this redox-active and high valent Cp*Co(III) catalytic system sheds light on the involvement of a new paradigm in the oxidative activation of alcohols unlike its high-valent noble metal analogues.\(^6\)

![Scheme 1](image)

**Scheme 1.** Cp*Co(III)-catalyzed C-C bond formations though borrowing hydrogen catalysis.

References

A Novel Tool for Accurate and Efficient Prediction of Conformations of Biomolecules

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Molecular dynamics simulations are widely used in understanding the mechanism of protein folding/unfolding, protein-drug binding/unbinding, and protein aggregation. In these simulations, it is vital to sample all relevant conformational states to accurately estimate free energetics. However, special molecular dynamics techniques like replica exchange are needed for sampling the conformational states efficiently in short simulations. Here we present a new molecular dynamics method in this direction to further improve the efficiency of the existing replica exchange methods for problems such as protein folding and ligand binding. The usefulness of the method is demonstrated by computing the folding landscape of solvated Trp-cage mini protein.

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Synthetic Strategies for Fluorination and Trifluoromethylation of Olefins

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Current interest in fluorine chemistry is essentially a consequence of the fact that the incorporation of fluorine into organic molecules may profoundly change their chemical, physical, and biological properties with minimal steric alteration, which leads to a wide range of applications in almost all aspects of the chemical industry ranging from materials and agrochemicals to pharmaceuticals and radiotracers for positron emission tomography (PET). A transition metal-free activation & fluorination followed by cyclization of Alkenols has been developed using Selectfluor® reagent is reported. Here Selectfluor is used as fluorinating reagent as well powerful oxidant that activates double bond via SET, which generates radical cation; after that, intramolecular cyclization gives monofluoromethylated Morpholines in good-to-excellent yield (Scheme 1a). Manganese dioxide catalyzed oxy-trifluoromethylation of styrenyl olefins and enol acetates using Langlois reagent is achieved under oxygen/air as the oxidant. The use of convenient reagents (Langlois reagent as the “CF₃” source), oxygen as the oxidant, and mild conditions render these transformations efficient (Scheme 1b).

(a)

(b)

Scheme 1. (a) Selectfluor® mediated Oxy-fluorination of Alkenols. (b) MnO₂ catalyzed aerial oxy-trifluoromethylation of Olefins

References

Electronic Structure, Lattice-Dynamics, and Superconductivity in Ag-Au Alloys

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Despite the fact that monovalent noble metals defy superconductivity at atmospheric pressure, it has been proposed recently evidence for room temperature superconductivity at ambient pressure in nanostructures of silver particles embedded into a gold matrix.\cite{1,2} The origin of this emergent phenomenon in these Ag-Au nanoalloys is unclear. The alloys may have different chemico-physical interactions\cite{3} leading to the formation of Cooper pair, the bosonic quasiparticle responsible for the superconductivity. To investigate this both in theory and computations, knowledge of the alloy structure is necessary. Therefore, here we predict crystal structures of Ag-Au alloys (3D crystals and 2D slabs) using knowledge and first-principles-based crystal structure prediction approaches. For the most thermodynamically stable and metastable structures resulted, the superconducting transition temperatures ($T_c$) are estimated by carefully calculating electronic structure and electron-phonon matrix elements. All the structures investigated are found to be metallic with a common fcc-like cuboctahedron Ag-Au structure motif, featuring similar electronic densities of states near the Fermi surface.

The $T_c$ are estimated within the Bardeen-Cooper-Schrieffer (BCS) formalism; it turns out that in calculations for all the Ag-Au structures we have predicted, the transition temperatures resulted in less than one milli Kelvin,\cite{4,5,6} The BCS calculations do not indicate any sort of room temperature superconductivity as proposed in references 1 and 2, but rather our results complement the observations of near absence of superconductivity in pulsed laser deposited Ag-Au modulated nanostructured thin films\cite{7} and ~2 K in Ag implanted in Au thin films.\cite{8} Probably, as proposed\cite{1-3} the superconductivity may be lurking in the domains of the grain-boundaries, may be vindicated in the Fermi-surface topology. Detailed methods, calculations, and results of our investigations will be presented.

References

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Cu-Catalyzed Chemodivergent, Stereoselective Propargylic Dearomatization and Etherification of 2-Naphthols

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Catalytic asymmetric dearomatization (CADA) reactions are acknowledged as useful strategy for constructing an optically active three-dimensional molecular architecture having contiguous stereogenic centers.[1] In this context, naphthol derivatives are anticipated to be valuable substrates because the resulting cyclohexadienone frameworks are present as the basic skeleton in various biologically active natural products and therapeutic reagents.[2] However, the dearomatization reactions of phenols/naphthols are relatively challenging due to the competitive O-alkylation (ether formation) and the Friedel-Crafts (alkylation) reaction pathways.[3]

Until now, different functionalization of naphthol has been reported for the dearomatization of 2-naphthol are allylic, alkene, aryl, and heteroatom, etc.[4] This presentation will focus on a Cu(OTf)₂ and chiral P, N, N-ligand complex catalyzed chemodivergent stereoselective propargylic dearomatization and etherification reaction of 2-naphthol derivatives. The methodology provides both the products in high yield and stereoselectivity with low catalyst loading (2 mol %) and follows a broad range of substrate scope.

Scheme 1. Chemodivergent propargylic dearomatization and etherification of 2-naphthols

References

Ruthenium Catalyzed Stereo- and Chemoselective Cross-Coupling reaction of Vinyl ketones and its application to Total Synthesis of FR256523

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FR256523 is a bioactive complex natural product, belongs to family of potent macrocyclic polyene and including other two members FR252921, FR252922 were isolated from the culture broth of pseudomonas fluorescens no. 408813 and act as an immunosuppressive agent, preferably used in the treatment of allograft repulsions and autoimmune- associated diseases. Due to their complexity and architect, FR molecules have sparked great interest in synthetic community. We report here the application of ruthenium catalyzed highly stereo- and chemoselective cross-coupling reaction of vinyl ketones and acrylates for the total synthesis of FR256523. The novel and concise synthesis of triene moiety and its further exploration towards total synthesis of FR256523 natural product.

References

Pd-Catalyzed Domino Cross-Coupling: Synthesis of Functionalized 4-(Arylethynyl)Coumarins

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Coumarin scaffolds are associated with various pharmacological and photophysical properties.[1, 2] The synthesis of 4-(arylethynyl)coumarin derivatives usually achieved through Sonogashira couplings of 4-bromo, 4-triflate, and 4-tosyl coumarin derivatives.[3] A few cross-coupling methods using organometallic reagents involving potassium alkynyltrifluoroborates and zinc pivalates derivatives have also been reported to synthesize the 4-alkynyl coumarin derivatives.[4] In contrast our present study is focused on developing a domino methodology for preparing a library of functional 4-(arylethynyl) coumarin scaffolds under Pd-catalyzed cross-coupling using triaryl bismuth reagents.[5]

Scheme 1. Pd-catalyzed synthesis of functionalized 4-(arylethynyl)coumarins.

References