(P1)

Luminescence Lanthanide complexes as universal phosphate sensor and their Application on Microalgal cell Chlorella vulgaris

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Luminescent lanthanides probes for recognition and sensing of phosphate ions such as ATP, ADP, AMP, PPi or total phosphate is of current interest because of their role in energy metabolism, DNA replication, DNA transcription and other fundamental function of living cells. We have recently synthesized phenanthroline based EuL₂Cl₃ and TbL₂Cl₃ complexes and shown their "red" and "green" emission for the detection of nucleoside phosphate. The emission property was meticulously investigated for sensing various anions and were demonstrated for selective recognition to phosphate and nitrite anions compared to other anions e.g., F-, Cl-, Br-, I-, HSO₄, CH₃COO-, HCO₃, NO₃. The binding constants of phosphate and nitrite ion with both the complexes were determined. Since both these complexes are giving change in the fluorescence intensity interacting with phosphate ions, it has been extended to nucleoside phosphates ATP/ADP/AMP. Among these two complexes, Terbium(III) showing similar quenching effect with all phosphate ions acts as "universal sensor for nucleosides phosphates". Using fluorescence microscope, these complexes were applied on microalgal cell chlorella vulgaris CCNM 107 and monitored the change in the emission with different time interval. The emission property, anion selectivity, binding constants determination and cell staining studies will be presented in detail.Fig 1: a) Eu and Tb complexes showing their luminscence activity b) Cell staining.

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(P2)

A turn-on fluorescence based quantification of cholesterol sulphate by its ionic selfassembly with tetracationic cyclophanes

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The positively charged imidazolium and its benzo derivative–based molecular architects due their dual electrostatic and hydrogen bonding interactions with negatively charged species have found many applications for the recognition of anions. Cholesterol sulfate is quantitatively the most important known sterol sulfate in human plasma with concentrations ranging from 328–924 μ g/100ml (6.71-18.92 μ M) and has emerged as an important regulatory molecule. It is widely distributed and has been involved in a wide variety of biological processes, e.g. regulation of cholesterol synthesis, sperm capacitation, thrombin and plasmin activities, and activation of protein kinase C isozymes. It serves as a substrate for adrenal and ovarian steroidogenesis. The

excessive cholesterol sulfonate deposition in the stratum corneum of the epidermis causes development of recessive X-linked ichthyosis. The cholesterol-cholesterol sulfate ratio in epithelial cells outside of the skin is normally about 500:1, whereas in the normal stratum corneum the ratio is as low as 10:1 or 5:1. In the recessive X-linked ichthyosis disorder, however, which is characterized by a deficiency in steroid sulfatase activity, the cholesterolcholesterol sulfate ratio in the stratum corneum is 1:1. The cholesterol sulfate due to its amphiphilic nature is also ideally suited for interactions with membrane constituents. This necessitates the development of simple and cost effective methods for the quantification of cholesterolsulfate. So we have synthesized Benzimiazolium based tetracationic cyclophanes display highly selective and sensitive ionic self-assembly based AIEE only with cholesterol sulfate amongst other steroidal sulfates under physiological conditions and with lowest detection limit of $< 0.4 \mu$ M. benzimidazolium based tetracationic cyclophanes BIMCP-1 and BIMCP-2 which on addition (50 equiv.) of various steroidal sulfates viz. cholesterol sulfate, pregnenolone sulfate, dehydroisoandosterone sulfate and taurocholic acid show aggregation induced emission enhancement (AIEE), only with Cholesterol sulfate. The SEM images of the films obtained form solutions of cyclophanes and Cholesterol sulfate (10 µM) point to the self-assembly of BIMCP-1 and BIMCP-2 with Cholesterol sulphate to form respective rod-like and nearly eliptical morphologies, respectively. This self-assembly process has been further supported by appearance of aggregates in DLS experiments and increase in emission intensity of such aggregates in confocal imaging. In solution phase fluorescence studies, BIMCP-1 and BIMCP-2 can quantitatively measure CH-S between 0.4 µM - 40 µM and is suitable for blood serum concentrations 6.7-18.9 µM. Significanlty, Pregnenolone sulphate and dehydroisoandosterone sulfate with BIMCP-1 show fluorescence enhacement at much higher concentrations (> 300 µM). BIMCP-1 is found to be significantly more sensitive to Cholesterol sulfate and other steroidal sulfates incomparsion to BIMCP-2 and points to the role of size of the cyclophane in self-assembly process. The titration studies, Job's plot, HRMS, SEM and structural optimization using Gaussian 09 confirm the encapsulation of CH-S. The salient features of these findings will be presented.

(P3)

Light-harvesting and efficient energy transfer in self assembled dendrimeric system V. Siva Rama Krishna, S. Bandyopadhyay INDIAN INSTITUTE OF SCIENCE EDUCATION AND RESEARCH KOLKATA

Light-harvesting antenna is essential for the prime energy-trapping process on earth, namely, the photosynthesis. There highly efficient natural systems possess several chromophores arranged in a circular fashion around a central reaction centre. The absorbed energy at the periphery is channelized efficiently through an "energy-funnel" resulting in an amplification at the reaction centre. Owing to their well-defined structure and efficient energy transfer, these light-harvesting systems serve as excellent models for mimicking. A coumarin based tripodal molecule with a amino coumarine at its centre has been synthesized. The molecule self associates in water into a spherical micelle that can encapsulates a Rose Bengal dye. On excitation, the peripheral chromophores absorbs light and transfer the energy to the N-diethyl aminocoumarin interior which subsequently relays it to the non-covalently attached Rose Bengal resulting in a strong emission from the dye. The energy cascade has been studied with steady-state and time resolved fluorescence methods.

(P4)

ESIPT induced AIEE active material for recognition of 2- Thiobarbituric acid

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Excited State Intramolecular Proton Transfer (ESIPT) based fluorescent molecules are recognized as highly significant functional materials because of their unusual photophysical behavior which leads to wide variety of applications as chemosensors, electroluminescent materials and in biochemistry etc. Aggregation Induced Emission Enhancement (AIEE) materials are also being extensively used as chemosensing templates. However, simultaneous application of both the phenomenon (ESIPT and AIEE) for molecular recognition may lead to development of high sensitivity chemosensors. Recently, we reported a new carbazole based molecule,1 synthesized in high yield through Condensation of 5-nitro-2-hydroxy benzaldehyde with equimolar amount of 3-Amino-9-ethylcarbazole. It exhibited ESIPT phenomenon and induces the AIEE behavior in H2O:THF (60:40). The aggregates of molecule in H2O:THF (60:40) have been utilized for recognition of 2-thiobarbituric acid (TBA) selectively. TBA is a heterocyclic compound known for its high medicinal value and its derivatives are used as sedatives, hypotonic drugs and for anticancer activity etc. Because of its industrial, clinical and pharmacological applications, detection of TBA is highly important and significant. A comparative study is accomplished using barbituric acid, urea, thiophene, carbon disulfide, and thiourea. It was observed that among all the analytes tested, aggregates of molecule recognized TBA with highest efficacy. The study is corroborated by fluorescence, UV-Vis. spectroscopy, TEM images, Naked eye and solid state detection (under illumination at 365 nm UV light) on silica coated TLC plate. Thus, the details of synthesis and studies of AIEE material for detection of 2-thiobarbituric acid and its further modifications shall be presented in the symposium.

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(P5)

Role of H-bonding on Self-Assembly of Naphthalene-Diimide Containing Amphiphiles in Aqueous Medium

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Inspired by nature chemists have utilized different non-covalent forces to generate synthetic supramolecular architectures. However, abiotic systems involving H-bonding in aqueous solution is still scarce due to the challenge in overcoming the competition from water. Recently, we have shown vesicular assembly of a bis-hydrazide functionalized naphthalene-diimide (NDI) bolaamphiphile (NDI-1) in water by synergistic effect of H-bonding among the hydrazides and π -stacking [1]. Interestingly electron rich pyrene derivatives could be intercalated in the NDI-membrane due to pyrene-NDI charge-transfer interaction. We have now studied this system in further detail with an objective of learning (i) the specific role of H-bonding on the self-assembly and (ii) influence of H-bonding on the intercalation phenomenon. We have compared NDI-1 with NDI-2, which differ only by the hydrazide units and show distinctly different assembly

properties in water. While both of them exhibit vesicular structure; the stability, critical aggregation concentration and aggregation propensity are better for the NDI-2 owing to the enhanced hydrophobicity in the absence of hydrazides. Conversely, NDI-1 showed lower critical solution temperature possibly related to the breaking of H-bonding among the hydrazides. More important they showed contrasting ability towards pyrene intercalation. While NDI-1 could engulf various pyrene donors, it was not possible with NDI-2 suggesting distinct role of H-bonding among the hydrazides in stabilizing the pyrene-intercalated NDI stack. A detail account of comparative self-assembly studies of NDI-1(a) and NDI-2(b) will be the topic of this presentation.

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(P6)

Chemosensors for biologically important cations and anions based on on imine/hydroxyl groups

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Currently, there is an immense research interest to develop the sensors that simultaneously bind both the cations as well as anions. The recognition of ions by chromogenic and fluorogenic sensors has gained importance due to their application in biological, environmental and chemical processes (1). The sensing of anions, especially F⁻ and CN⁻ ions are of particular interest (2) because of use of F ion in dental care, treatment for osteoporosis and due to its unwanted release during hydrolysis of nerve gas Sarin. Cyanide is highly toxic to animals and its release into the environment is hazardous but it is relentlessly used in various industrial processes, including gold mining and electroplating, production of organic chemicals and polymers, enhancing the chance of unwanted release. Similarly, sensors for cations such as Cu^{2^+} , Al^{3^+} , Ag^+ and Pb^{2^+} are important as these ions can directly affect human health (3). For practical applications, the need of the hour is to develop sensors that can be prepared easily, have low detection limit and display sensitive and selective recognition of ions in the aqueous medium. In present investigation, our work is focused on the synthesis of chemosensors (4) for anions as well as on cations. Various optical sensors, giving 'naked eye detection' and working on either binding site-signalling unit or chemodosimetry approach have been reported. We have designed and synthesized benzene/mesitylene based dipodal and tripodal Schiff bases which have Hbonding appendages. Anion sensing involves the chemosensors and chemodosimeters for F and CN^{-} ions, catechol based sensor works for both F^{-} and CN^{-} ions, albeit through different channels in DMSO. Its colorimetric response may be used to discriminate between the two anions within two minutes whereas its fluorogenic response may do so instantaneously and with high sensitivity. In DMSO: water mixture it behaves as a colorimetric sensor exclusively for CN⁻ ion. The phenol based sensor is a highly selective one for CN⁻ ion and may be used as a semiquantitative chromo/fluorogenic sensor, having different responses to different CN⁻ ion concentrations. The chemodosimeter response of these sensors towards CN⁻ ion is due to the Strecker's nucleophilic addition to imine bond of the Schiff bases. Cation sensing involves mesitylene based tripodal sensor for Cu^{2+} , which is capable of sensing nanomolar amounts of the metal ion in 80% aqueous medium with THF as a co-solvent and benzene based dipodal sensors for Al^{3+} in 70% aqueous medium with DMSO as a cosolvent.

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(P7)

Bay Functionalized Perylenediimides: Chromo-fluorescent Dyes for Molecular Recognition

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Perylene diimide (PDI) derivatives have been considered as a promising material for various optoelectronic devices with high molar extinction coefficient, fluorescence quantum vields and exceptional thermal, chemical and photochemical stability. However, we have seen slow growth in considering PDIs as chromo-fluorescent probes for sensing applications. For last few years, research has focused on developing chromo-fluorescent sensors as a safeguard for global ecosystem, for monitoring of toxic, carcinogenic metal ions and anions that impose serious human and environmental health hazards. Keeping this in view, we have synthesized two Perylenediimide (PDI) derivatives appended with 8-hydroxyquinoline (PDI 1) and benzimidazolium (PDI 2) derivatives and their photophysical and spectroscopic properties were experimentally determined using different solvents. The decreased quantum yield with increased solvent polarity indicates that PDI 1 have a charge transfer (CT) character. PDI 1 show ratiometric behavior to detect Cu2+ colorimetrically with visible color change from coral red to light pink concomitantly blue shift of the absorbance band, whereas it shows "turn-off" behavior in fluorescence with lowest limit of detection 5x10-7 M. Also PDI 1 can be further utilized for ratiometric CN- detection colorimetrically and as "turn-on" sensor for CN- detection fluorometrically with lowest limit of detection 8x10-6 M. PDI 2 shows fluorescence quenching with only perchlorate anions with minimum limit of detection 1 µM in pH 7.4 HEPES buffered (0.01 M) aqueous solution containing 10% DMSO (v/v). Moreover, PDI 2 shows solvatofluorism with 43 nm red shift on increasing the polarity of the solvent.

(P8) Dual Chemosensing properties of Azo Linked Thiourea based receptor in Nanomolar levels with Real sample Applications

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The developments of molecular systems for the colorimetric detection of anions and cations have gained most importance due to their significance in biological, analytical, medical and environmental applications. Generally, pyrrole -OH, -NH2, urea, thiourea, -CONH centers act as a binding site of both cations and anions. Sensing of fluoride anion in aqueous medium has attracted growing attention due to its detrimental roles (fluorosis) and beneficial effects (prevention of dental caries). The development of chemosensors for the transition metal ions, usually they deal with harmful pollutants in the environment. The selective detection of Cd2+ in the interference of other transition metal ions, particularly Zn^{2+} which belongs to the same group and exhibits many similar properties, is very difficult. Thus it is necessary to develop Cd^{2+} selective fluorescent sensors that can distinguish Cd^{2+} from Zn^{2+} and other metal ions. We are interested in fluorescent sensors that utilize photoinduced electron transfer (PET) to translate a cation binding event into a fluorescence signal. The Azo linked thiourea type Schiff base has been synthesized and characterized, and found to sense F, AcO, HO and Cd²⁺ ions in aqueous medium over the other anions and cations. The binding ability was confirmed by naked-eye analysis, optical and emission spectroscopic studies. Receptor with F, AcO, HO and Cd²⁺ shows higher binding constant with 1:1 stoichiometry. The detection limit of receptor with F is 5.1 nM, AcO- is 0.32 nM, HO⁻ is 0.27 nM and receptor with Cd²⁺ Shows 0.29 nM. Receptor with anions and Cd²⁺ shows fluorescence enhancement. F ion detection property of receptor in aqueous medium was also extended to the real samples like toothpaste and mouthwash.

(P9)

Substituted amino-alkyl-Rhodamines, tuning their selectivity towards mercury ion detection and subsequent applications

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Mercury toxicity due to its bioaccumulation in physiological functionalities leading to dysfunction of cells and consequently causing many health hazards, desirably presets its on-site, real time, selective analysis for biological, environmental and clinical monitoring purposes. Rhodamine based signaling probes for selective detection of mercury ion have been of enormous interest because of their ability to evaluate mercury ion's critical concentration as environmental pollutant and physiological hazardous substances; apart from their advantages as signaling module, a straight forward structure-function correlation protocol, and ability to modulate signal in aqueous media. In a modular approach, few substituted 'amino-alkyl-rhodamine' based probes were synthesized, where various parameters such as methodological designs, operational conditions, solvent medium, electronic decoupling etc. were tuned to address selectivity, sensitivity, response time, reproducibility/reversibility of signaling operation and probe's reusability issues in mercury ion detection at sub-micromolar level with monitoring window of dual channel chromogenic and fluorogenic signaling modulation. These probes were further

demonstrated their ability in in-situ mercury ion detection in plant tissues, microorganisms, algae and in solid phase through immobilized on a surface modified silica in alignment with their potentiality as sensory materials.

(P10)

TRANSITION METAL BASED-COORDINATION POLYMERS BUILT USING BENT FLEXIBLE LIGANDS

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Recent years have witnessed intense research activity in the rational design and synthesis of coordination polymers not only due to their interesting topologies but also because of their potential applications as functional materials in fields such as molecular magnetism, proton conduction, gas adsorption,(1) and so on. Synthesis of coordination polymers with desired magnetic properties are extremely important with an ever growing number of useful applications. A significant number of coordination polymers exhibiting ferromagnetic, antiferromagnetic, spin canting, metamagnetism, single chain magnets, spin glass behavior, etc. have been observed.(2) Recently, porous coordination polymers (PCPs) have emerged as an important new class of materials because of their ability to selectively adsorb gases. One of the most striking features of PCPs is their ability to sense guest molecules, which is predominantly governed by the window dimensions, presence of functional groups in the channels, and flexibility of these materials.(3) In addition to these, PCPs have attracted attention for potential uses in electrochemical devices and fuel cells as well as probes for studying transport dynamics and biological ion channels. Particularly, porous MOFs are finding more attention as proton-conducting separator materials to replace the existing proton exchange membrane in fuel cells.(4)

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(P11)

A new class of organic antacid 2,4,5-triaryl imidazole

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The potency and wide applicability of the imidazole pharmacophore can be attributed to its hydrogen bond donor-acceptor capability as well as its high affinity for metals, which are present in many protein active sites. Imidazole nucleus containing drugs are used as anti-inflammatory,

anti-cancer, antifungal and antibacterial drugs. A natural imidazole ring containing compound Histamine is involved in many regulatory responses, such as the control of gastric acid in the stomach, with an over-expression resulting in the over-production of acid as part of an allergic response. The imidazole-based drug, cimetidine (trade name, Tagamet) acts as an antagonist by blocking the histamine receptor site, thus reducing the production of gastric acid. Histamine is also involved in the inflammatory response. In this consequence, substituted 2,4,5triarylimidazole has been synthesized for the study of their antacid behavior. UV, NMR and Xray crystallographic study proves that imidazole nitrogen binds with hydrochloric acid.In vitro this molecule provided intramolecular C-H... π and intermolecular C-H...Cl and N-H...Cl interactions in solid as well as solution state. This result reveals that, in vivo tri phenyl imidazole nucleus can be developed as antacid drugs. The embedded HCl molecule bridges between molecules via C-H... π , C-H...Cl, Cl-H...N and N-H...Cl non-covalent interactions. Thus substituted imidazole behaves as a preorganized host molecule for HCl binding.

(P12)

Benzene Platform Based Hexa-amides as Anion Receptors: Conformational and Anion Binding Selectivity Studies

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A series of neutral hexa-amide receptors with different electron withdrawing substituent based on benzene platform are synthesized and explored towards anion recognition. Single crystal Xray diffraction studies reveal different conformations of the anion complexes with different anionic guests. For fluoride (F-) complexation in dioxane-acetone (1:1, v/v) mixture, we observe aaaaaa conformation with L1 (m-nitrophenyl substituted hexa-amide derivative), where all the amide arms are pointed in the same direction in order to encapsulate [F4(H2O)10]4- cluster inside the cavity of the dimeric capsular assembly. Acetate (CH3CO2-) shows aaabbb type of binding pattern with L1, L4 (o-nitrophenyl hexa-amide derivative), L6 (m-trifluromethylphenyl substituted hexa-amide derivative) & L7 (o-trifluromethylphenyl substituted hexa-amide derivative) where three consecutive arms are in upward direction and the other three arms are in downward direction. Interestingly, nitrate (NO3-) exhibits two different binding conformations with two different ligands L1 and L7 where L1 binds with ababab pattern and L7 binds with aabaab pattern. Solution state Isothermal titration calorimetry and 1H- NMR titration studies are carried out in order to investigate the anion binding selectivity.

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(P13)

Complementary Fusion between Self-Assemblies & CNT: Modulating Viscoelastic Properties

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Carbon nanotubes (CNTs) have emerged as a fascinating nanomaterial in the recent past owing to their versatile potentials in all domain of science. Recently, we have utilized this nanomaterial to develop supramolecular nanohybrids where single walled carbon nanotube (SWNT) has been incorporated within self-assemblies of amphiphiles leading to the development of softnanocomposite with superior viscoelastic properties. Peptide based hydrogelators and organogelators were amalgamated CNTs within self-assembled fibrillar network (SAFIN) of gel. Miniscule amount of SWNT-COOH triggers the self-assembled gelation of amphiphiles by infesting intertwined networks in free flowing solvent resulting in superefficient organogels.1 Surprisingly, the minimum gelation concentration plummeted up to 17-fold and the effect was seen even in presence of only 0.005 % w/v nanotube. Most strikingly the rigidity of the nanocomposite was found to be ~6 fold higher than that of the native gel at its MGC. To incorporate CNTs within the aqueous milieu we have synthesized imidazolium based hydrogelators which can accommodate a significantly high amount of pristine SWNTs (2-3.5% w/v) through complementary cation- π and π - π interactions.2 Remarkably, the developed nanocomposites showed manifold enhancement (~85-fold) in their mechanical strength compared with native hydrogel without SWNTs. The viscoelastic properties of these nanocomposites were readily tuned by varying the amount of incorporated CNTs.

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(P14)

Self-assembly of Cardanol Based Supramolecular Synthons to Photoresponsive Nanospheres: Light Induced Size Variation at Nanoscale Sankarapillai Mahesh, Dawn Raju and Kuruvilla Joseph Indian Institute of Space Science and Technology

Development of soft nanomaterials by the controlled self-assembly of molecules derived from renewable sources is attracting scientists all over the world. Herein we report the self-assembly of Cardanol based photoswitchable molecule in non polar solvents such as cyclohexane. Molecule 1 self-assembles to form nanospheres and transforms with UV light. The trans-cis photoisomerization and the associated surface dipole moment increase are responsible for the association of the nanospheres to microspheres. The observation described here reveals the advantages of versatile azobenzene chromophore which may encourage further studies towards stimuli responsive hierarchical structures from bio resources with controlled morphological features

(P15)

Architecture of isostructural Cd²⁺/Co²⁺ coordination polymer and its CO₂ sorption properties modulated by different anions

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The potential multidentate tris-pyridyl ligand has been synthesized, and later employed for the tailoring of four isostructural Cadmium (II)/cobalt (II) 2D isostructural coordination polymer $(ICPs), [[M(dmpt)2(X)2] \cdot xS]n, where S = solvent, M = Cd, (X = NO₃²⁻(1), Br (2), I (3)); M = Co$ $(X = Cl^{-}(4))$, dmpt = 4'-(3,4-dimethoxyphenyl)-4,2':6',4"-terpyridine). All of the complexes have been characterized by infrared spectra (IR), elemental analyses, thermogravimetric analyses (TGA), powder X-ray diffraction (PXRD) and further structurally characterized by single-crystal X-ray diffraction analyses. Single crystal X-ray diffraction analyses reveals that all these complexes are isostructural and crystallize in the monoclinic C2/c space group and possesses similar structural features such as metal-coordination environments, network topologies, $\pi^{\bullet\bullet\bullet\pi}$ interactions and exhibits a two-dimensional (2D) grid layer which possesses the cavity, though with tuning dimensions. In all isomorphous complexes, [[M(mptpy)2(X)2]•xS] coordination monomer act as the building block, building the 2D layer which is further piled up via vander waal interactions into three-dimensional (3D) frameworks with the anions directing to the pores and hence the impact of the different anions on the CO₂ adsorption was investigated. Furthermore, the effect of weak interactions on structural dynamics of the systems has also been studied.

(P16)

Selective Chromogenic and Fluorogenic Detection of Chemical Warfare Agents Vinod Kumar and M. P. Kaushik

Chemical warfare (CW) agents are the deadliest chemicals on exposure even in small quantities. These are broadly divided into two categories: vesicants and nerve agents. Apart from unfortunate history on the use of chemical weapons, recent attack of CW agents in Syria has again raised the grave concern over their illegitimate use on mankind. In order to protect the humanity from CW agents, it becomes necessary to develop the devices/protocols for selective and sensitive detection of CW agents. In our lab, we are directing the efforts for the development of chromogenic and fluorogenic techniques/protocols for the detection of these chemical agents. Using indicator displacement assay[1] (IDA) and chemososimeter approach[2], we have been successful in the selective and sensitive detection of the chemical agents [1-3]. The protocol has also been extended to explore the detection on various matrixes such as on the surfaces, water, and in soil sample.

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(P17)

Role of anions in fluorescence emission of N,N'-bis(3-imidazol-1-ylpropyl)naphthalene diimide

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Naphathlimide derivatives are greatly used as anion receptors and for anion detection. In these cases anion- π interactions are invoked (1) but not systematically studied with model compounds.(2) We have studied N,N'-bis(3-imidazol-1-ylpropyl)naphthalenediimide (L) as

model as it has a flexible tethers connected to imidazole moiety at a suitable distance for folding to hold an anion on protonation. The compound gets protonated in solution by various acids and shows fluorescence quenching with hydrochloric acid and hydrobromic acid, whereas it shows fluorescence enhancement with perchloric, sulphuric, phosphoric and nitric acid. A similar trend in fluorescence emission of the corresponding salt in solid state is also observed. The fluorescence quenching is attributed to the anion- π interactions of the chloride and bromide with H2L cations whereas the oxy-anion containing acids cause fluorescence enhancement by only protonation of L and they do not provide suitable orientation to imidazole to have charge transfer. The structures of the salts of L have been determined to exemplify the fluorescence properties. Chloride and bromide salts form hydrogen bonded halide-water chain; whereas hydrogen phosphate salt form one dimensional water bridged polymeric chain. The results on anion- π interactions interactions matches with theoretically predicted data on model ion channels derived from napthalenediimide derivative.(3) Receptor, L Chloride salt of L

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(P18)

Cu(II)Templated Amido-Amine Macrocycle Based Pseudorotaxanes

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An amido-amine macrocycle is explored as a wheel towards the construction of various Cu(II) template pseudorotaxanes with bidentate chelating ligands as axles. The macrocyle has shown selective formation of a particular self-sorted [2]pseudorotaxane out of nine components of a tridentate, four bidentate ligands and four transition metal ions assisted by Cu(II). Then Cu(II)-templated multinuclear non-fluorescent anti-[3]pseudorotaxane is synthesized on a fluorophoric axle using above macrocycle. Further axle substitution reaction via molecular transformation [3]-to [2]pseudorotaxane is established in solution and solid states studies. Finally, this macrocycle has been extensively explored to synthesize a series of Cu(II)-templated [2]pseudorotaxanes by various derivatives of 2,2'-bipyridine as axles. This study confirms metal coordination, aromatic π - π -stacking and second sphere hydrogen bonding interactions between the wheel and axle play crucial roles to maximize the template effect.

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Soluble Cocrystals of the Xanthine Oxidase Inhibitor Febuxostat <u>D. Maddileti</u>, Jayabun SK, and Ashwini Nangia* UNIVERSITY OF HYDERABD

Febuxostat is a novel nonpurine selective inhibitor of xanthine oxidase which is used for the management of hyperuricemia in patients with gout. It is a BCS class II drug (High Permeability, Low Solubility) having aqueous solubility 0.0129 mg /ml and D0 = 24. Synthesis and physicochemical characterization of co-crystals of the FEB with the GRAS co-formers urea, acetamide, nicotinamide, PABA, saccharin in 1:1 stoichiometry were reported for the first time. X-ray crystal structures were determined for the guest free form of the FEB and cocrystals with urea, acetamide, nicotinamide PABA, whereas the saccharin cocrystal was identified by IR, Raman, DSC,13C ssNMR and powder X-ray diffraction pattern. Analysis of the crystal structures revealed that cocrystals are sustained by the anticipated acid-acid homosynthon, acid-amide and acid-pyridine heterosynthons (with coformers URE, NIC and PABA) except in FEB-ACT. All the cocrystals showed higher IDR compared to FEB, in which FEB-ACT had the fastest dissolution rate (52 times) but it was prone to hydrate formation. Further, they exhibited good stability under accelerated humidity conditions (75% RH, 40 °C) except FEB-ACT cocrystal.

(P20)

Andrographolide: Solving Chemical Instability and Poor Solubility by Means of Cocrystals <u>Kuthuru Suresh</u>, N. Rajesh Goud, and Ashwini Nangia* UNIVERSITY OF HYDERABD

The bioactive agent Andrographolide was screened with pharmaceutically acceptable coformers to discover a novel solid form which will solve the chemical instability and poor solubility problems of this herbal medicine. Liquid-assisted grinding of Andrographolide with GRAS (generally regarded as safe) coformers in a fixed stoichiometry resulted in cocrystals with vanillin (1:1), vanillic acid (1:1), salicylic acid (1:1), resorcinol (1:1), and guaiacol (1:1). All the crystalline products were characterized by thermal, spectroscopic and diffraction methods. Interestingly, even though the cocrystals are isostructural, their physico-chemical properties are quite different. Andrographolide–Salicylic acid cocrystal completely inhibited the chemical transformation of Andrographolide to its inactive sulfate metabolite and moreover the cocrystal exhibited 3 times faster dissolution rate and 2 times higher drug release compared to pure Andrographolide.

(P21)

Selective recognition and extraction of uranyl ion by macrocyclic based tripodal receptor <u>Rahul Shrivastava</u>* and Suman Swami Department of Chemistry, Manipal University, Jaipur

Uranium is the most common radionuclide in nature. Among the four different oxidation states of uranium in aqueous systems: U(III), U(IV), U(V), and U(VI), soluble U(VI) species (e.g. Uranyl $UO_2^{2^+}$ ion) are the predominant forms of uranium in contaminated groundwater and soils. Different studies suggest the possibility of genetic, reproductive, and neurological effects from chronic exposure to uranium wastes. It is accepted now that when uranium enters the human

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body, radiation and chemical toxicity can increase the risk of bone and lung cancers and that uranium can accumulate in kidneys for a long period and cause renal dysfunction and structural damage. From last few years, various methods have been devised for uranium remediation in groundwater and soil but these methods are limited to nuclear power plants and do not have commercial implication due to their high cost, instability, toxicity and tedious extraction process in sophisticated laboratory. Thus paucity of simple and user-friendly method for in-house and municipal treatment encourages us to develop receptor molecules having high hydrophobicity for easy extractive removal of uranium from drinking water sources. In this context, a tripodal receptor capable of extracting uranyl ion from aqueous solutions has been developed. The new receptor features three carboxylates that converge on the uranyl ion through bidentate interactions. The NMR studies and crystal structure of the complex shows that the carboxylates coordinate to uranyl ion while the amides hydrogen bond to one of the uranyl oxo-oxygen atoms. The hydrophobic coating of the ligand and its rigidity contribute to its ability to selectively extract uranyl ion from dilute aqueous solutions.

(P22)

Highly Stable Ultra-Electron Deficient Naphthalenediimide and Radical Anion Crystal: Role of Multi-Faceted Phosphonium Ions

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Molecules with large electron deficiency are being intensely pursued for low-cost organic electronic devices and as vital scaffolds for self-assembly, etc[1]. Amongst these, the electron deficient naphthalenediimides (NDIs) have exhibited phenomenal applications as n-type semiconductors, electron transfer (ET) reactions, [2] etc. However, it has been realized that electron deficiency beyond a certain LUMO level makes the molecule highly unstable e.g. NDI-CN4 in spite of its commercial interest (dubbed to be the strongest NDI- π -acid) has not been achieved due to stability issues. In addition to these, significant applications of NDI moiety can be perceived if stable NDI.-radical anion (RA) is realized, which would lead to and magnetoconductive materials and plethora of applications. Although there have been pioneering strategies[3] to enhance the life-time of organic radicals, there is not a single example of a stable, chemically isolable NDI.-. The full potential of the rich opto-electronic properties of NDI.-/NDI.+ is yet to be realized due to its instability[2]. Herein we report the integration of the versatile phosphonium groups at the NDI-core (1a), leading to the lowest LUMO level recorded for a NDI molecule even surpassing one of the strongest electron acceptor i.e. TCNQ[2d]. Most significantly, we realized the first chemically isolable NDI.-(1a-RA) and stable single-crystals of 1a and 1a-RA. 1a and 1a-RA exhibited an unprecedented stability to air, light and probably for the first time for any radical ion system endurance to chromatography. Crystallographic evidence along with theoretical studies unearths the reason for the extraordinary stability of 1a and 1a-RA. The facile ET reactions of 1a and the panchromatic multi-channel absorption properties of 1a-RA makes it appealing as new generation of paramagnetic dyes.

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Design and synthesis of triazole-linked carbohydrate-based self-assembling materials <u>Mohit Tyagi</u>, Nikhil Taxak, Prasad V. Bharatam, K. P. Ravindranathan Kartha National Institute of Pharmaceutical Education and Research, Mohali

Triazole-based macrocycles possessing different pseudo-symmetry elements have been synthesized using the CuAAC reaction. The formation of the macrocycles was accompanied by their spontaneous self-assembly leading to solids with distinct layered structures as confirmed by scanning electron microscopy and supported by Density Functional Theory. The self-assembling property of the product and the "on water" reaction media seemed to form the driving force for the reaction in t-butanol-water system.(1) These observations on click-macrocycles led us to check the self-assembly of carbohydrate based click-conjugates. Molecules are diversified into two series. In series I, various click glycolipids are made, which exists in the form of long rods in water.(2) In series II, hexanoate protected click-glycoclusters are made, which shows gelation abilities in long chain hydrocarbons. These phase selective gelators can have a potential application in oil spill recovery from water. Solvent-free mechanochemical glycosylation is used for the scalable preparation of required propargyl glycosides, which serves as a building block for making self-assembling materials.(3)

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(P24)

A Bodipy based Mechanochromic Self-assembly

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Mechanochromic fluorescent materials belong to a class of "smart" materials which found extensive use in sensors (1), memory chips (2) and security inks (3). There are several examples highlighting the external-force-induced multicolored luminescence color change of mechanochromic molecules (4). We have earlier demonstrated the application of stimuli responsive supramolecular assemblies for erasable thermal imaging, authentic security labeling and currency counterfeit prevention (5). Herein we represent a novel self-assembled bodipy based p-phenyleneethynylene derivative which shows interesting mechanochromic luminescence

changes in the film as well as in the powder states. Upon shearing the powdered sample or the film, emission switches to green from yellow. This process could be reversed back by either exposing the sample towards heat or solvent vapor over certain period of time or just by leaving the assembly for a couple of days. When the recovery exposure period is insufficient to reorganize the molecular assembly completely to the initial stage, the process could be tuned into a third luminescent stage. The study reveals how the control of molecular self-assembly influences the luminescent properties of mechanochromic materials. Changing the mode of molecular assembly through mechanical force is the important step in achieving different luminescent colors from a single molecule. Details of the chemistry and experimental studies will be presented.

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(P25)

A common platform for Enzyme assay in a hydrogel matrix using Lanthanide luminescence

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Enzymes are the key protagonists of living organism catalyzing thousands of biochemical reactions involved in all biological processes. Variation of some enzyme levels in human body is associated with certain diseases, so many of them are routinely assayed for the diagnosis of diseases. Enzymes are usually assayed by a variety of methods using colorimetry, fluorimetry, radioisotopes, etc., but with time luminescent lanthanide-based probes are gaining prominence due to their unique features. Each lanthanide has its unique emission characteristics along with a long lifetime. Time delayed measurements, therefore, allow one to detect lanthanide luminescence thereby eliminating background emission from short-lived species. In this work we report a simple and efficient assay system for sensing enzymes. Our group has recently reported the sensitization of Tb3+ and Eu3+ by 2,3-dihydroxynaphthalene and 1-hydroxypyrene, respectively. By covalently modifying the functional group of the sensitizers we have designed novel "pro-sensitizers", and have successfully assayed carbohydrate metabolic enzyme splucosidase and β -galactosidase, fat metabolic enzyme lipase, protein metabolic enzyme chymotrypsin and alkaline phosphatase, an enzyme hydrolyzing phosphate ester in biological reactions. These results will be presented in this poster.

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A simple coumarin derived Michael addition based Turn-ON probe to detect CN⁻ ions Syed S. Razi, Priyanka Srivastava, Rashid Ali, Ramesh C. Gupta, Arvind Misra*

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A coumarin derived fluorogenic chemosensor has been synthesized and tested to detect anions in aqueous media through a Michael adduct reaction based chemodosimeter approach. Probe having coumarin group upon interaction with cyanide undergo nucleophilic addition reaction to form Michael adduct derivative in which fluorescence intensity enhances significantly, "turn-on" by intramolecular charge transfer (ICT) OFF-ON mechanism. The UV-Vis absorption spectra of probe (10 µm) in water shows a broad low energy ($n \rightarrow \pi^*$) intramolecular charge transfer (ICT) electronic transition band at 375-380 nm ($\varepsilon = 1.85 \times 104 \text{ M}$ -1 cm-1) and a high energy band at ~265 nm ($\varepsilon = 2.0 \text{ x } 104 \text{ M-1 cm-1}$) and upon excitation at 380 nm showed very weak broad emission band at ~ 450-500 nm. Upon addition of different anions (0-100 equiv) such as F-, Cl-, Br, I, SO_4^2 , CO_3^2 , SCN, AcO, CN, N_3^2 , S^2 , $H_2PO_4^2$ (sodium salt) to a solution of probe absorption spectra showed relatively high selectivity for cyanide in which absorption of electronic transition band, centered at 380 nm decreased with a blue shift of ~10-15 nm and a new band appeared at 366 nm ($\varepsilon = 1.1 \text{ x } 104 \text{ M-1 cm-1}$). This could be attributed to the formation of new entity in the medium. The color of probe solution switched-on to fluorescent blue which is visible to the naked-eyes. Job's plot analysis revealed a 1:1 stoichiometry for an interaction between probe and cyanide along with detection limit 0.21 µM (5.2 ppb). The mode of interaction has been confirmed by NMR, Mass, FTIR and DFT data analysis. Figure: The plausible mechanism of sensing of probe with CN- ion and change in color solution upon interaction with anions.

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(P27)

A blue fluorescent probe to detect Hg²⁺ in partial aqueous environment <u>Rashid Ali</u>, Priyanka Srivastava, Syed S. Razi, Ramesh C. Gupta and Arvind Misra* Banaras Hindu University

An efficient intramolecular charge transfer fluorescent probe bridging benzhydryl moiety and dansyl fluorophore through piperazine unit has been synthesized and characterized. The photophysical behavior of synthesized probe has been analyzed in the presence of different cations in aqueous acetonitrile solution. The probe shows quenching in the emission intensity on addition of Hg^{2+} metal ions only. The probe has shown sensitivity to detect Hg^{2+} ion selectively over other tested cations at 20 nM level. The probable mode of binding of Hg2+ through the nitrogen and oxygen atoms of piperazine and sulfonamide of dansyl fluorophore has been established by spectral data analysis. The mechanism of fluorescence quenching is due to electron transfer proven by the frozen temperature experiment.

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(P28)

New Paradigm in Band Gap Fine Tuning via Axial- and Core-Substitution Reactions of Naphthalenediimides:

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Band gap engineering has gained considerable attention due to its pivotal role for the preparation of modern organic semiconducting and light harvesting materials. It plays a vital role for the development of materials like dye sensitized solar cell, NIR absorbing/emissive dyes, nonlinear optical systems, polarity sensors, etc.[1] Naphthalenediimides (NDIs) are electron deficient organic building blocks that have been employed in several fascinating applications such as airstable n-type semiconductors, electron transfer (ET) reactions, [2a] generation of persistent/stable radical cations/anions,[2b] NIR absorption/emission dyes, etc.[2] Recently our group reported the synthesis of novel NDI-TTF-based molecules having low HOMO-LUMO energy band gap (~1.7 eV) and investigated their mixed-valance charge transfer properties. These observations encouraged us to pursue the band gap fine tuning in NDIs via core-substititon reaction with electron rich aryl amines. Herein we report new paradigm in the design and synthesis towards extremely narrow band gap (~1.1 eV) molecules by tuning the electronic properties of various dendrimeric units of aryl amine donor moiety.[2e] The secondary-bonding interactions (intraand intermolecular non-bonded interactions) in organochalcogen compounds have been utilised in handful of cases for tuning the HOMO-LUMO gap and for controlling supramolecular selfassembly.[3,4] Herein, we have integrated chalcogens (E = S, Se, Te) along with donor O or N atoms in NDI via core-substitution reactions. We have investigated the ability of E towards the modulation of the optical properties of these molecules due to the σ^* orbitals of E and the nonbonding orbitals of ONDI (i.e. $n \sigma^*$) interaction.

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(P29)

Colorimetric and highly selective turn-on fluorescence sensor for F[−] ion <u>Thangaraj Anand</u> and Duraisamy Chellappa MADURAI KAMARAJ UNIVERSITY

Construction of sensory molecules for recognition and sensing of anions is a forefront research topic in chemistry. Among the range of biologically important anions, $i\neg$, uoride is of particular interest due to its established role in preventing dental caries, important role in bone-growth and as a treatment for osteoporosis. An acute intake of a large dose or chronic ingestion of lower doses of F- can result in gastric and kidney disorders, dental and skeletal fluorosis, urolithiasis in humans, and even death. For these reasons, an improved method for the detection and sensing of F- with high selectivity is of current interest in the chemosensor research field. Herein we report a novel aminobenzohydrazide derivative PTAM was synthesised and evaluated as a chemoselective F- sensor utilising $\hat{a} \in Turn$ - $ON\hat{a} \in$ fluorescence measurements. There was a gradual fluorescence enhancement and colour change from colourless to orange colour upon the addition of one equivalent of fluoride ion; other anions had no significant effect of fluorescence. The receptor shows excellent selectivity and sensitivity towards F- over the other anions. Moreover, PTAM can be utilized for the quantification of fluoride ions in living systems.

(P30)

Triazole based ratiometric fluorescent probe for Zn²⁺ and its application in bioimaging <u>Murugan Iniya</u> and Duraisamy Chellappa MADURAI KAMARAJ UNIVERSITY

An efficient fluorescent chemosensor 4-((2-hydroxynaphthalen-1-yl)methyleneamino)-3-phenyl-1H-1,2,4-triazole-5(4H)-thione, based on triazole has been designed by condensing 2-hydroxy-1-napthaldehyde with amine, appended to 1,2,4-triazole unit. The probe displays excellent selectivity and sensitivity in both absorbance and fluorescence detection of Zn2+ over other essential metal ions. The nature of fluorescence behaviour of receptor upon addition of Zn2+ has been obtained from Density Functional Theory calculations. Imaging experiment indicates that probe works effectively for intracellular Zn2+ imaging with good cell permeability and biocompatibility.

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Fluoride induced Spirocyclic ring opening of fluorescein and its applicability in cell imaging BALASUBRAMAIAN VIDYA, GANDHI SIVARAMAN and DURAISAMY CHELLAPPA

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Fluorescein based highly selective fluorescent probe was rationally designed and synthesised as a novel fluorescein sensor for fluoride anion. Fluoride, the smallest anion with high charge density as unique chemical properties and its recognition and detection are of growing interest because it is associated with nerve gases and the refinement of uranium used in nucleus weapons manufacture. Equally fluoride plays an important role in the human life owing to its established role in dental care and clinical treatment for osteoporosis and deficiency are over exposure to fluoride causes gastric and kidney disorders dental and skeletal fluorosis urolithiasis in human and even death. Hence forth noble methods for detection of fluoride have become a hot topic. The receptor exhibits high sensitivity and excellent selectivity towards fluoride ion in aqueous buffer solution.

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C3-symmetric Cyanostilbenes: Dynamic, cooperative assemblies with Aggregation Induced Enhanced Emission (AIEE)

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Self-assembly of organic $\tilde{I}\in$ -conjugated chromophores offers a platform for the creation of ordered nanostructures.[1] A common drawback of these assemblies is 'concentration quenching' that limits their applications. We hereby present the self-assembled properties of novel C3-symmetric cyanostilbenes (C3-CSBs) where 1,3,5 benzenetricarboxamide (BTA) core leads to ordered assemblies through three-fold hydrogen bonding[2] and cyanostilbene moieties stack to form highly emissive aggregates by Aggregation Induced Enhanced Emission (AIEE) mechanism.[3] By incorporating chiral (s)-citronellyl chains in the C3-CSB system, we could investigate the cooperative self-assembly through circular dichroism (CD) measurements. Also, the combination of chirality and AIEE makes it an ideal system for studying Circularly Polarized Luminescence (CPL) in the self-assembled state.[4] Though cyanostilbenes are well-studied for AIEE, the exact mechanism of this phenomenon is yet to be unravelled. We aim to investigate this mechanism by exploiting the dynamicity of C3-CSB which, by itself, is a novel pursuit.

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(P33)

A New Benzimidazol Based Simple, Yet Highly Sensitive Receptor for Fluoride and Aceate ions DR. BOLIN CHETIA

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The sensing of anionic species by artificial receptors is an expanding area of supramolecular chemistry due to their significance in a number of biological, chemical, and environmental processes. The rate of growth in the development of anion binding agents is slow as compared to cation binding agents due to vast structural diversity of anions. Although two strategies, one based on cationic ligands, such as polyammonium, guanidium, quaternary ammonium etc, and the second on neutral ligands, such as amides, ureas, thioureas, calix[4]pyrroles and related ligands have been developed, the neutral ligand based receptors are given more importance due to $\hat{a}\in$ naked eye $\hat{a}\in$ TM sensing properties. Considering the importance of anion receptors, some newly developed benzimidazol based structurally simple synthetic receptors, capable of detecting different anionic guests in very low concentrations is presented here. The binding of anionic guest species with these receptors are studied using UV/Vis spectroscopy, fluorescence spectroscopy and 1H-NMR techniques. The results indicate that these receptors can be used as a chemical shift and optical modification based sensor for the detection of different anions. Anion binding studies using UV/Vis spectroscopy revealed that these receptors exhibit high selectivity for fluoride over other anions.

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(P34)

Fluorescein tagged highly sensitive and selective chemodosimeter for Fluoride Neeraj, Sharad Kumar Asthana, Rahul Prajapati, Ramesh, Abha Pandey, Siddharth Vishwakarma, Isha Sanskriti, Shweta, Uzra Diwan, Virendra Kumar, Ajit Kumar and K. K. Upadhyay *

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Anions play a variety of roles in living systems in the form of various chemical transformations. At the same time, they are also relevant for many industrial processes and are often found as harmful pollutants. The recognition and sensing of anionic analytes have emerged as a key research theme within the generalized area of supramolecular chemistry for last few decades. Herein we synthesized a highly sensitive chromofluorogenic chemodosimeter for fluoride ion based on a fluorescein conjugated probe. The proposed chemodosimeter showed excellent selectivity toward fluoride. When fluoride was added to the acetonitrile solution of the probe, a fast colorimetric along with fluorescence turn-on change was observed, thus allowing fluoride to be discriminated from other halide and carboxylate anions by the naked eye.

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(P35) Synthesis and Characterization of Novel Ferrocenyldendrimers with glucose as a core unit Avyavoo Kannan and Perumal Rajakumar*

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Dendrimers¹ are highly branched macromolecules and possess the ability to adopt with the other molecules through physical bonding. Dendrimer finds vast applications in the various fields, especially ferrocene and carbohydrate conjugates are known to have chemical and biological properties. They also find applications as electrochemical probes in electrochemical sensors², biosensors³ and in nanochemistry⁴. Show antimalarial activity⁵ and cytotoxic activity⁶. The ferrocenyldendrimers bearing glucose as a core unit have been synthesized via Cu(I)-catalysed click chemistry. The present investigation is mainly focus on the synthesis of ferrocenyldendrimers with glucose as a core unit. The electrochemical properties of such dendrimers will be also presented in detail.

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(P36)

Supramolecular Signatures of Adenine-Containing Organostannoxane Assemblies

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In view of the structural diversity of organostannoxanes, we were intrigued by the possibility of decorating them with nucleobases to investigate the supramolecular signatures that can detected in such systems. In particular, we were interested in capturing rare or unique nucleobase supramolecular motifs. To test this concept we chose to assemble different types of organostannoxanes that contained adenine units. In view of this interest, we have synthesized and structurally characterized [t-Bu2Sn(μ-OH)L]2•7H2O, [(n-Bu3Sn)3L3•H2O]n, [{n-Bu2Sn}2(μ3-O)(μ-OH)L]2, and [{n-Bu2Sn}2(μ3-O)L2]2 [LH = 3-(N9-adeninyl) propanoic acid]. The use of organotin motifs to support adenine peripheries has been successful. All the compounds reveal rich supramolecular structures as a result of intermolecular adeninea^^adenine interactions. Most remarkably, in [(n-Bu3Sn)3L3•H2O]n we have observed a new trimeric supramolecular signature for adenine in the form of a trimeric motif made up of alternating Watson-Crickâ^'Watson-Crick and Hoogsteenâ^'Watson-Crick interactions.

(P37)

Synthesis and characterization of dendrimers with Schiff's base as surface group via convergent approach

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Dendrimers¹ (Greek: dendron tree) are one of the most exciting classes of macromolecules that have sparked significant interest in recent years from synthetic, structural and functional points of view. Dendrimers are nanometer-sized, perfectly branched molecules with fascinating symmetrical architectures. In recent years, conjugated dendrimers and bioactive molecules show increased therapeutic efficacy and the delivery of bioactive molecules, is of great importance. Esters of anthranilic acid especially methyl anthranilate found versatile applications.2 Herein, we report the synthesis of Frechet type dendrimers containing anthranilate derived Schiff's base by means of O-alkylation methodology.³

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(P38)

Cyclotricatechylene based Self-Assembled Molecular Capsules: Synthesis and Guest Entrapment

Pardhasaradhi Satha, Giriteja Illa, Chandra Shekhar Purohit

Molecular capsules are a subject of great interest because of their potential utilizations in various fields of chemistry, medicine and nano science. They have been utilized as nano vessel for reactions and targeted drug delivery in recent years. Cyclotricatechylene (CTC) is a bowl shaped molecule in its crown structure. It has six phenolic groups as potential hydrogen bond donors. In this work, we utilize the hydrogen bonding capability of CTC to generate the supramolecular capsules1 with heterocyclic molecules such as 4,4'-bipyridine, pyrazine, 2,2'-bipyridine and 1,10-phenanthroline. One of these capsules was studied for guest entrapment. Planar molecules like naphthalene and pyrene were trapped inside its cavity without breaking the capsular assembly. These capsules were studied in solid state by X-ray crystallography.

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(P39)

Synthesis and Properties of Nonaromatic [20]Porphyrin

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Porphyrins are 18π aromatic macrocycles consisting four pyrroles that are connected in a coplanar fashion at their α -carbon atoms through four methine carbon bridges. The simplest higher homologue of 18π porphyrin (1.1.1.1) is the 20π expanded porphyrin macrocycle which contain an extra methine carbon between one of the methine and α -pyrrolic carbons. Thus, the 20π expanded porphyrin consists four pyrroles connected through five methine bridges and can be represented as [20] porphyrin (2.1.1.1). The nonaromatic $4n\pi$ porphyrinoid macrocycles are generally unstable [1]. However, recently several $4n\pi$ based antiaromatic stable expanded porphyrinoids with 24, 28, 32, 36, 40, 48 and 64π electrons were synthesized and structurally characterized [2]. Here we prepared core modified homoporphyrins by introducing two thiophene moieties in place of two pyrroles. The stable 20π dithiahomoporphyrins (2.1.1.1) which are the first members of the nonaromatic $4n\pi$ based expanded porphyrin macrocycles were prepared from [2+2] Macdonald condensation of butene-2,3-diyl-bisthiophene-2,5-diyl-bis(pmethoxyphenylmethanol) and different meso-aryl dipyrromethanes under mild acid catalyzed condensation. The dithiahomoporphyrins are non-aromatic as confirmed by various spectroscopic techniques. The synthesis, X-ray structure and spectroscopic properties of dithiahomoporphyrins will be presented in the poster.

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(P40)

Synthesis and Properties of BF2 and B(OR)₂-complexes of Smaragdyrins <u>Hemanta Kalita</u> and Mangalampalli Ravikanth* Department of Chemistry, Indian Institute of Technology, Bombay- 400 076, India

Smaragdyrin is a pentapyrrolic 22π -electron system bearing two direct pyrrole-pyrrole bonds. Smaragdyrin has received tremendous attention in recent years due to its significant photophysical and electrochemical properties [1]. Meso-triaryl 25-oxasmaragdyrin, which shows rich photophysical properties was synthesized using [3+2] MacDonald type condensation of meso-aryl dipyrromethanes and 16-oxatripyrrane under mild acid catalyzed condition [2]. The meso-triaryl 25-oxasmargdyrin was used for BF2-complexation where the BF2 unit was complexed with dipyrromethene moiety of 25-oxasmaragdyrin 1 [3]. Alkyl and aryl group substitution can be done on the boron center of the BF2-unit of the macrocycle using simple reaction conditions which greatly influence the absorption and redox properties [4]. Recently our group has synthesized the hydroxy substituted boron complex of oxasmaragdyrin which finds application in fluoride sensing [3]. We successfully synthesized B(OR)2 complexes of 25oxasmaragdyrin using BF2-oxasmaragdyrin as the key precursor under simple reaction conditions [5]. In the first part of the poster, we present the synthesis and properties of alkyloxy and aryloxy substituted boron complexes of smargdyrin. Although meso-triaryl 25oxasmaragdyrin and its derivatives showed novel photophysical properties, the functionalization of meso-triaryl 25-oxasmaragdyrin was found to be difficult because of the less reactivity of the Î²-pyrrole and Î²-furan protons. Functionalization of mono-meso free smaragdyrin is a significant approach to improve the electronic properties of the macrocycle. Since the free meso position of the macrocycle is reactive towards electorphilic and nucleophilic reactions, the limitation of functionalization of meso-triaryl oxasmaragdyrin can be overcome by using mono-meso-free 25oxasmargdyrin 2. In the second part of the poster, the functionalization of mono meso-free 25oxasmaragdyrin [6] and the synthesis of some selected derivatives using the functionalized BF2oxasmaragdyrins will be presented.

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(P41)

Crystal structure and supramolecular interactions in Mn(II) and Cu(II) complexes involving bioactive phenanthroline ligand

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Complexes of 1,10-phenanthroline and its derivatives are of great interest since they exhibit numerous biological activities such as antitumour, anti-candida, antimycobacterial, antimicrobial activities. It is well recognized that non-covalent interactions play a very important role in chemistry and biochemistry like functionalization of proteins, interaction of metal complexes with DNA, chemical sensors, etc.^{1,2} A few new metal-organic compounds has been synthesized by reacting M(II) salts with Phenanthroline (Phen) in presence of benzoate or substituted benzoates in aqueous medium and are characterized. Single crystal structures have been determined and solved. Phen ligands are coordinatedorthogonally to the metal centre forming distorted octahedral geometry. The benzoic or substituted benzoic acid hydrogen bonded dimer is encapsulated by inversion related two hosts within the cavity. The C-H…Cl and C-H… π interactions play the key role in constructing the 3D packing of the structures. The structure, thermal stability, magnetic behavior and bioactivity of the compounds have been investigated.

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(P42)

Crystal structure and properties of a complex with supramolecular architectures [Ni₂(pdc)(μ-pdc)(H₂O) ₅].2H₂O

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Supramolecular coordination solids are of great interest due to their potential applications in many areas, such as microporosity, electrical conductivity, molecular magnetism, linear optical behavior and catalysis. A new supramolecular metal-organic compound of composition $[Ni_2(pdc)(\mu-pdc)(H_2O)_5].2H_2O$ has been synthesized and characterized by elemental analyses, infrared (IR) spectrosopy, UV-vis spectroscopy, thermogravimetric (TG) analysis, and single crystal X-ray diffraction. The two pdc ligands are deprotonated in the complex. Both pdc²⁻ ligands are coordinated in a tridentate manner to one cobalt atom; one of the two dipic²⁻ groups also acts as a bridging ligand to the pentaaqua-Co(II) unit. Both of the two Co(II) ions exhibit distorted octahedral geometry. Hydrogen bonding between coordinated water and the carboxylate oxygen atoms of the dipic²⁻ links the binuclear cobalt molecules to form a one-dimensional chain. The water molecule which hydrogen bonded to three complex molecules stabilizes the chain structure. In addition, there are C–H···O hydrogen bridges between the pyridyl C–H and coordinated carboxyl oxygen atoms of the pdc ligands.

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(P43)

Aromatic Ring Cleavage of o-Aminophenols by Nonheme Iron(II) Complexes: Functional Model of o-Aminophenol Dioxygenases

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The catabolic pathway of o-nitrophenol proceeds through o-aminophenol followed by oxidative C-C bond cleavage to form 2-amino muconic acid semialdehyde which subsequently loose a water molecule to afford 2-picolinic acid.[1] 2-Aminophenol-1,6-dioxygenase (APD), a nonheme iron enzyme isolated from Pseudomonas Pseudoalcaligenes, catalyzes the C-C bond cleavage of o-aminophenols.[2] Furthermore, the degradation of 3-hydroxyanthralinate to quinolinate under aerobic conditions is catalyzed by 3-hydroxyanthranilate-3,4-dioxygenase (HAD).[2] Both APD and HAD are members of the superfamily of nonheme iron enzymes with the '2-His-1-carboxylate' facial triad motif and bear functional similarity with extradiol-cleaving catechol dioxygenases. To develop a mechanistic understanding of the reaction catalyzed by APD and HAD, a series of biomimetic iron(II)-o-aminophenolate complexes supported by tripodal N4 donor ligands were synthesized and characterized.[3] The model complexes undergo aromatic C-C bond cleavage of the coordinated o-aminophenolates during the reaction with dioxygen and functionally mimic the reactions catalyzed by APD and HAD. Proton plays an important role in directing the regioselective C-C bond cleavage. The influence of structural and electronic

properties of substituents on aminophenolate ring on the reactivity of iron(II) complexes and a possible C–C cleavage mechanism will be presented.

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(P44)

Nano Dispersion of 3D Cd(II) Co-ordination Polymer: Synthetic Blood Plasma Anticoagulant

Darsi Rambabu, Abhimanew Dhir,* Chullikkattil P. Pradeep*

Co-ordination polymers are synthesized by organic linker, which possesses donating groups (e.g. carboxylate) normally at both the ends with metal ion. They have wide variety of applications like gas storage, catalysis, adsorption, magnetism and sensors. However, their application in the field of biological sciences is still limited and need to be explored. Co-ordination polymers have a large surface area and may acquire hydrophobic and hydrophilic nature. Therefore, these surface properties of co-ordination polymers can be utilized for evaluating the recognition behavior toward different proteins. The protein adsorption on solid surfaces driven by different hydrophobicity like van der Waals and is а known phenomenon. forces Thus, with aim to develop new co-ordination polymer for synthetic anticoagulant we designed, synthesized and characterized new fluorescent Cd(II) 3D coordination polymer 3∞{Cd (NDC) (QN)}1 (RAM 1) utilizing 2,6 naphthalene dicarboxylate (NDC) and quinoline (QN) as ligands and cadmium as metal ion. Naphthalene and quinoline are utilized because of their fluorogenic nature and have shown potential applications in biological process. The Cd(II) ions are selected as they are good metal connector because of their high coordination affinity and cadmium in complexed state exerted a favorable anti-tumor effect in cancer cells. The polymer has been fully characterized by single X-ray analysis. The nano dispersion of RAM 1 behaves as an artificial blood plasma anticoagulant. The details of the synthesis, characterization techniques and the anticoagulant behavior of RAM 1 will be presented in the symposium.

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(P45)

Deiodination of Iodothyronamines by Iodothyronine Deiodinase Mimics Santanu Mondal and Govindasamy Mugesh

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The thyroid gland, a major hormone secreting gland in human endocrine system, produces thyroxine (T4). A group of selenoenzymes iodothronine deiodinases (IDs) deiodinates T4 into

biologically active hormone T3 and biologically inactive rT3, 3,3'-T2 to balance thyroid hormone (TH) concentration throughout the body. Besides deiodination, THs also undergo decarboxylation to form iodothyronamines (TnAMs).Recently, naphthalene-based sulfur and/or selenium containing molecules have been developed as functional mimics of ID-3. In our present study, the effect of decarboxylation of THs on the inner-ring deiodination has been investigated. Some new mimics have been designed and synthesized in order to increase the deiodination activity. TnAMs undergo much slower deiodination than THs by ID-3 mimics. This has been explained by means of charge on the iodine atoms, halogen bonding interaction and some kinetic parameters like order and activation energy. Intermolecular interactions in solution have been found to play a crucial role in deiodination of THs and TnAMs by ID-3 mimics.

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(P46)

Slow release of Cu(II)-based potential cancer chemotherapeutic agent using carrier protein HSA: Validated by high performance liquid chromatography (HPLC) technique <u>Mehvash Zaki</u>, Mohd Afzal, Ahmad Asim, Mohammad Usman, Sartaj Tabassum Department of Chemistry, Aligarh Muslim University, Aligarh-202002, U.P India

New potential cancer chemotherapeutic Cu(II) drug entity (1) derived from indole–3–propionic acid and 1,10 phenanthroline was synthesized and single-crystal X-ray diffraction study reveals that each Cu(II) ion has slightly distorted square planar geometry bounded by two carboxylate O atoms from IPA-1 ligand and two N atoms from phen ligand. In vitro DNA binding studies revealed phosphate oxygen binding of 1 with DNA duplex in the minor groove and inhibited Topo–I activity at a remarkable IC50~20 μ M concentration. To understand the drug–protein interaction of which ultimate molecular target was DNA, the affinity of 1 towards HSA was also investigated by the spectroscopic and molecular modeling techniques and further examined by time dependent HPLC experiment which revealed that bonded drug with protein was slowly released in the presence of DNA. The SDS–PAGE analysis of 1 at varying concentration showed efficient photoinduced protease activity and mechanistic investigation revealed the site–specific oxidative cleavage of HSA which is relatively rare in the literature. Furthermore, complex 1 exhibited remarkably good cytotoxicity against human cancer cell lines (GI50 values<10 μ g/ml), and live HeLa cell imaging studies of 1 clearly showed its nuclear specific localization into the cells.

(P47)

Mixed Ligand Zn (II) Complexes as DNA Condensing Agents Lalita B. Rane, Anupa A. Kumbhar* Department of Chemistry, University of Pune

Two mononuclear zinc (II) complexes $[Zn(L-His)(NIP)]NO_3$ (1) and $[Zn(acac)_2(NIP)]$ (2) where L-His = L-Histidine, acac= acetylacetone, NIP- 2 naphthylimidazo (f) 1,10 phenanthroline have been synthesized and characterized by elemental analysis, IR, 1H NMR, and ESI-Mass spectroscopy. Gel retardation assay, atomic force microscopy (AFM) and dynamic light

scattering (DLS) studies show that both the complexes induce the condensation of originally circular plasmid DNA under physiological conditions. Effect of structural variations on DNA - binding and –condensing properties and cytotoxicity of these complexes was assessed.

(P48)

Remote Substituent Effect of Ruthenium(II) Complexes on Non-covalent DNA Binding, pH Dependant DNA Cleavage, BSA Interaction and Cytotoxicity <u>SOMASUNDARAM SANGEETHA</u> and MARIAPPAN MURALI* DEPARTMENT OF CHEMISTRY, NATIONAL COLLEGE (AUTONOMOUS), TIRUCHIRAPPALLI-TAMIL NADU

Biological activities have been discovered for the most well explored ruthenium complexes of which two are currently in clinical trails; Ru(III) KP1019 and NAMI-A. Also Ru(II)-arene complexes have been developed. All these drugs were designed to obtain activity through covalent binding of the metal center to DNA. Non-covalent interactions with DNA and other macromolecules are observed in nature and are of great importance. Thus a series of Ru(II) complexes of the type, [Ru(bpy)2(L1/L2/L3)]PF6 (1-3), have been isolated. The coordination geometry around Ru(II) is distorted octahedral with planar salicylaldimine moiety containing dangling pyridine. 1H NMR spectra throw light on the nature of bonding and conformations. The non-covalent interaction of 1-3 with CT DNA has been explored and DNA binding affinity is moderate intercalative (1) and groove (2 and 3) binding. Interestingly, all the complexes exhibit pH dependent DNA damage; at which damage is greatest correlates well to the pH environment of cancer cells. The interaction between BSA and 1-3 is consistent with static quenching and the conformational changes of BSA observed. CD spectra of BSA in the absence and presence of 1-3 were similar in shape, predominantly alpha-helical. Docking studies support the experimental results. Complex 3 exhibits higher cytotoxicity against breast cancer due to distant methyl groups at dangling pyridine, potency similar to cisplatin, 1.5 times higher than 5-fluorouracil.

(P49)

Monitoring Cellular Uptake and Cytotoxicity of Copper (II) Complex Using a Fluorescent Anthracene Thiosemicarbazone Ligand

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Thiosemicarbazone derivative of anthracene (ATSC, anthracene thiosemicarbazone 1) and its copper(II) complex (CuATSC, 2) have been synthesized and characterized by spectroscopic, electrochemical and crystallographic techniques. Interaction of 1 and 2 with calf thymus (CT) DNA has been explored by using absorption and emission spectral methods and viscosity measurements reveal partial intercalation binding mode. Their protein binding ability has been monitored by quenching of tryptophan emission using Bovine Serum Albumin (BSA) as a model protein. Further, their cellular uptake, in vitro cytotoxicity testing on HeLa cell line and flow cytometric analysis has been carried out to ascertain the mode of cell death. The cell cycle analysis indicated that 1 and 2 cause cell cycle arrest in sub-G1 phase.

(P50)

Photocytotoxic Oxovanadium(IV) Complexes of Polypyridyl Ligands

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Oxovanadium(IV) complexes [VO(pyphen/pydpz)(L)]Cl₂ (1-4), where L is 1,10-phenanthroline (phen, 1 and 3) and dipyrido[3,2-a:2',3'-c]phenazine (dppz, 2 and 4), are prepared and characterized. The crystal structure of [VO(pyphen)(phen)](ClO4)2 (1a) shows pyphen in meridional binding mode and phen binds to the axial-equatorial positions of the VO²⁺ moiety in a distorted octahedral VIVN₅O geometry. The one-electron paramagnetic, 1:2 electrolytic complexes show a d-d band within 720-750 nm in DMF and exhibit an irreversible V(IV)/V(III) redox response near -0.85 V vs. SCE in DMF-0.1 M TBAP. The complexes exhibit excellent binding strengths to ct-DNA and efficient DNA photocleavage activity in near-IR light forming •OH radicals. Complexes 2-4 show remarkable photocytotoxicity in human cervical carcinoma (HeLa) cancer cells in visible light (400-700 nm) via apoptotic pathway. FACS analysis of the HeLa cells treated with 4 shows photo-induced cell death as observed from the sub G1 peak.

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(P51)

Impact of Co-ligands on the DNA interactions and BSA binding activity of bipyridine based copper(II) complexes

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The copper(II) complexes $[Cu(bpy)_2(ClO_4)](ClO_4)$ (1), $[Cu(bpy)_2(CH_3COO)](ClO_4)$ (2), $[Cu(bpy)_2(Cl)](ClO_4)$ (3), $[Cu_2(bpy)_2(OH)](ClO_4)_2$ (4) and $[Cu_2(bpy)_2(OH)(H_2O)(CH_3COO)]$ $(ClO_4)_2$ (5) (where bpy = bipyridine) have been synthesized and characterized. The single crystal X-ray study showed that the complex 3 crystallize in a monoclinic P21/n space group and the other complexes (1, 2, 4 and 5) crystallize in triclinic P-1 space group. The mononuclear copper(II) complexes (1-3) show one quasi-reversible cyclic voltammetric response and the binuclear complexes (4 and 5) show two quasi-reversible one electron reduction near cathodic region in DMF assignable to the Cu(II)/Cu(I) couple and Cu(II)Cu(II)/Cu(respectively. Binding interaction of the complexes with calf thymus DNA (CT DNA) investigated by absorption studies and fluorescence spectral studies showed good binding affinity to CT DNA in the order as follows: 5 > 4 > 3 > 2 > 1. Complexes (1-5) also exhibits good binding propensity to bovine serum albumin with relatively high binding constant values. DNA cleavage studies of the complexes showed efficient oxidative cleavage in the presence of 3-mercaptopropionic acid as reducing agent through a mechanistic pathway involving formation of singlet oxygen as the reactive species. The complexes were also screened for antimicrobial activities which indicate that the complexes exhibited similar activity to that of standard drugs.

(P52)

Cu(I) and Cu(II) complexes of thiosemicarbazone: Synthesis, structure and study of anticancer activity

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Thiosemicarbazones have received considerable attention since the discovery of their cytotoxic activity against cancer cell and bacteriostatic effects [1]. The biological properties of thiosemicarbazones are often related to metal coordination, the lipophilicity is modified by coordination and the metal complex can be more active than the free ligand as the metal complex can be a vehicle for activation of the ligand as the cytotoxic agent [2]. Cancer cells have shown to take up greater amounts of copper than normal cells, [3] and Cu metabolism has been linked to angiogenesis and metastasis [4]. Therefore, development of compounds that chelate Cu has become a therapeutic strategy showing significant promises [4]. To extend these observations, at present, an attention is focused on the synthesis, characterization, X-ray crystal structure of copper complexes of different thiosemicarbazone ligands and study of their cytotoxic activity against HeLa cell line.

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(P53)

Ethoxo bridged dioxidodivanadium(IV) complexes featuring azo ligands: Synthesis, structure and study of reactivity

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Azo compounds have gained paramount attention due to their use in the dyeing industry and involvement in the inhibition of DNA, RNA, and protein synthesis, nitrogen fixation, and carcinogenesis [1]. Transition metal complexes of azo dyes have been well documented but the vanadium complexes of azo ligands still remain scarce [2]. The presence of vanadium in biological systems, its insulin-enhancing action [3] and anticancer activity [4] has driven a considerable amount of research. Keeping the wide applicability of azo complexes in mind [5] and the immense biological and catalytic application of vanadium complexes, we have synthesized and characterized some new dinuclear oxidovanadium(IV) complexes featuring azo dyes as coordinating ligands and have explored their biological activity.

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(P54)

Interaction of flexible binuclear ruthenium (II) polypyridyl complexes with DNA <u>Sushma B.Singh</u>, Avinash S.Kumbhar and Ayesha Khan Department of Chemistry, University of Pune

DNA condensation into compact structures, threading intercalation, conformational change in DNA is essential for gene therapy and cell imaging. Several organic polymers are studied for DNA aggregation and condensation such as cationic lipids, peptides, polyamines, polysaccharides, spermidine and dendrimers. Few mononuclear Ru (II) polypyridyl complexes have exhibited potential tools for gene delivery, cell imaging probe etc, but binuclear complexes of high cationic charge with diverse chemical structures are less explored. Therefore a series of binuclear ruthenium (II) polypyridyl complexes using flexible bridging ligand has been synthesized and characterized. The interaction of these complexes with DNA is studied by UV-Visible and Fluorescence spectroscopy. Orange flocculent material is observed with increment of DNA in metal complex –DNA titration. These DNA aggregations are further studied by fluorescence microscopy and transmission electron microscopy. The interaction of complex with CT-DNA shows peculiar honey comb like structure observed by fluorescence microscopy.

(P55)

ENHANCEMENT OF CYTOTOXIC ACTIVITY BY AQUATION OF CHLORIDO COMPLEXES [(P-CYM)RuX(PZ4LUT)]n+ AND [{(P-CYM)RuX}2(µ-PZ4LUT)]n+ TOWARDS HUMAN CANCER CELLS

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Herein, we report the synthesis, characterisation and anticancer activity of mononuclear [(p-cym)RuCl(pz4lut)]Cl (1) and dinuclear [{(p-cym)RuCl}₂(μ -pz4lut)]Cl₂ (2) and their corresponding aqua derivatives [(p-cym)Ru(H₂O)(pz4lut)](ClO₄)₂(3) and [{(p-cym)Ru(H₂O)}2(μ -pz4lut)](ClO₄)₄ (4) (p-cym = 1-isopropyl-4-methylbenzene) comprising of bis(pyrazol-1-yl)methane based heteroscorpoinate ligand α , α , α' , α'' -tetra(pyrazol-1-yl)-2,6-lutidine (pz4lut). All complexes have shown dose dependent suppression of cell viability with moderately good IC50 values ranging from 35 – 92 μ M for chlorido and 3.5 – 20 μ M for their

corresponding aqua derivatives in human breast (MCF7), lung (A549) and colon (HCT116) cancer cell lines. It is notable that significant enhancement of cytotoxic activity (10 times) is achieved through mere aquation of chlorido complexes against colon (HCT116) cancer cell line.

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(P56)

New chloro-bridged dinuclear nickel(II) and copper(II) complexes: Structural characterization, DNA binding, cleavage and apoptotic activity

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A new class of chloro-bridged dinuclear nickel(II) and copper(II) phenolate complexes (1 & 2) was synthesized from 2-((2-(piperazine-1-yl)ethylimino)methyl)-4-bromophenol (HL). The molecular structure of the complexes, $[(NiHL(CH3OH)_2)_2(\mu-Cl)]$ (Cl)₃.(H2O)₂, 1 and [(Cu(HL)Cl)2(µ-Cl)]Cl.(H2O)7, 2 was confirmed by single crystal XRD technique. The geometry around the metal ions in the complexes 1 & 2 are distorted octahedron and distorted square pyramidal, respectively. The ESI-MS result of the complexes exhibit peaks corresponds to mononuclear species, because the chloride bridge (µ-Cl) is easily breakable. Variable temperature magnetic studies of the complex 2 express the presence of a strong intramolecular antiferromagnetic interaction between the copper(II) ions with the magnetic exchange constant – 2J values of 228 cm-1. The binding studies of the complexes 1 & 2 with CT DNA were examined and, intercalative/electrostatic interaction mode was strongly proposed. Both the complexes exhibit better nuclease activity against pBR322 DNA. The IC50 value of the complex 2 against hepatoma cancer (Hep G2) cell lines is comparable with that of cisplatin indicating that the complex may act as an effective anticancer drug in time and dose-dependent manner. To find the extent of nuclear chromatin cleavage, propidium iodide (PI) staining and comet assay have been employed.

(P57)

Metallation of Proteins

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Metallation of protein is the study of interaction between metal ion and protein. Metal ions are important in the biological systems, as they have several roles viz; maintenance of ionic balance, binding with proteins and DNA molecules. Almost one half of all proteins are associated with a particular metal ion for its structure and functions.1 Metallation can also used to study proteinprotein interactions. Some of the examples of proteins which have been studied for metal binding are albumin, globulin, lysozyme and lectins; the sugar binding proteins. Because of the critical roles of these metal cofactors in protein function, many studies have been carried out to understand the factors governing metal binding and selectivity in metalloproteins.2 However, when the 3-dimensional structures of proteins are being examined, there seems to be several potential metal ion binding cores formed by the presence of one or more of the side chains of His, Lys, Asp, Glu and/or Cys.3 It would be of great interest to explore the potential of such sites for metal ion binding. Since such metal ions in the matrix of protein are expected to show unusual reactivity and thereby one can generate artificial metalloenzymes of the corresponding protein. The effect of metal ions on the secondary structure of these proteins, overall change in conformation and other properties of the proteins were studied by using different methods, including spectroscopy, microscopy and calorimetry. Our spectroscopy studies of metallation covers data from fluorescence, UV-Visible absorption, circular dichroism and MALDI-TOF, microscopy work encompasses that of AFM, SEM and TEM and the calorimety studies includes the isothermal titration calorimetry. In this poster we would like to present the results of the metallation of different proteins.

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(P58)

Synthesis, characterization, DNA binding and cleavage studies of macrocyclic binuclear copper (II) complexes containing ferrocenyl unit

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The interactions of transition metal complexes with DNA have been a subject of intense research in the field of bioinorganic chemistry, ever since the discovery of cis-platin as an anticancer agent. However clinical drawbacks of cis-platin, which include acquired resistance and the limited spectrum of the anticancer activity, gave an impetus to develop alternative transition metal complexes which are less toxic and more effective for chemotherapeutic application¹. Many ferrocenyl derivatives shows good results as anti-tumor agents and some of them are now in clinical trials. Jaouen et al² synthesized several ferroenyl derivatives based on the structure of tamoxifen and hydroxyl tamoxifen. Several derivatives of polyphenolic compounds containing ferrocene moiety can act as more potent anticancer agents. In continuation of our earlier studies3, here we report a series of new binuclear Cu (II) complexes.. Ferrocenyl moiety containing macrocyclic ligands and complexes were prepared from condensation of 1,1-diacetylferrocene di hydrazone with 2,6-diformyl-4-methyl phenol and various diamines in presence of metal salts. The Complexes were characterised using IR, ESI-Mass, electronic absorption and elemental analysis. The DNA binding and cleavage and cancer (HeLa) cell line studies of the binuclear complexes were investigated. All the binuclear Cu(II) complexes are found to be effectively promote the hydrolytic cleavage of plasmid pBR322 DNA under and aerobic conditions. The interactions of complexes with calf thymus DNA were studied by absorption, fluorescence spectroscopic techniquies and Viscometric method.

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(P59) Biochemical behaviour of newly synthesized multinuclear complexes of molybdenum <u>Vinay Kumar Srivastava</u> Department of Chemistry D.S College, Aligarh 202001

Molybdenum is only second row transition element known to possess defined Biological functions and has been identified as cofactor in a variety of Bacterial, plant, Mammalian and NonMammalian enzymes. Multinuclear complexes of Molybdenum with dithiocarbamates have been synthesized. The strong metal binding properties of dithiocarbamates are directly related with the presence of donor sulphur atoms (L----->M) which primarily determine the nature of the metal that can be bound and the strength of complexes formed. The purity of complexes have been checked by various physical and analytical measuements. Physico-chemical methods like IR,FT NMR, Electronic spectral studies and Single X -ray diffraction techenique have been used to findout the Geometry of the synthesized complexes. Enzyme inhibition activity and cytotoxicity studies of complexes also reported under different conditions. The invitro Biocidal studies revealed that Molybdenum complexes are potentially active against Bacterial and Fungal species and exhibit greater Biocidal effect as compared to the ligand fragments.

(P60)

Lower/upper rim derivatives of calix[4]arene as organogelators and hosts for molecules/ions

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Supramoleculaar organogels are interesting soft materials that have received particular attention due to their fascinating properties and promising practical applications in various fields, such as sensors, tissue culture, drug release and self-healing materials. There are very limited number of reports that focused on the doping or release of guest molecules in the gel state in comparison to the host–guest chemistry in solution state. Non covalent interactions play a crucial role in the entire gelation phenomenon which include hydrogen bonding, ï °â€¦ï °, electrostatic interactions, vander Waals forces etc. In this scenario, calixarene derivatives would be of justifiable choice to opt for the gelation studies because they can provide all afore mentioned interactions via a well functionalized groups on the calix platform. Thus we have synthesized a cholesteryl derivatized calixarene (L1) that can gel variety of solvents e.g. CH3CN, acetone, MeOH, DMF, and DMSO. This calix scaffold form gel instantatneously and that can be even reversible to sol by heating at ~45- $50\hat{A}^{\circ}C$. Gelation can be done by doping with some dyes and fluourescent molecules also. Studies are underway for drug encapsulation and their release. Whereas L2, which is tetra benzimidazole derivative on the upper rim has a bowl like architecture which showed greater quenching with TNT when compared to its nitro analogues which retain its sensing ability of TNT vapors in the solid state when coated over SU-8 cantilever by change in its piezo resistivity. On the other hand, in the quest for ion recognition we synthesized a 1, 3-bis triazole linked phenylene derivative of calix[4]arene (L3) that showed to be highly sensitive and selective toward Mg^{2+} through enhancement in its fluorescence intensity by ~ 70 folds among all the metal ions studied. The binding of Mg²⁺ was also confirmed by absorption, electron spray mass spectrometry and 1H NMR studies. AFM studies showed that spherical featured L converts into metal ion aggregates in presence of Mg^{2+} . This in

situ generated fluorescent complex $\{L^{3+}Mg^{2+}\}$ exhibited to be non-fluorescent in presence of phosphates.

(P61)

Synthesis, Characterization and DNA Binding Studies of Novel Ruthenium(II)-Platinum(II) Polypyridyl Complex

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Platinum chemotherapeutics based upon the success of cisplatin remain the first point of call for the treatment of a variety of tumor types, including ovarian cancers; however, the issue of drug resistance remains one of the greatest challenges in modern, non-targeted chemotherapy. Accordingly, there is great interest in the anti-cancer properties of metal complexes, particularly those able to interact with DNA. Mixed metal complexes consisting of ruthenium light absorbers and a cisplatin unit represent an emerging class of bioactive molecules of interest as anti-cancer agents. We have synthesized a novel ruthenium(II)-platinum(II) polypyridyl complex and characterized by standard spectroscopic methods. Its DNA binding behavior was studied by UV-Vis, Luminescence spectroscopy, and viscosity studies. Cytotoxicity and anti-proliferative activity was tested against the human ovarian cancer cell line. Detailed studies reveal that this reagent is anti-proliferative rather than cytotoxic and thus, operates via a significantly different mechanism to cisplatin.

(P62)

Hetero-metallic trigonal cage shaped dimeric Ni₃K core complex of L-proline ligand: Synthesis, structural, electrochemical and DNA binding and cleavage activities S. Nagasubramanian, A. Jayamani, N. Sengottuvelan Sri Raajaraajan College of Engineering and Technology, Karaikudi , and DDE, Department of

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Hetero-metallic trigonal cage shaped dimeric Ni₃K core complex of L-proline ligand has been synthesized and characterized. Single crystal X-ray diffraction analysis showed that the hetero-metallic Ni(II)-K(I) complex has a dimeric structure with nine coordinated potassium atoms and six coordinated nickel atoms. The cyclic voltammograms of complex exhibited two successive quasireversible reduction waves at (E1pc =-1.02 V and E2pc = -1.33 V) and two successive irreversible oxidation waves (E1pa = 0.95 V and E2pa = 1.45 V) versus Ag/AgCl in DMF solution. The interaction of the complex with Calf-Thymus DNA (CT DNA) has been studied using spectroscopic techniques. The complex is an avid DNA binder with a binding constant of 3.6 x 108 M-1. The complex showed efficient oxidative cleavage of supercoiled pBR322 DNA in the presence of the reducing agent hydrogen peroxide involving hydroxyl radical ($\hat{A}^{\circ}OH$) species. As evidenced from the control experiment, DNA cleavage in the presence of $\hat{A}^{\circ}OH$ radical was inhibited by quenchers, viz. DMSO and KI. The complex showed invitro antimicrobial activity against four bacteria and two fungi and the activity is greater than that of the free ligand.

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Synthesis and characterization of CuO nanomaterials: Biological applications

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Biocompatible CuO nanoparticles were synthesized at a relatively low temperature ($80\hat{A}^{\circ}C$) for 2h using polyethylene glycol-glycerol mixture which acts as a capping agent. A detailed characterization of the synthesized nanomaterials were performed utilizing X-ray diffraction (XRD), infra-red spectroscopy (IR), thermogravemetric analysis (TGA-DTA), transmission electron microscopy (TEM) and photoluminescence (PL) The effect of annealing on the asprepared nanoparticles were studied and compared with their corresponding bulk counterpart. The synthesized nanoparticles have been screened for in vitro cytotoxicity (IC50) studies against the human cervical adenocarcinoma cell line (HeLa). The standard disc diffusion method has been used to study the antibacterial activity of the samples against the human pathogenic bacteria such as Escherichia coli (MTCC 729), Proteus mirabilis (MTCC 425) and Klebsiella pneumoniae sub sp. pneumoniae (MTCC 432).

(P64)

Theoretical Perspectives on Redox "Non-innocent" Oxazolidine-N-oxide Iron and Cobalt Nitroxide Complexes Subrata Tewary and Gopalan Rajaraman*

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One electron redox processes in ligands exhibiting non-innocent behaviour invariably leads to the generation of radical species which when coupled with redox-active metal centres can lead to strong magnetic exchange, ambiguous electronic structures and even spin-crossover (SCO).1 We have chosen two radical complexes (1) [FeII(L•)2](BF4)2 and (A) [CoII(L•)2](NO3)2 along with their two electron reduce species (2) [FeIII(L•)2](BPh4) (B) [CoIII(L•)2](BPh4) (L• = 4-dimethyl-2,2-di(2-pyridyl) oxazolidine N-oxide) to undertake an extensive theoretical study to underpin the influence and interplay of the strong magnetic exchange, the redox non-innocent behaviour and any possible spin transitions.2,3 A series of calculations establishes the low-spin character of both the metal ion as well it gives us a valuable insight into the electronic structure.

(P65)

Oxo, alkaoxo, phenoxo bridged homoleptic square based Ln_4 ($Ln^{3+}=Gd$, Tb, Dy) clusters: Synthesis, Magnetic properties

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Three new homometallic tetrameric square based μ 4-oxo bridged clusters are isolated as single crystals and the structures are solved as Gd(III)4(μ 4-O)(C1₂H₁₅NO₅)₄(CH₃OH)₂(H₂O)₂]Br₂ (1), [Tb₄(μ 4-O)(C1₂H₁₅NO₅)₄(MeOH)₄]Cl₂ (2) and [Dy₄(μ 4-O)(C1₂H₁₅NO₅)₄ (CH₃OH)₄]Cl₂ (3). These clusters were characterized by single crystal X-ray diffraction analysis and by dc and ac magnetic susceptibility measurements. All the four lanthanide ions in these complexes are occupied on the corners of a square and a μ 4-oxo group in the middle of the cluster links all the
four lanthanide ions. Although all four lanthanide ions occupy the corners of a square, they are not co-planar. Among these molecular based magnetic systems, Dy4 complex exhibits slow relaxation of Magnetization below 5K associated with single molecule magnet behavior.

(P66)

Design and synthesis of DNA and Protein Binding Ruthenium(II) complexes of Diimines for Cellular Imaging applications

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In the last few decades, due to attractive photophysical properties, much of this research has focused on complexes based on ruthenium(II) centres and, more recently, attention has turned to the use of these complexes in biological contexts. As the rules that govern the cellular uptake and cellular localisation of such systems are determined they are finding numerous applications ranging from imaging to therapeutics.1 In this work, a series of Ru(II) complexes of the type $[\operatorname{Ru}(5,6-\operatorname{dmp})_2(\operatorname{diimine})]^{2+}$ 1-3 and $[\operatorname{Ru}(\operatorname{tmp})_2(\operatorname{diimine})]^{2+}$ 4-6, where 5,6-dmp is 5,6-dimethyl-1,10-phenanthroline, tmp is 3,4,7,8-tetramethyl-1,10-phenanthroline and diimine is dipyrido-[3,2-d:2',3'-f]-quinoxaline (dpq), dipyrido[3,2-a:2',3'-c]phenazine (dppz) and 11,12-dimethyldipyrido[3,2-a:2',3'-c]phenazine (11,12-dmdppz), has been isolated and the DNA binding mode of the complexes studied by using emission and circular dichroic (CD) spectral techniques. The complex $[Ru(tmp)_2(dpq)]^{2+}$ 4 exhibits enhancement in luminescence higher than [Ru(5,6 $dmp)_2(dpq)$ ²⁺ 1 upon binding to DNA. Among the complexes, 4 exhibits the highest enhancement in fluorescence intensity upon binding to the protein bovine serum albumin (BSA). The efficiency of the complexes as fluorescent probes for detection of nuclear morphology and proteins has been evaluated by using fluorescence microscopy. Remarkably, 4, which shows strong hydrophobic forces of interaction when bound to DNA and protein, acts as fluorescent probes for detection of nuclear components in the head, and proteins in the tail, of sperms.

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(P67)

Design, Synthesis, Characterization and In Silico molecular docking studies of Tetraaza Macrocyclic Chelating Agent

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The use of cyclic polyamine compounds as ligands for metals has expanded over years. Interest in the coordination chemistry of these chelators is due in part their relevance in bioinorganic and catalytic studies, as well as their application in biology, medicine and modern clinical imaging protocols. The macrocyclic complexes are considered to mimic the synthetic models of metalloporphyrins and metallocorrins due to their intrinsic structural properties. The macrocyclic complexes have also received special attention because of their mixed soft–hard donor character and versatile coordination behaviour and their pharmacological properties, i.e., toxicity

against bacterial growth. Macrocyclic ligands form metal complexes more thermodynamically stable and also kinetically more inert. Acyclic ligands do not usually require harsh condition for complexation but they are more prone to release off the metal in-vivo because of transmetallation by endogenous metal ion competition or transchelation by endogenous ligands (eg. phosphates). A tetraaza mono-thia macrocyclic chelator $[C_{10}H_{20}N_4O_2S]$ has been synthesized and characterized by IR, NMR (1H & 13C) spectroscopy and ESI-Mass spectrometry. DFT study based on B3LYP method with 6-311G**(d,p) basis set for all atoms by Gaussian 03W programme which results dipole-moment, vibrational frequency and optimized structure of chelating agent. Energy, dipole moment and point group of optimized structure was found - 1160.9941 a.u., 10.0831 Debye and C1. In silico study (molecular docking) of ligand with proteins OSC, HMGCR of human and mouse gives significant results in terms of free energy of binding, inhibition constant , VdW+H-bond+desolvation energy, electrostatic energy, total intermolecular energy and interaction surface which concludes this compound showed good binding affinity with these proteins (which are potential enzyme of cholesterol biosynthetic pathway), so have potential ability to reduce high cholesterol level by binding these proteins.

(P68)

VARYING ELECTRONIC STRUCTURAL FORMS OF RUTHENIUM PHENANTHRENEQUINONOIDS Abhishek Mandal and G. K. Lahiri*

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The intricate mixing of the frontier orbitals of ruthenium and of biochemically relevant quinonoid moieties renders such systems with redox non-innocently behaving ligands as prototypical models to study electronic structural aspects.1 These could result in complex phenomena such as valence tautomerism or redox induced electron transfer (RIET) at the metalquinonoid ligand interface, yielding an intermediate resonance situation instead of any specific configuration. In this regard, the electronic structural features as well as potential applications in catalysis of ruthenium-o-benzoquinonoid derivatives have been widely investigated in combination with varying ancillary ligands. However, ruthenium complexes of 9,10phenanthrenequinone and 9,10-phenanthrenequinonediimine derivatives are relatively limited.2 In this context, a variety of bis(acetylacetonato)ruthenium complexes [Ru(acac)₂(Q1-3)], incorporating redox non-innocent 9,10-phenanthrenequinonoid ligands (Q1 = 9 10-=9,10-phenanthrenequinonediimine, phenanthrenequinone, Q2 Q3 9,10 phenanthrenequinonemonoimine) have been characterized structurally, electrochemically and spectroscopically.3 The electrochemically generated redox states for the three complexes have been further analyzed by UV-vis-NIR spectroelectrochemistry and by EPR for the paramagnetic intermediates in conjunction with DFT and TD-DFT calculations.

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(P69)

Diruthenium Complex of "Nindigo", a Ligand Trying to Remain Innocent <u>Prasenjit Mondal</u> and G. K. Lahiri*

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Diruthenium complexes of potentially non-innocently behaving bridging ligands have become rewarding subjects of electron transfer research1 because they offer a readily analyzed alternative between a (Class II or Class III) mixed-valent metal-metal configuration with a superexchanging bridge versus a homovalent dimetal arrangement with an oxidized radical bridge. A recent addition to the set of bis-chelating unsaturated bridging ligands has been the (R-Nindigo)n system, $H_2(R-Nindigo) = indigo-N,N/-diarylimine, derived from the indigo$ structure.2

Thus, the present deliberation involves the first structurally characterized nindigo bridged diruthenium complex {(-Nindigo)[Ru(acac)_2]_2} (1)3 (H₂(Nindigo) = indigo-N,N/-diphenylimine and acac- = 2,4-pentanedionate). The metric parameters of 1 suggest a neutral-acceptor bridge containing coupled s-trans configurated -diimines which are coordinated by two ruthenium(II) centers. 1 exhibits a very intense MLCT absorption band at 630 nm (= 66800 M⁻¹ cm⁻¹) and a weaker near-IR band at 1120 nm (= 3000 M⁻¹ cm⁻¹) in CH3CN solution. The electronic structural aspects of reversible one-electron reduction and oxidation steps have been investigated by experimental and theoretical calculations.

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(P70)

Activation of C-H Bonds by High-Valent Iron Complexes: A Computational Investigation Azaj Ansari

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The experimental work on iron catalyzed ortho-hydroxylation shows that regioselective hydroxylation of aromatic acids with hydrogen peroxide proceeds readily at room temperature in the presence of iron(II) complexes with ligands like [FeII(TPA)(CH₃CN)₂](OTf)₂ where TPA=tris-(2-pyridylmethyl)amine and [FeII(BPMEN)(CH₃CN)₂](OTf)₂ where BPMEN=N,N'-dimethyl-N,N'-bis(2-pyridylmethyl)ethane-1,2-diamine).^{1,2} In this comprehensive study, we have investigated the ortho-hydroxylation of aromatic compounds by iron complex and reactivity of two different BPMEN and TPA ligands with iron complexes by using hybrid density functional theory.³ Two distinct isomers of the FeIII-OOH species are modelled where the O---O bond is found to cleave exclusively either via heterolytic (FeV=O) or via homolytic (FeIV=O) fashion. Apart from having favourable formation energies, the FeV=O species also have significantly less barrier height compared to the corresponding FeIV=O species for the aromatic

ortho-hydroxylation reaction. The transient FeV=O prefers an electrophilic attack on the benzene ring. A large thermodynamic drive for the formation of a radical intermediate is encountered in the mechanistic scene and this intermediate substantially diminishes the energy barrier required for the C-H bond activation. The spin density distribution and the frontier orbitals of the computed species have been utilized to rationalize the oxidative abilities of these oxidants and to shed light on the preferred choice of the mechanistic pathways for the aforementioned catalytic transformation. Our results predicted that the reactivity in BPMEN is higher than TPA ligand with iron complexes during the course of ortho-hydroxylation of aromatic compound.⁴ Our computed results are in excellent agreement with the experimental results.

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(P71)

Dimer- to Dodecametallic-Manganese SMMs - A DFT Study

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SMMs aroused a large interest in the co-ordination chemistry community, due to its varied potential applications such as memory storage device, molecular refrigeration, spintronics, quantum computing. The studies on the 3d-clusters pave us the parameters, total spin (S), axial anisotropy (D) and along with these, strong exchange interaction between the metal centres is found to govern the spin-reversal barrier but the unique SMMs with practical applicability towards the classical magnets remains unexplored. Ever since the exploration of magnetic properties of {Mn12} clusters, several 3d-3d, 3d-5d, 3d-4f, 4f-4f, 3d-5f, 5f-5f clusters are reported till date. The theoretical exploration of the magnetic properties will help in the betterment of the way the problems are approached and in this regard, we have explored magnetic properties of several Mn(III) clusters using DFT methodology. Apart from extracting the different exchange pathways and mechanism which underline the nature of exchange interaction is explored. The parameters which control the sign of the exchange have been detected and in addition magneto-structural correlations are developed to find the ways to amplify the parameter in a positive direction.

(P72)

SYNTHESIS, STRUCTURE AND INTERATION OF COBALT COMPLEXES OF N, N'-DONOR HETEROCYCLIC BASES WITH BIOLOGICAL TARGETS Anirban Chandra and Ashis K. Patra* Department of Chemistry, Indian Institute of Technology Kanpur

Transition metals complexes possess a variety of advantages over organic compounds and can act as versatile platforms for the development of potent therapeutic and diagnostic agents.1 Metal complexes have wide range of geometries and structural diversity, accessible oxidation and electronic states and tunable thermodynamics and kinetics of ligand substitution. Bioactive

luminescent transition metal complexes are suitable as sensing and imaging probes.2,3 Several cobalt complexes have been reported to exhibit antiviral, antibacterial and anticancer activities.4,5 Despite of their versatile biological effects and different mechanism of actions, cobalt complexes received less attention as metallodrugs compared to other metal complexes.

Herein, we will highlight the synthetic methodologies, characterization, spectroscopic and electrochemical properties, and structures and of a series of cobalt complexes having planar N, N'-donor heterocyclic bases, viz. dipyrido[3,2-a:2',3'-c]phenazine (dppz), terpyridine (tpy) and their substituted analogs. We will describe the effect of these substituents towards electronic and structures of the complexes. Detailed binding interactions of these complexes with potent biological targets (e.g. nucleic acids, proteins) using various spectroscopic methods will be described.

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(P73)

Robust Three-Dimensional Chiral Metal Sulfates: Synthesis and First Principles Calculations

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NISER

Two chiral three-dimensional metal sulfates of the compositions, $[NH_4]_8[Mn_8(SO_4)_{12}]$, (1) and $[NH_4]_8[Mg_8(SO_4)_{12}]$, (2), have been synthesized under hydro/solvothermal conditions and studied from first principles. Both the two compounds 1 and 2 are isostructural and crystallize in the cubic chiral space group P2 (1)3. In the presence of NH⁴⁺ cations, the frameworks of 1 and 2 have three-dimensional structures formed by corner sharing of metal octahedra and sulfate tetrahedra through M-O-S linkages, which leads to a pinwheel arrangement of metal octahedra surrounded by six sulfate tetrahedra. First Principles calculations suggest stable crystalline phases of similar stability for both the compounds before and after de-ammoniation. However, upon de-ammoniation while compound 1 largely preserves its crystal structure and keeps its interstitial voids unencroached by the framework, compound 2 evolves into a more compact configuration with higher bulk-modulus and smaller unit-cell volume.

(P74)

Synthesis, characterization, properties and structure of lanthanide complexes with Ureabisdithiocarbamate

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In the present study, the disodium salt of bisdithiocarbamate has been prepared from urea, with carbon disulfide under strong alkaline medium use a sodium hydroxide. Dithiocarbamates highly versatile mono-anionic chelating ligands which form stable complexes with all the transition

elements and also the majority of main group, lanthanide and actinide elements. Its possessed good chelating ability for various metal ions. Metal complexes of Urea bisdithiocarbamates was synthesized with Lanthanides. The prepared ligand and complexes were characterized by chemical analysis, IR spectra, electronic spectra, conductivity and magnetic measurements. The electronic spectra and magnetic measurements indicate that some of the complexes have square planer, tetrahedral and the other contain octahedral geometry.

(P75)

Preparation, characterization and anti-microbial activity of transition metal complexes of hydrazine and trimesic acid

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Hydrazinium metal trimesiate hydrates of composition $(N_2H_5)_2M(Htms)22H_2O$ where, $(M = Mn, Co, Ni, Cu, Zn or Cd; H_3tms = trimesic acid)$ have been prepared and characterized by elemental analysis, IR, electronic and EPR spectral, X-ray powder diffraction and thermal studies. IR studies revealed the coordination of $N_2H_5^+$ cation as a monodentate in the complexes. On the basis of electronic spectral studies, an octahedral geometry is assigned for all the prepared complexes. During heating, dehydration and dehydrazination followed by decomposition of the organic component produced the corresponding metal oxide as the final residue. The coordination of water has been substantiated by thermal analyses. The X-ray powder diffraction patterns show isomorphism among similar set of complexes. These complexes have been screened for their antimicrobial activities against a few bacteria and fungi.

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(P76)

Synthesis, characterization and magnetic properties of an oxido-bridged tetranuclearcopper(II) complex

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Multinuclear complexes of copper(II) are of great interest to the researchers because of their diversity in structural aspects as well as their applications in the field of magnetism, biology, catalysis, etc. [1]. Multinuclear complexes can be prepared by choosing appropriate ligand systems with suitable donor atoms. Mononuclear complex can be transformed into multinuclear complex by the judicial choice of bridging ligand, metal ion and reaction conditions. Cu(II)–Schiff-base complexes have found numerous applications in catalysis, biological sciences, magnetism, etc. Cu(II) complexes produce variable and distorted geometries and have a simple electronic configuration. These properties encourage the researchers to explore magnetic properties of multinuclear metal–organic complexes of Cu(II). Schiff-base complexes with μ 4– oxo–Cu4 moiety have been reported in literature and magnetic properties of these complexes have been extensively studied [2]. A copper(II)-Schiff-base complex, [Cu₄(O)(L)₂(CH₃COO)₄]

(1) where HL = 4-methyl-2,6-bis(((2-tri-fluoromethyl)phenyl)methyliminomethyl)phenol has been prepared. It has been characterized by elemental analysis, different spectroscopic methods and single crystal X-ray diffraction study. Single crystal analysis of 1 reveals that four copper atoms coordinate with one oxygen atom forming a distorted tetrahedron in which oxygen atom occupies the center and copper atoms reside in the corners. Temperature dependent magnetic property of complex 1 shows strong antiferromagnetic interactions among the copper atoms.

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(P77)

RhCl₃-mediated N(sp²)–H, C(sp²)–H and C(sp²)–O bond Activations: Novel NNO pincer complexes of Rh(III) from symmetrical NNN Azo-aromatics

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Platinum group metal based non-carbon pincer complexes are currently the subject of much attention due to their immense reactivity toward organic transformation. The framework of a pincer ligand can be modified in terms of both steric and electronic factors to modulate the property of a metal center. Notably, nitrogen-based 'NEN' type pincers are based basically on the di-imine fragments due to their easy accessibility. While the analogous ligands with strong π -acidic azo chromophores are rarely cited. This has prompted us to explore the novel NNN type pincer incorporating two azo moieties in place of two inime functions. Notably, the reaction of RhCl3 with 1 leads to an ineresting chelation viz. NNO instead of expected NNN type, where one ortho C-H bond is activated in situ following the incorporation of O atom to furnish a phenolato function. Here we report a novel class of rhodium(III) complexes 2 with NNO pincer based on the organic framework 2,5-bis(aryllazo)-1H-pyrrole 1. X-ray diffraction study reveals the metal center is asymmetrically ligated with the symmetrical ligand (C2v) and furnishes two contiguous five-membered chelate rings. It should be noted that N-H bond of pyrrole group is activated during metalation. The one azo group (dN-N = 1.303 (1) Å) is ligated with the metal while the other (dN-N = 1.269 (1) Å) remains free. Complexes exhibit rich spectral properties in the UV-vis region with multiple low energy bands near λ max 464, 652 and 698 nm. Theoretical investigation reveals that these excitations are ILCT in nature. The complexes containing redoxinert rhodium(III) display one quasi-reversible oxidative couple couples near 1.0 V vs SCE along with reductive couples. The former response can best be described as ligand center oxidation from the EPR and DFT studies, indicating noninnocent nature of NNO pincer.

(P78)

Investigations on the mesomorphic potential of aryl-ether substituted aroylhydrazones: a structure-property relationship study

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The present study addresses the first example of synthesis and characterization of a series of liquid crystalline compounds based on the aryl-ether substituted aroylhydrazones. These compounds, which have different alkyl chains (alk; formyl, methyl, dimethyl, decyl) at alkylidene moiety (n=10, 12) and di- and tri- alkoxy (n= 6-16) benzylidene derivatives, are non mesogenic in nature. Mono-alkoxy benzylidene derivatives (n=6-16) display SmC mesophase with very low thermal mesophase range. In the nickel (II) and copper (II) complexes of these ligands, only methylidene (alk=formaldehyde) derivatives (n=6-16) showed SmC mesophase with wide temperature range with glass transitions at higher temperatures, as evidenced by polarising optical microscopic (POM) and differential scanning calorimetric (DSC) studies. Furthermore, the temperature dependent Raman studies of nickel (II) methylidene derivative with n=16 indicate that intramolecular rotations of benzyl-ether bond occur during phase transitions. As suggested by molecular optimization using DFT calculations by Gaussian 09 package combined with the experimental data, the non- coplanarity of benzyl-ether linkage at aroylhydrazone moiety does not confer the proper geometric requirements for the complexes to exhibit mesomorphic properties.

(P79)

Synthesis, Characterisation and Application of TM doped and neat MnO₂ nanoparticles for Stoichiometric benzylic oxidation

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Nano-sized MnO₂ Catalysts having the composition M_xMn_1 -xO₂ (where M=Co, Fe, Ni, Cu, Ag and X=0 and 0.10) were prepared by co-precipitation method. The samples prepared were then characterised by X-ray diffraction, FTIR spectroscopy, and BET surface area studies. The surface morphology of the catalysts was studied by AFM and SEM. IR data of the samples showed characteristic Mn–O bands. The catalytic study was carried out with benzyl alcohol as the model alcohol to test for catalyst reactivity and selectivity. The popularity of benzyl alcohol as a probe molecule results from its extremely high reactivity and the limited number of side products. In this experimental studies stoichiometric amount of MxMn1-xO2 nanoparticles were used to carry out benzylic oxidation using Molecular oxygen as the oxidant. The obtained results would discussed be in the poster with reasoning.

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(P80)

Five new mononuclear Zinc(II) complexes with tetradentate N-donor Schiff base: Syntheses, structures and influence of anionic coligands on luminescence behaviours and supramolecular interactions

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The present report describes the syntheses, crystal structures and luminescence properties of five mononuclear complexes, $[Zn(L)Cl]ClO_4$ (1), $[Zn(L)Br]ClO_4$ (2), $[Zn(L)I]ClO_4$ (3), $[Zn(L)N_3]ClO_4$ (4), and [Zn(L)(NCS)](SCN) (5), derived from the tetradentate ligand (L = N,N'-(bis(pyridin-2-yl)methylidene)propane-1,3-diamine). The geometry around the Zn²⁺ is best described as a square pyramidal structure although significant distortion towards the trigonal pyramidal geometry is noticed especially for halide complexes, of them chloro (1) and bromo (2) complexes are isostructural and isomorphous. The stabilization of the crystal lattices is maintained by interesting, relatively strong hydrogen bonds and $\pi \cdots \pi$ interactions which lead to various supramolecular architectures. All the five complexes show photoluminescence property and their trend can be correlated with the position of apical anionic coligands in the spectrochemical series of ligands.

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(P81)

A Stable Eight-coordinate Mo(VI)-dioxo Complex by Oxidative Addition of Di-oxygen and its Catalytic OAT Function

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Oxidative addition of di-oxygen via, a net four electron transfer process at a single metal site is a rare type of chemical reaction and is primary to meet the long standing challenge of using metal catalyzed oxygen atom transfer (OAT) with direct participation of aerial oxygen. Though observed in biological systems, such a process could scarcely be mimicked in transition metal complexes in general and at mono-metallic system, in particular. Here, we introduce a rare example of metal-ligand cooperation in oxidative addition of di-oxygen in a Mo-system. Participation of ligand redox in 4e⁻ transfer process in producing a di-oxo molybdenum complex

using air is demonstrated by isolation and characterization of intermediate and end products. The end product is an eight coordinate Mo(VI) complex with a distorted square-antiprism structure and a powerful, benign oxidant in OAT processes with the use of air as terminal oxidant.

(P82)

FORMATION OF UNUSUAL POLYNUCLEAR NI(II) COMPLEXES BY 5-SUBSTITUTED TETRAZOLE LIGANDS GENERATED BY [2+3] CYCLOADDITION Manideepa Saha,^a Rajendar Nasani,^a Shaikh M. Mobin,^a Eva Rentschler,^b Suman

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Metal mediated cycloaddition reactions between organonitriles and coordinated azide contribute to the development of 5-substituted tetrazole complexes, over the years (Mukhopadhyay et al. [1]). However, limiting the nuclearity of the synthesized complex to a finite number remains a challenge in this field (Mota et al. [2]). Herein, we report the synthesis of polynuclear nickel complexes through cycloaddition starting from $[Ni(N_3)L]$ [L= p-chloro-2-{(2-(dimethylamino)ethylimino)methyl}phenol] 1. Under microwave irradiation technique, complex 1 reacts with benzonitrile, 3-cyanopyridine and 1,2-dicyanopyridine leading to the formation of $[Ni_3L_2(5-Phenyltetrazolate)_4(DMF)_2]$ 2, Ni_3L_2 {5-(3-pyridyl)-tetrazolato}4 (DMF)_2].H2O 3 and $[Ni_5L_4$ {5-(2-cyanophenyl)-tetrazolato}4 (OH)_2(H_2O)_2].3H_2O.DMF 4 respectively. The magnetic susceptibility data in the temperature range of 2 - 300 K shows dominant antiferromagnetic interactions between the nickel centres for all the complexes.

(P83)

SYNTHESIS, CHARACTERIZATION, DNA BINDING AND CLEAVAGE STUDIES OF MACROCYCLIC BINUCLEAR COPPER (II) COMPLEXES CONTAINING FERROCENYL UNIT

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The interactions of transition metal complexes with DNA has been a subject of intense research in the field of bioinorganic chemistry, ever since the discovery of cis-platin as an anticancer agent. However clinical drawbacks of cis-platin, which include acquired resistance and the limited spectrum of the anticancer activity, gave an impetus to develop alternative transition metal complexes which are less toxic and more effective for chemotherapeutic application 1. Many ferrocenyl derivatives show good results as anti-tumor agents and some of them are now in clinical trials. Jaouen et al.,2 synthesized several ferroenyl derivatives based on the structure of tamoxifen and hydroxyl tamoxifen. Several derivatives of polyphenolic compounds containing ferrocene moiety can act as more potent anticancer agents. In continuation of our earlier studies3, here we report a series of new binuclear Cu(II) complexes.. Ferrocenyl moiety containing macrocyclic ligands and complexes were prepared from condensation of 1,1diacetylferrocene di hydrazone with 2,6-diformyl-4-methyl phenol and various diamines in presence of metal salts. The Complexes were characterised using IR, ESI-Mass, electronic absorption and elemental analysis. The DNA binding and cleavage and cancer (HeLa) cell line studies of the binuclear complexes were investigated. All the binuclear Cu(II) complexes are found to be effectively promote the hydrolytic cleavage of plasmid pBR322 DNA under and aerobic conditions. The interactions of complexes with calf thymus DNA were studied by absorption, fluorescence spectroscopic techniquies and Viscometric method.

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(P84)

Formation of π -cation Radicals in Diheme Centers: Unusual Stabilization of 'U' Conformer

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Multiheme cytochromes c constitutes a widespread class of proteins with essential functions in electron transfer and enzymatic catalysis. Their functional properties are in part determined by the relative arrangement of multiple heme cofactors. Understanding the consequences of these motifs is crucial for the elucidation of the highly optimized properties of multiheme cytochromes c, but their spectroscopic investigation is often restricted by the presence of a large number and efficient coupling of the individual centers. These attractive features have prompted us to investigate on the model diheme centers as a part of our ongoing research. In the present work, we have oxidized both the Fe(III) and Zn(II) complexes of cis-1, 2-Bis(meso-octaethylporphyrinyl)ethene shepherds the formation of π -cation radicals of the corresponding trans-isomer, that have two different orientation: P-conformer and U-conformer. The crystal structure of these species provides the first structural evidence of the U-conformation of trans-1, 2-Bis(meso-octaethylporphyrinyl)ethane. The electronic, chemical and electrochemical properties of these systems will also be discussed here.

(P85)

Modulation of Iron Spins by External Stimuli: Effect of Hydrogen Bonding, Counter Ion and Interring Interactions

Dipankar Sahoo, Debangsu Sil, Firoz Shah Tuglak Khan and Sankar Prasad Rath*

Elucidation of the electronic structure of iron porphyrins is quite important to understand the function and catalytic activities of naturally occurring heme proteins. Spin-state phenomena associated with (porphinato)iron derivatives have been recognized as an important aspect of the biological control of hemoprotein function. Extensive work on model systems and hemoproteins has established that spin state of Fe in an iron-porphyrin complex is primarily controlled by the nature of axial ligands, macrocycle, and geometry around metal center. Dependence of spin on counter ions has been found rarely, particularly the anions, which are far away from metal center and not directly involved in any kind of interaction with the metal. The consequences of H-bonding, interaction with counter ion and inter-ring interactions in heme proteins on the spin state of iron centre will be discussed here.

(P86)

Syntheses and characterizations of square planar nickel(II) complexes with pendant ligands: Examples of bi-dentate bonding modes of potentially tri- and tetra-dentate Schiff bases

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The study of Schiff base ligand system is linked with many of the key advances made in inorganic chemistry. The term 'pendant ligand' is applied a to potential polydentate ligand that has additional donor groups attached to its periphery. A large number of pendant ligands are produced for a variety of different chemical applications, e.g. in enzyme simulations, for the purpose of carrying a radionuclide into a target cell, in magnetic resonance imaging reagents and for progressively more elaborate investigations for their structure/activity relationship. In the present study, four square planar nickel(II) complexes, $[Ni(L1)_2]$ (1), $[Ni(L2)_2]$ (2), $[Ni(han)_2]$ where $[Ni(L3)(NHEt_2)]$ (3) and (4), HL1 1 - (3 hydroxypropyliminomethyl)naphthalene-2-ol, HL2 = 1-(5-hydroxy-3-oxapentyliminomethyl)naphthalene-2-ol, $H_2L_3 = 2$ -(2-hydroxy-3-methoxybenzylideneamino)phenol and Hhan = 1hydroxy-2-acetonaphthone, have been prepared and characterized by elemental analyses, IR and UV-Vis spectroscopy and single crystal X-ray diffraction studies. H-bonding, C-H...pi and pi...pi interactions form supra-molecular assembly.

(P87)

Control of molecular architectures of nickel(II) complexes with the variation in the coordinating ability and acidity of the counter anions and denticity of the chelating ligands: Isolation of a novel tetranuclear nickel(II) complex with end-on and end-to-end azide

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Three nickel(II) complexes, $[Ni(HL1)_2](ClO_4)_2$ (1), $[{Ni2(L2)_2(\hat{1}_{4}^{+}1, 1-N_3)(H_2O)}(\hat{1}_{4}^{+}1, 3-N_3)(H_2O)](\hat{1}_{4}^{+}1, 3-N_3)(H_2O)]$ N_3 $N_2(L2)_2(\hat{I}_4^{+}1, 1-N_3)(H_2O)$ CIO_4 . CH₃OH (2) and $N_2(dmpn)_2(hap)_2(N_3)_2$ (3) {where HL1 3-(dimethylaminopropyliminomethyl)naphthalen-2-ol, HL2 = 2-(3-(dimethylamino)propyliminomethyl)-6-methoxyphenol, dmpn = N,N-dimethyl-1.3diaminopropane and Hhap = 2-hydroxyacetophenone} have been synthesised and characterized by elemental analysis, IR, UV-Vis and fluorescence spectroscopy and single-crystal X-ray diffraction studies. Complex 1 is mononuclear and contains square planar nickel(II). In complex 1, the Schiff base is present in its zwitterionic form. Complex 2 is tetranuclear and contains both End-On and End-to-End azide, whereas complex 3 is dinuclear and contains double end-on azide bridging. Both the complexes 2 and 3 contain octahedral nickel (II). The weak forces like hydrogen bonding, lone pair...pi/pi...pi/C-H...pi interactions lead to various supramolecular architectures.

(P88)

Rhodium(III)-triphenylphosphine complexes with NNS donor Schiffs base ligand: synthesis, electronic structure and catalysis of transfer hydrogenation of ketones and oxidation of alcohols

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The rhodium (III)-triphenylphosphine complex having general formula $[Rh(PPh_3)(L)Cl_2]$ (1) with NNS donor Schiffs base ligand (L) (L = 2-(methylthio)-N-((pyridine-2-yl)methylene)benzenamine) has been synthesized and characterized by various spectroscopic techniques. The pseudo octahedral geometry of the complex has been confirmed by single crystal X-ray study. Cyclic voltammetric study shows quasi-reversible Rh (III)/Rh(IV) oxidation and ligand based reduction in aetonitrile. The electronic structure and redox properties are supported by DFT computation. The complex acts as an efficient catalyst of transfer hydrogenation of ketones and oxidation of alcohols.

(P89)

BISPHOSPHINES WITH HETERO DONOR ATOMS: SYNTHESIS, TRANSITION METAL CHEMISTRY AND CATALYTIC APPLICATIONS IN SUZUKI CROSS-COUPLING REACTIONS

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The interesting coordination chemistry and potential applications in various organic transformations is essentially the motive behind designing various phosphorus based ligand systems and their metal complexes. Although bisphosphines with a variety of frameworks are known, the chemistry of bisphosphines based on heterocyclic backbones such as bis(imidazolyl,pyrazolyl and triazolyl)methane and N,N-bis(-bromobenzyl)-N-phenylamine, Bis(2-bromobenzyl) ether frameworks is less extensive. Copper(I) complexes of phosphines have attracted considerable interest because of their rich structural and photophysical properties[1] and also their potential applications as inexpensive materials in optoelectronics,[2] catalysis,[3] and biological systems[4]. In the present investigation, the ligands of type $C_7H_6N_4(PPh_2)_2$ [bpizm] (1), $C_7H_6N_4(PPh_2)_2$ [bppzm] (2), $C_5H_6N_6(PPh_2)_2$ (3), [C1₄H1₄O(PPh₂)₂] (4) and [C₂₀H₁₉N(PPh₂)₂] (5) have been synthesized in good yield.

A series of Pd(II), Pt(II), Ru(II), Cu(I) and Au(I) complexes of these ligands have been synthesized. In case of copper complexes diverse structural types such as monomers, one dimensional polymers, tetranuclear stairâ \in step and cubane type clusters are observed. Pd(II) complexes has shown good catalytic activity in Suzuki C-C cross coupling reactions. Further, exploration of the catalytic applications of other ligand systems and photophysical properties of Cu(I) complexes is in progress.

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(P90)

Cation Recognition by an Azo-phenol Zn(II) and Cd(II) Complexes: Selective Receptor Copper(II) ion

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More recently, metal-based receptors are developed as a class of efficient receptors which provide some important advantages over purely organic hosts by combining the structural and functional properties of metal centres with the recognition capabilities of organic ligands. The structural and geometrical flexibility of metals can provide an excellent way of organising neutral/cation/anion binding groups (e.g. hydrogen bonding moieties) for optimal host–guest interactions. In addition, careful choice of the metal centre can confer useful optical, electrochemical or catalytic properties to the receptor. This metal's organic approach to binding is used by Nature in certain enzymes and receptors. It is well conceived that in these systems, the organometallic core imparts two important features to the receptor: structurally, it preorganises the hydrogen bonding substituents for optimal interaction with the guest; in addition, the electronic and emission properties of the metal can be successfully employed as a read-out for the detection of the specific guest. In this context, colorimetric azobenzene based Zn(II) and Cd(II) metalloreceptor of type $[M(LH)_2(bpy)_2]$ where, $\{M = Zn(II), Cd(II), LH_2 = 4-(2-hydroxy$ naphthalen-1-ylazo)-benzoic acid, bpy= 2,2'-bpy) 1 and 2 were designed and synthesized. Resulting complexes are characterized using elemental analysis, spectroscopic (IR, NMR, UVvis), single crystal X-ray diffraction studies. The colorimetric sensing property of the complexes 1 and 2 by Cu(II) ion are further supported by concomitant change in their UV-vis spectra and emission spectra which were recorded in aq. DMF. The results indicate that the receptor exhibits a strong affinity and selectivity for transition-metal ions such as Cu(II) under physiological pH conditions. A detailed account of the study will be presented.

(P91)

Sonochemical synthesis and characterization of nanoparticles of Chromium(III) and Cobalt(III) coordination complexes

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The design and construction of nano-materials are an important area of research, because of the chemical and physical properties of solid material depend upon both the size and the shape of the microscopic particles1-3. The properties of inorganic nano-material depend strongly on their morphologies 4. Here, we are reporting the sonochemical synthesis of nano particles of chromium(III) and Cobalt(III) complexes. The particle size and size distribution of nanoparticles of [Cr(urea)₆]Cl₃.3H₂O and [Co(en)₃]Cl₃ have been determined by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The characterizations of these nano-sized coordination complexes were done with the help of physiochemical, spectroscopic (UV and IR) and XRD techniques.

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(P92)

SIX-COORDINATE HOURGLASS SHAPED CHROMIUM(III) COMPLEX AS AN ANION RECEPTOR FOR ANIONS: ([M(SCN)4]2- WHERE M = Zn2+, Cd2+, Hg2+)

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In recent years, anion binding by synthetic receptors is receiving increased attention in the field of coordination chemistry 1- 3. The rapid growth in this area is due to countless roles that anion play in biology, medicine, catalysis as well as contributing significantly to environmental pollution 4-7. In the present work an hourglass shaped metal-based receptor, $[Cr(CO(NH_2)_2)_6]^{3+}$, has been recognized and its binding properties with complex anions $([M(SCN)_4]^{2-}, M = Zn, Cd, Hg)$ were determined by standard UV-vis titrations in aqueous medium. The newly synthesized receptor-anion complexes were also characterized by elemental analyses and IR spectroscopy. The single crystal X-ray structure of NH₄[Cr(CO(NH₂)₂)₆][Hg(SCN)₄]2.H₂O reveals the presence of two cations, one anion and one water of crystallization. The hourglass shape cation contains twelve NH₂ groups which bind the anions through hydrogen bonding interactions (HNH...NCS) apart from electrostatic force of attractions.

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(P93)

Multifunctional Zeolitic Phosphazne Cluster Frameworks (ZPCFs) with luminescence, sorption and redox properties.

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The rapidly emerging field of Metal organic frameworks (MOFs) or porus coordination polymers (PCPs) is of upsurge interest because of their structural and topological novelty as well as their applications in gas storage, separation, electrical conduction and catalysis.1 A review of literature reveals that the designing of MOFs is mainly confined to linkers with hard donor atoms such as Bipyridine and Carboxylates. Here in we report for the first time, the synthesis of Zeolitic Phosphazane Cluster Frameworks (ZPCFs) where cyclodiphosphazane ring having soft donor P atoms acting as a bidentate linker and Cu_4X_4 clusters are acting as tetrahedral nodes. The most prominent feature of these frameworks having SOD topology is the presence of large cages

of 2.4nm diameter. This represents unique multifunctional MOFs having a combination of redox activity in addition to its photoluminiscent and porus properties.

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(P94)

Chalcogenide and Transition Metal derivatives of Triphenylphosphole- Synthesis, Structure and Photophysical properties.

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Heterocyclopentadienes of Group 15 and 16 play a prominent role in contemporary research. Many well-defined linear -conjugated oligomers for optoelectronic functions, infact have been designed from these cycopentadienes (pyrroles, thiophene, silole..etc).[1] Phospholes are superior to these heterocyclo-pentadienes since they exhibit certain characteristics which make them attractive synthons.[2] Firstly, the aromaticity of phospholes is generally much lower than that of furan, pyrrole or thiophene. Since the P-atom has a pyramidal geometry, the efficient orbital interaction with the butadiene unit is hindered. This property has an impact on the molecular engineering of the HOMO-LUMO separation of linear π -conjugated systems, since π electron delocalization along the chain is favoured when the backbone features heterocycles of low resonance energy. Secondly, unlike thiophene or pyrrole, phospholes possess a heteroatom (P with lonepair) which retains a versatile reactivity. Thus, by simple chemical modification, the HOMO-LUMO gap can be tuned. One such representative, the 1,2,5-Triphenylphosphole has been chosen due to its easy synthesis with readily available starting materials. Group 11 and platinum group metal complexes have been prepared by choosing the appropriate stoichiometry and metal precursors. Further, its chalcogenide derivatives have been synthesized and structurally characterized. After examining the photophysical properties, the ability of phosphole oxide for detection of nitroaromatics have been explored with fluorescence quenching experiments.

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(P95)

Conducting Metal Organic Framework Behaving as Schottky Barrier Diode Biswajit Bhattacharya, Dilip Kumar Maity, Debajyoti Ghoshal* Jadavpur University

MOFs are the assembly of inorganic and organic moieties with crystalline network. Extensive studies on this class of materials have done; which essentially exploit the high surface area and porosity of their structure, conducting behavior of proton in a MOF channel, magnetism, drug delivery, catalysis and sensing applications. Here we have prepared a new metal organic framework with bivalent cadmium, a bent dicarboxylate (5-hydroxy isophthalate) and an N, N'

donor 4,4'-azobispyridine (azpy) ligand at room temperature and characterized by single-crystal X-ray diffraction and other physicochemical methods. The crystal structure shows a two dimensional arrangement with azpy in the lattice. The experimental and theoretical band gap of this compound is around Eg= 2.0eV. The electrical conductivity of this compound is 1.86 Scm-1. The ab initio calculations reveal that the compound will be n-type semiconductor and its Fermi level (EF) is located much above the EF of aluminium, a precondition for current rectification. The current-voltage behavior of the compound in an ITO/Cd-MOF/Al structure exhibits non-linear behavior with an on/off current ratio in the order of ~10^2 (at ±10 V) signifying sound rectification behavior. This rectification behavior certainly suggesting the prospect of this MOF for its use as an electronic device such as Schottky barrier diode.

(P96)

Synthesis, spectroscopic and biological studies on copper(II) complexes containing equatorial-apical chloride bridges: Crystal structure of [Cu₂(μ-Cl)₂(O-2butoxyethylpyridine-2-carboximidate)₂Cl₂] R.K.Bindiya Devi and R.K. Hemakumar Singh Department of Chemistry, Manipur University Canchipur

Three new $[Cu_2(\mu-Cl)_2(O-2-alkoxyethylpyridine-2-carboximidate)_2Cl_2]$ complexes where alkoxy = methoxy, ethoxy and butoxy were synthesized and characterized by the elemental analysis, FTIR spectrum, electronic spectra, EPR, conductance, magnetic moment, powdered XRD, TGA and X-ray single crystal diffraction. The X-ray crystal structure of the complex $[Cu_2(\mu-Cl)_2(O-2-butoxyethylpyridine-2-carboximidate)_2Cl_2]$ shows that it crystallizes as centrosymmetric dinuclear species in which each of copper(II) ion is in a distorted square pyramidal structure. Magnetic field-induced partial molecular alignment has been observed in the polycrystalline samples of complex (2) and (3) when cooled in a magnetic field of 1 T at 77 K. The interaction of these complexes with Calf thymus DNA has been explored and the values of binding constant, Kb for complexes (1), (2) and (3) are found to be 1.524x103, 5.587x103 and 6.362x103 (molL-1)-1 respectively. Complexes were screened for antimicrobial activities by the agar well diffusion technique.

(P97)

Sonogashira Cross Coupling Reaction Catalyzed by Schiff Base Palladium Complex in Aqueous Media

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Transition metal catalysts, incorporated into organic or inorganic supports, can combine the advantages of homogeneous and heterogeneous catalysts ^[1]. Palladium catalyzed C-C cross-coupling reactions are the constructive reactions in organic synthesis and in organometallic chemistry, because these are primary tools for the synthesis of large variety of complex compounds ^[2]. The palladium-catalyzed coupling of terminal acetylenes with aryl and vinyl halides (Sonogashira reaction) is one of the important and widely used carbon-carbon bond-

forming reactions in organic synthesis ^{[3].} Adding in concert to this work we have successfully synthesized an ionic liquid-supported Palladium(II) complex of Schiff base moiety which was found to be a highly proficient catalyst in Sonogashira cross coupling reaction (Scheme 1). Short reaction time, effortless workup and reuse of the catalyst even up to six cycles without much loss of catalytic activity are the main advantages of our designed protocol. Details of synthesis and characterization will be shown in main presentation.

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(P98)

Fe(III) complex of phenyl substituted biuret-amide based macrocylcic ligand as peroxidase enzyme mimic : Kinetic and mechanistic studies

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We have reported the synthesis and characterization of Fe(III) complex of a biuret-amide macrocyclic ligand (1) which showed excellent peroxidase activity, huge acid stability and has very low intramolecular deactivation rate in aqueous media. In another approach, we have been able to generate a high valent FeV=O reactive intermediate from 1 in organic media (Acetonitrile) and used for oxidation of unactivated C-H bonds (cyclohexane) at room temperature. However to check the electronics effect in the tail part of the biuret moiety, we introduced N-phenyl moiety in the parent biuret-amide macrocycle ligand instead of N-Me moiety and synthesized (Et₄N)₂[FeIII(Cl)(N- phenyl-biuret-amide)] (2) successfully. Single crystal XRD data suggested that the incorporated phenyl group in complex (2) is perpendicular with respect to macrocyle plane. Detailed acid stability, inactivation parameter measurement and peroxidase activity of 2 is going on in our laboratory to decide whether substituted phenyl group has innocent or noninocent character towards electron transfer in course of the reaction. In acetonitrile medium 2 reacts with mCPBA (1:1) at room temperature gives FeV=O species that was already characterized by EPR, HR-MS. This FeV=O species can able to do hydroxylation of unactivated C-H bond like cyclohexane. Suitable findings like electronics and steric around metal center would provide a great deal in synthetic organic transformation.

(P99)

SYNTHESIS OF CARBOXY AND PHOSPHONIC ACID CORROLES FOR MATERIALS APPLICATIONS

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Except for nuclear fuel and geothermal energy in the form of geysers, our energy sources ultimately solar. Wood and fossil fuels (oil and coal) represent solar energy stored through photosynthesis. Solar energy is a clean and unlimited renewable energy source. Further, Dye-Sensitized Solar Cells (DSSC) have proven their potential as feasible energy device for solar

energy conversion. Recently, the electron donor such as triarylamine or pyrene appended porphyrins have shown remarkable performance and highest power conversion efficiencies (10-13%). Unlike porphyrins, corroles were rarely used for DSSC applications due to their synthetic difficulties. With these objectives, we focused to synthesise carboxylic/phosphonic acid substituted corroles for DSSC applications. Herein, we report the elegant synthesis and characterization of 5,10,15-tris(4'-phosphoryl/carbomethoxy/carboxyphenyl)corroles, 5,15dimesityl-10-(4'-phosphoryl/carbomethoxy/carboxyphenyl)corroles and their corresponding Cu(III) and Ag(III) complexes. The triester/triphosphoryl substituted corroles exhibited marginal triphenylcorrole (TPC) red-shift than that of whereas dimesityl mono carbomethoxy/carboxyphenyl substituted corroles are marginally blue-shifted than TPC. In this presentation, we will discuss about the elegant synthesis, spectral, electrochemical and DSSC studies of these corroles and their metal complexes in detail.

(P100)

SYNTHESIS OF MIXED β-SUBSTITUTED 'PUSH-PULL' PORPHYRINS FOR NONLINEAR OPTICAL (NLO) APPLICATIONS

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Recently considerable attention has been focused on optical limiters, with the goal of protecting sensitive optical systems and human eyes against accidental exposure to high energy laser beams. For this purpose, Porphyrins and phthalocyanines constitute a promising group of NLO compounds due to high nonlinearities upon irradiation with high intense laser light. The main advantage of porphyrins is their chemical versatility which provides a tool for tailoring the linear and NLO properties for specific applications. With these objectives, we focused to synthesize the porphyrin-based donor- π -acceptor systems for NLO applications. A new family of β -pyrrole mixed substituted [C₆H₅, NO₂, CHO, CH₂OH, Br] free-base tetraphenylporphyrins and their metal complexes [Co(II), Ni(II), Cu(II) and Zn(II)] have been synthesized and characterized. These porphyrins were examined to modulate the various properties of the macrocycle and they showed dramatic differences in their optical spectral, stereochemical and electrochemical redox properties relative to their corresponding tetraphenylporphyrins with homosubstitutents at the β -pyrrole positions.

(P101)

Synthesis and Studies on Sterically Crowded Porphyrins <u>Nivedita Chaudhri</u> Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee, India

Highly sterically crowded porphyrins are of considerable interest due to their unique physicochemical properties. Besides, they serve as model compounds of nonplanar porphyrinoids in biology. Of particular interest, the porphyrins with polyhalogen substituents have been employed as robust catalysts for the oxidative transformation of organic substrates. The synthesis and properties of porphyrins with mixed electron withdrawing substituents are less explored. The present work involves the synthesis of 2-nitro-3,7,8,12,13,17,18-heptachloro-mesotetraphenylporphyrin and their metal (Co(II), Ni(II), Cu(II) and Zn(II)) complexes. Further, we examined their optical absorption spectral and electrochemical redox properties. $MTPP(NO_2)Cl_7$ exhibited profound red-shift of the Soret (B band) and longest wavelength band energy, Qx(0,0) (~ 10 - 15 nm) relative to $MTPPCl_8$ due to strong electron withdrawing nature of nitro group. In this presentation, we will discuss about the synthesis, spectral and electrochemical properties of these porphyrins in detail.

(P102)

Synthesis and application of Zinc Oxide Nanoparticle <u>Meenakshi.M</u>, Nithya.P Vellore Institute of Technology UNIVERSITY, Vellore, Tamil Nadu.

Zinc oxide is a direct band gap semiconductor with a band gap around 3.4 eV and a large exciton binding energy of about 60 meV. ZnO occurs naturally in the form of hexagonal wurtzite-type structure and is named as Zincite. Various methods are employed for the preparation of Zinc oxide Nanoparticles, such as precipitation, hydrothermal, solvothermal, physical vapour deposition, chemical vapour deposition, laser ablation, sol-gel method, micro-wave, sonochemical and so on. However sol-gel method was found to be more promising than the others. Zinc oxide find its own application in various fields like rubber industry for vulcanisation process, sunscreen for antiseptic properties, pigments in paints, as a heterogeneous catalyst in many organic reactions and also in transparent conducting oxide layer in solar cell applications. Herein, the zinc oxide nanomaterials were prepared by the sol-gel method at various temperatures (55C, 70C, room temp) and compared with the nanomaterial obtained using the microwave method. The nanomaterial was prepared using Zinc nitrate or Zinc acetate as a precursor and dissolved in sodium hydroxide or ammonia and the reactions are carried out at various temperatures. The morphology of the sample was studied by FE-SEM and TEM. The crystal structure has been viewed by using X-ray diffractometer. The band gap of the sample has been calculated by using UV-Visible Specrophotometer. The surface area has been analysed using the BET method. Herein, the zinc oxide nanomaterials were prepared by the sol-gel method at various temperatures (550C, 700C, room temp) and compared with the nanomaterial obtained using the microwave method. The nanomaterial was prepared using Zinc nitrate or Zinc acetate as a precursor and dissolved in sodium hydroxide or ammonia and the reactions are carried out at various temperatures. The morphology of the sample was studied by FE-SEM and TEM. The crystal structure has been viewed by using X-ray diffractometer. The band gap of the sample has been calculated by using UV-Visible Specrophotometer. The surface area has been analysed using the BET method. Herein, the zinc oxide nanomaterials were prepared by the solgel method at various temperatures (550C, 700C, room temp) and compared with the nanomaterial obtained using the microwave method. The nanomaterial was prepared using Zinc nitrate or Zinc acetate as a precursor and dissolved in sodium hydroxide or ammonia and the reactions are carried out at various temperatures. The morphology of the sample was studied by FE-SEM and TEM. The crystal structure has been viewed by using X-ray diffractometer. The band gap of the sample has been calculated by using UV-Visible Specrophotometer. The surface area has been analysed using the BET method.

(P103)

Photochemical assisted synthesis of silver nano dendrites by phenothiazine and its application in amperometric sensing of nitrite

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Here in, we describe photochemical route for synthesis of silver (Ag) dendrites nanostructure using phenothiazine (PTZ) as a reductant as well as stabilizer without any extra control viz. surfactant, pH etc. This hybrid material derived from nanoscale silver capped with phenothiazine (PTZ) and its oxidation product (PTZH) has been explored for development of highly sensitive electro-sensing of nitrite ions. Further, a possible mechanism for the formation of silver dendrites nanostructure has also been proposed. The synthesized hybrid material (Ag-PTZH) has been characterized by UV-visible spectroscopy, cyclic voltammetry, transmission electron microscopy, field emission scanning electron microscopy and Xray photoelectron spectroscopy. One of the objectives of the present finding is to utilize the nanomaterials based platform for the electro-catalytic sensing of nitrite ions since dendrite nanostructure is attractive due to their high surface area to volume ratio and their high degree of connectivity throughout the structural surface. Modified electrode with hybrid material (Ag-PTZH) efficiently catalyzes the electrochemical oxidation of nitrite at the potential of 0.442 V vs. AgCl/Ag and shows linear response toward nitrite ions sensing with 2.434µA/µM sensitivity and 2.3 nM limit of detection at S/N (signal-to-noise ratio):3. This hybrid nanomaterial modified electrode offers a selective, sensitive, enzyme less electroanalytical determination of nitrite and field deployable onsite measurements where one cannot afford to carry costly equipments like ICP-OES or spectrometers.

(P104)

Synthesis and characterization of end-off mono and binuclear copper(II) complexes: DNA/BSA binding and nuclease activity

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The current research area of "inorganic chemistry" widely offers a versatile platform for the design of novel anticancer agents.¹ However the drug interactions at protein binding level significantly affect the apparent distribution volume also affect the elimination rate. Therefore clear understanding on such interactions will facilitate the design and development of new drugs of metal complexes possessing anticancer activities also with protein have received the great attention of the recent research.² Within these expectation synthesis of novel end-off mono and binuclear copper(II) complexes containing a ligand with piperazine and aliphatic, aromatic substituted diamines. Electrochemical studies by cyclic voltammetry in the potential range from - 0.5 to -1.4 V. DNA/BSA binding and DNA cleavage results of the complexes, the best activity as encountered in naphthalene substituted binuclear copper(II) complex. The binding constant value is 3.3 x 104 M-1, 5.8 x 106 M-1 for DNA binding studies in UV and Flurescent technique, 2.32 x 105 mol L-1 s-1 for the Stern-Volmer quenching constant of BSA binding in Flurescent technique. DNA cleavage studies result, maximum cleavage occurred for more aromatic substituted complex and the mechanistic investigation, singlet oxygen plays the role in the cleavage process.

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(P105)

Synthesis and anticancer activity of novel 2-(4-pyrrolidine-1-yl) phenyl benzothiazole derivatives

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In recent years, the synthesis and functionalization of benzothiazole has become a major area of focus for synthetic organic chemists because of their several pharmacological functions including antitumour activity¹, neurotransmission blockage, calmodulin antagonists and neuroprotective activity. Some phenybenzothiazole derivatives, especially interesting are 2phenyl benzothiazoles that exhibit potent and selective antitumour activity. Such as 2-(3,4dimethoxyphenyl)-5-fluorobenzothiazole (PMX 610) 1 has been shown to exhibit exquisitely potent (GI50 < 0.1 nM) and selective in vitro antitumor properties in human cancer cell lines (e.g., colon, nonsmall- cell lung and breast subpanels) of the National Cancer Institute (NCI) 60 human cancer cell line screen. 2-(4-amino-3-methylphenyl) benzothiazole (DF 203) and the 2-(4-amino-3-methylphenyl)-5-fluoro benzothiazole (5F 203)16 (2a and 2b) have been reported to poseess potent and selective in vitro antitumour properties in human cancer cell lines particularly against colon, non-small cell lung and breast cancer lines of the National Cancer Institute (NCI) 60 human cancer cell line screen. Other benzothiazole derivatives such as 4-(benzothiazol-2yl)- 4-hydroxycyclohexa-2,5-dienones 17 (PMX 464) 3 exhibited potent and selective antitumour activity concentrated in certain colon, renal and breast cancer cell lines, that acts via inhibition of the cellular redox protein thioredoxin(Trx-1).

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(P106)

3d-4f MOLECULER COOLANTS FOR MAGNETIC REFRIGERATION TECHNOLOGY

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Magnetic refrigeration technology exploits the intrinsic magnetocaloric efficiency (MCE) associated with the materials of interest. Achieving sub-milliKelvin temperature with alloy and nanoparticles are impractical. However, discrete molecular clusters can be used and the MCE of these molecular clusters is better than the alloy and/or nanoparticle system. There are several parameters (ground state, anisotropy and the excited states) required to be refined for better

magnetocaloric efficiency of molecular clusters. These clusters could be potential substitute of 3Helium which is becoming very rare and expensive. In this vein, a 3d-4f cluster $[Ni_2IIGdIII(L)_6](NO_3)$ (where $L = C_{12}H_{12}NO_2$) has been isolated and the magnetothermal properties of this complex and the importance of mass density ratio has been emphasized.

(P107)

Tuning of anisotropy by change in co-ordination environment in Co(II) tetrahedral complexes

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The magnetic anisotropy in co-ordination complexes can be very well tuned by changing the coordination environment. The change of halide groups have been known to change the anisotropy in many Mn(II), Cr(II or III) and Ni(II) complexe[1]. By simply changing the ligand with oxygen to sulphur the anisotropy can change its sign from positive to negative which is very well documented in literature[2]. In this line we have synthesised a series of isostructural complexes of general molecular formula [Co(L)(CH₃CN)X₂] (where $L = C_{13}H_{10}N_4O_1$ or $C_{13}H_{10}N_4S_1$ and X = Cl or Br) by changing the halide group or by changing the ligand with oxygen to sulphur.

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(P108)

Linking of Discrete D4R Zeolitic SBUs by ditopic ligands, 4,4'-bipyridyl-N,N'-dioxide and 4,4'-bipyridyl-N-oxide into 2-dimensional supramolecular assemblies: Application in Fluoride Encapsulation and molecular recognition <u>Aijaz Ahmad Dar</u>

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D4R zinc cubanes of 2,6-diisopropylphenyl phosphate (dippH₂) with a variety of ancillary ligands [ref] and N-donar ditopic ligands lead to formation of supramolecular 3-D assemblies[ref]. The surface area and gas adsorption potential of these MOFs are moderate and not sufficient for practical applications. Hence we aimed at design of 2-D MOFs by functionalising D4R-Zn cubanes and using 4,4'-bipyridyl-N-oxide (BIPYMO) and 4,4'-bipyridyl-N,N'-dioxide (BIPYDO) as linkers. These compounds have two types of voids, smaller intra D4R- Zn cubane and larger inter D4R-Zn cubane voids, which can be used to host molecules of different sizes. We have shown the smaller intra D4R-Zn cubane cages encapsulate fluoride ions, while the larger cages recognise and host the benzil molecules.

(P109)

Designing redox potentials for analytical applications

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The mismatch of redox potentials can often block desired redox reactions in biology, analysis and catalysis. Complexation modifies the redox potential of a redox system involving metal ions as complexing agents (ligands) bind to the two oxidation states of same metal with different binding constants thereby altering their affinities to get oxidized or reduced in the complexed state relative to their free or aqueous state. (Equation 1). E (complex) = E(aqua) - (59.16 mV) log β III / β II.....1; Where β III and β II are the stability constants of the ligand with the higher and lower oxidation state of the metal. Thus ligand effect on redox potentials is a promising phenomenon to design the redox potentials for the development of new redox reactions with aimed applications. With the choice of a suitable ligand for different metal systems, the redox potentials have been tailored for some unique analytical applications which will be presented as case studies:-

a) Iron-phenanthroline b) Cobalt-Phenanthroline c) Copper- neocuproine d) Iron-EDTA

e) Cysteine + Iron+ Phenanthroline f) Copper + Iron + neocuproine.

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(P110)

DNA binding and cleavage properties of Mono and Binuclear polydentate ligand copper (II) complexes.

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We have reported some of the side-off, macrobicyclic, macrocyclic dinuclear copper(II) and nickel(II) complexes, which avidly bind and efficiently cleave DNA under physiological conditions.1 Very recently, we have found that the bis-phenanthroline water bridged dicopper(II) complex plays a pivotal role in the DNA hydrolysis and mechanism underlying induction of cell death.2 Encouraged by the results here we report DNA-binding and cleavage properties of novel mono and binuclear copper(II) complexes [CuL(bpy)] and [Cu₂L(bpy)(ClO₄)], {L = 2-(4-hydroxy-3-methoxy-5-[3,3'-Iminobis(N,N-dimethylpropylamin-1-yl) methyl] phenyl) imidazo [4,5-f]-[1,10]phenanthroline}. The DNA binding properties were investigated using electronic absorption spectroscopy, fluorescence spectroscopy and viscosity measurement. The complexes acts as mixed intercalating/groove-binding complexes with an intercalating ligand on one metal centre and nonintercalating ligands on the other, with both flexible or rigid bridging ligands. The increased aromatic moiety in the polydentate ligand of the Cu(II) complex facilitates its potential intercalative and/or DNA major groove binding. The DNA cleavage properties of the complexes were also investigated by gel electrophoresis.

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(P111)

Synthesis, Characterization and Application of Cellulose ANSA Resin for removal of Toxic metal ions from Industrial wastewater

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A new cellulose based resin containing 1-amino-2-naphthol-4-sulfonic acid group has been synthesized by modified Porath's method of functionalisation of polysaccharides. The adsorption behavior of CANSA resin for toxic metal ions has been investigated by batch and column experiments. The prepared resin was characterized on the basis of ion exchange capacity, distribution coefficients (Kd), elemental analysis,pH titration and FT-IR spectra. Owing to large differences in Kd values of toxic metal ions at different pH, the removal and recovery of metal ions from their aqueous solutions and effluents of Bhawana Steel Industry, Jodhpur has been studied systematically. The adsorption capacity of different metal ions on CANSA resin follows the order; Zn(II)>Fe(II)>Cd(II)>Cu(II)>Pb(II). Keywords-Distribution coefficients, Ion exchange capacity, Toxic metal ions,CANSA resin.

(P112)

Synthesis, characterization of polyaniline based composite and its application for the removal of organic and inorganic pollutants

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A novel polyaniline based composite cation exchange material has been synthesized by sol-gel method and characterized by standard analytical techniques such as XRD, TGA-DTA FTIR, SEM and TEM analysis. The XRD and SEM analysis show amorphous morphology of the material which also exhibits improved ion exchange capacity along with thermal stability. The partition coefficient studies of different metal ions on the ion-exchanger were performed in DMW and Water: DMSO solutions of different concentrations. The K_d values of the metal ions show its selectivity for toxic metal ions. Quantitative separation of some important metal ions was achieved from industrial wastewater samples by using columns of this exchanger. The conducting behavior, antimicrobial activity of the material was also performed. The photocatalytic activity of this material was also investigated by using the photocatalytic degradation of organic pollutant.

(P113)

Polarity of Choline Chloride Based Deep Eutectic Solvents Ashish Pandey and Mahi Pal Indian Institute of Technology Delhi

Deep Eutectic Solvents (DESs) developed as green solvents, share many characteristics with ionic liquids (ILs) but are cheaper to make, less toxic and mostly biodegradable. An estimate of polarity of DESs is essential if they are to be used as green alternatives. Polarity of DESs is assessed through solvatochromic optical spectroscopic responses of several uv-vis absorbance and molecular fluorescence probes. Hydrogen bonding and other specific solute-solvent interactions are found to play an important role in solvatochromic probe behavior within the DESs. The cybotactic region of probe dissolved in a DESs affords information on the polarity of DESs towards solutes of similar nature and functionality.

(P114)

Selective Colorimetric Probe for Sensitive Detection, Quantification, and On-Site Analysis of Nitrite Ions in Natural Water Resources

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Nitrite ions are highly toxic reactive species and are known to cause diseases like esophageal cancer, infant methemoglobinemia, spontaneous abortion and birth defects in the central nervous system. Therefore, determination of nitrite levels is extremely important in monitoring drinking water quality and clinical diagnosis. Of the various optical methods reported, the spectrophotometric technique is simple and can be used for the visual on-site analysis. In this context, we designed a novel NIR absorbing aza-BODIPY dye,(1-4) which selectively detects nitrite ions through distinct visual color change from bright blue to intense green with a lowest detection limit (LOD) of 20 ppb. Importantly, the nitrite ions detection thus achieved is far more sensitive than the allowed levels of 1 ppm by the U.S. Environmental Protection Agency (EPA). Uniquely, this probe can be coated on a glass surface to fabricate a simple solid-state dipstick device that can be used for the visual detection of nitrite ions in the presence of other competing anions in distilled as well as natural water resources like sea, lake and river. This efficient dipstick strategy can be used as the spot test for nitrite ions in the undergraduate laboratory practicals and can also be used for the detection of nitrate ions when coupled to a simple reduction step. As far as we know, this is the first report, which demonstrates the simple, convenient, sensitive, on-site analysis and quantification of nitrite and nitrate ions through a direct method (3). Our results demonstrate that the aza-BODIPY probe is highly selective, sensitive and economically viable molecular probe that can be used for the on-site detection and quantification of the nitrite and nitrate ions under the environmental conditions (3-4).

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(P115)

Homogenous vs. heterogenous reaction: a kinetic and mechanistic investigation of oil-water interface.

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Water is very different from other solvents of similar molecular weight and polarity. This discrepancy arises owing to the unique properties of water such as high cohesive energy density, polarity and hydrogen bonding ability. The literature is piled-up with plethora of studies on both physical and chemical properties of bulk water. The interface of water plays an important role in various physicochemical and biological processes. However unlike bulk water, study of the interface of water is still an open challenge for further exploration. Hardly any reports are available on the nature and extent of forces acting at the oil-water interface. One of the predominant interaction mediated by water-hydrophobic interaction is very intriguing. There existence and predominance has been well established in bulk water. But still there is a controversy on whether hydrophobic forces exists at the interface or not? This raises the question of closely examining the impact of hydrophobic forces at the oil-water interface. Herein we have made an attempt to delineate the role of such forces at the interface. 1,3-dipolar cycloaddition of phenyl azide and an alkene has been undertaken to quantify the effect of such forces. For comparative analysis of the rate of reaction, the investigation was carried out under both homogenous (i,e within the solubility limit of the reactants) and heterogenous condition at the oil-water interface (created with the presence of reactants above their solubility limit in water). Effect of prohydrophobic and antihydrophobic salts has been used as an investigating tool to have a better understanding of the role of hydrophobic forces at the interface.

(P116)

Deep Eutectic Media: Solvent with Sustainable Properties

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One of the critical issues in optimization and design of new separation processes lies on the selection of a suitable solvent that improves process efficiency and cost, but also minimizes environmental damages. Over the past years, ionic liquids (ILs) appear as promising candidates mainly due to their properties tunability and low vapor pressure.^[1] More recently, deep eutectic solvents(DES) formed by combination of a quaternary salt and a hydrogen-bond donor showed analogue solvent characteristics with promising advantages regarding low cost preparation, no need for purification, no water incompatibility, tuneable phase behaviour and solubility, low toxicity and biodegradability.^[2] A new family of DES based on unique combination of carbohydrates and organic salts are introduced and characterized here as a cheaper and greener alternative to ILs as solvents for organic reactions and separation technologies. The DES provide better perspective in each process carried out in organic reactions and are likely to be effective in separation technologies as compared to other solvents.^[3]

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(P117)

Nitro-substituted Bishomocubanes: synthesis, characterization, and Application as an energetic material.

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High energy and high density materials (HEHDMs) are common ingredients in various volumelimited applications such as rockets, gas generators, and explosives which demand high performance parameters. An ideal HEHDM should possess high gravimetric and volumetric energy density, high positive heat of formation (HoF), high density, as well as low operational hazards. Cage compounds are a new class of potential HEHDMs with severely strained molecular structures. This study demonstrates the synthesis, thermodynamic characterization, and energetic properties of cage compounds, nitromethyl-1,3-bishomocubane (NMBHC), nitromethylene-1,3-bishomocubane (NMyBHC), and bis(nitromethyl)-1,3-bishomocubane (DNTMBHC) which have higher HoFs and higher energy densities than traditional hydrocarbon fuels. The compounds were synthesized from bishomocubanone for applications as standalone fuels in liquid bipropellant systems, or as additives in liquid and solid propellant formulations. The DFT-B3LYP/6-31G (d) level of theory was employed for their geometry optimization, and to determine density, heats of formation, and other thermodynamic properties. The density specific impulse, determined through equilibrium thermodynamics, demonstrated an improvement of 75 seconds for NMBHC and NMyBHC over standard liquid hydrocarbons. The detonation properties showed that these oxygen-deficient carbon-rich systems possess low potential as explosives. TGA, coupled with IR spectroscopy, revealed that NMBHC and DNTMBHC evaporate readily with activation energies of 61.5 kJ/mol and 58.4 kJ/mol. NMyBHC undergoes a two-stage decomposition, the first stage being initiated at 95 °C to form the parent bishomocubanone and a polymeric form of HNCO.

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(P118)

PEDOT –A Versatile Material

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Since the invention of electronic conductivity in otherwise insulating synthetic polymers in last three decades, conjugated polymers have evolved from the academic curiosity to one of the most important commercial material for wide ranging applications in many modern electronic devices such as Displays, Photovoltaics, Field Effect Transistors (RF tags), Chemical and biological sensors etc. Organic electronics is leading this new revolution of so called "pervasive

electronics" wherein the electronic devices are becoming more and more personal with each passing year and soon will become an integral part of our life. The total market size for "Organic Electronics and Electrics" has been projected to be of USD 96 Billions by year 2020. This is possible because of the low cost of materials as well as low fabrication cost. In this direction, polythiophene based conjugated polymers have taken significant lead over other conjugated polymers in printable electronic applications. Commercially the most successful conducting polymer, PEDOT, is used as a transparent conductor and hole transport layer in electronic displays as well as for flexible transparent conductor. Many applications such as light emitting diodes, touch panels, electronic displays, photovoltaic cells and electrochromic devices require good conductivity as well as high optical transparency. PEDOT, as electrochromic material, has become increasingly important due to the widespread application of these devices in fields such as displays (both transmissive and reflective), e-paper, optical shutters, smart windows, and night vision. Development of low cost flexible devices with high contrast ratio and fast switching time is the need of the hour. PEDOT is emerging as important ingredient of solar cells especially of dve sensitized solar cells (DSSCs). It is being used not only as a replacement of TCO layer but also as solid electrolyte and catalytic layer on cathode of DSSC due to its good conductivity and catalytic nature. Use of highly conducting PEDOT films not only diminishes the requirement of expensive platinum but also TCO.

Our recent results in the aforementioned applications of PEDOT will be discussed in the presentation. A summary of those results are mentioned below.

1. Transparent conductor

The simultaneous enhancement of electrical conductivity (C) and transparency {figure of merit $(\sigma DC/\sigma OP)$ } of PEDOT: PSS films by a combined posttreatment. The treatment provides PEDOT: PSS thin films suitable for use in organic optoelectronic device possessing metal-like conductivity of 3230 S/cm coupled with a high $\sigma DC/\sigma OP$ value of 139. A multi-technique approach was taken to elucidate information regarding film structure. Combined results of XPS, FTIR, EDS and Raman indicated change in structure of these films due to PSS removal and doping of the system. Increase in conductivity of films was found to be associated with a change in film morphology.

2. Electrochromic material-ECDs

We have found the effect of electrode surface on electrochromic contrast of PEDOT. Effect of solvents is previously known to give high contrast PEDOT (\sim 70%). Our recent findings do suggest that it is possible to get high contrast (> 70%) in PEDOT films via electropolymerization on different substrates. This high contrast is attributed to changes in the morphology which in turn is the manifestation of higher conjugation length or molecular weight. Now we are exploring various methodologies wherein we are interested in increasing the electrochromic contrast in case of thin films derived from Clevios-P. Our recent results in this direction will be discussed in the presentation.

3. TCO and platinum replacement-DSSC

We demonstrate high efficiency DSSC with FTO and platinum free counter electrode made up of PEDOT-PSS. This counter electrode has catalytic activity equivalent to Pt electrode without catalytic electropolymerized PEDOT.

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(P119)

Palladium Catalyzed Regioselective C-O and C-C Bond Formation of 2-Arylbenzazoles via Substrate Directed C-H Activation

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Selective functionalization of C-H bonds is one of the key challenges in recent synthetic organic chemistry. The advent of techniques such as directing group assisted C-H bond functionalization and cross dehydrogenative coupling have made possible to process the selective functionalization of inert CH bonds. Pertinent to these seminal achievements, protocols have been developed for the direct ortho-hydroxylation and ortho-aroylation of of 2- arylbenzazoles using Pd(OAc)₂ as the catalyst in the presence of suitable oxidants and solvents. In C-O bond formation approach (diacetoxyiodo) benzene (DIB) is acting as hydroxyl source whereas in the C-C bond formation approach aldehyde is acting as aroyl equivalent. Both of these methodologies tolerate a diverse array of substituents giving good to excellent yields of corresponding ortho-hydroxylated and ortho-aroylated products.

(P120)

1,2,4-Triazole-5-thiones: Novel Class of Inhibitors of Enoyl Acyl Carrier Protein Reductase from Mycobacterium tuberculosis

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In view of the worldwide spread of multidrug-resistant, extensively drug-resistant and totally drug-resistant forms of tuberculosis, there is an urgent need to discover anti-tubercular agents with novel structure. InhA, the enoyl acyl carrier protein reductase from Mycobacterium tuberculosis (Mtb), is one of the key enzymes involved in the mycobacterial fatty acid elongation cycle of cell wall synthesis and has been validated as an effective antimycobacterial target. We hereby report the discovery of a series of 1,2,4-triazole-5-thiones as a novel class of potent InhA inhibitors. These direct InhA inhibitors require no mycobacterial enzymatic activation and thus circumvent the resistance mechanism to anti-tubercular prodrug such as isoniazid that is most commonly observed in drug-resistant clinical isolates. The 1,2,4-triazole-5-thione compounds

were rationally designed and molecular similarity studies were performed. Based on the results of similarity studies, they were synthesized and spectral characterization using IR, 1H NMR and 13C NMR spectroscopies confirmed their structures. Biological evaluation was performed using resazurin microtiter assay on Mtb H37Rv strain followed by InhA enzyme inhibition studies. The most active compound in the series exhibited Mtb H37Rv MIC of 0.19 μ g/ml and InhA IC50 of 90 nM. Molecular docking, pharmacophore generation and 3D-QSAR studies were performed on our compounds.

(P121)

Greener approach in the synthesis of some novel class of isoxazolidine and isoxazoline derivatives using N-benzyl fluoro nitrones via cycloaddition reaction

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1-Butyl-3-methylimidazolium based ionic liquids are found to accelerate significantly the intermolecular 1,3-dipolar cycloaddition reactions of N-benzyl-fluoro nitrones derived in situ from 2,6-difluoro benzaldehyde and N-benzylhydroxylamine, with active alkene & alkynes to afford enhanced rates and improved yields of fluoro isoxazolidine and isoxazoline derivatives. Synthetic potentiality of the novel isoxazolidine/isoxazolines and nitrenes have been also tested successfully as they could be utilized in the synthesis of 1,3-amino alcohols, aldehydes and ketones respectively. All the novel fluoro isoxazolidine and isoxazoline derivatives have been screened for antimicrobial activities and found to be very active.

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(P122)

Highly Efficient Synthetic Routes to Carbocyclic Enaminonitriles/ 4,5-Dihydropyrroles via Lewis Acid Catalyzed Domino-Ring-Opening-Cyclization (DROC) of Donor-Acceptor Cyclopropanes/ Aziridines with Malononitrile.

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Malononitrile is versatile reagent having a wide range of reaction scope in organic synthesis. Utilizing this reagent, we have developed highly efficient synthetic protocols for the synthesis of functionalized carbocyclic enaminonitriles from DA-cyclopropanes and enantiopure 4,5-dihydropyrroles from aziridines.DA-cyclopropanes are important class of small ring carbocycles in which the inherent ring strain is responsible for their reactivity towards various nucleophiles. Here we show a facile synthesis of 5 membered carbocyclic enaminonitriles by reacting such DA-cyclopropanes with malononitrile anion. Enaminonitriles are extensively used for building

large heterocyclic molecular frameworks having wide range of usabilities. The greatest features of this work being its smooth reaction course, mild conditions, use of environmentally benign reagents, high yields and ease of product purification. The reaction is generalised over various substrates. It is needless to say these enaminonitriles hold the potential to flourish as important asymmetric building blocks aided by their built-in multifunctionalities. On the other hand enantiopure aziridines when reacted with malononitrile in presence of a base enantiopure 4,5-dihydropyrroles can be synthesized.

(P123)

Synthesis of Polysubstituted Quinolines via Copper(II)-Catalyzed Annulation of 2-Aminoaryl Ketones with Internal Alkynes

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Quinolines represent a major class of nitrogen-containing heterocyclic compounds which are found as key structural units in many natural products with interesting biological activities.^[1] Due to their wide range of bioactivities, synthesis of 2-arylquinoline derivatives has gained special attention. Based on our continuing efforts to achieve copper-catalyzed C-C and C-heteroatom bond formations,^[2] we envisaged an application of copper triflate for the synthesis of 2-arylquinoline derivatives by the annulation of 2-aminoaryl ketones with internal alkynes under solvent-free conditions. Various types of substituted quinolines could be synthesized by choosing proper alkynes employing this methodology. To extend our methodology, phenylpropiolic acid was used as an internal alkyne. Furthermore, H_2O as the only byproduct makes this transformation atom efficient. In nutshell, simple reaction procedure, environmentally friendly reaction conditions avoiding toxic organic solvent, cheap catalyst and aerobic reaction conditions make this procedure convenient and useful for the synthesis of diversified quinolines.

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(P124)

Metal nanoparticles in "on-water" organic synthesis: one-pot nano CuO catalyzed synthesis of isoindolo [2,1-a]quinazolines

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In recent times, much attention has been drawn to the synthesis of biological active compounds using a sustainable reaction medium. Indeed, water is a unique green solvent for the chemical transformations in view of its low cost, safety, and environmentally benign properties. The reactions under heterogeneous conditions in which, water plays the role of medium only and not of solvent are termed as "on-water" reactions.[1] Quinazolinone and its derivatives are an important class of bioactive nitrogen-containing heterocycles.[2] Herein we report a copper oxide nanoparticle catalyzed synthesis of isoindolo[2,1-a]quinazoline derivatives via a water

mediated three-component coupling of 2-carboxybenzaldehyde, isatoic anhydride and various amines. The substrate scope of the present method has proven to be broad. Reusability of the catalyst was also studied to make this protocol more effective in greener way. In summary, we have developed an environmentally benign one-pot nano CuO catalyzed "on-water" strategy for the synthesis of isoindolo[2,1-a]quinazolines. Water plays a major role to accelerate this transformation through hydrogen bond mediated 'electrophile–nucleophile dual activation'.

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(P125)

Functionalization of sp3 C-H bond via redox-neutral domino reaction: diastereoselective synthesis of hexahydropyrrolo[2,1-b]oxazoles

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Functionalization of C-H bonds into C-C and/or C-X bonds (X = O, N, halogen, etc.) is an important area of organic synthesis for the construction of biologically active complex molecules.^[1] however, functionalization of sp3 C-H bonds have been developed either by transition metal catalysis or by internal redox processes under thermal conditions during last few vears.^[2] Pyrrolidinooxazolidines are the key intermediates in synthetic as well as in pharmaceutical chemistry and are important building blocks for the syntheses of various biologically active nitrogen containing heterocycles.^[3] Herein we present a new diastereoselective synthesis of hexahydropyrrolo[2,1-b]oxazole through a redox-neutral domino reaction under microwave irradiation Overall process becomes redox-neutral due to the combination of reductive N-alkylation and oxidative α -functionalization. High yields, simple operation, atom-efficient, transition metal-free and environmentally benign reaction conditions which attractive are the features of this one-step protocol.

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(P126)

PIDA-Mediated Synthesis of Aromatic Azo Compounds via Oxidative Dehydrogenative Coupling of Anilines: Scope and Mechanism

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Aromatic azo compounds are widely used as organic dyes, indicators, pigments, and food additives. Various synthetic methods have been developed over the past few decades.

Conventionally symmetric azobenzenes are prepared by the reduction of nitrobenzenes and by oxidation of anilines.^[1] Hypervalent iodine reagents have been drawn considerable interest as oxidizing agents in organic synthesis due to^[2] considerably mild, selective and non-toxic oxidizing reagents and a good alternative to common metal oxidants. Among the various iodine derivatives, PIDA has been used extensively for oxidizing the nitrogen atom in C-N or N-N^[3] bond formations. An efficient method has been developed for the synthesis of azobenzenes via PIDA mediated homo- and cross-dimerization of anilines. Gratifyingly we have successfully synthesized various unsymmetrical azobenzenes with high yields in ethanol. The mechanistic path of the reaction has been studied through the isolation of the intermediate. The substrates scope of this reaction is broad for both homo- and cross-dimerization. Solvent plays a vital role make highly efficient cross-dimerization. to this protocol for

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(P127)

Copper-Catalyzed C-H Amination: Synthesis of Imidazo[1,2-a]pyridines from Ketones <u>Avik Kumar Bagdi</u>, Sougata Santra and Alakananda Hajra* Visva Bharati University

Transition metal catalyzed oxidative C-H bond amination has been received great interest in recent days of synthetic organic chemistry.^[1] These types of reactions are very useful as the prefunctionalization of the substrate is not required, avoiding the multistep synthesis and contribute to changing the way chemists think about chemical reactivity and planning chemical syntheses. Direct C-N bond formation through C-H bond functionalization is commonly catalyzed by Pd or Cu. The synthesis of biologically and medicinally active heterocyclic compounds using copper salts in aerobic conditions is an emerging field of organic synthesis. Here a new copper-catalyzed oxidative cyclization via C_H amination between 2-aminopyridines and methyl aryl/heteroaryl ketones has been developed under ambient air.^[2] Imidazo[1,2-a]pyridines containing a wide range of functional groups have been synthesized from basic and easily available starting materials. This one-pot simple reaction protocol is applicable for the direct preparation of zolimidine (the marketed antiulcer drug) in large scale.

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(P128)

Carbazole Substituted Boron Dipyrromethene Dyes Praseetha E. K. and <u>Dr. Iti Gupta</u>* Department of Chemistry, Indian Institute of Technology Gandhinagar The BODIPY (4,4-difluoro-4-bora-3a,4a-diaza-s-indacene) dye was first discovered by Treibs and co-workers in 1968.^[1] This fluorescent dye has remarkable photophyical properties ^[2] like: intense absorption in the 480-600 nm region, high quantum yield, negligible triplet-state formation, good thermal and photochemical stability. Good solubility and easy functionalization of the BODIPY core has made them very popular among chemists. BODIPYs have been shown useful for variety of applications such as chemosensors ^[3], laser dyes ^[4], fluorescent switches ^[5] etc. Halogenated ^[6] BODIPY derivatives are also used for the treatment of cancerous cells in PDT (photo dynamic therapy) ^[7] due to low dark toxicity and less photo-bleaching and good ISC (inter system crossing). In spite of having numerous applications, the major limitations of such dyes are the emission range (about 600 nm) and small Stokes shifts (5-15 nm). One simple way to induce bathochromic shift in their absorption and emission bands is the introduction of electron releasing groups ^[7] (like carbazole) at the various position of BODIPY core.

Our group at IIT Gandhinagar is involved in the synthesis of functionalized N-Confused porphyrin derivatives and in the synthesis of novel BODIPY dyes linked to suitable donor moiety to study energy/electron transfer process in such systems.

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(P129)

Efficient Syntheses of the A-band Trisaccharide Related to Pseudomonas aeruginosa Aritra Chaudhury, Sajal K. Maity and Rina Ghosh Jadavpur University

The present work describes highly efficient syntheses of the trimeric repeating unit { α -D-Rhap-(1 \rightarrow 3)- α -D-Rhap-(1 \rightarrow 3)- α -D-Rhap} associated with the A-band polysaccharide of Pseudomonas aeruginosa via two different synthetic pathways. Conventional 4,6-O-benzylidene derivatives of D-manno thioglycosides were found to give three D-rhamno thioglycosides as building blocks with remarkably high yields and selectivity via radical mediated redox rearrangement. The D-rhamno thioglycosides so obtained allowed efficient access to the above trimeric target. Moreover, synthesis of the target trisaccharide from D-mannose involving an alternate pathway has also been achieved. Judicious selection of the protection profile led us to the D-rhamnose based trisaccharide directly with a global 6-deoxygenation in a single step from a D-mannose based trimer, which was obtained from the corresponding 4,6-O-benzylidenated mannose based building blocks. The yield and selectivity offered by this global protocol were highly rewarding.

(P130) Green Synthesis of substituted Esters and Amides using Sintered Calcium Phosphate supported Zinc Oxide [ZnO/SCaP] B.R. Saikishore Kumar, S. Sumathi* and P.S. Raghavan*

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Designing organic synthesis with an eco-friendly approach continues to receive a wide attention among the synthetic organic chemists as it offers many advantages over conventional reactions ^{[1, ^{2]}. In such green reactions, catalysts play an important role ^[3]. Herein, we report the effect of ZnO deposited on sintered calcium phosphate [ZnO/SCaP] on the acylation of phenols, alcohols and amines .The above catalyst prepared by chemical method was characterized by XRD, UV-DRS, SEM and TEM. This catalyst (~30nm) proved to be highly efficient for the synthesis of esters and amides under solvent free conditions ^[4]. These reactions proceeds at room temperature and goes to completion in a shorter time (30-60 min). The products were obtained in high yields (85-95%). In addition, is observed that this catalyst can be reused up to 5 cycles with consistent activity and good yield.}

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(P131)

A Synthetic Approach Towards (-)-Muricatacin and Related Compounds

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Muricatacin is a member of the hydroxy-lactone class of compounds that are notable for their biological activity. It was isolated several years ago by McLaughlin and co-workers from the seeds of Annona Muricata. Both the enantiomers are found in nature, and both exhibit the same potent cytotoxicity towards several human tumor cell lines. The chiron approach is one of the most widely used approaches toward the total synthesis of natural products in which chiral templates such as amino acids, carbohydrates, hydroxy acids, and terpenes are used as the starting materials. A simple and efficient route for the total synthesis of (-)-muricatacin has been achieved starting from commercially available and inexpensive D-mannitol. The stereochemistry inherited from C-3 and C-4 of D-mannitol was translated to the desired stereochemistry of (-)-muricatacin. The synthetic route is flexible enough to give access to potentially interesting natural analogues of muricatacin.

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(P132)

Palladium catalyzed intramolecular cyclisation of 3-(2-bromobenzyl)chromonol – Stereospecific synthesis of cis and trans-homopterocarpanes

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Homopterocarpanes1 are the dimeric flavonoids, many natural flavonoids exists as dimers and have been shown possess a wide range of physiological and biological properties.2 The first synthesis of cis-homopterocarpane 4 was reported in 1976.1a During the course of our study using various substituted homopterocarpanes, we were surprised to find that the trans-homopterocarpanes has not been reported so far. Herewith, we report the synthesis of cis and trans-homopterocarpanes, viz., (+/-)-trans-6a,12a-dihydro-6H,7H-[1]-benzopyrano-[4,3-b]-[1]-benzopyran via intramolecular palladium catalysed Buchwald coupling of the respective cis and trans 3-(2-bromobenzyl)chroman-4-ols (Scheme 1).

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(P133)

Titanocene(III) chloride mediated stereoselective synthesis of trisubstute tetrahydrofurans and spirolactone via tandem radical reactions

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Carbon-carbon bond formation and functional group transformation are the most important reactions in organic chemistry for design of molecular framework. Radical mediated reactions became an important synthetic tool for the development of efficient carbon-carbon bond forming reactions in organic synthesis due to mild reaction conditions with high levels of region- and stereoselectivity along with significant functional group tolerance. Due to widespread occurrence in nature and broad range of biological activities, trisubstituted tetrahydrofurans specially containing α -methylene- γ -butyrolactone moiety have attracted much attention of the organic chemists over the years. Spirolactones are also an important fragment in wide range of natural products and related biologically active compound. So, synthesis of substituted tetrahydrofurans and spirolactones has received much attention for years and still a challenge to organic chemists to develop a viable method. Titanocene(III) chloride (Cp₂TiCl) mediated stereoselective synthesis of highly substituted tetrahydrofurans has been achieved using Baylis-Hillman adduct and activated bromo/iodo compounds via tandem radical cyclization reaction. The reaction of epoxide with Baylis-Hillman adduct furnished spiro-lactone via radical cyclization followed by in situ lactonization. Cp₂TiCl was prepared in situ from commercially available Cp₂TiCl₂ and zinc dust in THF. The details will be discussed during presentation.

(P134)

Palladium/Lewis Acid Mediated Reaction of Pentafulvene Derived Diazabicyclic Olefins: Efficient Access to Indoline-Pyrazolidine Fused Cyclopentenes Sarath Chand S and K V Radhakrishnan*

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Aza-heterocycle units are attractive scaffolds for drug discovery because of their potentially diverse bioactivities.1 Efficient and divergent production of such polycyclic scaffolds is an important challenge for synthetic and medicinal organic chemists. We have unraveled a facile method for the construction of alkylidenecyclopentenes2,3,4 through Lewis acid catalyzed ring opening of fulvene-derived azabicyclic olefins with o-iodoaniline. The alkylidenecyclopentenes obtained were successfully utilized for the construction of novel spiropentacyclic framework having cyclopentene fused to indoline and pyrazolidine skeletons via intramolecular Heck cyclization.5 A catalytic tandem protocol was also developed for synthesis of indoline-pyrazolidine fused cyclopentenes. The details of the investigation will be presented.

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(P135)

Borax catalyzed synthesis of highly functionalised pyran-annulated heterocycles

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IIT PATNA

Pyran annulated heterocycle are of immense interest because of its wide range of biological and pharmacological properties.¹ These are used as anti-coagulants, diuretic, anticancer agents, spasmolytics, anti-anaphylactics, anti-tumoral, anti-HIV etc.² Moreover, these compounds can be used as cognitive enhancers for the treatment of neuro degenerative diseases, including Alzheimer's disease, as well as for the treatment of schizophrenia and myoclonus. With ever-increasing level of global environmental concern, there is much incentive to find new and strategically important process with wide applicability using a robust, inexpensive and innocuous catalyst. For these reasons and in continuation of our research in extending the scope of boron compounds in catalysis for various reaction, we report herein our results of borax3 catalysed one-pot three-component condensation of aldehyde, alkyl nitriles (malononitrile and ethyl cyano acetate) and an active methylenic diketo compounds (dimidone, cycloalkan-1,3-dione, 4-hydroxy coumarin and 1,3 diketoesters) to pyran annulated heterocycle in very good yields.

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A. Molla, E. Hossain and S. Hussain, RSC Adv., 2013, 3, 21517.

(P136)

Synthesis and evaluation of novel monoarylated and symmetrical /unsymmetrical diarylated Imidazo[1,2-a]pyrazines as anticancer agents Richa Goel, Vijay Luxami and Kamaldeep Paul*

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Cancer is a group of disease characterized by uncontrolled cell proliferation, cell development and inhibition of apoptosis. It can spread to more distant parts of the body through the lymphatic system or bloodstream and is the world's second largest killer after cardiovascular disease. Many factors are known to increase the risk of cancer, including tobacco use, certain infections, radiations, lack of physical activity, obesity and environmental pollutants. In 2013, cancer caused about 20% of all human deaths worldwide (7.9 million). National Center for Health reported total of 1,638,910 new cancer cases and 577,190 deaths from cancer are projected to occur in 2013. Keeping in consideration about the present status of cancer, side effects of anticancer drugs (resistance and toxicity) and drugs in clinical trials, we plan to synthesize novel imidazopyrazine derivatives and evaluate its efficacy against different types of cancer. Library of Imidazopyrazines was synthesized from readily available 2-aminopyrazine which on bromination gives 2-amino-3,5-dibromopyrazine followed by cyclization gives Imidazo[1,2-a]pyrazines. These dibromo imidazo[1,2-a]pyrazines were further reacted with variety of boronic acids using Palladium-catalyzed Suzuki–Miyaura cross-coupling to give symmetrical and unsymmetrical imidazopyrazines in moderate to good yields. These compounds were well characterized by NMR and Mass spectra as well as single X- ray crystallography. These synthesized compounds were then evaluated for anticancer activity against 60 human cancer cell lines.

(P137)

Synthesis of Polyfunctionalized 2,3-Dihydro-4H-pyran-4-ones via Tandem Cyclisation Strategy and Its Synthetic Applications <u>P. Sakthivel</u> and A. Ilangovan Bharathidasan University, Tiruchirappalli

The 2,3-Dihydro-4H-pyran-4-one ring system is an important biological scaffold found in many natural products especially in polypropionate class of natural products and pestaloficiol A-E.^[1] In addition is also found in several pharmacologically relevant synthetic molecules. Moreover, this structural motif have been widely employed as versatile intermediates in the synthesis of natural products, tetrahydropyran, y-pyrone, carbohydrarates and highly substituted aromatic compounds.^[2] Some of the well-known methods^[3] for the construction of 2,3-dihydropyran-4ones are coupling of Danishefsky's diene with aldehydes via hetero-Diels-Alder reaction, palladium(II)-catalyzed oxidative cyclizations of β -hydroxyenones, cyclizations of β hydroxyynones by Au(I), β -ethoxy- α , β -unsaturated lactones, 5-hydroxy-1,3-dicarbonyl compounds or related compounds, α,β -unsaturated-1,3-diketones and rearrangement of 1alkynyl-2,3-epoxy alcohols. However, these methods are associated with drawbacks such as the use of expensive Lewis acid or metal catalyst, multistep preparation of the starting material and in most of the cases 2,3-dihydro-4H-pyran-4-one obtained as lack reactive sites/functionalities. A simple method was developed for the synthesis of polyfunctionalized 2,3-dihydro-4H-pyran-4one ring system from readily accessible starting materials such as active methylene compounds and acid chloride. This method allows for the synthesis of variety of 2,3-dihydro-4H-pyran-4ones in a one pot procedure. Further, making use of 2,3-dihydro-4H-pyran-4-one as crucial synthon some pharmacologically relevant synthetic heterocycles were synthesised.

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(P138)

Iodobenzene-Catalyzed C-H Functionalization of N-Substituted Amidines using m-Chloroperbenzoic Acid

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The benzimidazole moiety has become important over the past decades as it displays widespread biological and therapeutical activities. The traditional method for the construction of this basic core structure involves condensation followed by oxidative cyclization of benzene-1,2-diamine with carboxylic acids or its equivalent. The development of the concept of direct functionalization of C-H bonds under metal-free conditions by using hypervalent iodine (III) involved catalytic process has proven valuable in the area of organic synthesis, developing effective, safe and environmentally benign protocols for carbon-carbon and carbon-heteroatom bond formation. This process obviates the need of hypervalent iodine (III) reagents in stoichiometric amounts which leads to co-production of iodoarenes in equimolar amounts. In this presentation, we would like to report an iodobenzene catalyzed oxidative C-H amination for the preparation of N-substituted benzimidazoles from N"-aryl-N'-tosyl/N'-methyl sulfonylamidines and N,N'-bis(aryl)amidines using mCPBA as a terminal oxidant at room temperature. The protocol is simple and general providing a potential route for the construction of a library of benzimidaozles with structural diversity in high yields. In this catalytic process, the desired transformation is achieved by using iodine (I) containing compound in catalytic amount together with a stoichiometric oxidant. The oxidant generates the hypervalent iodine (III) species in situ, which leads the reaction giving the oxidation product accompanied by the liberation of iodine(I), which is reoxidized to Iodine(III) by the oxidant.

(P139)

Design, Synthesis and evaluation of Tacrine-(s-allylcysteine) hybrids as potential bifunctional anti-Alzheimer drug candidates with anti-oxidant and copper-binding properties

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Alzheimer's disease (AD), characterized by memory loss, language impairment, personality changes and decline in intellectual ability, is a highly complex and progressive neurodegenerative disorder in the elderly population [1]. Many factors are considered as the key pathological hallmarks of AD, such as cholinergic system dysfunction, accelerated aggregation of β -amyloid (A β) peptides and the dyshomeostasis of biometals [2]. These factors provide a basis for the cholinergic, amyloid and biometal hypotheses for AD pathology, respectively. The current treatments for AD involve the use of acetylcholinesterase (AChE) inhibitors, such as tacrine and donepezil, however their effect does not stop the progression of the disease, only providing symptomatic benefits. With this in mind and the recent interest on natural-based drugs [3], we have explored and performed an integrated study on a set of nature hybrid compounds combining the tacrine and S-allylcystein (garlic constituent) moieties in order to tackle the acetylcholine esterase (AChE) inhibition and neuroprotective activity, respectively. The compounds were evaluated for some representative biological properties, including AChE inhibitory (AChEI) activity and cell neuroprotective activity (viability of A β -stressed neuronal-like cells) and also for some relevant physico-chemical properties, namely the antioxidant

activity (DPPH) and the Cu(II) chelating ability. The most promising results were presented by compound 9d, especially the remarkable neuro-regenerative role.

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(P140)

Ruthenium catalyzed chelation-assisted transformation of an unreactive ortho C-H bond of aromatics to C-C or C-O bonds via C-H bond activation

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The transition-metal-catalyzed chelation-assisted C H bond activation and subsequent alkenylation at the ortho position of hetero-atom substituted aromatic or heteroaromatic ring with alkenes is a practical and highly atom-economical method to synthesize highly substituted alkene derivatives in organic synthesis. This type of alkenylation reaction has been widely used to synthesize various organic materials, natural products and drug molecules. The selection of directing group is highly important in order to success this type of alkenylation reaction. While the C H bond activation reaction in the presence of strong directing groups is well documented in the literature. But, activation in the presence of weak directing groups such as aldehydes, esters, cyano and ketones are still a challenging task. In meantime, only palladium and rhodium complexes have been widely used as catalyst in this type of alkenylation reaction. Until now, a less-expensive ruthenium complex as a catalyst has not been explored in the literature. In this poster presentation, we would like to discuss a ruthenium catalyzed ortho-alkenylation of heteroatom substituted aromatics with alkenes. The reaction of aryl ketones with olefins in the presence of ruthenium catalyst gave ortho-alkenylated aromatic ketones in a highly regio- and stereoselective fashion1a. Further, weakly coordinating CHO as well as ester substituted aromatics and heteroaromatics underwent alkenylation reaction with alkenes to provide orthoalkenylated aromatic and heteroaromatic aldehydes or esters in a highly regio- and stereoselective manner.1b-c It is interesting to note that this catalytic reaction was conducted under the air atmosphere and only catalytic amount of terminal oxidant Cu(OAc)₂ has been used, the remaining amount of copper source being reoxidized by air. The coupling of carboxylic acids with aromatics is more challenging due to rapid complex formation of the carboxylic acids with the metals. Oxidative ortho-benzoxylation of substituted acetanilides1d with benzoic acids in the presence of $[{RuCl_2(p-cymene)}_2]$, AgSbF₆ and $(NH_4)_2S_2O_8$ afforded ortho-benzoxylated acetanilide in a highly regioselective manner. The catalytic reaction was also compatible with acetic acid.

(P141)

Efficient and green synthesis of dihydropyrido[2,3-d]pyrimidines via a one-pot [4+2]cycloaddition strategy and their in-vitro evaluation for antimicrobial activities <u>MANAS MAUSUM SARMAH</u>, DIPAK PRAJAPATI CSIR-NORTH EAST INSTITUTE OF SCIENCE AND TECHNOLOGY, JORHAT, ASSAM The Diels-Alder reaction is a versatile method for the construction of six-membered heterocycles.^[1] Over the past decade, the intensifying influence on developing "green" synthetic methodologies has renewed interest in the Diels-Alder reaction, as it ensures 100% atomeconomy. In recent years, organic reactions in aqueous media has become a popular branch in synthetic organic chemistry, the disadvantage of poor solubility of organic reactants in water can be overcome by using phase-transfer catalysts (PTCs)^[2]. The presence of an appropriate side chain on the heterocyclic ring frequently made possible ring transformation into other heterocyclic ring systems.^[3] In a continuation of our study on the reactivity of uracils possessing a suitable side chain at the 6-position together with our interest in developing eco-friendly technologies^[4], we have reported a two component, one-pot Diels-Alder reaction of nitro alkenes with mono-methyl uracil amidine in aqueous medium for the construction of dihydropyrido[2,3-d]pyrimidine derivatives in excellent yield. The antimicrobial tests of the products was carried out and observed their anti-fungal and anti-bacterial activities.

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(P142)

Synthesis of some novel 3-aminoalkyl-2-hydroxynaphtho-quinones and their application in the synthesis of naphthofuroquinones

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Naphthoquinone and its annelated derivatives are widely distributed in nature. Ongoing studies have widely established the medicinal value of a range of natural and semisynthetic naphthoquinones.[1] 3-alkyl-2-hydroxynaphthoquinones represent an important class of such compounds possessing antimalarial as well as activity against sapsucking insects.[2] Similary, Naphthofurandione constitutes the basic moiety of a varied number of naturally occurring biologically active compounds possessing anticancer, antifungal, antibacterial as well as antiviral activities. Therefore, there has been a continuous effort towards the synthesis of these molecules.[3] Multicomponent reactions (MCRs) have emerged as an efficient and powerful tools in modern synthetic organic chemistry. MCRs contribute to the requirements of an environmentally friendly process by reducing the number of synthetic steps, energy consumption and waste production.[4] In continuation of our work on heterocyclic chemistry,[5-6]here we would like to report the synthesis of some novel 3-aminoalkyl-2-hydroxynaphtho-quinones 1 via one-pot three component reaction in ethanol under catalyst free condition. The compound 1 was further utilized to synthesize naphthofuroquinones using pyridinium ylide and 1,8-Diazabicycloundec-7-ene.

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(P143)

Novel and green approaches for efficient synthesis of trisubstituted-triazoles

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1,2,3-Triazoles are an important class of compounds because of their wide coverage of biological and industrial applications including antiviral, antimicrobial, anti-HIV, anticonvulsants, antiallergic, dyes, corrosion inhibitors, sensors and photo-stabilizers etc. Room temperature ionic liquids, PEG-400, water have shown great promise as attractive alternatives to conventional volatile and toxic organic solvents and considered as green reaction medium. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) is a sterically hindered amidine base and has been used in many organic transformations in recent years. In view of the emerging importance of ionic liquids, water, PEG-400 as green reaction media. We have investigated the synthesis of 1,2,3triazoles and their novel hybrids in ionic liquids, DBU-water system, PEG-400 under different reaction conditions. We report herein an efficient and environmentally benign synthesis of different 1,2,3-triazoles and their novel hybrid hetrocycles by reaction of various aryl azides with active methylene compounds and by copper (1) catalyzed azide-alkyne cycloaddition reaction in ionic liquids, DBU-water system and PEG-400 under different reaction conditions. The reactions can be achieved efficiently and yield the corresponding triazoles in high yields. Biological activities such as antibacterial, antifungal and antioxidant of these compounds have also been examined. The details will be presented.

(P144)

A Novel Tandem Sequence to Pyrrole Syntheses by 5-endo-dig Cyclization of 1,3-Enynes with Amines

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Highly substituted pyrroles are important structural motifs of many natural products and pharmaceutically active substances. Moreover, they are widely used in material science and supramolecular chemistry. Therefore, a large effort has been made to develop more valuable synthetic method to obtain this heterocycle. Thus, several classical and modern methods have been developed for the synthesis of pyrroles and their derivatives. However, the strategies for the synthesis of tetra and pentasubstituted pyrroles from the readily available substrates is somewhat limited due to lack of selectivity and harsh reaction conditions. Thus, it remains highly desirable to develop methods requiring milder condition as well as avoiding the toxic metal catalysts.

More recently, electrophilic iodocyclization of alkynes has been found to be powerful tool for the synthesis of carbocycles and heterocycles. The designing of enynes makes this process attractive for the construction of the target cyclic compounds. In continuation of our studies on heterocycle synthesis, we wish to report herein a synthetic approach to tetra and pentasubstituted pyrroles from 1,3-enynes and amine source using molecular iodine via a tandem aza-Michael addition, iodocyclization and oxidative aromatization at ambient conditions. The protocol provides a potential route for the synthesis of pentasubstituted pyrroles in moderate to good yields.

(P145)

Synthesis and Characterization of novel series of fatty acid chain substituted pyrazoline derivatives

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Pyrazolines are well known and important nitrogen containing 5-membered heterocyclic compounds and various methods have been worked out for their synthesis. Pyrazolines are known to possess antimicrobial, antitubercular, antiviral, anti HIV, molluscicidal and cerebroprotective properties, etc. They also possess some potent receptor selective biological activity like nitric oxide synthase (NOS) inhibitor and cannabinoid CB1 receptor antagonist activity. As a result, a large number of pyrazolines derivatives using different synthetic methods have been studied. The introduction of fatty acid chains into organic molecules also can produce important changes in their chemical and physical properties. In this context, to study the influence of fatty acid chains on the biological activity of organic compounds, our research group has developed methodologies for synthesizing new nitrogen containing heterocycles of pharmacological and technological interest. Bearing in mind the aforementioned facts to the pharmacological and biological importance of pyrazoline nucleus we herein report the synthesis of a novel series of fatty acid chain substituted pyrazoline derivatives by the cyclization reaction of different chalcones with selected fatty acid hydrazides. These selected fatty acid hydrazides were previously synthesized in our laboratory. The newly synthesized compounds were characterized by their IR, 1H NMR, 13C NMR and MS data.

(P146)

H-Bond Activated Glycosylation of Nucleobases: A Probable Prebiotic Synthesis of Nucleosides

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Formation of nucleosides under laboratory as well as natural (biotic/abiotic) conditions carries vital biological, astrobiological and medicinal importance. As nucleosides are formed from a nucleobase and a sugar, but it was confront to find an efficient procedure that how these components combine in primitive earth. Although there are many reports for the nucleosides synthesis in primordial earth conditions, most of them involve enzyme/metal catalysed condensation of de novo formed nucleobases and sugars, but no clear cut report is available on un-catalyzed glycosylation of nucleobases. We achieved glycosylation of nucleobases by heating metal free aqueous solution of nucleobase and sugar. It seems that abstraction of N9/N1 H by

C1'-OH promotes N9/N1(nucleobase)-C1' (sugar) covalent bond formation. The details of the experimental procedure along with mechanism of the reactions will be presented.

(P147)

A novel and efficient synthesis of 6-{(5-aryl-1,3,4-oxadiazol-2-yl)methyl}-6H-indolo[2,3b]quinoxalines

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The utility of microwave energy in developing green protocols in synthetic organic chemistry has been widely recognized. The microwave irradiation has been applied to organic reactions in solvents as well as solid phase heterogeneous reactions to shorten the reaction time. Microwave assisted heterocyclic synthesis has emerged as an efficient and eco-friendly strategy in recent years. In this presentation, a novel multi-step synthesis of a new series of sixteen 2-{(9-H/F/Br-6H-indolo[2,3-b]quinoxalin-6-yl)methyl}-5-aryl-1,3,4-oxadiazole derivatives (7) starting from isatine and o-phenylenediamine, utilizing only microwave energy is disclosed.

(P148)

Brønsted Acid Catalyzed in situ Acetal Formation, Intermolecular Alkyne-Carbonyl Metathesis and Annulation: A Facile Access to Substituted Fluorenes Seetharaman Manojveer and Rengarajan Balamurugan*

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Polycyclic aromatic hydrocarbons (PAHs) such as naphthalenes, fluorenes, antharacenes etc. play important role in the field of medicinal as well as material chemistry due to their unique properties. For their synthesis in a regioselective manner cyclization reactions of type [4+2], [2+2], [2+2+2], etc have been developed. In contrast to the synthesis of naphthalene derivatives, only very few methods are available in the literature for the construction of fluorene framework. Hence, development of simple method for the construction of fluorene from readily available starting materials is desirable. Yamamoto and co-workers studied extensively the cyclizations involving o-alkynylbenzaldehyes and alkynes under Lewis/Bronsted (LA/BA) acid catalyst condition for the synthesis of naphthalenes via [4+2] benzannulation pathway. In our endeavor to develop reactions using in situ generated acetals, we have found that reaction of o-alkynylbenzaldehyes and alkynes in the presence of trimethyl orthoformate and catalytic Brønsted acid results in fluorene derivatives in one pot efficiently. It undergoes [2+2] cycloaddition of in situ formed acetal with alkyne to give chalcone followed by annulation to furnish substituted fluorene in the same pot.

(P149)

MnO₂ Promoted Sequential C-O and C-N Bond Formation via C-H Activation of Methylarenes: A New Approach to Amides

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The development of novel chemical reactions and recuperating the reaction conditions to maximize product selectivity, energy efficiency, and environmental safety remains the main thrust of current chemical research. Hydrocarbons, derived from oil and natural gas, constitute the most inexpensive and readily available feed stocks for chemical industries. Therefore, direct formation of C-C and C-X linkage via carbon hydrogen (C-H) bond activation of hydrocarbons is of immense importance and has currently emerged as a challenging goal. This idea has been mainly realized by means of chelation-assisted C-H activation and cross-dehydrogenative coupling (CDC) strategy. Although these advances have been extensively explored for C-C and C-O bond formation, there is still a dearth of information on C-N bond creation. In this perspective, C-N bond formation and eventual synthesis of amides involving C-H bond activation of alkylarenes remains the cherished target. The amide is one of the most important functional groups in chemistry, forming the basic building block of a number of natural products, pharmaceuticals, and polymers. Amides are commonly formed via reactions of a carboxylic acid with an amine. A number of alternative methods for amide bond formation have been developed including Beckmann rearrangement, aminocarbonylation of aryl halides and alkynes, crosscoupling of formamide with alkyl/aryl halides, oxidative amidation of aldehydes/alcohols, and transamidation. However, more economical, environmentally friendly, resource efficient and highly selective methods are in demand.

(P150)

Synthesis of Tetrasubstituted Thiophenes from Activated Donor-Acceptor (D-A) Cyclopropanes <u>G. Sathishkannan</u> and K. Srinivasan* School of Chemistry, Bharathidasan University, Tiruchirappalli.

Thiophene ring is encountered in many medicinally active agents, including the drugs articaine, banminth, cymbalta, plavix and zyprexa and in certain bioactive natural products such as echinothiophene and xanthopapin-C.1 More importantly, several thiophene-based materials find applications in organic electronics as semiconductors, molecular wires, light emitting diodes, field effect transistors, non linear optical materials, photovoltaic materials, etc.2 Some important methods for the synthesis of thiophenes include the cyclocondensation of 1,4- dicarbonyl compounds with phosphorous pentasulfide (Paal synthesis), the base-induced cyclocondensation of α -diketones with thiodiglycolates (Hinsberg synthesis) or α , β -acetylenic esters with thioglycolates (Fiesselmann synthesis) and variations thereof.3 We have discovered a de novo synthesis of tetrasubstituted thiophenes from activated donor-acceptor (D-A) cyclopropanes (which are popular building blocks in organic synthesis4). Accordingly, trans-2-aroyl-3-arylcyclopropane-1,1-dicarboxylates undergo [3+3] annulations with 1,4-dithiane-2,5-diol in the presence of aluminium(III) chloride in dichloromethane to give diastereomeric mixtures of thiopyran derivatives, which upon further treatment with DBU furnish highly substituted thiophenes in good yields. The reaction is of wide scope and tolerates various substituents on the aryl rings. The details will be presented in the poster.

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(P151)

Diversity oriented approach to phenylalanine derivatives via the Diels-Alder reaction involving sulfolene intermediates

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We have synthesized a series of highly functionalized unusual phenylalanine derivative by using the DA reaction as a key step and here diethyl acetamidomalonate has been used as a glycine equivalent. There are various diversity points embedded in our strategy and thus provides opportunity to generate a library of unusual phenylalanine derivatives. By our methodology these unusual AAAs are accessible readily from easily available starting materials in three steps The strategy demonstrated here can provide access to bis armed AAA derivatives such as 24, which are not accessible by conventional coupling strategies. For example, dibromo compound 29 on coupling with diethyl acetamidomalonate gave 1,2,3,4-tetrahydro isoquinoline 3-carboxylicacid (tic) derivative 30.

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(P152)

Trapping azidocarbeniumion: an unique activation mode for the synthesis of azides <u>Suman Pramanik</u>, Prasanta Ghorai

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 α -Azidocarbeniumion intermediate is well known in literature since middle half of twentieth century as the intermediate in Schmidt rearrangement. A theoritical calculation has revealed that the azido group can stabilize the α -carbocation better than an α -HO-group, albeit slight lower than the α -NH₂ group. Although, there are overwhelming reports for the trapping of oxocarbeniumion as well as iminiumion for the synthesis of alkoxides and amines, respectively; the trapping of analogous azidocabeniumion for the synthesis of azides has never been developed. The real challange associated with such startegy is to stop the easy removal of nitrogen (N₂) gas followed by rearrangement to occur. Here, we envisioned an unprecedented approach for the trapping of highly sensitive azidocarbeniumion intermediate with numerous nucleophiles to provide a diverse class of benzylazides from aldehydes with excellent chemoselectivity.

(P153)

A simple and efficient mechanochemical route for the syntheses of 2-aryl benzothiazoles and substituted benzimidazoles

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The development of simple, efficient and environmentally friendly chemical processes for the preparation of biologically active molecules continues to be one of the major challenges for the synthetic organic chemists. In this direction, a mechanochemical process (such as ball-milling and grinding) is a reasonable approach for reducing waste, and such strategies due to their simplicity provide a sustainable alternative to the classical solution based methods of chemical synthesis. Both benzimidazoles and benzothiazoles are considered as privileged motifs in the field of medicinal chemistry as well as industrial processes. Although some mild and "green" protocols for the synthesis of these systems have been documented in recent time, development of a more efficient and simpler method is always worthy to pursue. Like our earlier efforts in this direction,2 herein, we report a simple and "green" method for the synthesis of a variety of arylsubstituted benzothiazoles and benzimidazoles through solvent assisted grinding of the corresponding aromatic aldehydes with o-phenylenediamine / o-aminothiophenol under ambient conditions. In a typical procedure, o-phenylenediamine / o-aminothiophenol and aldehydes were taken in an agate mortar and pestle and gradually ground for 5-30 min to afford corresponding benzazoles in 70-85% of yields. Total 26 entries. The formation of the products was confirmed by determination of melting point, 1H NMR and ESI-MS. The method is not useful for the preparation of benzoxazoles.

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(P154)

PALLADIUM CARBENOID BASED CROSS-COUPLING REACTIONS IN ORGANIC SYNTHESES

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Aryl halides are employed as electrophiles in the Pd-catalyzed cross-coupling with tosylhydrazones affording di-, tri-, and tetrasubstituted olefins. The versatility of this coupling reaction is demonstrated in showcasing the selectivity of coupling reaction in the presence of hydroxyl and amino functional groups containing aryl halides. This method allows to synthesize a variety of vinyl-heterocyclic compounds. This development was further extended to synthesize a regioselective highly substituted branched dienes. The regioselective formation of highly branched dienes is a challenging task. Design and exploration of alternative working models to achieve such a regioselectivity to accomplish highly branched dienes is considered as a historical advancement of Heck reaction. Based on the utility of carbene transfer reactions, a coupling of N-tosylhydrazones with Pd(II), under oxidative conditions was envisioned to obtain Pd-biscarbene complex with α -hydrogens, which can lead to branched dienes. Herein we report, a

novel Pd-catalyzed selective coupling reaction of hydrazones in the presence of LiOtBu and benzoquinone to form the corresponding branched dienes. The utility of Pd-catalyst for the crosscoupling reactions for synthesizing branched conjugated dienes is unprecedented. The reaction is versatile and compatible with a variety of functional groups and is useful in synthesizing heterocyclic molecules. We anticipate that this Pd-catalyzed cross coupling reaction to open new avenue for synthesizing useful compounds. The synthesis of branched dienes were highly selective towards sensitive functional groups such as bromo arenes and also electron rich heterocyclic rings. The outcome of the reaction was postive for the unactivated systems like alkyl substituted tosylhydrazones. Typical reactions conditions was also utilized to synthesize the cyclic conjugated dienes, which furnished the expected quinolines in good yield.

(P155)

Chiral Oxo-Rhenium(V) Complex as Catalyst for Enantioselective Reduction of Imines Braja Gopal Das and Prasanta Ghorai*

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The secondary amines or their protected analogues are crucial assynthetic tools for the synthesis of various natural products and pharmaceuticals. Therefore, their synthesis has fueled considerable research into the asymmetric reduction of imines. These reductions generally performed by catalysts derived from transition metals in low-oxidation states. In contrast, recently, oxo-rhenium complexes in the high oxidation state have emerged as mild,non-toxic, and air/moisture stable catalysts for efficient hydrosilane activation as well as various organic transformations. Herein, we describe the development of a novel chiral rhenium(V)-oxo complex for the catalytic enantioselective reduction of imines with good to excellent enantioselectivities.

(P156)

Desymmetrization of Trehalose via Regioselective DIBAL Reductive Ring Opening of Benzylidene and Substituted Benzylidene Acetals

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Trehalose containing glycolipids and lipooligosaccharides are isolated from mycobacteria, fungi and worms.¹ These glycoconjugates play significant biological roles in survival of these organisms and display immunological properties. Due to presence in micro-heterogeneous form in nature, they are not available in ample amount and with desired purity for biological studies. A general methodology of desymmetrization of trehalose is essential for the synthesis of unsymmetrically substituted trehalose derivatives.^{1,2} Regioselective reductive opening of one of the benzylidene acetals constitutes a short route for desymmetrization of trehalose. We carried out a systematic study to establish conditions for selective ring opening of only one of the 4,6-Obenzylidene groups of the trehalose dibenzylidene acetals and substituted benzylidene acetals at O_6 or O_4 , by using DIBAL solution in toluene or in CH_2Cl_2 , respectively to get access to unsymmetrically substituted 6-OH and 4-OH trehalose derivatives. The method was applied to synthesize various biologically important trehalose glycoconjugates substituted at O_4 and O_{6_2} including a mycobacterial trisaccharide, a 4-epi trehalosamine analog and a maradolipid.³ References

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(P157)

Expeditious Synthesis of Bacterial Glycoconjugates

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Bacteria have unusual glycans on their surfaces which distinguish them from the host cells. These unique structures offer avenues for targeting bacteria with specific therapeutics and vaccines. However, the rare sugars are not accessible in acceptable purity and amounts by isolation. Availability of orthogonally protected monosaccharide building blocks through efficient chemical synthesis is the crucial step toward the development of glycoconjugate vaccines. Herein, we describe a general and divergent strategy for the synthesis of the bacterial deoxy amino hexopyranoside building blocks from a common sugar intermediate. The methodology is applied to the first total synthesis of the L-serine linked trisaccharide of Neisseria meningitidis and synthesis of a rare disaccharide fragment of the zwitterionic polysaccharide A1 of Bacteroides fragilis. The short and efficient protocol is expected to speed up bacterial glycan assembly and give a rapid access to the prokaryotic glycome.

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(P158)

Facile, diastereoselective synthesis of functionally enriched Tetra/Octahydro-isoquinolone hexahydroisoquinolines, hexahydroisoquinolones and hexahydroisochromones via inter-/intramolecular amidolysis of C-3 functionalized 2-azetidinones

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The isoquinoline and isoquinolone have attracted the attention of synthetic and medicinal chemists not only because of their pharmacological profiles but also their intermediacy in the synthesis of different types of chemical compounds. Recent revelation from our lab has shown the utilization of β -lactam synthon protocol for the synthesis of functionally decorated heterocycles.1 The present work describes the synthesis of Tetra/Octahydro-isoquinolone, hexahydroisoquinolines, hexahydroisoquinolones and hexahydroisochromones via inter-/intramolecular amidolysis of C-3 functionalized 2-azetidinones. Since the described protocol does not include the use of highly functionalized intermediates, stringent conditions or toxic reagents, the developed methodology does not suffer from the typical intricacies associated with the conventional protocols.

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(P159)

4-aminoquinoline-β-lactam conjugates: Synthesis, and in vitro Antimalarial Evaluation <u>Raghu Raj</u>, Vipan Kumar Department of Chemistry, Guru Nanak Dev University, Amritsar.

With approximately 500 million infections and 2.5 million deaths annually, malaria remains one of the most serious health problems of the developing world. The causative agent of the most lethal form of malaria, Plasmodium falciparum, has developed resistance to multiple drugs including chloroquine (CQ), previously the first line drug to treat malaria in most endemic countries. In present work, a library of urea/amide/oxalamide tethered 4-aminoquinoline- β -lactam based hybrids were synthesized with well modulated chain lengths and tested for their antimalarial activities.^{1,2} The results reveal the dependence of activity profiles on the N-1 substituent of the β -lactam ring, the nature of the linker as well as the length of the alkyl chain. The most potent of the test compounds showed better antiplasmodial activity compared to chloroquine and desethylamodiaquine, having an IC50 of 34.97 nM against cultered W2 resistant strain of P. falciparum.

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(P160)

Facile construction of fused quinolyl-4H-thiopyran via three-component reactions catalyzed by L-proline Mahul P. Kanani and Manish P. Patal*

Mehul B. Kanani and Manish P. Patel* Sardar Patel University

Three-component reactions of 2-mercaptoquinoline-3-carbaldehyde, malononitrile and thiolbased nucleophiles were developed, by using L-proline as a catalyst, which generated various substituted quinolyl-4H-thiopyran derivatives in good to excellent yields. The reactions were performed in ethanol under mild conditions. In these reactions, the use of L-proline as a catalyst was proven to be key for rendering the reactions possible because replacing L-proline with other acids or bases resulted in the generation of many side products. Many nucleophiles, such as thiophenols and mercaptans could be successively used to assemble with malononitrile and various 2-mercaptoquinoline-3-carbaldehyde. The structures of new derivatives were characterized by 1H NMR, 13C NMR, FT-IR, mass spectra and elemental analysis.

(P161) Development of solid supported platinum(0) nanoparticles as heterogeneous catalyst and its applications in diversified organic transformation

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From the very dawn era 'Platinum' has attracted organic chemist's attention due to its potential catalytic properties mainly in oxidation and reduction reactions for laboratory scale as well as industrial process development.[1] But in the recent years i.e., in era of 'Green Chemistry' we are more interested in the development of environmentally stable, easily recoverable, highly recyclable and low loading heterogeneous catalytic system with high activity and negligible metal contamination in the product. As a part of our recent investigation,[2] our group has developed a facile process for the preparation of solid supported platinum(0) nanoparticles (SS-Pt) as heterogeneous catalyst through reduction deposition method.[3] Characterization of SS-Pt was performed by SEM, TEM, EDX and XRD analysis. Further, the SS-Pt catalyst was applied in various organic transformations such as oxidation of alcohols to aldehydes and ketones, chemo-selective controlled reduction of nitroarenes to N-arylhydroxylamines and hydration of nitriles to primary amides. In all the above organic transformations the SS-Pt catalyst was found to be air/moisture stable, highly recyclable and negligible metal leaching.

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(P162)

Total Synthesis of L-Asparagine Linked Hexasaccharide of the surface Glycoprotein of Methanothermus fervidus

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Chronic periodontitis is an oral disease, arising from polymicrobial infection. It may cause loss of teeth and has been involved in endocarditis, atherosclerosis, stroke, and preterm delivery of low birth weight infants.¹ There is a little information about the relationship between methanogenic archaea and chronic periodontitis.² It is plausible that they are secondary colonizers of infection process.³ L-Aparagine linked hexasaccharide was isolated from the surface glycoprotein of methanothermus fervidus.⁴ We herein describe the first total synthesis of aspargine linked hexasaccharide through a convergent [3+3] glycosylation approach. This strategy employs thioglycosides as key building blocks that access the synthesis of 3-O-methyl mannose disaccharide and construction of other glycosidic linkages. Galactosamine derivative

was accessed from the glucosamine building block via the Lattrell–Dax invesion of 4-OH and aspargylation was embedded in later stage.

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(P163)

Novel Multicomponent Cascade Assembly for Quinolinopyranpyrazole Architectures Manickam Bakthadoss, *^[a,b] <u>Anthonisamy Devaraj</u>^[a] and Damodharan Kannan^[a] ^aDepartment of Organic Chemistry, University of Madras, Guindy Campus, Chennai. ^bDepartment of Chemistry, Pondicherry University, Pondicherry.

Heterocyclic frameworks, especially nitrogen containing polyheterocycles are most prevalent class of compounds in the arena of agrochemical productions and pharmaceutical sectors with wide range of applications. A multicomponent reaction (MCRs) is an appealing convergent strategy where three or more substrates are put together towards the formation of complex heterocyclic molecules with significant portions of all substrate components. The utilization of multicomponent domino reactions in organic synthesis is a preferred way to improve synthetic efficiency and selectivity particularly for the construction of complex molecular units. It is well clear from the literature that the polycyclic quinolinopyran and pyrazole frameworks are widely found in several bioactive compounds and natural products with potential utility in medicinal chemistry. In continuation of our interest in the field of heterocyclic chemistry, we herein describe an efficient, novel and new protocol towards the synthesis of fused tetracyclic quinolinopyrappyrazole frameworks via multicomponent domino reaction. The present method involves an in situ formation of edaravone from phenylhydrazine and methyl acetoacetate followed by domino Knoevenagel intramolecular hetero Diels-Alder (IMHDA) reaction which leads to the formation of three rings encompassing two six membered rings and one five membered ring in a stereoselective manner. Formation of wide variety of tetracyclic quinolinopyrappyrazole frameworks in excellent yields with high stereoselectivity pronounces the efficiency of the reaction.

(P164)

Studies Towards Synthesis of Tumor Associated Carbohydrate Antigens (TACAs) Archanamayee Behera, Madhu Emmadi and Suvarn S. Kulkarni* Department of chemistry, IIT Bombay

Truncated glycocalyx is a universal hallmark of cancer. The difference between the normal glycocalyx and the truncated one with the exposed tumor associated carbohydrate antigens (TACAs), is exploited for the development of anti-cancer vaccines.1–6 Many syntheses of TACAs are reported in literature.1–5 Our divergent approach involves synthesis of an orthogonally protected Tn antigen and its application in assembly of all important TACAs (scheme 1).7

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(P165)

Lewis acid-mediated ring opening reactions of 2-aryl-3-nitro-cyclopropane-1,1dicarboxylates: Access to aroylmethylidene malonates <u>T. Selvi</u> and K. Srinivasan*

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Nitrocyclopropanes are highly useful building blocks in organic synthesis. They act as precursors for cyclopropane amino acids which are employed in the constuction of structurally defined peptide units.¹ They have been used as key intermediates in the total synthesis of antibiotic natural products, belactosins A and C, harmaomycin.² Further, nitrocyclopropanes undergo nucleophilic ring opening reactions which lead to many valuable products, including isoxazoline-N-oxides, pyrroles and chiral amines and ethers.³ Due to such diverse applications, many racemic and asymmetric methods have been developed for the synthesis of nitrocyclopropanes.⁴ We are interested in trans-2-aryl-3-nitro-cyclopropane-1,1-dicarboxylates because of their easy accessibility and enormous synthetic scope. They are readily synthesized by Michael addition of halomalonates to nitroolefins followed by base-induced ring closure ⁵ or from the oxidative cyclization of Michael adducts of nitroolefins with malonates using iodobenzene diacetate.⁶ Even though, these nitrocyclopropanes were known as early as 1969, their chemical properties or synthetic applications have been scarcely investigated. In the poster, we will describe Lewis acid-mediated ring-opening reactions of these nitrocyclopropanes for the facile access of aroylmethylidene malonates. In addition, the applications of the resulting products in the synthesis of various heterocycles will be presented.

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(P166)

Sodium metal in Silica Gel (Na_SG): A new reagent for decarbamoylation of Carbamates Chandra kant Maurya & Pradeep Kumar Gupta*

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Sodium metal stabilized on silica gel (Na_SG) has been reported as a powerful reducing agent. In comparison to the free metal, it is less pyrophoric and can easily be handled. Owing to the merits, this reagent has been used to carry out a variety of organic transformations including desulfonation of amines, Birch reduction, Bouveault-Blanc Ester Reduction, etc. In this paper, we describe a newer method describing its use for decarbamoylation of carbamates to corresponding alcohols. On contrary to the reported methods, the present method requires milder reaction conditions and proceeds at room temperature. During the present course of work, the reaction conditions including solvent and reaction time have been optimized and the process has been extended for decarbamoylation of a variety of carbamates.

(P167)

Synthesis, molecular docking and anti-inflammatory activity studies of some novel pyrazolothiazole derivatives.

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Non-steroidal anti-inflammatory drugs (NSAIDs) alleviate pain by counteracting the cyclooxygenase (COX) enzyme. On its own, COX enzyme synthesizes prostaglandins, creating inflammation. This enzyme has two recognized forms: COX-1 and COX-2. COX-1 is important for the basic housekeeping throughout the body and COX-2 enzyme is induced to signal pain and inflammation. In whole, the NSAIDs prevent the prostaglandins from ever being synthesized, reducing or eliminating the pain1-3. The present work is focused on the selective inhibition of COX-2 enzyme so as to reduce the side effects associated with inhibition of COX-1 enzyme. Continuing our effort to build novel biologically active heterocyclic derivatives, here we report some novel Pyrazolothiazole derivatives as anti-inflammatory agents4-7. All the synthesized compounds were characterized by FT-IR, 1HNMR, 13CNMR, HRMS and elemental analysis techniques. The in vivo anti-inflammatory assay of the synthesized compounds was carried out by using the functional model of carrageenin-induced paw edema in mice initially proposed by Winter et al.8 The compounds showed average to good anti-inflammatory activities. The molecular docking studies of the synthesized compounds were done with COX-2 enzyme using Autodock Vina software9. The crystal structure of the COX-2 protein was obtained from Protein Data Bank (PDB ID: 6COX). Most of the docking scores complemented the in vivo antiinflammatory activity results.

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(P168)

Synthesis of Indole alkaloids using In/TFA as catalytic combination

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Indoles and their derivatives constitute an important class of biologically active natural products, possessing antitumor, anticancer, antimicrobial, antibacterial, and anti-inflammatory activities,¹ and dozens of methods for the construction of indoles have been developed.² Among the indole alkaloids, tetrahydro- β -carbolines (THBCs) skeleton form a class of alkaloid, which have been studied extensively.³ Further, the synthesis of tetracyclic [6,5,5,6] indole ring systems is gaining momentum due to it bioactive moiety and presence in natural products, which led organic chemists to hunt for novel synthetic strategies.⁴ On the basis of the above considerations and in the context of our efforts on developing strategies towards bioactive heterocycles.⁵ We are reporting the synthesis of tetrahydro-beta-carbolines (THBCs) and tetracyclic [6,5,5,6] indole ring system in presence of In2(SO4)3 /TFA combination as catalyst in DCM as solvent using tryptamine as common reactant. The methods developed are mild and efficient protocol for the synthesis of tetrahydro- β -carbolines and tetracyclic [6,5,5,6] indole ring in good yields. The methods are one-pot and used tryptamine as the common starting reagent.

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(P169)

Design and Synthesis of Pyrazolopyran Derivatives Possessing Anticancer Activities Targeting Various Receptor Aurora Kinases <u>Ashok Sharma</u>, Paritosh Shukla Department of Chemistry, BITS Pilani, Rajasthan.

Functionalized pyrazolopyran small molecules and their derivatives have been shown to possess broad spectrum of biological activities such as anticancer activities targeting receptor aurora kinases and CHK inhibitors, antifungal, and antibacterial etc. To be more specific, inhibition of aurora kinases, a member of serine/threonine kinase family involved in the regulation of cell division is emerging as a promising targeted cancer treatment option. Hence, based on the emerging success of Aurora kinase inhibitors in the development of kinase-based cancer therapy, we have started a synthesis initiated biological activity-cum-virtual screening program for the identification of Aurora kinase inhibitors. In this regard, the development of simple and effective methods of obtaining functionally substituted pyrazolopyrans is a challenging task worth taking up. A series of novel pyrazolopyran derivatives were synthesized first by the usual condensation reactions and then using microwave reactions of 3-Methyl-5-pyrazolone with a variety of substituted aldehydes. The resulting pyrazolopyran compounds were characterized by the usual analytical techniques such as IR, NMR etc. The compounds are presently being evaluated for their in-vitro activity against various cell-lines such as anticancer, anti HIV and antimicrobial. In silico studies such as docking will be carried out to understand their specific interaction with the target enzyme. After optimizing their SAR, QSAR and docking studies, the results shall be combined go to the next level of hit to lead development.

(P170)

Catalytic activity of Copper(II) Complexes Derived from Succinoyldihydrazones

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Copper-catalyzed cross-coupling reactions have lead to the formation of C–N, C–O, C–S and C– C bonds and have been recognized as one of the most useful strategies in synthetic organic chemistry. Actually, the past decade has witnessed a sharp increase on the attention to Cu catalyzed coupling transformations due to the low cost and low toxicity and also due to important discovery on organic ligand facilitated copper catalysis, which significantly lowered the demand on reaction conditions and expanded the compatibility of Cu-catalyzed couplings.¹ As an important step towards the ideal synthesis of atom economics, employing the Cu-catalyzed coupling reaction in the design of tandem reactions is now gaining worldwide attention for their great efficiency in assembling structurally diversified small molecules. Copper catalysts have been proven to tolerate a great variety of different reaction conditions. Accordingly, the research on exploring new application of Cu-catalyzed coupling has gained extensive interest. So, in importance and our interest in copper complexes² playing an important role in catalysis, we, present in here copper complexes of succinoyldihydrazones³ which have been synthesized, characterized and their catalytic properties studied in the synthesis of 1,3-divnes. The dihydrazones used as ligands for complex formation are multidentate ligands possessing as many as eight bonding sites and can utilize utmost six bonding sites simultaneously in bonding to the metal ions. The complexes show equal reactivity both with electron donating and electron withdrawing substituted phenylactylenes in good yields. The advantages of the present protocol are low catalytic loading of the catalyst (1 mol%) with good yields in less time. The 1,3-diynes play a significant role in the construction of macrocyclic annulenes, organic conductors, supramolecular switches and carbon-rich materials.⁴

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(P171) A facile one-pot multi-component synthesis of thiazolidin-4-ones via Staudinger/aza-Wittig reaction

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Thiazolidin-4-ones exhibit diversified bioactivities such as anti-fungal, cardioprotective, antihistaminic, anti-HIV, analgesic, cytotoxic, COX-1 inhibitors, and non-nucleoside inhibitors of HIV-RT. Hence considerable interest towards their synthesis has attained importance. In particular, synthetic methodologies through one-pot multi-component reaction is emerging. Perusal of literature indicates that synthesis of thiazolidinones involve the preparation of imine (from amine and carbonyl compounds) followed by its reaction with thioglycolic acid. The methodology involves the use of dehydrating agents or azeotropic removal of water and hence time consuming and laborious. In view of this, it was envisaged to develop a simple and elegant methodology avoiding the dehydrating agents or azeotropic removal of water. In this regard, in the present investigation, a one-pot multi-component sequential Staudinger/aza-Wittig reaction has been conveniently utilized to eradicate the above said limitations in the synthesis of the title compounds.

(P172)

Cerium(IV) ammonium nitrate mediated catalytic oxidation of 1, 3-dicarbonyl compounds to vicinal triketones

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1,2,3-Tricarbonyls or VTCs are compounds with three adjacent carbonyl groups in an array and have gained attention by the organic chemist ever since the synthesis of diphenyl triketone in 1890 by von Pechmann and de Neufville[1]. The chemistry of these compounds has been extensively studied by Rubin, Wasserman and their co-workers[2]. Among the various methods developed for the synthesis of VTCs, those from β -dicarbonyl compounds constitute an

important route[3]. The use of single electron oxidants for the formation of carbon-carbon and carbon-heteroatom bonds has received much attention in the field of organic synthesis. Cerium (IV) ammonium nitrate (CAN) occupies a unique position among the various single electron oxidants, owing to its low cost, ease of handling, solubility in organic solvents and its high reduction potential value of 1.61V vs SHE. Its synthetic versatility is revealed from the numerous organic transformations it can mediate[4]. Oxidative addition of (CAN) to activated methylene compounds produce electrophilic radicals, which can be successfully trapped by using several electron rich substrates like alkenes[5a], glycols[5b], vinyl sulphides[5c] and MCPs[5d]. We were also successful in the synthesis of multisubstituted furans by the oxidative addition of 1, 3-dicarbonyl compounds to terminal acetylenes [6]. However the fate of the radical cation of 1,3-dicarbonyl compound in presence of catalytic amounts of CAN is unknown and we have carried out a detailed study in this direction. Our studies have shown that 1,3-dicarbonyl compounds in presence of catalytic amounts of CAN led to the facile synthesis of VTCs in moderate to good yields[7]. The reaction was found to be general with various β -ketoesters, 1,3diketones and β-diesters. The detailed experiential procedure, optimization studies and the mechanistic rationale will be presented. The single step synthesis of commercially important compounds like ninhydrin, alloxan and oxoline has been accomplished by this methodology. Further studies towards the synthesis of vicinal tetra and pentacarbonyl compounds are underway.

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(P173)

Environ-friendly water mediated synthesis of 1,2,3-triazolyl-pyrazoline hybrids

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In general, heterocyclic molecules exhibit potent pharmacological activities. Among active heterocycles, 1,2,3-triazole and pyrazoline nucleus have attained importance due to their varied bioactivity profiles. During the past two decades, synthesis of novel pharmacologically interesting hybrid heterocycles has received attention in drug discovery and thus emerging.

Nowadays, synthesis of organic molecules in aqueous environment provokes interest among organic chemists. As a reaction medium, water offers many practical and economic advantages including low cost, environmental compatibility and safety compared to other solvents, thus leading to eco-friendly chemical processes. In view of this, it was envisaged that synthesis of hybrid molecules containing two bioactive skeletons via environmentally friendly protocol is worth the attempt. Thus, in the present research work, an efficient and facile water promoted synthesis of 1,2,3-triazolyl-pyrazoline hybrids has been achieved in excellent yields from easily accessible 1,2,3-triazole linked chalcone precursors.

(P174)

A multicomponent cascade reaction for the synthesis of novel chromenopyranpyrazole scaffolds

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Heterocyclic rings are present as fundamental components in the skeleton of biologically active compounds produced by nature. Among them, benzopyran and pyrazole heterocyclic ring systems are present in a vast number of natural products and bioactive substances. Domino Knoevenagel-hetero-Diels-Alder reaction has proven to be a useful tool for the synthesis of polyheterocyclic compounds. Multicomponent reactions (MCR), which encompass numerous bond-forming reactions in a one-pot operation, represent appealing strategy for the facile construction of novel molecular architecture. The compounds containing a pyranopyrazole unit have shown antimicrobial, anti-inflammatory, and molluscicidal activities. On the other hand, photochromic compounds having a benzopyran nucleus have practical applications in data storage, optical filters and displays. The Baylis–Hillman adducts have become a valuable source for various organic transformations and have been transformed into a number of carbocycles and heterocyclic frameworks of medicinal importance. In continuation of our ongoing research program in the field of heterocyclic chemistry, we herein report a convenient, facile, and new method for the synthesis of novel tetracyclic chromenopyranpyrazole frameworks through a multicomponent cascade reaction (MCCR). Interestingly, this cascade reaction proceeds via the insitu formation of edaravone from phenyl hydrazine and methyl acetoacetate followed by domino Knoevenagel intramolecular hetero Diels-Alder reaction, which creates the annulation of three rings in a stereoselective fashion.

(P175)

Synthesis of spirooxindole derivatives via isatin based MCRs <u>Suman Pal</u> and Lokman H. Choudhury* Department of Chemistry, Indian Institute of Technology Patna

The oxindole core with a spirocyclic quaternary stereocenter at the C3 position is considered as a privileged heterocyclic motif which is found in a number of natural products as well as in synthetic pharmaceuticals.1 In continuation of our efforts towards the development of functionalized heterocycles using multicomponent reactions2 we have developed some isatin-based MCRs. A simple and efficient method to synthesize various spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-3'-carboxylate derivatives using triethylamine mediated four-component

reactions will be reported. Using the similar type base catalyzed reaction, the three component reaction of isatin, malononitrile and 5,7-dihydroxy-4-methyl-2H-chromen-2-one will also be discussed. The notable features of these protocols are simple and metal free reaction conditions, easy isolation of products, applicable to a wide range of readily available starting materials and good yields.

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(P176)

An environmentally benign solvent/scavenger-free protocol to 2-iminothiazolidin-4-ones <u>M.Dinesh</u>, M.Sathish kumar and A.Ponnuswamy*

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Iminothiazolidinones possess some potential bioactivities such as anti-HIV, anti-tubercular, cardiovascular, platelet activating factor (PAF) antagonist, anti-cancer and anti-diabetic activities. their synthesis inhibitory Hence. has attained importance. Prevailing synthetic methodologies for 2-iminothiazolidin-4-ones uses scavengers and organic solvents which are not environmentally benign. In particular, various bases are employed in the synthesis envisaging their role as acid scavengers. From an insight into the mechanism, it was presumed that use of acid scavenger would not promote rather retard the reaction. In view of this, a one-pot solvent/scavenger-free protocol for a rapid and efficient synthesis of 2iminothiazolidin-4-ones has been accomplished which regionselectively affords the regioisomer, 2-iminothiazolidin-4-ones as the exclusive product. The selectivity is directed by allylic strain encountered during the reaction.

(P177)

A Facile Multicomponent Reaction Involving Isoquinoline, Dimethyl Allenedicarboxylate, and 2-Oxo-1-H-indole-3-ylidenes

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The history of transient zwitterions dates back to 1932 when Diels and Alder reported that the reaction of pyridine with dimethyl acetylenedicarboxylate gave a 1:2 adduct [1]. Although the studies of Acheson and Huisgen enriched the chemistry of zwitterions [2, 3], the synthetic utility of these versatile intermediates remained largely unexplored. It is noteworthy that the ubiquitous presence of nitrogen containing heterocycles in drugs [4], has motivated synthetic chemists to design novel methods for rapid conversion of pharmacologically important drug- like compounds [5]. A major part of the work in zwitterion chemistry has involved the addition of

nucleophilic species to acetylenic esters [6]. Allenoates [7], an important class of activated π systems were first utilized in this protocol only very recently [8]. In view of the success of the reaction involving cyanoacrylates leading to highly functionalized pyrido[2,1-a]isoquinoline derivatives, we investigated the activity of the nucleophilic allenoate zwitterion towards 2-oxo-1H-indol-3-ylidenes.

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(P178)

Ruthenium-Catalyzed Synthesis of Isoquinolones Using 8-Aminoquinoline as an Auxiliary Bidentate Directing Group in C-H Functionalization

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Transition metal catalyzed C-H functionalization is an important tool in construction of various synthetic targets which are potentially useful in medicinal and materials chemistry.[1] In this work, we have developed a novel method for the synthesis of isoquinolones using 8-aminoqunoline as an auxiliary bidentate directing group.[2] A variety of functional groups were tolerated in this oxidative annulation process. This method is applicable for both symmetrical and unsymmetrical alkynes. High regioselectivity was achieved in the case of unsymmetrical alkynes. Reactions with heteroaryl amides also successful in this catalytic process. All the key products were characterized by X-ray crystallography.

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(P179)

Enantioselective NHC-Catalyzed Annulations of 2-Bromoenals with 1,3-Dicarbonyl Compounds, Enamines and Enolizable Aldehydes

Santhivardhana Reddy Yetra, Trinadh Kaicharla, Anup Bhunia, Atanu Patra and Akkattu T. Biju*

The N-Heterocyclic carbene (NHC)-catalyzed generation of α,β -unsaturated acyl azoliums followed by its interception with various nucleophiles, the formal [3+3] annulation reaction is well documented.1 Intriguingly, however, the NHC-catalyzed generation of chiral α,β unsaturated acyl azoliums is rare. Recently we reported the enantioselective NHC-catalyzed annulations of 2-bromoenals with 1,3-dicarbonyl compounds and enamines via chiral α,β unsaturated acyl azoliums. The reaction resulted in the asymmetric synthesis of synthetically and medicinally important dihydropyranones and dihydropyridinones, and the reaction tolerates a wide range of functional groups.2 Moreover, very recently, we demonstrated that enolizable aldehydes as nucleophilic partners for chiral α,β -unsaturated acyl azoliums, and the reaction furnished 4,5-disubstituted dihydropyranones.3 In addition, based on DFT calculations, a mechanistic scenario involving the attack of nucleophile from the below the plane of the α,β unsaturated acyl Azoliums, and the mode of enantioinduction is presented. The details of this work will be presented.

(P180)

Studies Towards Total Synthesis of Oligosaccharide OSE-1 of Mycobacterium gordonae (Strain 990)

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OSE-1 is highly antigenic glycan isolated in 1993 by Besra from the cell surface of Mycobacterium gordonae (strain 990).¹ Mycobacterium gordonae also known as $\hat{a} \in \alpha$ ap-water bacillus $\hat{a} \in \alpha$ is a slow-growing scotochromogenic acid-fast bacillus with characteristic cultural and biochemical properties. In AIDS patients this strain causes pulmonary infections similar to Tb but it is resistant to anti-Tb drugs like isoniazid, pyrazinamide, ethambutol and cycloserine.² It is observed mainly in patients with prosthetic devices, compromised immunity, chronic pulmonary disease or history of trauma.³ It is considered as a potential opportunistic respiratory tract pathogen in patients with advanced HIV-1 infection. Also a number of infections involving skin, soft tissues, liver, respiratory tract and underlying immunosuppression have been reported.² Synthesis of OSE-1 would enable speedy serodiagnosis and vaccine development. The key step involved in the synthesis of OSE-1 is Intramolecular Aglycone Delivery method to obtain the right hand terminal desymmetrized trehalose unit. Remaining part of the molecule is assembled in a convergent fashion via stereoselective glycosidation reactions using trichloroacetimidate and thiol donors.

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(P181)

Synthesis and biological evaluation of cholesteryl glycinates and cholesteryl carbonates

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Steroids play a crucial role in biological systems. Many of steroids are generated by the body system and also exist in plants. In the development of medicinal chemistry, these steroids are connected with small organic unit and studied their response to the biological system. Among all the steroids cholesterol is one of the most important one because it is main precursor to other steroids in the steroidogenesis. Cholesterol is precursor to pregnenolone which is a naturally available neurosteroid. Recently, Kakati et al reported the antimicrobial activity of pregnenolone derivatives. But the biological inhibitory activities of cholesterol or its derivatives has been reported in very few litratures. We could expect these derivatives maid show good response. For this purpose we started a program to study the antimicrobial, anti-fungal and antioxidant activities of cholesterol derivatives. Several novel carboxamide, sulphonamide, carbamate, urea and thiourea derived cholesterol glycinate and carbonate derivatives were designed and the results of antimicrobial, anti-fungal and antioxidant activities are presented here.

(P182)

A simple, efficient and green procedure for Michael addition catalyzed by [C4dabco]OH ionic liquid

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In the last two decades ionic liquids (ILs) are emerging as potential 'greener'alternatives to volatile organic solvents and they have been used as environmentally benign media for many important organic reactions.¹ The Michael addition is one of the most important carbon-carbon bond forming reactions² and is catalyzed by strong bases and Lewis acids that lead to undesirable side reactions.³ A dabco-based basic ionic liquid, 1-butyl-4-aza-1-azaniabicyclo[2.2.2]octane hydroxide,⁴ has been developed as a catalyst for a convenient and rapid method for Michael addition of active methylene compounds to α , β -unsaturated carboxylic esters and nitriles. The method is very simple and yields are very high. The catalyst can be recycled for several times without loss of activity.

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(P183)

Engaging Isatins in Solvent-Free, Sterically Congested Passerini Reaction

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The Passerini reaction, the three-component reaction between a carboxylic acid, a carbonyl compound such as an aldehyde or a ketone, and an isocyanide, offers direct access to α -acyloxy carboxamide derivatives.¹ In many cases, the Passerini reaction employing ketones is generally slower and in some cases, the reactions carried out with bulky carbonyl substrate and the bulky isocyanide fail to afford the desired product.² In the context of our interest in the chemistry of isatins, we recently reported a practical and efficient solvent-free Passerini reaction of 3,3-disubstituted oxindole derivatives, and interestingly the reaction is carried out under air.³ Moreover, electrophilic phenols are used as the acid component in these reactions and the utility of the reaction was established by a one-pot synthesis of oxindoles with free -OH group at the benzylic position. The details of this work will be presented.

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(P184)

Synthesis of π-conjugated dibenzoheterocycles using Diels-Alder reaction <u>Nandakumar, M.</u> and Mohanakrishnan, A. K. University Of Madras.

Dibenzofluorenone and dibenzothiophene derivatives are the class of condensed aromatic heterocyclic hydrocarbons having promising opto-electronic applications in the area of material science. The Diels-Alder reaction of benzo[c]furan¹ with dieneophiles namely, indenone, naphtho[b]cyclopentenone, benzo[b]thiophene S, S-oxide and naphtho[b]thiophene S, S-oxide followed by cleavage of the furan bridge lead to the formation corresponding heterocycles. Also, the one pot synthesis of Dibenzofluorenone and dibenzothiophene S, S-dioxide also achieved through the Diels-Alder reaction followed by aromatization. The various types of dibenzoheterocycles reported herein may find application in the area of field-effect transistors and also in organic solar cell (OSC) applications.

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(P185) Iodine–alumina as an efficient and useful catalyst for the synthesis of N-substituted 2aminobenzothiazole under solvent free conditions

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Benzothiazoles are a class of heterocycles that possess diverse array of biological properties.¹ Benzothiazoles moieties are found in a variety of biologically important natural products and are used as drugs for several diseases such as, inflammatory, epilepsy, viral infections, insomnia and atherosclerosis.² Indeed, benzo[d]thiazoles may be regarded as a 'privileged class' of structure from which drug like bioactives can be reasonably developed. Among the benzothiazoles, 2-(Narylamino)benzothiazoles have found a broad application in drug development for the treatment of various ailments.³ There are only few reports on the synthesis of 2-(N-arylamino) benzothiazoles. For the synthesis of 2-(N-arylamino)benzothiazoles, a ligand-free coppercatalyzed reaction of 2-halobenzenamines with isothiocyanataes using TBAB as the promoter has been developed recently.⁴ In our previous work, we reported the solid phase synthesis of 2-(N-arylamino)benzothiazoles using polymer supported tribromide (PST) under microwave irradiation in solvent-free condition.⁵ Herein, a new example of iodine-alumina (I2-Al2O3) catalyzed cyclization reaction of thioureas to N-substituted-2-aminobenzothiazoles will be reported. The method has several advantages, such as short reaction time, good yields and environmentally benign procedure. Moreover, the catalyst could be recovered conventionally and reused again without loss of activity.

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(P186)

Synthesis of novel 1,2,3-triazole tagged pyrazolo[3,4-b]pyridine derivatives and their cytotoxic activity

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A large number of heterocyclic compounds containing pyridine rings are associated with diverse pharmacological properties. The pyrazolo[3,4-b]pyridine skeleton is an important structural fragment of many heterocyclic compounds showing a broad spectrum of biological activity such as antibacterial, anticancer, anxiolytic, antiviral and GSK-3 inhibition activity. Alternately, the 1,2,3-triazoles due to their unique chemical and structural properties, received much attention

over the past decade and found wide application in medicinal chemistry. Based on the importance of these two scaffolds i.e., the pyrazolo[3,4-b]pyridine and triazole, it was proposed to conceive both the scaffolds in a single molecule to have promising activity. These two scaffolds are connected through the click reaction under Sharpless conditions and obtained triazole tagged pyrazolo [3,4-b] pyridine derivatives. All the products were screened for cytotoxicity against five human cancer cell lines such as A549 - Lung cancer (CCL-185), MCF7 -Breast cancer (HTB-22), DU145 - Prostate cancer (HTB-81), HepG2 - liver cancer (HB-8065) and COLO 205- Colon cancer (CCL-222), compounds which showed promising activity have been identified.

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Synthesis of novel N-triazolalkyl tagged quinolin-2(1H)one derivatives and their cytotoxic activity

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Quinolinones are important class of pharmacologically active agents¹ and are frequently recognized in the structure of numerous naturally occurring alkaloids.² Functionalized quinolinones are attractive compounds for drug discovery since many of them have been shown to exhibit excellent biological activities^{3,4} which includes anti-oxidative,⁵ nitric oxide production inhibition6 and cytotoxic activity.⁷ Similarly, 1,2,3-triazoles are also found as useful building blocks in organic synthesis because of their wide range of biological activity.^{8,9} Based on the importance, we synthesized a series of novel N-triazolalkyl quinolin-2(1H)one derivatives (6, 8) and screened for cytotoxic activity against four human cancer cell lines and compounds 6d and 6k which showed promising activity at micro molar concentration have been identified.

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Exploration of in vitro free radical scavenging potential and molecular docking studies of synthesized 8-substituted xanthine derivatives as potential NADPH oxidase inhibitors

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The NADPH oxidase (NOX) is the major source of Reactive Oxygen Species (ROS) in the artery wall in conditions such as hypertension, hypercholesterolaemia, diabetes and ageing and therefore, they are the important contributors to the oxidative stress. Herein, we demonstrate the synthesis of 8-substituted xanthine derivatives (6a-s, 4a-r) via aldehede route using NBS/ AIBN at room temperature and via carboxylic acid route using polymer supported coupling reagent PS-IIDQ, respectively, followed by evaluation of their NOX inhibitory and free radical scavenging activities. Derivatives 4b, 4a, 6k, 6j and 4c showed promising NOX inhibitory and 4b, 4j, 6c exhibited significant free radical scavenging activities as revealed by IC50 values (2.85-3.59 μ M). Significant dock score of 4b (-72.127 kcal/mole) compared with ascorbic acid (-75.233 kcal/mol) has been figured out using molecular docking. From the molecular docking studies, it is evident that hydrophobic groups substituted at 8-positions of the xanthine ring possessing strong hydrophobic interactions with non-polar active residues are likely to enhance NADPH oxidase inhibition.

(P189)

Synthesis of Functional Conjugated Polymers as a Generic Platform for Next Generation of Organic Electronics, Chemical and Biomedical Sensor: Recent Advances, Challenges and Opportunities

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In recent times, Organic electronics is leading this new revolution of so called "pervasive electronics" wherein the electronic devices are becoming more and more personal with each passing year and soon will become an integral part of our life. In this direction, polythiophene based conjugated polymers have taken significant lead over other conjugated polymers in printable electronic applications. Commercially, two of the most successful polythiophenes are a) regioregular poly(3-hexylthiophene), rr-P3HT [1], used as an active semiconducting layer for various electronic devices such as photovoltaics and RF tags and b) Poly(3,4ethylenedioxythiophene), PEDOT [2], used as a transparent hole transport layer in electronic displays as well as for flexible transparent conductor. Large scale syntheses with controlled molecular properties still remain a major challenge in this area. In this direction we have initiated a program to design new synthetic routes which are amenable for large scale syntheses with complete control over Critical Molecular Design Parameters (CMDPs) such as chemical purity, regioregularity, molecular weight and polydispersity. Grignard Metathesis (GRIM) polymerization [3] is one of the most commonly used method for the synthesis of high quality conjugated polymers based on aryl and heteroaryl monomers and was first reported in US patent. Poly(3,4 ethylenedioxythiophene), PEDOT is best applicable in devices as an aqueous dispersion. However, the tedious purification processes and the stability of the final dispersion (shelf life) are the major drawbacks in this process. Therefore, it will be advantageous if one can synthesize PEDOT powders which can be dispersed in water in presence of stabilizers as when needed. This will increase the ease of purification, improve shelf life as well and one can control the surface charge of the colloidal particles based on the added stabilizer. The powder method allows us the synthesis of PEDOT powder which then can be dispersed in water in presence of various stabilizers resulting in the syntheses of stable dispersions with particle size ranging from 200-1200 nm wherein surface charge can be controlled from highly negative to positive. However there are certain bottlenecks in this process which hampers large scale syntheses of these materials with controlled CMDPs. Our approaches, including flow syntheses [4], in solving these issues will be discussed in this presentation.

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(P190)

Computational Investigation on the Mechanism and Stereoselectivity in the Michael'Addition Reaction Catalyzed by a Thiourea-Cinchona Catalyst <u>Bangaru Bhakararao</u> and Raghavan B. Sunoj* Department of Chemistry, Indian Institute of Technology Bombay.

Organocatalysis has been used in the synthesis of a large group of chiral compounds.¹ The naturally occurring cinchona alkaloids are known to be effective for asymmetric C-C bond formation.² In an earlier study, we have established the factors affecting enantioselectivity in a cinchona-thiourea catalyzed decarboxylation.³ In the present work, we have examined the mechanism and of a related Michael addition reaction between dioxolane and ortho-bromonitrostyrene catalyzed by thiourea based cinchona catalyst4 using DFT methods. In this reaction, catalyst plays a dual role by simultaneously activating both the nucleophile and electrophile. Calculations show that H-bonding between the catalyst and substrates plays a crucial role in the stereoselective C-C bond formation. Three different pathways for the C-C bond formation have been identified, which differ in the H-bonding pattern of nucleophile and electrophile towards the catalyst. A quantitative scheme for comparing the relative hydrogen bonding strengths has been proposed as a way to rationalize predicted energy difference between the transition states. Computed stereoselectivities (ee >99% and de=87%) are found to be in good agreement with the experimental results (ee >89 and de=98%).

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(P191)

Chemical synthesis of damaged DNAs to study structure and function of Y-family polymerases

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DNA damage is a constant threat caused by endogenous and exogenous sources; presence of these damages block the progress of DNA replication process by replicative polymerases. An important mechanism to overcome this problem entails the use of specialized DNA polymerases (Y-family) to carry out Translesion synthesis (TLS). TLS is defined as the bypass of damaged sites by incorporation of a nucleotide across the damage, which can be error-free or error-prone. Compared to the replicative polymerases, additional little finger domain of the TLS polymerases enhances the binding with template DNA and influences fidelity and activity. Among the Y-family polymerases, the structure of DinB polymerase (DNA polymerse IV from E. Coli) is yet to be determined with damaged DNAs. A recent study suggests that DinB polymerase and its orthologs can efficiently bypass the different N2-dG potential lesions. To understand the structural and functional requirement of DinB polymerase, we carried out synthesis of oligonucleotides containing site-specific N2-modified-dGs. The clear perspective of lesion

induced conformational changes in DinB polymerase with N2-modified-dG oligonucleotides is currently being studied by X-ray crystallography.

(P192)

Mechanistic Investigation of a Palladium Acetate Catalyzed Phosphorylation Reaction <u>Pritha Verma</u> and Raghavan B. Sunoj Department of Chemistry, Indian Institute of Technology Bombay.

The past decade has witnessed an unprecedented growth in the domain of palladium-catalyzed ligand directed C-H bond functionalizations (ref 1). These reactions typically employ a highly site-selective C-H bond activation strategy towards making new C-X bond (X = C or any heteroatom). While the C (aryl)-C coupling reactions continue to fluorish, other C(aryl)-heteroatom bond formations are now becoming rapidly popular. One such important transformation is C-P bond formation. Aryl phosphonates, which could be generated using such phosphorylation methods, have broad application in the fields of medicinal chemistry, material chemistry, and catalysis. Over the years, these molecules have been prepared by employing various cross coupling strategies. Very recently, a palladium catalyzed directed C-H phosphorylation reaction was reported by Yu and co-workers (ref 2). A number of additives were found to be important for the success of this challenging transformation. Our continued interest in transition metal catalysis (ref 3) prompted us to investigate a detailed mechanism of this reaction. Our Density Functional Theory investigations have provided a molecular understanding of the mechanism and some early insights into the role of additives in various elementary steps of the reaction. The details of the key findings will be presented in the poster.

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(P193)

New Methodologies for the Synthesis of Novel Multi-functionalMoleculeswith Interesting Properties

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Our group's research interests encompass organic synthesis, development of new synthetic methodologies, asymmetric catalysis, mechanistic studies and materials chemistry. The reactivity of nitroalkenes as substrates in the Morita-Baylis-Hillman reaction and applications of the Morita-Baylis-Hillman adducts in the synthesis of novel multi-functional and bioactive molecules, including heterocycles, have been investigated for the first time by our research group. The hitherto unexplored reactivity of the Bestmann-Ohira reagent and its sulfone analogs as 1,3-dipolar cycloaddition partners has been exploited by us recently in the synthesis of highly functionalized pyrazoles, including pyrazole alkaloid Withasomnine. The catalytic asymmetric synthesis of aminophosphonates, the transition state analogs of amino acids, and aminosulfones via Michael addition, application of Mg/CHBr3 reagent system for 1,4-addition, 1,2-addition and

cyclopropanation, stereoselective synthesis of carbocycles and heterocycles via cascade reactions involving curcumins and various Michael acceptors, synthetic and mechanistic studies on the vinylidenecarbene-acetylene rearrangement, application of polycyclic cage compounds as energetic materials and application of carbon nanotube (CNT)-metal hybrids as heterogeneous catalysts in various organic reactions are other highlights of our research work. Detailed synthetic and mechanistic studies carried out by us have applications in areas as diverse as drug design, materials chemistry and asymmetric synthesis.

(P194)

Template-Free and Direct Electrochemical Deposition of Hierarchical Dendritic CuNi and Graphene-CuNi Microstructures: Growth and Their Application as Glucose Sensor

<u>M. Kaleesh Kumar</u> and Shailendra K. Jha* CSIR-Central Electrochemical Research Institute, Karaikudi.

Hierarchical dendritic CuNi and graphene-CuNi microstrutures with secondary and tertiary branches are directly electrodeposited on Cu foil substrate without the use of any templates, surfactants, or stabilizers. The effects of electrodeposition potential and electrolytes concentration on the formation of microstrutures and time-dependent morphological evolution are investigated in detail. A diffusion-limited aggregation (DLA) mechanism is used to explain the formation of hierarchical dendritic microstructures (HDMs). Typically, the as-synthesized graphene-CuNi HDMs exhibited much higher electrocatalytic activity towards the electrooxidation of glucose in alkaline solution compared to CuNi HDMs electrode.

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(P195)

Inhibition of Brass Corrosion in NaCl Solutions by Self-assembled Monolayers of n-Alkanethiols and Anti-tarnishing Effect

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Monolayers of n-alkanethiols (1-dodecanethiol) were grafted from ethanolic solution on brass substrate. Self-assembly of n-alkanethiols on brass has been investigated by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization curves. Electrochemical results indicated that self-assembled monolayer (SAM) of 1-dodecanethiol inhibited the corrosion of brass in NaCl solutions significantly and obeys the Langmuir adsorption isotherm. Atomic force microscopy (AFM) and ellipsometry characterizations have been made to understand the modification and thickness of SAM on brass. Static water sessile drop contact angle measurements (S-CAMs) were also performed to understand the wetting properties of the surface of brass before and after modification with n-alkanethiols. The reflectance of visible light has been made to understand the tarnishing effect of brass before and after anti-tarnish treatment.
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V. Mullaivananathan, V. K. Pillai, S. K. Jha* Langmuir (To be communicated)

(P196)

Shape modulated electro-catalytic Activity of Au Nanostructures

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Noble metal nanomaterials create an emerging performance in different field of application like optoelectronics, sensors, electrocatalysts, photocatalysts etc. In particular, Au NPs are fetching towards a large number of applications due to their better optical, electronic and catalytic properties. The negligible cytotoxicity and greater affinity of Au nanoparticles towards the thiolated bio molecules have been attracted for biomedical applications. However, the performance of nanomaterials can be triggered by controlling the shape and structure. Many synthesis protocols have been established to develop different shaped Au nanoparticles. In General, inorganic and organic reducing and stabilising agents are used to synthesize such nanomaterials. Therefore, the development of different shaped NPs by green method is an ongoing challenge for many researchers. In this work, we develop a completely new and bio inspired approach for shape control synthesis of Au NP using different bio-molecules. The assynthesized AuNPs were characterized by different techniques. The TEM measurements reveal the formation of Icosahedral and dendritic nanostructures. It has been observed that the structure and functional groups of the reducing/stabilizing agent play a vital role in the shape evolution of nanostructures. The growth mechanism for their formation and role of the molecular precursor were investigated by using TEM and UV/Vis spectral measurements. The electro catalytic activity of the as synthesized different nanostructures was investigated towards the reduction of oxygen. The catalytic performance of different Au NPs was found to be shape-dependent.

(P197)

Theory for Quasi-Reversible Charge Transfer with Ohmic Effects at Rough Electrodes: Verification in Ionic Liquid Medium

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Complex Systems in Electrochemistry & Materials Group Department of Chemistry, University of Delhi, Delhi

We experimentally verify our recent theory, "Quasi-reversible charge transfer with ohmic effects at rough electrodes^{1, 3}", in ionic liquid medium at the glassy carbon electrode. The roughness of glassy carbon electrode is characterized through the power spectrum (PS) obtained from SEM micrographs². Chronoamperometric measurement was made on morphologically characterized Glassy carbon rough electrode in a solution of ferrocene in room temperature ionic liquid interface [BMIm+][BF4-]. This ionic liquid is about 173 times more viscous than water hence it will cause slowing down of diffusion process hence fine roughness^{4, 5} of electrode will influence the dynamic experimental response. The PS obtained from SEM shows only a finite bifractal nature. Roughness factor R* obtained from chronoamperometric (current step) measurements is used to determine the actual electrochemically active area of a glassy carbon rough electrodes.

SEM image, image process provides knowledge of electrode surface morphology such as fractal dimension (DH), topothesy length ($\ell \tau$), lower cutoff length scale (ℓ) and upper cutoff length scale L. Chronoamperometric response observed experimentally is compared with the theoretical equation for average chronoamperometric response. The anomalous response is seen in intermediate time in the chronoamperometric. Finally, we illustrate that electrode roughness influence on electrochemical response is enhanced in RTIL⁶ medium.

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(P198)

Nitrogen-Doped Reduced Graphene Oxide-Mn3O4 Hybrid Material for Oxygen Reduction Reaction

Sourav Bag, C. Retna Raj IIT KHARAGPUR

The high cost of Platinum as a catalyst for cathodic oxygen reduction reaction (ORR) for fuel cell is the major disadvantage. To develop a non precious efficient electrocatalyst is a challenging and tough task. Here, we describe a new facile protocol for the synthesis of hybrid functional electrocatalyst based on nitrogen-doped reduced graphene oxide (N-rGO) and Mn3O4 with pronounced electrocatalytic activity towards ORR in alkaline solution. The synthetic route involves one-step in situ reduction of both graphene oxide (GO) and Mn (VII) and nitrogen doping onto the carbon framework using a single reducing agent. The X-ray photoelectron (XPS), Raman and FTIR spectral and X-ray diffraction measurement confirms the reduction of GO as well as formation of Mn3O4 nanoparticle. The XPS profile reveals that N-rGO has pyridinic, pyrrolic, and pyridinic N oxide nitrogen. The average size of the nanoparticles is 37nm and randomly distributed over the wrinkled N-rGO sheets. The hybrid catalyst reduce oxygen molecule at a potentials of -0.075V, which is 60 millivolts positive than the state-of-the-art carbon-supported platinum. The synergistic effect of N-rGO and Mn3O4 enhances the catalytic activity with remarkable durability, methanol tolerant property, and an excellent four electron selectivity.

(P199)

Spectrochemical and Electrochemical Studies of Quinones with Ruthenium(II) Complexes containing bathophenanthroline Ligands

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Quinones and their intermediates play important roles as mediators in the electron transfer reactions occurring in photosynthesis and phosphorylation. Neutral quinones are good electron

acceptors in the cascade of electron transfer reactions initiated when photosynthetic reaction centers are excited and the reduced forms of guinones are very active with donor protons to generate mainly hydroquinone or hydrogen bonded complexes. Redox chemistry of naturally occurring quinines is an essential aspect of biological processes. A unique combination of photophysical and redox properties makes the ruthenium(II)-polypyridyl complexes as ideal candidate for the role as photosensitizers for artificial photosynthetic systems. The photochemistry and electrochemistry of ruthenium(II)-polypyridyl complexes with parabenzoquinone as model for photosynthetic reaction centers have been investigated for a very long time. Ruthenium(II) complexes containing bathophenanthroline as ligands in the above mentioned model has not been explored. [RuII(bathophenanthroline)] complexes as interesting alternatives (bathophenanthrolineÂ¹/₄4,7-diphenyl-1,10-phenanthroline). They show excellent chemical and thermodynamic stability, and the relatively long decay time for their luminescence in the microsecond range also allows highly sensitive time-resolved measurements. Meanwhile, we have applied these complexes in combination with suitable donor or acceptor chromophores to robust fluorescence resonance-energy-transfer (FRET) systems either in peptides or DNA fragments. These molecules are applied to fluorescent labeling of molecules, mainly for the detection of protein molecules and in cell biology. Keeping in view, the above model, reduction of quinines with ruthenium complex containing bathophenanthroline ligands were subjected to electrochemical studies for qualitative and quantitative information. The change in the shape of the resulting voltammograms is used to quantify the hydrogen bonding interaction/Ï€-Ï€ stacking interactions of the aromatic rings of the ligands and the quinone. In the present work, the photophysical and electrochemical properties of the complexes and the various quinones are studied. The association between the metal complex and the substituted quinones was treated in terms of single global association equilibrium constants (Keq(1) and Keq(2)) and the number of ruthenium polypyridyl molecules (n and m) bonded with anion and dianion of quinones are calculated. A linear relationship was found between the anodic shifting waves and corresponding equilibrium constant values with the increasing concentration of ruthenium complex. The effect of substituents of hydrogen bonding equilibrium was also analyzed.

(P200)

Comparison of electrochemical oxidation of methanol over Polyanilne modified electrodes Richa Singh and P C Pandey

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A comparative study on electrochemical oxidation of methanol over Polyanilne modified electrodes is reported using different acidic dopants. Three acids viz. HCl, H2SO4 and HClO4 are used for electropolymerization of aniline. It is found that the size of dopants influences the rate of polymerization and electrochemical behavior of resulting polymer films. The efficiencies of these electrodes in methanol oxidation are examined and their electrochemical properties are investigated using cyclic voltammetry. The maximum yield of polymer with excellent electrochemical behavior is observed in case of polyanilne grown in HCl suggesting high level of doping of chloride ion as compared to other anions. Such finding may be attributed to the smallest size of chloride ion among three dopants used. Further, the electrochemical oxidation of methanol is studied over these modified electrodes in nearly neutral medium and following conclusion were drawn; (i) the increase in anodic peak current is observed in all cases; (ii) significant shift in the anodic peak potential is also observed; (iii) the dependence of anodic peak

current on the nature of different acidic dopants and (iv) the chloride ion accelerates the oxidation of methanol by increasing anodic peak current while perchlorate ion facilitates the oxidation by reducing the peak potential required for the oxidation of methanol. All these results suggest the electrocatalytic oxidation of methanol over these modified electrodes which are attributed to the nature and unique properties of different dopant ions.

(P201)

Application of ionic liquid as salt-bridge Mosarrat Perween and Divesh N.Srivastava* CSMCRI.

The conventional reference electrodes have several drawbacks because of essentiality of liquid electrolyte, which need to be rejuvenated by refilling or diluting on regular basis. Moreover a liquid component is not convenient for portable devices. The problem enhances many folds when it is being used by the semiskilled or unskilled persons. Owning to that there is a genuine demand of solid state and disposable reference electrode which can provide precise and reproducible potential for on-site electrochemical measurements.Several unconventional electrodes, including our 'plastic chip electrode' fabricated from composite of graphite in polymer, are reported and successfully used as disposable working electrode. However, equivalentreference electrode is still lacking because of unavailability of suitable junction. Various attempts were tried to minimize the junction potential by tailoring the saltbridge. In this work we tried ionic liquid and its composite as salt-bridge in a solid state reference electrode and the performance of such reference electrode was evaluated in various electrochemical processes

(P202)

Glucose Oxidase-PANI Based Electrochemical Sensor For Escherichia Coli. <u>A.Shaikh¹</u>, L. H. Mujawar¹, M. G. Walawalkar¹, A. Q. Contractor¹* Department of Chemistry, Indian Institute of Technology Bombay.

Food and water quality control methods rely on the detection of fecal coliforms viz. Escherichia coli, as indicators of fecal contamination. Till date, various methods are available for the detection of Escherichia coli, viz. antibody-based methods [1] and culture-based, use of genetically engineered cells, various enzymatic assays, etc. Previous work on PANI+GOD as glucose sensors has been done by our group [2]. The aim of this study is to prepare an electrochemical sensor for Escherichia coli based on the conducting polymer polyaniline (PANI) and the enzyme glucose oxidase (GOD). PANI has been used as a conducting polymer as well as an immobilization matrix for GOD due to its higher stability, ease of synthesis, low cost and good electrical conductivity [3]. In our study, we exploit the natural ability of Escherichia coli to utilize glucose as a source of energy. Electrochemical detection of glucose has been done using gold coated polycarbonate membrane (Au-PCM). Polyaniline was synthesized electrochemically on Au-PCM. Glucose oxidase was immobilised potentiostatically on the polyaniline coated Au-

PCM. The above sensor was checked for its response with glucose at 0.2 V. Glucose gets hydrolyzed in presence of glucose oxidase to gluconic acid, releasing protons which change the local pH of the microenvironment in the PANI matrix. This change in pH is measured as a change in conductance of the sensor. The optical detection of live as well as lysed samples of Escherichia coli was performed for validation. The electrochemical detection and sensor response for Escherichia coli will be discussed during the presentation.

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(P203)

Acetylcholinesterase-Based Conductometric Biosensor For Inhibitive Determination of Arsenic(III)

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The presence of arsenic in natural waters is of concern because of its toxicity and carcinogenicity. In groundwater, they are found as arsenite and arsenate. Arsenite is more toxic than arsenate. The World Health Organization's maximum permissible contaminant level of arsenic(III) in drinking water is 10 ppb. India, China, Bangladesh, Mexico, Argentina, USA and many other countries in the world have reported arsenic contamination in ground water. Various techniques are available for detection of arsenic(III), viz inductively coupled plasma atomic emission spectrometry [1], graphite furnace atomic absorption spectrometry [2], hydride generation atomic absorption spectrometry [3] used for determination of arsenic in drinking water. These techniques are very laborious and expensive. Hence, there arises a need to develop a sensor which is simple, inexpensive, and easy to use. The aim of this study is to prepare an electrochemical sensor for arsenic(III) based on the conducting polymer polyaniline (PANI) and the enzyme acetylcholinesterase (AChE). PANI has been used as a transducer as well as an immobilization matrix for enzyme due to its higher stability, ease of synthesis, and good electrical conductivity[5]. The principle of the determination is based on the inhibition effect of arsenic(III) on the activity of the enzyme AChE. PANI films were formed on Au-coated polycarbonate membrane (PCM) by cyclic voltammetry between -0.2V and 0.8V vs. saturated calomel electrode, and AChE was immobilized on PANI matrix. Au/PANI/AChE sensor has been used for the detection of arsenic(III). Acetylthiocholine is hydrolyzed in presence of AChE to thiocholine and acetic acid. Thiocholine, being an electroactive species gets readily oxidized to release protons which change the local pH of the microenvironment of the PANI matrix. This change in pH is measured as a change in conductance of the sensor using dc conductivity method. The presence of arsenic(III) inhibits the AChE activity, resulting in a lower thiocholine production.

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(P204)

A facile synthesis of symmetric diaryldisulfides by nucleophilic ring opening of benzo[b]thiophene-2, 3-diones

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Bisalkyl-and bisaryl-disulfides have been synthesized and characterized as mimics of various cysteine-containing proteins, especially to understand the biologically important thiol disulfide interexchange reaction. It can also be used with aspirin as a medication for patients with rheumatoid arthritis and in pharmaceutical products such as eye drops, in which it serves as an antibacterial and antifungal preservative. We report a facile synthesis of symmetrical diaryldisulfides by ring opening of benzo[b]thiophene-2,3-diones accomplished by an equimolar mixture of 5-methylthioisatin and diethylamine was heated to reflux in toluene for 4 hr. After evaporation of the solvent, a solid yellow crystalline compound was obtained. A single crystal X-ray crystallographic study revealed the molecular skeleton of the product (Figure). A possible mechanism is presented.

(P205)

The Photophysics of 7-(diethylamino)coumarin-3-carboxylic acid N-succinimidyl ester in Different Solvents and in Reverse Micelle

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In this work, we have reported the photophysics of 7-(diethylamino)coumarin-3-carboxylic acid N-succinimidyl ester (7-DCCAE) in different neat solvents, and in aqueous reverse micelles by using steady state absorption, fluorescence emission and picosecond time resolved spectroscopy. Several well-established empirical solvatochromic models (such as Lippert, Dimroth, Kamlet-Taft, Catalán 3P and Catalán 4P model) was used to analyze the solvatochromic shift of 7-DCCAE in different solvents. The different empirical models show that the observed results are better correlate for non-chlorinated solvents and provide statistically significant best fits data. The ground state structure of 7-DCCAE was optimized by using Density Functional Theory (DFT). The ground state dipole moment (μ g) of 7-DCCAE obtained from the DFT analysis was used to estimate the dipole moment of 7-DCCAE in the locally excited (LE) state (μ e). We used sodium dioctylsulfosuccinate (AOT) as surfactant to prepare the reverse micelles. The excitation wavelength dependent excited state dynamics of 7-DCCAE was observed in the reverse micelles. With the increase in w0 value (w0 = [water]/[AOT]) the extent of REES gradually decreases, due to the increase of mobility of water molecule inside the reverse micelles. The rotational relaxation time [r(t)] of 7-DCCAE decreases with increasing the w0 value of the reverse

micelles. The fluorescence anisotropy decays were found to be biexponential in nature; this is explained by two steps and "wobbling-in-cone model".

(P206)

Torsional Dynamics of Thioflavin T in Room-Temperature Ionic Liquids: An Effect of Heterogeneity of the Medium

Aninda Chatterjee, Banibrata Maity, and Debabrata Seth* Department of Chemistry, IIT Patna.

The ultrafast excited state dynamics of a fibril binding dye thioflavin T (ThT), has been studied temperature ionic liquids (RTILs): 1-Butyl-1-methylpyrrolidinium in two room bis(trifluoromethylsulfonyl)imide ([BmPr][NTf2])methyl-trioctylammonium and bis(trifluoromethylsulfonyl)imide ([N1888][NTf2]). Previously, in most of studies, it was observed that the excited state dynamics of the ThT dye were dependent on the viscosity of the medium. In our study, by using RTILs, we have showed that the excited-state dynamics of ThT are not only viscosity dependent, but also dependent on the heterogeneous nature of the medium. For both the RTILs the excitation wavelength dependent emission behaviour of ThT was observed. It was found that in both the RTILs, with gradual increase in temperature the emission quantum yield and the fluorescence decay time of ThT gradually decreased. The fluorescence quantum yield and fluorescence decay time values are always higher when $\lambda exi = 445$ nm, than $\lambda exi = 405$ nm in [N1888][NTf2]. This is mainly due to the presence of structural heterogeneity in the medium. This is further confirmed by the comparison of activation energy for viscous flow of RTILs and the activation energy for the nonradiative decay of ThT. So beside viscosity the structural heterogeneity of the medium is also responsible for the excited state dynamics of ThT in RTILs.

(P207)

Dye based photogalvanic solar cell: Energy conversion device for sustainable development <u>K R Genwa</u>, Jayshree Rathore Department of Chemistry, Jai Narain Vyas University, Jodhpur.

Electricity generation from renewable is assuming increasing importance in the context of large negative environmental externalities caused by electricity generation.1 The utility of solar energy is one from many renewable sources of energy especially in photogalvanic cells, so the photogalvanic cells are worthwhile source of energy and have future applications and uses. The photogalvanic effect was first reported by Rideal and Williams2, but Rabinowitch3-4 made the first photogalvanic cell using thionine-iron system. Later on Kaneko and Yamada5 were reported the photopotential and photocurrent induced by tolusafranine ethylenediaminetetraacetic acid system and Kaneko and Wohrle6 was used cation radical formed electrochemically in the presence of oxygen. Recently, attention has been paid to use of some new dyes as photosensitizer in photogalvanic systems and surfactants as stabilizing agents7-8. In the present work, electrical output of DSS – Sunset Yellow – EDTA system examined experimentally to increase storage performance of cell and to development cost effective photogalvanic cell system for sustainable development. The photogalvanic behavior of Sunset Yellow dye was studied in DSS – Sunset Yellow – EDTA system. The experimental studies were performed of different at pH conditions and dye concentrations. The effects of electrode area, light intensity and diffusion length on cell

electrical parameter are studied in various experimental conditions. Cell generates maximum power of 126.73 μ W in ideal conditions. Conversion efficiency was calculated by observed photopotential and photocurrent values at power point.

(P208)

Molecular Recognition in Biomolecular Assemblies: Photochemical Perspective of Thioflavin T on G-quadruplex DNA A.C. Bhasikuttan

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Structural diversity of biomolecules and the intricate details of their folding at physiological conditions have attracted immense attention as prospective targets for chemical intervention of biological functions. Targeting the activity of these intriguing functional templates through noncovalently interacting guests poses challenges to identify such structure specific ligands, which can discriminate it from other forms and report its presence fluorescently. This quest for a G-quadruplex specific fluorescent sensor amongst other DNA forms under physiological salt conditions has been addressed by us in a recent study. We demonstrated the application of a water soluble fluorogenic dye, Thioflavin T (ThT), in dual role of exclusively inducing quadruplex folding in the 22AG human telomeric DNA, both in the presence and absence of Tris buffer/salt, and sensing the same through its fluorescence light-up (~ 2100 fold) in the visible region. The distinction of ThT as a quadruplex inducer has been contrasted with the erstwhile used structurally related dye, Thiazole Orange, which did not induce any quadruplex folding in the 22AG strand. The striking fluorescence light-up in ThT on binding to the human telomeric G-quadruplex is shown to be highly specific compared to the less than 250 fold enhancement observed with other single/double strand DNA forms. This work has implication in designing new generation dyes based on ThT scaffold, which are highly selective for telomeric DNA, for potential diagnostic, therapeutic and ion sensing applications.

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(P209)

Studies on conversion and storage of solar energy in solar cells. <u>R.C.Meena</u> Department of Chemistry, Jai Narain Vyas University, Jodhpur

Conversion of solar energy is the important phenomena that are due to electron ejection by the photo sensitized dyes may more by random transform to a vacant site when they will be localized for a period of time that depends on the trop site depth relative to the conduction bond, electron may also be transformed to the oxidized dyes. In this paper we studies containing Congo red-ascorbic acid system when used for solar energy conversion into electrical energy gave very good results. The system gave a photo current of 187μ A, photo potential 770 mV and power 42.46 μ W. The system has a conversion efficiency of 1.06% and can be used in dark for 130 min. various factors on which efficiency of solar energy conversion is depends are also studied and reported here.

(P210)

Ultrafast Charge Separation Dynamics in CdS quantum dot Sensitized by Re(I)-polypyridyl Complexes with Catechol moiety

<u>Partha Maity</u>, Tushar Debnath, Tanmay Banerjee, Amitava Das, and H. N. Ghosh Radiation & Photochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai.

Exciton dissociation of the quantum dots (QD) is very crucial step to design a QD sensitized solar cell because exciton-exciton annihilation take place within 10-100 ps time scale in most of the QD materials. In the present report we demonstrate ultrafast exciton dissociation of CdS QD via transferring the photo-excited hole to Re(I) molecular adsorbate. The Re(I) dye anchored onto CdS surface which serves as a photosensitizing (through injecting electron) dye also act as hole accepting material. This dual role of the Re dye has been successfully demonstrated where Re is very stable dye towards solar radiation. Optical absorption measurement clearly suggests the dye molecule adsorb on CdS surface and form a weak charge transfer complex. Energy level diagram of CdS and the sensitizer reveals that photoexcited hole of CdS can be transferred to the dve molecule and excited Re(I) can inject electron into the conduction band of QD which has been confirmed by steady state and time-resolved photoluminescence studies with selective excitation. Femtosecond transient studies have been carried out to monitor charge transfer dynamics in early time scale. Transient absorption spectra of the dye quantum dot composite shows transient absorption 550 - 650 nm region with a peak at 590 nm which is attributed to Re(I) cation radical and a broad absorption in 650 -1000 nm region attributed to injected electron in CdS QD. Electron injection time was found to be pulse width limited (<100 fs) however charge recombination dynamics found to be extremely slow.

(P211)

Super Sensitization of Mn Doped CdSe Quantum Dot with Bromo Pyrogallol Red (Br-PGR) molecule: A New Route to Achieve Slower Back Electron Recombination Dynamics <u>Tushar Debnath</u>, Partha Maity, and Hirendra N. Ghosh

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In search for a suitable super sensitizer and to find the effect of doping on super sensitization we have synthesized CdSe and Mn doped CdSe (MnCdSe) quantum dots (QDs) to see the effect of charge transfer process by sensitizing with bromo-pyrogallol red (Br-PGR) molecule. Steady state absorption studies suggest that both CdSe and MnCdSe QDs form strong charge transfer (CT) complex with Br-PGR. Both steady state and time-resolved emission spectroscopic measurements shows on selective photoexcitation of CdSe and MnCdSe QDs, in the composite sytems complete quenching of QDs emission was observed which has been attributed to hole transfer from CdSe to Br-PGR. Ultrafast transient absorption studies in the above composite system after exciting the sample at 400 nm shows a broad bleach in the 500-700 nm region and positive absorption in 700-900 nm regions due to Br-PGR cation radical and injected electron in QDs. Electron injection for both the super sensitized system are found to be pulse width limited (<100fs). Hole transfer dynamics are found to be quite similar (600-700fs) for both the systems, however charge recombination dynamics found to be much slower in MnCdSe/Br-PGR system as compared to that of CdSe/Br-PGR system. From our above investigation we can conclude that

MnCdSe/Br-PGR system can be used as better super sensitizer in quantum dot sensitized solar cell (QDSSC).

(P212)

Ultrafast Hot Hole Transfer From CdSe Quantum Dot to Molecular Adsorbate Pallavi Singhal and <u>Hirendra N. Ghosh</u> Radiation & Photochemistry Division, Bhabha Atomic Research Centre, Trombay

To design higher efficient quantum dot solar cell it is very important to dissociate the exciton before they annihilate which takes place within 10-100 ps. In the present studies to demonstrate both hot and thermalized hole extraction in photoexcited quantum dot (QD), we have synthesized CdSe QD and different catechol derivatives are chosen as hole accepting material. Energy level diagram suggest that photoexcited hole in CdSe QD can be transferred to catechol derivatives. Since different catechol derivatives have different redox levels the driving force for hole transfer reaction will be different for different derivatives. Steady state and time-resolved luminescence studies clearly suggest the hole trasfer process in the above systems. Hole trasfer time has been determined to be 1-20 ps as measured from Femtosecond fluorescence upconversion studies. Femtosecond transient absorption studies indicate extraction of hot hole from upper excitonic level to catechol derivatives prior to cooling to first excitonic level of CdSe QD. Bleach recovery kinetics was monitored at two different excitonic wavelengths and different recovery rate was observed for different catechol derivatives. Observation of different hole transfer rate for different catechol derivatives is correlated in terms of difference in Gibbs free energy for hole transfer reaction and results are fitted in Marcus theory of electron transfer.

(P213)

Effect of spacer length on conformational changes of bichromophores

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Development in the area of switchable systems is of utmost importance for a variety of applications such as information processing and storage, molecular recognition and controlled release devices[1]. The amount of information stored could be increased by several orders of magnitude by expanding the concept of information storage from macroscopic devices to molecular level[2]. In almost all the work reported so far, the intermolecular association of two chromophoric units results in the formation of dimers. Further addition of monomers can lead to the formation of higher order aggregates and it is difficult to control the spatial dimension. A better control on the spatial disposition of the interacting chromophores in aggregates is possible through a rational design and, bichromophores are a group of molecular systems which have gained attention in this regard. Thomas et.al.[3] have done extensive studies on the conformational changes in hemicyanine-based bichromophores. In the present work the effect of the length of the polyoxoethylene spacer on the aggregation properties of the bichromophores is studied.

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(P214)

Investigation of photophysics of proflavine encapsulated into the nanoporous host materials in presence of ZnO nanoparticles

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ZnO nanoparticle inside the nanoporous host materials (Zeolite-Y, ZSM-5 and MCM-41) were prepared by ion-exchange method and characterized by UV-DRS, BET, and XRD techniques. The loading of ZnO nanoparticle in porous materials was determined by ICP-OES. The characteristics band edge absorption of the zinc oxide nanoparticles in nanoporous host materials were found to be blue shifted due to the quantum confinement effect. The influence of zinc oxide nanoparticles on the photophysical properties of co-adsorbed organic dye proflavine (3,6diaminoacridine) present in the nanoporous material was studied by using steady state and time resolved fluorescence techniques. The fluorescence intensity of the dye was enhanced with red shift by increasing loading of ZnO nanoparticle. The loading of ZnO nanoparticles influences the protonation of proflavine and acidity of the host materials will be presented in details.

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(P215)

Study of photocatalytic degradation of few reactive dyes with metal- non metal codoped TiO₂ under visible light

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Organic dyes are one of the largest groups of pollutants released into waste waters from textile and other industrial processes. Because of potential toxicity of the dyes and their visibility in surface waters, removal and degradation of organic dyes have been a matter of considerable interest. To address these problems, advanced oxidation processes (AOPs) play an important role in the waste water treatment. Among various oxide semiconductor photocatalysts, titanium dioxide has proven to be the most widely used due to its strong oxidizing power, non toxicity and long term stability. However conventional TiO_2 is active only under UV light which is accountable for 3-5% of solar light. So, TiO_2 has been modified by various methods to expand its photoresponsive region into visible light which is the major component of solar light. Doping of TiO_2 with metals and non metals individually could reduce the band gap energy, resulting in the absorption band shifted to visible region; furthermore, metal dopants also bring down the electron-hole recombination rate. Therefore, the modification of TiO_2 by co-doping metal and non metal ions is a novel issue for improving efficiency of TiO_2 . In light of this, we have synthesized N/Cu codoped TiO_2 by sol gel method and well characterized by XRD, TEM, FTIR techniques. The results of photocatalytic degradation of few reactive dyes with N/Cu codoped TiO_2 will be presented.

(P216)

Evidence for existence of two different conformations in amino substituted acridinedione dyes - A femto upconversion study

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Acridinedione dyes are a group of Laser dyes, widely applied as a fluorescent chemosensors via intramolecular PET process and these dyes have structural similarities with NADH. 9-N,N-dimethyl aniline decahydroacridinedione dye exhibits dual emission in non polar and polar aprotic solvents. Quantum mechanical studies reveal that, the presence of two different conformation of the same molecule in the ground state has lead to two close lying excited states, local excited (LE) and charge transfer (CT), and thereby results in the dual fluorescence of the dye. However there is no experimental report supplementing the origin of the CT state. We have prepared 9-aniline decahydroacridinedione dye for the current study and time resolved fluorescence studies reveal the origin of the CT state. Two different conformation of the molecule leads to two different local excited state (LE), each with different fluorescence lifetime of 1 ps and 2.5 ns respectively in acetonitrile. The ultra short lifetime (1 ps) of one of the conformer is due to the strong intramolecular PET process from the primary amino group to the ring nitrogen which results in the formation of a new PET promoted CT state with a lifetime of 0.2 ns. The femto second fluorescence decay monitored at different wavelength reveals the existence of mother-daughter relationship between these two states (rise time of 1 ps observed at the red end of the CT emission). Since the geometry of the other conformer does not facilitate the intramolecular PET process, it exhibits the local excited fluorescence lifetime of 2.5 ns, which is similar to the protonated form of the dye in acetonitrile.

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(P217)

Femtosecond to Nanosecond Dynamics of 2,2'-Bipyridine-3,3'-diol inside the Nano-Cavities of Molecular Containers

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Femtosecond fluorescence upconversion measurements are employed to elucidate the mechanism of ultrafast double proton transfer dynamics of BP(OH)₂ inside molecular containers (cucurbit[7]uril (CB7) and β -cyclodextrin (β -CD)). Femtosecond up-converted signal of BP(OH)₂ in water consists of growth followed by long decay component (~650 ps). The apperance of growth component (~35 ps) in the up-converted signal indicates the presence of two-step sequential proton transfer process of BP(OH)₂ in water. Surprisingly, the up-converted signal of BP(OH)₂ inside the CB7 nano-cavity does not exhibit any growth component characteristic of two-step sequential process. Interestingly, the growth component exists inside the nano-cavity of β -CD (having similar cavity size as that of CB7), infering the presence of two-step sequential process of PT inside the β -CD nano-cavity. The different features of PT dynamics of BP(OH)₂ in the above mentioned two macrocyclic hosts may be attributed to the presence and absence of water solvation network surrounding the BP(OH)₂ inside the nano-cavities of β -CD and CB7, respectively. Finally, docking and DFT calculations have been employed in deciphering the molecular pictures of the interactions between BP(OH)₂ and macrocyclic host.

(P218)

Graphene oxide-based molecular switch for sensing biomolecule

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Recently, graphene, a two-dimensional nano-material and its derivatives, namely, graphene oxide (GO), reduced graphene oxide (RGO) are mostly considered as nano-carriers for certain anticancer drugs.[1-4] Here, we have studied the loading of an anti-cancer drug, ellipticine (E) on GO surface and its subsequent release to intra-cellular biomolecules like DNA/RNA. Interestingly, the green fluorescence of ellipticine in aqueous solution, switches to blue in GO and switches back to green by the addition of polynucleotides. The intensified blue emission of the ellipticine-GO (E-GO) complex with human serum albumin (HSA), switches to bluish green upon addition of dsDNA. Electron microscopy reveals the formation of distinctive 3D assemblies involving GO and biomolecule(s) probably through non-covalent interactions and is primarily responsible for the biomolcule(s) assisted fluorescence-switching of ellipticine. To our knowledge, such morphological pattern of GO-DNA complex is very unusual, reported here the first time and could find applications in the fabrication of biomedical devices. Moreover, our approach of direct optical detection of drug loading and releasing is very cheap, appealing and will be useful for clinical trial experiments once the cytotoxicity of GO is duly taken care.

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(P219)

Photochemical conversion and storage of light energy into electrical energy by employing dye sensitized photogalvanic cells

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Photogalvanic cells are dye solution based photo-electrochemical cells for solar energy conversion and storage. These cells have good output in terms of potential, current density, power, conversion efficiency and storage capacity. They may be energy source for the future, if their electrical performance is further increased, and their some drawbacks are removed. For this, a lot of work has been done by using various synthetic dyes as well as natural photo sensitizer with Fructose as reductant, NaOH as alkaline medium and sodium lauryl sulphate as surfactant. Radically high cell performance has been observed. The potential 1071 mV, current 1049 μ A , power 244.02 μ W, efficiency 7.58% and storage capacity(in terms of half change time) 3.6 h is reported for Rhodamine B – Fructose based photogalvanic cells. It is concluded that photogalvanic cells may be promising future devices for solar power and storage capacity, can give electrical output comparable to that for commercially used power storage property lacking solar cells.

(P220)

A Study of Thermodynamic , Diagnostic & Thermophysical parameters and their excess values for ternary liquid mixtures

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An attempt has been made to determine internal pressure, energy of vaporization, enthalpy of vaporization, pseudo Gruneisen parameter and the excess parameters of the first two parameters from experimentally determined values of ultrasonic velocity and density for four ternary liquid mixtures at 298.15 K. Cohesive energy density and solubility parameters for the four multicomponent liquid mixtures under investigation has also been computed. Due to scarcity of data on ternary and higher order multicomponent liquid mixtures , the aim of the present work is to determine the aforementioned parameters with the help of experimentally determined values of ultrasonic velocity (u) and density (ρ) at 298.15 K for four ternary mixtures viz., where ρ and ρ at 298.15 K for four ternary mixtures viz.,

- I. chlorobenzene(1) + cyclohexane(2) + n-heptane(3).
- II. chlorobenzene(1) + cyclohexane(2) + iso-octane(3).
- III. chlorobenzene(1)iso-octane(2) + n-heptane(3).
- IV. chloronapthalene(1) + iso-octane(2) + n-heptane(3).

The idea behind the selection of the aforementioned systems lies in studying the influence of a polar component (chlorobenzene or chloronapthalene) on the mixture of alkanes (viz., components 2 and 3 of the ternary system). The results and discussions have been compiled taking into consideration the size, shape, polarity, chemical nature and flexibility of the polar molecule and the induced conformational changes in the alkane mixture.

(P221)

Preferential solvation and association constants of 2-exo and 2-endo methyl norbornyl chlorides in water-acetone mixtures

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Molecular dynamics simulations of 2-exo and 2-endo methyl norbornyl chlorides are performed in water-acetone mixtures to investigate the role of preferential solvation on the dissociation process of methyl norbornyl chlorides. New potential model are developed to match the gas phase PCM model based ab-initio potentials. We have studied the association of methyl norbornyl chloride ion pair with the help of potentials of mean force. The running coordination number and the excess coordination numbers are used to investigate the solvation structure and preferential solvation of methyl norbornyl chloride ion pair in water-acetone mixtures.

(P222)

Thermophysical properties of N, N/-ethylenebis-(salicylideneiminato)diaquochromium(III) chloride in aqueous Dimethylsulphoxide solution at T = (298.15, 308.15 and 318.15) K

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The densities, viscosities and refractive index data of N,N/-ethylene-bis(salicylideneiminato)diaquochromium(III) chloride, [Cr(salen)(H₂O)₂]Cl, in the binary mixtures of dimethyl sulfoxide and water at different mass percentage composition (i.e. 100%-80%) of dimethyl sulfoxide have been determined at 298.15, 308.15 and 318.15 K temperatures and atmospheric pressure. The apparent molar volumes were calculated from density data and the experimental slope were derived from the Masson equation and interpreted in terms of solute-solute and solute-solvent interactions. Apparent molar expansibilities of [Cr (salen)(H₂O)₂]Cl solutions; the partial molar expansibilities were then determined from the relation. The temperature dependence of values yielded; the sign of values were discussed to reveal the structure promoting ability of [Cr(salen)(H₂O)₂]Cl in the experimental solvent/solvent mixtures. The activation parameters of viscous flow for the ternary solutions were also derived and discussed in terms of transition state theory.

(P223)

Reorientation of Water Molecules around Ionic Liquids: Probing Salt Effects Raju Nanda, Anil Kumar National Chemical Laboratory, Pune.

Ionic liquids (ILs) are the molten salts constituting of large organic cation and inorganic or organic anions having negligible vapour pressure, high thermal stability, recyclability, large liquidus range and electrochemical window. There are many reports available in the literature dealing with the study of different physicochemical properties of ILs and their mixtures for their applications in different fields of science and technology. Besides these, there has been an on going research on the viscosity of ILs as these materials possess very high viscosity. This is one of the major drawbacks of ILs for their potential use as solvents in carry out different organic reactions. Recently it has been shown from from our group that there is a dramatic decrease in the viscosity of ILs was observed by adding different cosolvents into it. But to the best of our knowledge no reports are available in the literature describing the effects of different electrolyts

and non-electrolytes on the viscosity of aqueous solutions of ILs mixtures. We have observed for the first time in our research group some of the contrasting behaviour of different electrolytes on the viscosity of ILs mixtures. These unusual behaviours of electrolytes are specific to specific kind of electrolytes and also specific to the ionic liquids.

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(P224)

Towards Tuning the Inter-Ionic Interactions in Ionic Liquid Solutions: A Calorimetric Approach

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Ionic Liquids (ILs) are the alternative solvents to conventional, volatile organic solvents. ILs can be used as solvents or catalysts due to their novel properties such as negligible vapour pressure, high thermal stability, and high degree of recyclability to name a few [1]. The physico-chemical properties of ILs such as viscosity, conductivity and surface tension are the reflection of the inter-ionic interactions prevailing between the ionic components of these ILs. The quantitative measurement of these interactions can be achieved by employing several techniques such as spectroscopy and other physico-chemical measurements. An alternative methodology to elucidate these molecular level interactions is the thermal analysis, which can be successfully used for the dilute solution of ILs [2]. In this study we have used an isothermal titration calorimeter to investigate these interactions in the binary mixtures of ILs in a common solvent i.e. DMSO [3]. The basic experimental quantity, which is further analysed to deduce the quantitative information on ion-solvent and ion-ion interactions, is the excess partial molar enthalpy (HEIL). From the present study we have concluded that

1. ILs with DMSO show weak interactions as compared to the other solvents like water, aliphatic alcohols, and DMF.

2. Upon increasing the alkyl chain length of alkyl groups substituted on IL cations, the endothermic behaviour shifts towards exothermic in very dilute solutions of ILs with DMSO.

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(P225)

What Causes Enhanced Acidic Strength of Carboxylic Acids in Protic Ionic Liquids? Shashikant Shukla*, Vijay Beniwal, Anil Kumar SRF, CSIR-National Chemical Laboratory, Pune.

Acidity of a medium is an intrinsic number. However, the strength of an acid in a medium varies with the (i) nature of the acidic species and (ii) ability of the solvent to dissociate it. Protic ionic liquids (IL) are the class of IL that contain proton in their continuum and hence acidic. The acidity of a PIL was far below the acidity of weak carboxylic acid as noted by Hammett function (H0). However, acidity of carboxylic acids (HCOOH, CH₃COOH, CH₃CH₂COOH) in PILs was opposite in order and acidic strength on Hammett scale as compared to that in water. The ratio between H0 values of organic acids in water and in PIL, say, 1-methylimidazolium formate ([HmIm][HCOO]) is 1.14:0.94:0.88 at 0.48M. The lowest ratio for CH₃CH₂COOH indicates higher acidity in [HmIm][HCOO]. This reversal in acidic strength does not depend on the structural and electronic differences of PIL and water as both of them analogously behave towards promoting the acidity. Acidic strength of carboxylic acids in PILs depends on the more favorable arrangement of cations and anions according to the hard-soft acid-base (HSAB) principle. Thus, an unstable combination of cation and anion acts as a powerful media in promoting the acidity of weak carboxylic acid. It is hoped that this knowledge will be of great importance for various processes where a suitable combination of PIL and carboxylic acids can be used in place of hazardous and corrosive acids.

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(P226)

Effect of different counter ions of the metal ion on the resorcinol based BZ system in non aqueous-aqueous acid media

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The response of various non aqueous solvents to the Mn-ion catalysed resorcinol-based BZ system in addition to the effect of various counter ions of the metal ion has been investigated at 30oC under batch conditions. It has been observed that out of several non aqueous solvents used only a few like DMF, Acetonitrile, DMF+Acrylonitrile play role in affecting oscillatory behavior whereas DMSO doesn't show any oscillations. All these non aqueous solvents have been used (% v/v) in aqueous acid media. It has been observed that there is decrease in amplitude of oscillations due to the fact that there is bromination of solvent in addition to the substrate (resorcinol), hence, decreasing the concentration of Br2 required for bromination. The use of organic/inorganic counter ions in this reaction shows selective behavior towards non aqueous/aqueous media. Further, the limitation for the partial solubility of organic based counter ions is over, because they get easily dissolved in partial non aqueous medium. This study helps in using various organic based Mn salts as catalysts and also can play a role in studying the behavior of hydrophobic additives like antioxidants, hormones, proteins, etc in such nonlinear chemical systems, which can pave way for understanding their mechanism.

(P227) Ring Closing Metathesis of a Bispyrenyl Long Chain Compound within Ionic Liquid and Cosolvent-Modified Ionic Liquid

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within an ionic liquid 1-butyl-3-methylimidazolium The ring closing metathesis hexafluorophosphate ([bmim][PF6]), a 'green' solvent tetraethylene glycol (TEG), and their equimolar mixture is investigated through the intramolecular excimer formation of 6-(1pyrenyl)hexyl-11-(1-pyrenyl)undecanoate [1]. The excimer formation efficiency of [1] correlates directly with the inverse of the bulk viscosity of the system. A simplistic double exponential decay model based on Birk's scheme is enough to fit the excited state intensity decay of [1] in these liquids. This behavior is in stark contrast to that reported in organic solvents and in scCO2, where three exponentials are required to fit the fluorescence decay. The activation energies of the excimer formation (Ea), viscous flow (Ea, nbulk), and microviscosity (Ea, nµ) were estimated from the temperature dependence. Ea and Ea, nu are significantly higher for the equimolar mixture as compared to that for [bmim][PF6] or TEG, whereas Ea, Î-bulk is close to the average. This highlights the important outcome that the cyclization dynamics scales with the microviscosity rather than the bulk viscosity of the systems investigated.

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(P228)

Silica Nanostructures as Scaffold for Energy Transfer <u>Anjali Dhir</u>, Anindya Datta Department of Chemistry, Indian Institute of Technology Bombay.

Silica nanostructures have been used as the medium and/or spacer to study various processes like metal enhance fluorescence, resonance energy transfer, etc. These applications are based on either core-shell like architecture or porous nature of silica. Here, using arrays of chromophores on silica nanoparticles (SNPs) FRET was studied with an aim of developing light harvesting antennae. Silica-dye nanoconjugates were prepared by co-condensation of dye in the matrix. Rhodamine B and Fluorescein were used as FRET pairs. Steady state study of nanoparticles showed enhanced emission of acceptor at preferential excitation of donor molecule. Further, time resolved analysis using time correlated single photon counting (TCSPC) system and Up-conversion technique for ultrafast process clearly indicates fast decay of donor molecule in the presence of acceptor. The ultrafast decay at emission end of acceptor (with minimum contribution from donor) shows a growth, that further supports the FRET process. The spectroscopic studies were performed at $\lambda ex = 440$ nm and $\lambda em = 520$ nm and 630 nm with magic angle polarization (54.7°). The decays were fitted in single or multiexponential function using an iterative reconvolution method using IBH DAS 6.0, Fluofit and IGOR software.

(P229)

Cobalt manganite nanocubes embedded graphene nanoribbons: High performance supercapacitor with short relaxation time

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Energy storage devices have attracted great attention due to the increasing demand for sustainable energy. Among energy storage devices, Supercapacitors offer transient but extremely high power for electrical vehicles and mobile devices. The ever-growing need for high energy and/ or high power for emerging new applications have promoted numerous research efforts toward developing new electrode materials. Recently, great attention has been paid to the nanostructured spinel oxides exhibiting a high pseudocapacitance due to better electrical conductivity and enhanced electrochemical activity. Graphene nanoribbons supported CoMn₂O₄ (CoMn₂O₄/G) are synthesized under facile hydrothermal conditions. Inclusion of Graphene nanoribbons in the synthesized composite offers a conducting matrix entailing fast diffusion of the electrolyte ions and fast conduction of electrons to the electroactive sites. More significantly, graphene nanoribbons prevent interparticle agglomeration resulting in uniform dispersion of CoMn₂O₄ nanocubes on graphene nanoribbons as analyzed by Transmission Electron Microscopy (TEM). CoMn₂O₄/G exhibits high energy 22.3 Wh Kg-1 and power density 3.1k W Kg-1 with short relaxation time of 2 ms. It maintains 97% of the capacitance after 5000 charge discharge cycles. The superior electrochemical performance of CoMn₂O₄/G is attributed to short ion diffusion length of Na⁺ ions endowing a promising material for supercapacitor electrode.

(P230)

Tribological studies of Stearic acid-modified CaCu₃Ti₄O₁₂ nanoparticles as potential lubricant additive in paraffin oil

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The CaCu₃Ti₄O₁₂ (CCTO) nanoparticle with an average diameter of 60nm has been synthesized by sol-gel method followed by surface modification with stearic acid (SA) for developing ecofriendly lubricant additive. The surface modified CCTO (SA-CCTO) nanoparticle has been characterized by FTIR and TEM. Tribological behavior of these nanoparticles (CCTO and SCCTO) in liquid paraffin oil has been evaluated using four-ball lubricant tester and compared with conventional high SAPS containing zinc dialkyldithiophosphates (ZDDP). The concentration of the additives have been optimized by conducting the test for different concentration 0.5, 1.0, 1.5 and 2.0 % w/v at applied load of 392N load. The optimum concentration of the additive has been found to be 1.0 % w/v. Various tribological parameters such as mean wear scar diameter (MWD), friction coefficient (μ), mean wear volume (MWV), running-in, steady-state and overall wear rates show that all the SCCTO nanoparticle act as efficient antiwear additives and possess high load carrying capacity. The enhanced tribological efficiency of SCCTO nanoparticle was due to their strong tribochemical film on interacting surfaces. The worn surface has been characterized using SEM, AFM, EDX and XPS in order to understand the action mechanism.

(P231)

Magnetic and Semiconducting Oxide and Chalcogenide Nanocrystals <u>Arunava Gupta</u> University of Alabama

Monodisperse inorganic nanocrystals have been intensively investigated in recent years, both because of fundamental scientific interest and technological applications arising from the unique properties in reduced dimension. In particular, the spinel ferrites of composition MFe2O4 (M=Co, Ni, Mn, Fe, etc.) exhibit interesting magnetic and magneto-optical properties that are potentially useful for a broad range of applications, including magnetoelectric devices, drug delivery, ferrofluidics, etc. Their magnetic properties can be systematically varied by changing the identity of the divalent M^{2+} cation or by partial substitution. The properties can additionally be tuned by controlling the shape, size and crystallinity of the nanocystals. Another class of spinel nanocrystals that remain largely unexplored are the chromium-based spinel chalcogenides, ACr_2X_4 (A = Cu, Cd, Hg, Fe, Co; X = S, Se, Te), which are ferromagnetic insulators, semiconductors, or even metals and display unique properties in the bulk. We have synthesized monodisperse nanocrystals of a number of spinel ferrites and chalcogenides using facile solutionbased methods and investigated their magnetic properties. The synthesis of the chalcogenides has been further expanded to semiconducting nanocrystals of varying compositions and band gaps, such as CuInxGa1-xS₂ and Cu₂ZnSnS₄, with different anisotropic shapes and crystal structures. Colloidal suspensions of these nanocrystals are attractive for use as inks for low-cost fabrication of thin film solar cells by spin or spray coating.

(P232)

Ureido di-peptides as novel material for Molecular Self-Assembly leading to Nanostructures

M.M.V. *Ramana, <u>S.A. Shete</u>, M.J.Gawli. Department of Chemistry, University of Mumbai.

Studies of peptide-based nanostructures provide general insights into biomolecular self-assembly and can lead material engineering toward technological applications. Biological building blocks construct complex architectures and machinery through the process of molecular self-assembly. This process offers a new direction for the design and fabrication of novel materials that can be used in various applications such as microelectronics, drug delivery, and tissue engineering. One such example is of simple diphenylalanine peptide (FF) which self-assembles into discrete, hollow, well ordered nanotubes, and its derivatives form nano assemblies of various morphologies [1]. These assemblies can serve as casts for the fabrication of silver nanowires and have remarkable stiffness[2]. Self –Assembly is a result of molecular building blocks that can undergo spontaneous organization into a well-defined and stable macroscopic structure using non-covalent bonds. These typically include hydrogen bonds, ionic bonds, water-mediated hydrogen bonds, hydrophobic and van der Waals interactions. Although each of these forces is rather weak, their collective interactions can produce very stable structures. Based on these observations and our interest in the synthesis of soft-materials for nanotechnology, we have successfully synthesized novel dipeptides with ureido functional group. These derivatives have been prepared by using cost effective solution phase synthesis protocol. These ureido di-peptide formed nanostructures with high yield under mild and controlled condition in aqueous media. The morphology of nanostructures can be controlled by using variety of hydrophobic amino acids. e.g., Isoleucine forms nanotubes and Leucine forms nanofibril. These novel ureido dipeptides nanotubes can be used in fabrication of biocompatible peptide-based nanostructures and they will undoubtedly have nanotechnological applications.

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(P233)

Homochiral coordination polymeric gel: Zn2+-induced conformational changes leading to J-aggregated helical fibers formation

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Chiral gelators have attracted immense interest because gelation often leads to helical twisting of the fibres, inducing chirooptical effects. Though there are few reports on the conformational change pertaining to helix formation involving organic derivatives such an observation has not been made with coordination polymeric gel. Considering these points, recently, we reported¹ the facile synthesis of novel chiral coordination polymeric (CP) gel from L-tyrosine derived symmetrical ligand, specific base and Zn^{2+} has been described. The Zn^{2+} induced conformational reorganization in the ligand leading to gelation has been monitored by fluorescence, CD, NMR spectroscopy. Moreover, twisted helical fibrous morphology has been revealed by AFM. The CP gel shows thermo-reversible behavior which is uncommon property for CP gel.² Fluorescence experiment exhibited a red shift of ~32 nm in the position of $\pi - \pi^*$ emission band upon addition of Zn^{2+} , which may arise due to $\pi - \pi$ stacking between phenolic rings like excimer formation. This unique red shift may be due to J-type aggregation.³ Circular dichroism spectral study indicates that chirality transfer becomes more effective with the growth of π - π stacking of phenolic units. Further, the π - π stacking interactions have been confirmed by 1H NMR titration studies. Rheological studies revealed phase transition at Tgel via gel-semi sol-solid. The present gel may find applications in chiro-optical, optoelectronic devices and gelator can be used for sensing metal cations.

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(P234)

Utilization of wheat husk ash as silica source for the synthesis of nanoporous materials: a sustainable approach towards valorization of a significant agricultural waste stream ISAK RAJJAK SHAIKH

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After acid pre-treatment, the product extracted from the wheat husk ash is utilized as a silica source for the preparation of mesoporous siliceous material(s). The MCM-41 type samples using hexadecyltrimethylammonium bromide (CTAB) as template were synthesized using commercially available silica and wheat husk ash silica at room temperature. The materials were characterized to prove crystallinity, siliceous framework, overall material morphology, etc. A comparison is also made between the characteristics of (i) MCM-41 synthesized from the commercially available silica source; (ii). MCM-41 synthesized using wheat husk ash as silica source, and (iii). the MCM-41 reported earlier. This methodology opens up new methodology for the utilization of renewable sources and also for the concepts of 'valorization of agricultural waste stream' and the 'silicon elemental sustainability.' The crystalline siliceous mesoporous MCM type silica presents an interesting potential for their applications in adsorption, ionexchange and shape-selective catalysis. The material synthesized were characterized using X-Ray Diffraction (XRD) patterns, Scanning Electron Microscopy (SEM), etc. While the low-angle XRD pattern is consistent with the existence of mesoporous silica MCM-41, the wide-angle XRD pattern exhibits quite strong reflections, which are not due to MCM-41. Therefore, a second phase or material is present which needs to be identified. This leads to understand the importance of TEM and porosimetry data that are required before one can reasonably state the purity of the as-synthesized material. We developed the use of MCM-41 type silica, prepared from wheat husk in Pechmann reaction. When resorcinol is reacted with the ethyl acetoacetate in the presence of this catalyst, three reactions, hydroxyalkylation, transesterification, and dehydration occur concomitantly condensing together the two reactants at two sites to form the coumarin derivative. This is an example of acid catalysis. In an another work, titanium was successfully incorporated into the framework of MCM-41 to use the Ti-MCM-41 material as heterogeneous catalyst for the oxidation using aqueous hydrogen peroxide. In our future works, we also aim to develop the use of this siliceous material as an environmentally benign catalyst for the synthesis of benzimidazole derivatives from o-phenylenediamine and benzoyl chlorides. Synthesis of ZSM-5 (similar to Panpa, W. et al. Applied Catalysis B: Environmental, 90, 389-394, 2009) was also successful with tetrapropylammonium bromide (TPABr) as template and wheat husk ash the silica source. The researchers focus to make sincere attempts to bring forth development of chemical technologies benefiting sustainability or ecological and environmental health on the planet by identifying and implementing scientific trends in utilization of biomass and valorization of ashes.

(P235)

Synthesis And Self-Assembly Of Novel N-Phenylureido Dipeptide Esters Leading To Nanostructures *Ramana, M.M.V., Gawali Manoj J., Shete, S.A.

Department of Chemistry, University of Mumbai.

Self-assembly at the nanoscale is becoming increasingly important for the fabrication of novel supramolecular structures, with applications in the fields of nanobiotechnology and nanomedicine. Peptides represent the most favorable building blocks for the design and synthesis of nanostructures because they offer a great diversity of chemical and physical properties, they are biocompatible, can be easily synthesized in large amounts, can be decorated with functional elements and can be used in various biological and non-biological applications. Short peptides can spontaneously associate to form nanotubes, nanospheres, nanofibrils, nanotapes, and other ordered structures at the nano-scale. The simplest peptide building blocks are dipeptides. Nanostructures derived from self -assembly of dipeptides are the widest amongst peptide nanotubes. The self- assembly process is mediated through weak intermolecular bonds, such as van der waals bonds, electrostatic interactions, hydrogen bonds and stacking interactions. These relatively low energy interactions are combined together to form intact and well-ordered supramolecular structures. The driving force for the formation of these structures is most likely the intermolecular association of the hydrophobic moieties in the aqueous solution to form ordered structures similar to a micellization process. These self-assembled nanostructures have use as transport vehicles in drug delivery systems as well as in the specific ion sensors, easily tailored molecular reaction vessels, molecular sieves, or nanoscale fluidic transport systems. In the present work, we have synthesized a series of novel N-Phenylureido dipeptide esters which showed a tendency to form nanostructures through self-assembly.

(P236)

Metal Coordination Polymeric Nanoparticles with Morphology Dependent Non-enzymatic Peroxide Sensing

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Hydrogen peroxide (H_2O_2) is a reactive oxygen species which is produced not only in several chemical and industrial processes such as disinfection and waste water treatment but also as a by-product of several oxidative metabolic pathways. Peroxy radicals is implicated to a variety of disease and sensing these can be of great value for early detection of diseases. For this reason, a number of H₂O₂ sensors have been fabricated based on enzyme and enzyme free working electrode. In the present work, Metal Coordination polymers (MCPs) nanoparticles (NPs) with different shape and dimension synthesized using single precursor are employed to fabricate enzyme free peroxy radical electrochemical sensor. These MCPs NPs exhibits semi-infinite diffusion controlled phenomenon of electron transfer with highest apparent diffusion coefficient (Da) observed for MCPs nanocubes is apparently 2 times higher than nanotubes & nanosheets. The amperometric response to the successive increasing H_2O_2 concentration exhibits large linear ranges with highest sensitivity 1.23 µAcm-2mM-1 and lowest limit of detection (LOD) 6.0 µM at S/N ratio 3 for nanocubes. The sensors also displayed high reproducibility and excellent stability over range of temperature, time and pH. These highly stable non enzymatic H₂O₂ sensors can be used in the area of diagnostics for early detection of diseases and to study progression of diseases caused or promoted by free radicals.

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Effect of functionalization of the SiO2 nanoparticles on the adsorption of Ru onto them and their activity in degradation of congo red

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The catalytic activity of the Ru nanoparticles supported on SiO_2 particles has been investigated as an application in waste water treatment. The microwave synthesized Ru nanoparticles were adsorbed on bare, lysine and arginine functionalized SiO_2 nanoparticles. The purpose of functionalization was to increase the interaction of the SiO_2 and Ru nanoparticles. Using transmission electron microscopy, Energy-dispersive X-ray spectroscopy and dynamic light scattering, it was found that Ru nanoparticles are adsorbed maximum on arginine functionalized SiO_2 nanoparticles. The mechanism for this adsorption has been understood by zeta potential on their surface. The catalytic activity of these particles was studied by taking a model degradation reaction, i.e. the reduction reaction of congo red, an azo dye. The kinetics of the reaction was calculated using UV-vis spectroscopy and SiO_2 -Ru nanoparticles were found to be more active in the degradation of congo red than amine functionalized SiO_2 nanoparticles adsorbed by Ru nanoparticles.

(P238)

Oxadiazole based Donor-Acceptor Luminescent Materials for OLED Applications <u>M. Ongungal</u>, Deepak D. Prabhu and Suresh Das*

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In the search for ideal materials for OLEDs, solution processable ambipolar small molecules are extremely attractive since they offer the possibility to achieve efficient and stable devices. A straightforward strategy to achieve bipolar transport in organic materials is to incorporate both electron-donating and electron-withdrawing building blocks into the same molecule.[1]

Novel carbazole functionalized benzo[2,1,3]oxadiazole derivatives have been developed which have strong emission in the red region. The derivatives exhibited excellent photoluminescence in solution state and in solid state with high fluorescence quantum yields. The high photoluminescence efficiency in their solid state could be attributed to their non-planar structure which suppresses molecular aggregation. Star shaped oxadiazole derivatives were also developed which exhibit columnar mesophases at elevated temperatures and transform into a highly luminescent ordered glasses at ambient conditions. The photophysical properties of these materials in solution and the solid state will be presented.[2]

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(P239)

Photoluminescence properties of Tb⁺³ doped SrF₂ @BaF₂ nanomaterials. Premananda N.¹ & S.K.Srivastava^{1*}

Lanthanide ion doped nanomaterials are increasingly used as luminescent devices, bio-imaging, catalysts, and other functional materials based on their optical and chemical characteristics. Pure SrF2 and lanthanide Tb^{3+} doped SrF₂ (3 at.%) @BaF₂ at two different shell ratios was synthesized by ethylene glycol route. Characterisation of the as-prepared nanomaterials was done through XRD, SEM, FTIR, TEM and PL analysis. All the XRD peaks pattern for pure and 3 at.% Tb doped SrF₂ correlates to cubical structure. In case of SrF₂:Tb @BaF₂, the peak patterns for shell BaF₂ are found to be face center cubical structure. The lattice parameters and unit cell volume of the prepared samples were calculated. FTIR spectra of as-prepared sample shows O-H stretching and bending vibrations around at 3300-3600 cm⁻¹ and 1500-1600 cm⁻¹. Stretching vibration corresponds to C-O and C-C linkage appeared around 1350-1450 cm⁻¹ and 1000-1200 cm⁻¹, indicating the nanoparticles are capped successfully by ethylene glycol. In Photoluminescence spectra, absorption spectra from 200-280 nm is related with 4f - 5d charge transfer transition of Tb3+ ion and found to be consists of strong band at 213 nm and a shoulder at 238 nm. The peaks having lower intensity from 280-400 nm is related with the 4f-4f transition of Tb³⁺ ion. The peak at 316, 337, 350, 368 and 376 nm can be assigned to the 7F6â⁺ '5L8, 7F6â†'5G5, 7F6â†'5L10, 7F6â†'5G6, and 7F6â†'5G3 transition of Tb3+ ion. The emission spectra monitor at two different excitation wavelength spectrum 213 and 350 nm for SrF2:3Tb nanoparticles shows the characteristic emission peaks of Tb3+ ion originating from 5D4â†'7Fj (j = 6, 5, 4 and 3). The peaks at 487, 543, 583 and 619 nm can be assigned to $5D4 \rightarrow 7F6$ (electric dipole), 5D4 \rightarrow 7F5 (magnetic dipole), 5D4 \rightarrow 7F4 and D45 \rightarrow 7F3, respectively. The 213 nm excitation is related to CT transition and 350 nm excitation is related to direct 4f-4f transition of Tb3+ ion. Intensity of CT transition is much more intense than 4f-4f transition of Tb^{3+} ion predicts there is good energy transfer from host SrF2 to Tb3+ ion. The calculated value of life time of $SrF_2:3Tb$, $SrF_2:3Tb@BaF_2(1:1)$ and $SrF_2:3Tb@BaF_2(1:2)$ are 3.1, 3.4 and 5.0 S, respectively. The life time value of $SrF_2:3Tb@BaF_2(1:2)$ is highest. The size of the samples were well correlates with data given by XRD, SEM and TEM images.

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(P240)

Fabrication, characterization, transportation of ions and antibacterial potential of Polystyrene based Cu3 (PO4)2/ Ni3 (PO4)2 composite membrane <u>Mohd Arsalan</u>, Rafiuddin Aligarh Muslim University

Novel organic-inorganic composite membrane was successfully prepared by sol-gel process. Such composite material shows better thermal, mechanical, chemical stability and good ion exchange property. Structural configuration of membrane was confirmed by TEM, XRD and FTIR analysis where as the thermal properties examined by TGA/DTA and LCR analysis. Teorell, Meyer and Siever method, method was used to determine the theoretical values of the potential. The observed potentials and charge densities seems to follow KCI<NaCI<LiCl and

LiCl<NaCl<KCl respectively. By potential reading the transport number, mobility ratio, distribution coefficient, charge effectiveness, and fixed charge density of ions were calculated easily.

(P241)

Controlled Fabrication of Intercrossed Sheet like α-Bi₂O₃ on Ag-ZnO Heteroarchitectures and its multifunctional applications

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Heteroarchitectured α -Bi2O3 on Ag-ZnO was synthesized through simple, cost effective, template free photodepositionâ[^] hydrothermal method. This composite material represents a potential new class of photocatalysts wherein the enhanced light absorption, hydrophobic and electronic properties of Ag-ZnO is anticipated to couple with the observed benefits of composite ZnO/Bi₂O₃ systems. The synthesized α -Bi₂O₃-Ag-ZnO was characterized using X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), high-resolution transmission electron microscopy (HR-TEM), and nitrogen adsorption analysis. The XRD patterns indicated that well-crystallized α -Bi₂O₃ on the hexagonal wurtzite phase of Ag-ZnO was formed in a hydrothermal process. The FE-SEM images indicated the formation of well-organized intercrossed Sheets and peanut shell like structure, which were composed of nanoparticles and microsheets. This Heteroarchitectured system exhibits enhanced photocatalytic activity for the degradation of azo dyes, Acid Black1 (AB 1) and Acid Violet 7 (AV 7) under UV light (365nm), far exceeding those of the single component systems. α -Bi2O3 on Ag-ZnO is found to be reusable without appreciable loss of catalytic activity up to five runs.

(P242)

Aryl Pyrazaboles: A New Class of Highly Fluorescent Materials

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Organoboron compounds have recently proved to be promising candidates for OLEDs, OFET, OPV, and NLO materials.[1] Pyrazaboles are a class of tetra-coordinated organoboron compounds, with two nitrogen, and two carbon atoms.[2] The photophysical properties of the pyrazaboles can be tuned by the incorporation of different aryl groups. In this context, novel aryl substituted pyrazaboles were synthesized by the Pd-catalyzed Suzuki, and Sonogashira cross-coupling reactions.[3] These aryl substituted pyrazaboles show good thermal stability, and tunable photophysical properties. In this poster we will discuss about the effect of aryl substituents on the structural, thermal, and photophysical properties.

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(P243)

Design, synthesis and characterisation of sugar based gels <u>Thangamuthu Mohan Das</u>

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Design and synthesis of novel class of molecular scaffolds with unique structural and biological properties is an increasingly active area of current chemical research.¹ Recently, the chemistry of glyco-hybrids has gained enormous attention and it is due to the vital role played by these carbohydrates in several biological events.² Thus, the synthesis of glyco-hybrids becomes one of the most important and challenging field in synthetic organic chemistry and also in chemical biology. The present lecture will highlight the recent research on synthesis and applications of sugar based -inden-1-ol/indenones, --lactams, -spiro compounds, -pyrazoles, -quinolines, - coumarins, -triazoles and -fluorescein derivatives.³ Synthetic methodologies such as, Morita-Baylis-Hillman (MBH) reaction, cycloaddition reactions, Multi-Component Reaction (MCR), Aldol condensation, Michael addition and glycosylation strategy were used for the synthesis of above mentioned glyco-hybrids.³ In addition, applications of these sugar derivatives as gelator will also be discussed in the presentation.

(P244)

Flower shaped ZnO nanorod bundles: synthesis, characterization and its photocatalytic activity study

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The synthesis of ZnO nanostructures are currently attracting intense worldwide interest due to its remarkable performance in electronics, optics and photonics.1 Numerous ZnO nanostructures have been demonstrated, for example, nanowires, nanotubes, nanobelts etc.¹ The methods generally applied to synthesize ZnO nanostructures include electrochemical deposition technique,² hydrothermal method,³ sputter deposition technique⁴ and carbothermal reduction methods.⁵ In this report we synthesized flower-shaped homocentric pencil like ZnO nanorod bundles (or ZnO flowers) by hydrothermal method. The characterization was done by PXRD, PL spectroscopy, UV-Visible spectoscopy, FTIR spectroscopy and morphology was confirmed from FE-SEM images. The synthesized ZnO flowers were efficiently tested as an excellent photocatalyst for self sensitized photodegradation of a cationic triphenylmethane dye, Malachite Green (MG) under solar light. The amount of degradation of MG was almost 94% when initial dye concentration was 0.2 gL-1 and initial catalyst amount was 0.02g. Photodegradation of the dye leads to its complete mineralization under solar light which was confirmed by measuring the CO₂ produced.

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(P245)

Electrochemical Synthesis and Photocatalytic Behaviour of ZnO-SnO Microstructures

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Mixed metal oxides of Zinc and Tin (ZnO and SnO) microstructures have been synthesized using electrochemical method by electrolyzing an aqueous solution of Sodium Bicarbonate and Sodium Stannate using Zinc electrodes. Investigation on the effect of current density showed that better structures were formed at lower current density while irregular clusters were formed at higher density. The resulting particles were calcined at different temperatures. The characterization of these microstructures were carried out using powder XRD, SEM, FTIR and UV-Visible spectra. Photocatalytic behaviour of the synthesized product was investigated using different dyes like Methylene Blue, Eriochrome Black-T and Methyl Red. The effect of operating parameters like catalyst load and initial dye concentration on the rate of dye degradation was studied. Nearly 100% decolourisation was achieved under optimum experimental conditions suggesting photochemical degradation of dyes by nanostructures of ZnO-SnO.

(P246)

Triarylborane-Luminescent Dye Conjugates: Intriguing Optical Properties and Anion Sensing Applications

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Recently, inherent Lewis acidity of triarylborans has been exploited in linear/nonlinear optics, two-photon materials, OLEDs and anion recognitions1. In this poster, we will portrait our recent ventures in understanding such triarylborane-luminescent Dye conjugates 2,3. Linear2 and 'V'-shaped boryl-BDY have been synthesized. These dyads exhibit dual fluorescence peaks, which are due to partial electronic energy transfer (EET) from donor borane to acceptor BDY units. The EET process can be conveniently exploited for the selective detection of F in organic medium. For colorimetric detection of F⁻ and CN⁻ a new triad containing triphenylamine-triarylborane-BDY has been synthesized4. The new triad was used for colorimetric detection of F⁻ and CN⁻. To discriminate the interfering anions, a smart sensor which contains dual Lewis acidic centers such as TAB and Zn has been designed4. Using this smart sensor it is possible to selectively distinguish interfering anions F⁻ and CN⁻. In order to achieve colorimetric detection of F- in aqueous medium, dyads decorated with (ArNMe₃)⁺ have been synthesized. The new sensor detects F- in aqueous medium with visual color change from green to yellow. This is the first molecule which can detect fluoride colorimetrically as low as 1 ppm in aqueous medium.

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(P247)

Large Centimetre-size Macroporous Ferritin Gels as Versatile Nanoreactors

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Organized assemblies of ferritin provide templates that can be exploited for nanotechnological applications. Organization of ferritin into well-defined three dimensional assemblies is challenging and has attracted considerable attention recently. We have synthesized, for the first time, large (centimeter-sized) self-standing macroporous scaffold monoliths from ferritin bionanoparticles, using dynamic templating of surfactant H1 domains. These scaffolds comprise three-dimensionally connected strands of ferritin, organized as a gel. The organization of the ferritin into a scaffold dramatically simplifies the purification protocols associated with replacement of the iron oxide nanoparticle into catalytically active zero-valent transition metal nanoparticles inside the ferritin. Since the ferritin is crosslinked in the scaffold, it is significantly robust with enhanced thermal stability and better tolerance towards several organic solvents. The monoliths of apo-ferritin that contain catalytically active Pd or iron oxide nanoparticles can be used as a recyclable heterogeneous catalyst for the oxidation of 2,3,6-trimethyl phenol to 2,3,6trimethyl-1,4-benzoquinone (precursor in Vitamin E synthesis) and for C-C bond formation via Suzuki reaction in both aqueous and organic solvents since the scaffold macropores facilitate substrate and reagent transport. The protein shell around the nanoparticles protects them from agglomeration, a phenomenon that otherwise plagues nanoparticles-based catalysis. Finally the Pd@apo-ferritin scaffold was immobilized inside a steel cartridge and used for the continuous flow hydrogenation of alkenes to their corresponding alkanes for 15 cycles without any loss of activity.

(P248)

Effect of molecular structure on corrosion inhibition properties of 2-(substituted phenyl) benzimidazole derivatives on mild steel in 1 M HCl solution

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The molecular configuration has been found to have a profound effect on corrosion inhibition efficiency of benzimidazole (BI) derivatives. In this endeavour, we have studied the effect of positional variation of electron withdrawing and electron donating groups in the phenyl ring present as substituent at 2-posotion of BI moiety using a series of benzimidazole derivatives namely 2-phenyl benzimidazole (PB), 2-(2-nitro phenyl) benzimidazole (2NPB), 2-(4-nitro phenyl) benzimidazole (4NPB), 2-(2-amino phenyl)benzimidazole (2APB), 2-(4-amino phenyl)benzimidazole (4APB)towards corrosion inhibition of mild steel in 1 M HCl. We have employedpotentiodynamic polarization (Tafel extrapolation) and electrochemical impedance

spectroscopy (EIS) techniques which showed the corrosion inhibition efficiency (IE) of the inhibitors increases in the order 4APB > 2APB >4NPB >2NPB >PB.The inhibitors are all found to act as mixed type inhibitors as observed from the polarisation study. Impedance measurements showed that with increase in the inhibitor concentration, the double-layer capacitance decreases with gradual increase in charge-transfer resistance, indicating the formation of adsorbed layer of the inhibitors on the metal surface which retards the rate of charge transfer processes. The nature of adsorption is explained according to the Langmuir adsorption isotherm model. The negative values of $\Delta G0$ ads indicate the spontaneous adsorption of the inhibitors on mild steel surface. Quantum chemical calculations using the density functional theory (DFT) were performed on benzimidazole derivatives to determine the relationship between molecular configuration and their inhibition efficiencies. The efficiencies of the corrosion inhibitors have been found to be related to energy gap between the frontier molecular orbitals of the molecules ($\Delta Eint=ELUMO$ -EHOMO). EHOMO often indicates the electron donating ability of the molecule, whereas ELUMO is a measure of electron accepting potentiality. As the observed IE of the molecules are related with both the frontier molecular orbitals, it may be concluded that the overall adsorption process and subsequent corrosion inhibition depend simultaneously on electron donation from the inhibitors to the vacant metal orbitals as well as back electron transfer from metal to the LUMO of the inhibitors.